



Significance of the long-chain organic cation structure in the sorption of the penconazole and metalaxyl fungicides by organo clays

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ABSTRACT

Sorption–desorption of two different hydrophobic fungicides, penconazole and metalaxyl, by a series of clay minerals layered and non-layered (montmorillonite, illite, kaolinite, muscovite, sepiolite and palygorskite) modified with the two-chain cationic surfactant, dihexadecyldimethylammonium (DHDDMA) was studied by first time in this work. DHDDMA-clays showed a good capacity to sorb both fungicides from water. Freundlich sorption constants (K_f) increased 22–268-fold for penconazole and 4–112-fold for metalaxyl in relation to natural clays. High sorption irreversibility was observed for penconazole for all modified clays, while for metalaxyl this occurred only for some of the modified clays. Additionally, a comparative study of the sorption of the fungicides by clay minerals modified with organic cations of different structure was carried out by a statistical approach. Non-layered and layered clay minerals modified with the two-chain alkylammonium organic cation DHDDMA, and with single-chain organic cations octadecyltrimethylammonium (ODTMA) and hexadecylpyridinium (HDPY) were used as sorbents. The study indicated a significant linear regression between the distribution coefficients K_d of fungicides and the organic carbon (OC) content of the organo clays ($r^2 \geq 0.80$, $p < 0.001$). According to this sorption of fungicides by partition between the aqueous solution and the organic medium created by the alkyl chains of the exchanged ammonium cations regardless of the type and structure of these cations is suggested. However, linear relationships between K_d values of each pesticide by the different organo clays and their relative OC contents revealed higher increase in sorption for HDPY-clays (penconazole) and for ODTMA-clays (metalaxyl) pointing out different effectiveness of the OC provided by each organic cation. These effects were also supported by the values of K_d relative to OC, $K_{d_{oc}}$. The results evidenced the different relative weight of alkyl cations to make organo clays effective barriers to prevent the mobility of pesticides from a point source of pollution.

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1. Introduction

In the past years, organo clays or clay minerals modified exchanging their inorganic cations by quaternary ammonium cations, with chains with a high number of carbon atoms have been proposed as sorbents of industrial organic contaminants and pesticides with the purpose to immobilise these compounds [1–7], to remove pesticides from water [8–10], to develop slow release pesticide formulations [11–13], or to examine the potential bioavailability [14,15] and the photostabilization of sorbed pesticides [16,17].

Sorption of non-ionic organic contaminants by organo clays depends on different factors. Molecular structure of the ammonium cation used to modify clays affects both the magnitude and

the mechanism of non-ionic solute sorption [2,6,18]. On the other hand, the clay type and the fraction of its cation exchange capacity (CEC) satisfied by the organic cation, and sorbate characteristics such as size, shape, and solubility/hydrophobicity are important factors in this process [3,5,19].

Organo clays synthesized with large hydrocarbon chains (greater than 12 carbons in the chain) possess high OC and are most effective sorbents for removing non-ionic organic compounds from liquid media than those synthesized with short hydrocarbon chains [6,20]. These large organic cations create an organic partition medium through the conglomeration of their flexible alkyl chains and tend to sorb non-ionic organic contaminants through partitioning or hydrophobic interactions (sorption). This process is characterized by a non-competitive sorption and the achievement of linear isotherms over a wide range of solute concentrations [9,21,22]. However, organo clays synthesized with small organic cations create a relatively rigid, non-polar surface favourable to non-ionic solute uptake by adsorption [6,18,23]. Short-chain organo clays are

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better sorbents for relatively hydrophilic or slightly hydrophobic compounds, and the adsorption is characterized by competitive sorption and non-linear isotherms (dependent of concentration), which are associated with specific sorption sites between the modified clay surface and the organic compound being sorbed.

Generally, sorption of organic compounds by organo clays is considered as a function of its total OC content [22,24]. However, El Nahhal and Safi [25] indicated that the chemical structure (size and shape) of the organic cation used to modify the clay is more important than the fraction of OC. In this sense, a number of studies on sorption of organic pollutants by bentonite modified with different organic cations have also indicated the influence of the interlayer arrangement of the quaternary ammonium cation alkyl chains in this process, and the increase of sorption capacity with increasing the surfactant chain length and the number of alkyl chains per surfactant molecule [26,27].

Pesticides are compounds with different polar groups and with a structure that differentiate them from non-ionic organic pollutants. Sorption of these compounds by organo clays has been usually studied using montmorillonite as clay mineral and organic cations with single hydrocarbon chains. However, the sorption of pesticides by other clay minerals (layered and non-layered) exchanged with organic cations of different structure is not well documented. All clay minerals have a higher or lower amount of exchangeable inorganic cations and their saturation with a given cationic surfactant may generate organo clays with a broad range of OC contents. Furthermore, their specific surface area and charge density can affect the organization and distribution of organic cations at the clay surface [7,19], and in consequence the sorption and the stability against desorption of hydrophobic compounds sorbed by them.

We studied in this work the sorption–desorption of two fungicides with different hydrophobicity, penconazole and metalaxyl ($\log K_{ow}$ of 3.72 and 1.75, respectively), by a series of low cost clay minerals saturated with a two 16C aliphatic chain cationic surfactant, dihexadecyldimethylammonium (DHDDMA) bromide. The novelty and originality of this work is based on: (1) the use of a two long-chain organic cation (not usually used in these studies) and the comparison of results with those obtained using the same clays modified with single-chain organic cations of different structure (octadecyltrimethylammonium (ODTMA), and hexadecylpyridinium (HDPY)) and (2) the use of a series of clays with different structure and properties, montmorillonite (M), illite (I), kaolinite (K), muscovite (Mu) (layered structure) and sepiolite (S) and paligorskite (P) (non-layered structure) to know the influence of base clays of the organo clays in the sorption of fungicides. The comparative study of the effect of the organic cation structure is through statistical approach using the data obtained in this work as well as those of our previous studies [7,28].

The results obtained contribute to evaluate the capacity of different clay minerals modified with a two long-chain organic cation for their possible use as sorbents of hydrophobic pesticides from point sources of pollution [29,30] and to clarify the influence of the long-chain organic cation structure in the ability of organo clays to sorb pesticides with different hydrophobic character.

2. Materials and methods

2.1. Natural clay minerals

A series of clay minerals (<1 mm) with different structures and cation exchange capacities CECs both in natural form and saturated with DHDDMA were used in the study. Tidinit montmorillonite (M) (Morocco), Cuenca kaolinite (K) (Spain), Peñausende muscovite (Mu) (Spain), Vallecas sepiolite (S) (Spain) and Bercimuelle palygorskite (P) (Spain) are minerals of low cost and Fithian illite (I) (Illinois) is a reference clay from the American Petroleum Institute.

The characteristics of the samples included in Table 1, were determined as described in Sánchez-Martín et al. [7]. The samples were considered to be representative of the different types of clay minerals and were used with their impurities since it was considered of interest to know their properties and behaviour as marketed for their possible use.

2.2. Preparation of organo clays

Clays saturated with DHDDMA were prepared by treating clays with a solution of the cationic surfactant in warm deionised water containing an amount of organic cation equivalent to 1.25 times the CEC of clay mineral. The suspensions were shaken for 1 h, centrifuged, washed with deionised water until free of bromide ions as indicated by AgNO_3 , freeze-dried and kept in an atmosphere at controlled humidity for later use. From the organic carbon (OC) determined for each organo clay, the amount of DHDDMA cation, and the percentage of CEC saturation were calculated. The characteristics of DHDDMA-clays are presented in Table 1. The DHDDMA with two 16C alkyl chains was more effective to increase the OC of clays studied than the organic cations with one alkyl chain (ODTMA and HDPY) [7,28]. The higher the CEC of clay the more was the exchange of surfactant, resulting organo clays with higher OC. The sepiolite and kaolinite, with the lowest CEC had the lowest total OC content. The intercalation of organic cation in the interlayer space of the organo clays was only observed for DHDDMA–montmorillonite (34.6 Å).

2.3. Pesticides

Unlabelled and ^{14}C -labelled pesticides were used in the study. Penconazole (1-[2-(2,4-dichlorophenyl)pentyl]-1H-1,2,4-triazole) is a solid hydrophobic compound with water solubility of 73 $\mu\text{g}/\text{mL}$ and $\log K_{ow}$ of 3.72. Metalaxyl (methyl *N*-(2,6-dimethylphenyl)-*N*-(methoxyacetyl)-DL alaninate) is a solid compound with water solubility of 8400 $\mu\text{g}/\text{mL}$ and $\log K_{ow}$ of 1.75 [31]. ^{14}C -Penconazole (specific activity 1.02 MBq/mg and 98.1% purity) and ^{14}C -metalaxyl (specific activity 1.37 MBq/mg and 97.2% purity) and the same pesticides unlabelled (>98% purity) were supplied by Novartis Crop Protection AG (Basel, Switzerland).

2.4. Sorption–desorption isotherms

Sorption isotherms of pesticides by natural and organo clays were obtained using the batch equilibrium technique. Duplicate 50 mg samples were treated with 10 mL solutions of each pesticide in deionised water at concentrations 5, 10, 15, 20 and 25 $\mu\text{g}/\text{mL}$ and an activity of 100 Bq/mL. The suspensions were shaken intermittently at $20 \pm 2^\circ\text{C}$ for 24 h in a thermostatted chamber (2 h every 4 h). Preliminary experiments revealed contact for 24 h to be long enough for equilibrium to be reached. Subsequently, the suspensions were centrifuged at $5000 \times g$ for 15 min. To determine the pesticide concentration at equilibrium, a 1.0 mL aliquot of supernatant solution was mixed with 4 mL of scintillation liquid and its activity was measured in disintegrations per minute (dpm) on a Beckman LS 6500 Liquid Scintillation Counter (Beckman Instruments Inc., Fullerton, CA). The dpm value recorded for the supernatant aliquot was related to the dpm obtained for the aliquots of the respective standards of pesticide solutions and the equilibrium concentration was determined. The amount of pesticide sorbed was considered to be the difference between that initially present in solution and that remaining after equilibration with the clay mineral.

Desorption isotherms of the pesticides were studied in clay samples initially treated with 25 $\mu\text{g}/\text{mL}$ solution of each pesticide

Table 1
Characteristics of natural and DHDDMA-clays studied

Parameters	Montmorillonite	Illite	Kaolinite	Muscovite	Sepiolite	Palygorskite
Natural clays						
CEC ^a (cmol/kg)	82	15	6.1	21	5.0	27
OC ^b (%)	0.06	1.74	0.10	0.10	0.08	0.46
<i>d</i> (001) (Å)	13.4	10.0	7.16	10.0 (12.6) ^c	12.3	10.6
Penconazole adsorption ^d						
K_f	40.2	24.1	11.3	9.39	13.4	8.11
n_f	0.53	1.06	0.83	0.98	1.12	0.88
Penconazole desorption ^d						
K_{fd}	79.3	128	78.2	121	97.5	57.2
n_{fd}	0.31	0.49	0.20	0.15	0.49	0.21
Metalaxyl adsorption ^d						
K_f	1.27	14.1	0.05	1.08	5.02	2.15
n_f	1.54	1.23	1.84	1.15	1.24	1.12
Metalaxyl desorption ^d						
K_{fd}	3.17	39.0	8.93	26.5	48.0	33.9
n_{fd}	1.31	0.91	0.17	0.29	0.48	0.24
DHDDMA-clays						
OC (%)	29.8	9.63	2.49	5.20	2.60	10.6
OCS ^e (%)	89	127	96	60	123	92
<i>d</i> (001) (Å)	34.6	10.0	7.16	10.0 (19.2) ^c	12.3	10.6

^a Cation exchange capacity.

^b Organic carbon.

^c Montmorillonite impurities.

^d K_f , Freundlich adsorption constant, K_{fd} Freundlich desorption constant taken from Sánchez-Martín et al. [7].

^e Organic cation saturation.

during the sorption study. After sorption equilibrium had been reached, 5 mL were removed from the solution and immediately replaced by 5 mL of deionised water. The resuspended samples were shaken for 24 h at 20 ± 2 °C, after which the suspensions were centrifuged and the desorbed pesticide was measured as reported above. This desorption procedure was repeated four times for each sample. The amount of compound sorbed by the clay at each desorption stage was calculated as the difference between the initial amount sorbed and the amount desorbed. All experiments were carried out in duplicate.

2.5. Statistical analysis

Standard deviations were used to indicate variability in the sorption and desorption coefficient values among duplicates. Simple linear regression models between sorption parameters and properties of organo clays were obtained with the SPSS 12.0 software package to study the effect of the organic cation structure on the sorption through a statistical approach.

3. Results and discussion

3.1. Sorption–desorption of penconazole and metalaxyl in DHDDMA-clays

Figs. 1 and 2 show the sorption–desorption isotherms of penconazole and metalaxyl by the six clay minerals modified with the DHDDMA cation, and by the six natural clay minerals taken from our previous work [7]. The sorption isotherms of both fungicides by the DHDDMA–M and DHDDMA–I are of C-type according to Giles et al. [32]. They are almost linear, showing that these compounds are sorbed by partitioning in these organo clays. However isotherms obtained by the other DHDDMA-clays are of L-type, in general, indicating sorption could also occur by physical forces [27].

All isotherms fit the Freundlich sorption equation ($\log C_s = \log K_f + n_f \log C_e$), with r^2 values ≥ 0.90 . The values of the Freundlich adsorption constants K_f and n_f are shown in

Tables 1 and 2 for natural and DHDDMA-clays, respectively. K_f is the fungicide amount sorbed (C_s) when the equilibrium concentration (C_e) is equal to the unity. This constant is considered in the work as a measure of the sorption capacity of fungicides by the different natural and DHDDMA-clays. The parameter n_f (slope of logarithmic equation) is a measure of inflection in the curve that fits the isotherm data. It has also been shown mathematically that n_f is a measure of the heterogeneity of adsorption sites on the adsorbent surface [33]. As n_f approaches a value of zero, surface site heterogeneity increases, indicating that there is a broad distribution of adsorption site types. The homogeneity of surface sites increases when n_f approaches the unity, indicating that there is a narrow distribution of adsorption site types on the adsorbent surface. The n_f values obtained for the sorption isotherms of fungicides by natural and DHDDMA-clays were close to 1 in a lesser or greater extent. They were always <1 for penconazole and they were >1 for sorption of metalaxyl by natural clays and <1 for sorption of this fungicide by DHDDMA-clays according to the type of isotherms obtained. The greater change in n_f values (towards the unity) was seen for the sorption isotherms of both fungicides by DHDDMA–M in relation to those obtained by the natural clay. The change indicate an increase in the homogeneity of adsorption sites of this mineral due to the modification of its surface by the OC derived of the DHDDMA organic cation, and suggests the importance of this OC on the sorption of the fungicides. Sánchez-Martín et al. [34] and Andrades et al. [35,36] have already indicated the influence of the organic matter in the sorption of penconazole and metalaxyl by soils.

For each DHDDMA-clay and for both pesticides, the K_f value was always greater than that calculated for the natural clay included in Table 1. In the case of DHDDMA–M, the K_f value was 268-fold higher for the sorption of penconazole and 112-fold higher for the sorption of metalaxyl than that calculated for the natural clay. The Freundlich constants K_f for the sorption of penconazole by the natural clays varied between 8.11 (P) and 40.2 (M). These values increased for sorption of the fungicide by the clays saturated with

Table 2Sorption–desorption Freundlich coefficients of penconazole and metalaxyl by DHDDMA-clays (K_f , n_f , and K_{fd} , n_{fd}), hysteresis coefficients (H), and efficiency coefficients (E)

Pesticide/clay ^a	$K_f \pm S.D.$ ^b	$n_f \pm S.D.$	$K_{fd} \pm S.D.$	$n_{fd} \pm S.D.$	$H^c \pm S.D.$	E^d
Penconazole						
DHDDMA–M	10793 ± 27.5	0.84 ± 0.08	10700 ± 33.5	0.06 ± 0.01	13.2 ± 2.94	133
DHDDMA–I	2997 ± 355	0.92 ± 0.03	4469 ± 17.1	0.16 ± 0.04	5.60 ± 2.04	57.2
DHDDMA–K	530 ± 3.48	0.72 ± 0.01	1050 ± 47.1	0.44 ± 0.02	1.62 ± 0.09	8.20
DHDDMA–Mu	1364 ± 62.8	0.73 ± 0.02	3189 ± 2.63	0.17 ± 0.01	4.24 ± 0.44	26.4
DHDDMA–S	857 ± 4.74	0.71 ± 0.01	2224 ± 140	0.25 ± 0.02	2.81 ± 0.23	22.8
DHDDMA–P	1234 ± 3.40	0.79 ± 0.01	2106 ± 70.3	0.43 ± 0.01	1.84 ± 0.07	36.8
Metalaxyl						
DHDDMA–M	142 ± 44.0	0.96 ± 0.09	277 ± 20.9	0.72 ± 0.03	1.34 ± 0.19	87.4
DHDDMA–I	54.8 ± 2.34	0.84 ± 0.02	111 ± 7.57	0.61 ± 0.02	1.36 ± 0.06	2.85
DHDDMA–K	9.13 ± 0.51	0.78 ± 0.01	47.1 ± 0.02	0.27 ± 0.04	2.89 ± 0.40	5.27
DHDDMA–Mu	9.62 ± 6.12	0.82 ± 0.21	104 ± 6.12	0.23 ± 0.05	3.58 ± 0.09	3.92
DHDDMA–S	25.0 ± 2.46	0.72 ± 0.04	108 ± 15.8	0.37 ± 0.04	1.96 ± 0.33	2.25
DHDDMA–P	13.9 ± 2.96	0.81 ± 0.08	127 ± 45.7	0.22 ± 0.09	3.70 ± 1.13	3.75

^a M, montmorillonite; I, illite; K, kaolinite; Mu, muscovite; S, sepiolite; P, paligorskite.^b Standard deviation of two replicates.^c $H = n_f/n_{fd}$.^d $E = K_{fd}(\text{organo clay})/K_{fd}(\text{natural clay})$.

the organic cation in all the samples studied ranging between 530 (DHDDMA–K) and 10793 (DHDDMA–M).

Metalaxyl, a less hydrophobic pesticide than penconazole, was sorbed by the natural clays with K_f values ranging between 0.05

(K) and 14.1 (I). The sorption of this fungicide by the organo clays increased, although to a lesser extent than that of penconazole. K_f constants varied between 9.13 (DHDDMA–K) and 142 (DHDDMA–M).

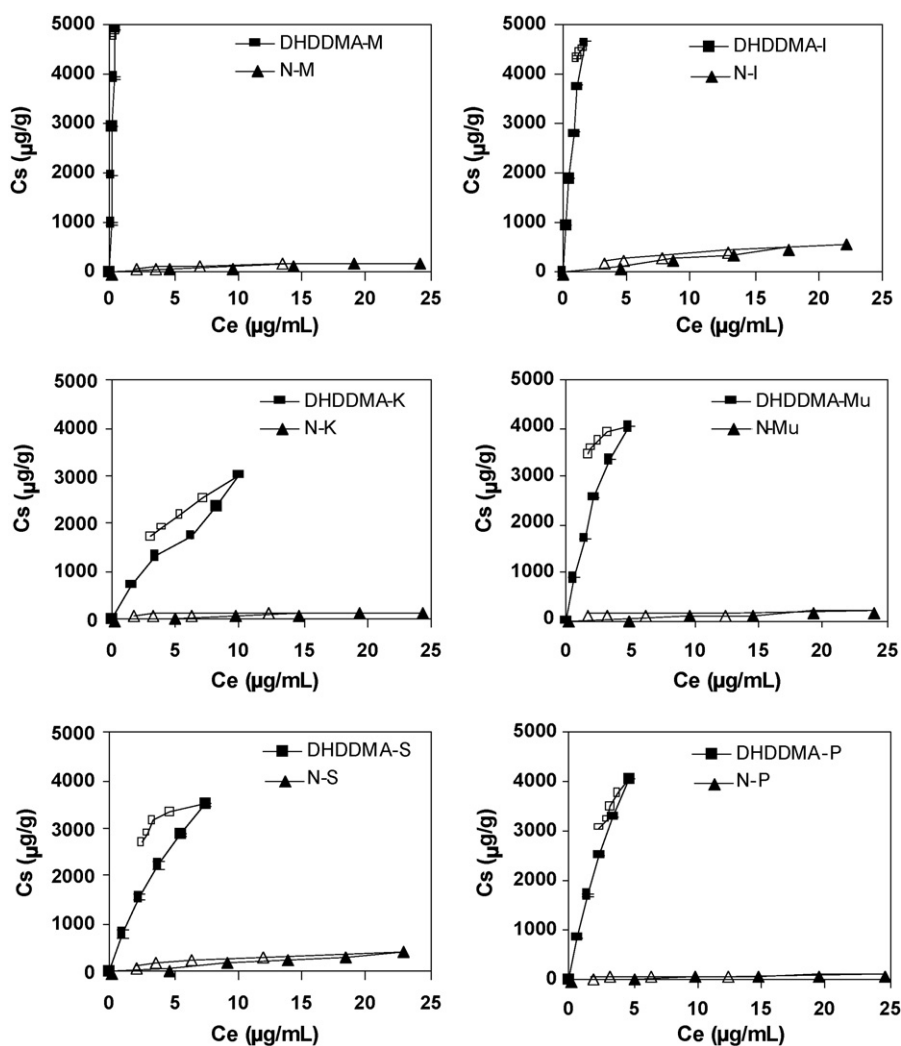


Fig. 1. Sorption–desorption isotherms of penconazole by the natural clay minerals (N), montmorillonite (M), illite (I), kaolinite (K), muscovite (Mu), sepiolite (S) and paligorskite (P), and by these clay minerals modified with DHDDMA cation. Filled symbols correspond to sorption and unfilled symbols correspond to desorption.

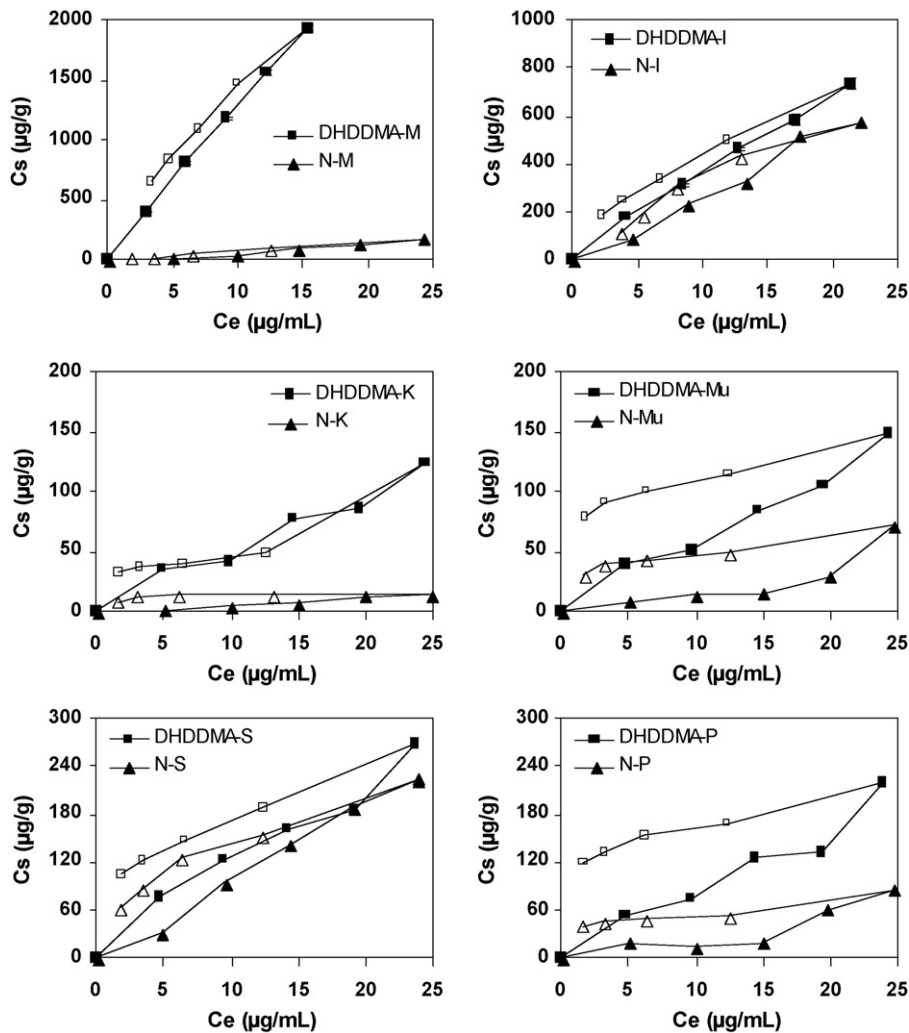


Fig. 2. Sorption–desorption isotherms of metalaxyl by the natural clay minerals (N), montmorillonite (M), illite (I), kaolinite (K), muscovite (Mu), sepiolite (S) and paligorskite (P), and by these clay minerals modified with DHDDMA cation. Filled symbols correspond to sorption and unfilled symbols correspond to desorption.

DHDDMA–M proved to be the most effective adsorbent, especially as regards the removal of the fungicide only sparingly water-soluble. Montmorillonite with highest CEC value resulted the organo clay with the highest organic cation exchanged (higher OC, Table 1). Under the working condition used here, this organo clay may adsorb up to 98.4% of the penconazole present in solution and, in the case of metalaxyl, may adsorb up to 38.5% of the fungicide in a solution of 25 µg/mL concentration. The results obtained indicate that the sorption of fungicides by organo clays from an aqueous

solution depends on the hydrophobic character of the fungicide and the clay structure. The influence of native clay nature is due to the OC content (derived of DHDDMA organic cation) supported by each clay which depends on its structural properties [37].

The desorption isotherms of both fungicides from the DHDDMA-clays fitted the Freundlich equation ($\log C_s = \log K_{fd} + n_{fd} \log C_e$) with r^2 values ≥ 0.80 . K_{fd} and n_{fd} are two characteristic coefficients of fungicide desorption, their values are included in Table 2. These isotherms display hysteric behaviour in a greater or lesser extent,

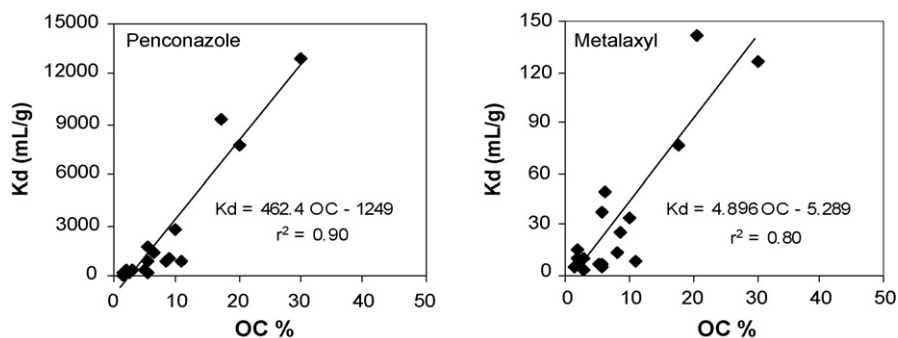


Fig. 3. Relationship between K_d values of penconazole and metalaxyl by the HDPY-clays, ODTMA-clays and DHDDMA-clays and the organic carbon content of these organo clays.

Table 3

Linear sorption distribution coefficients (K_d) of penconazole and metalaxyl by organo clays, correlations coefficients (r^2), $K_{d_{oc}}$ values, and organic carbon content (OC) of organo clays

Organo clays ^a	OC (%)	Penconazole			Metalaxyl		
		K_d (mL/g)	r^2	$\log K_{d_{oc}}$	K_d (mL/g)	r^2	$\log K_{d_{oc}}$
HDPY-M	17.2	9,309	0.98	4.73	78.1	0.99	2.66
HDPY-I	5.42	1,777	0.98	4.52	38.9	0.99	2.86
HDPY-K	1.60	367	0.95	4.36	7.87	0.94	2.69
HDPY-Mu	4.87	452	0.92	3.97	7.78	0.99	2.20
HDPY-S	1.19	147	0.97	4.09	5.67	0.88	2.68
HDPY-P	8.01	947	0.98	4.07	14.7	0.98	2.26
ODTMA-M	20.1	7,844	0.99	4.59	143	0.99	2.85
ODTMA-I	6.05	1,493	0.99	4.39	50.2	0.99	2.92
ODTMA-K	1.61	434	0.99	4.43	11.5	0.95	2.85
ODTMA-Mu	5.39	293	0.99	3.74	7.94	0.95	2.17
ODTMA-S	1.55	260	0.99	4.22	16.4	0.99	3.02
ODTMA-P	8.50	1,167	0.99	4.14	25.6	0.98	2.48
DHDDMA-M	29.8	13,035	0.99	4.64	128	0.99	2.63
DHDDMA-I	9.63	2,866	0.97	4.47	34.9	0.99	2.56
DHDDMA-K	2.49	302	0.97	4.08	3.25	0.93	2.12
DHDDMA-Mu	5.20	942	0.91	4.26	5.86	0.98	2.05
DHDDMA-S	2.60	512	0.94	4.29	11.1	0.96	2.63
DHDDMA-P	10.6	937	0.97	3.95	8.34	0.95	1.90

^aM, montmorillonite; I, illite; K, kaolinite; Mu, muscovite; S, sepiolite; P, paligorskite.

due to desorption points do not fall on the sorption isotherm, i.e. nonsingularity is observed. The desorption pathway does not return to zero sorption when the equilibrium concentration is going to zero, and the effect is an apparent increase in the sorption constant K_{fd} in relation to K_f [38]. The irreversibility of sorbed compound has been proposed by different authors [33] as a potential reason to explain the nonsingularity of sorption isotherms. A hysteresis coefficient (H) has been defined by the relation between the slopes of sorption and desorption isotherms (n_f/n_{fd}) [39] as a measure of the irreversibility of sorption processes. The H values (Table 2) corresponding to desorption of penconazole were, in general, higher than those corresponding to desorption of metalaxyl. The highest value was observed for DHDDMA-M, where fungicide partitioning must be mainly in the DHDDMA adsorbed in the interlayer space of the montmorillonite ($d(001)$ of the DHDDMA-M increased 24.4 Å in relation to natural clay). Sorption irreversibility was observed for both fungicides in all DHDDMA-clays but in general it was greater for penconazole than for metalaxyl.

K_{fd} value represents the fungicide amount that remains sorbed for an equilibrium concentration equal to unity when the equilibrium is approached after desorption. This sorption coefficient represents the real sorption of fungicides by natural and/or exchanged clay minerals (Tables 1 and 2). With the aim to know the increase in the sorption capacity of the natural clay mineral after saturation with DHDDMA an efficiency coefficient, E , was estimated and calculated by the relationship between K_{fd} for the sorption of fungicides by the organo clay and K_{fd} for the sorption by the corresponding natural clay ($E = K_{fd} \text{ organo clay} / K_{fd} \text{ natural clay}$). E values obtained (Table 2) indicated an increase in the sorption capacity of natural clays from 8.20 to 133-times for penconazole and from 2.25 to 87.4-times for metalaxyl when they were modified with the organic cation DHDDMA.

The results showed that the sorptive properties of different clays for penconazole and metalaxyl can be greatly enhanced by simple ion exchange reactions of naturally occurring inorganic exchangeable ions with large organic cations. In this work we confirm and extend our previous results [7,28] on the increased sorptive capabilities of HDPY-clays and ODTMA-clays by examining sorptive capabilities of DHDDMA-clays.

3.2. Comparison of sorption of penconazole and metalaxyl by exchanged clays with organic cations of different structure

Penconazole and metalaxyl sorption by exchanged clays with DHDDMA (two 16C alkyl chains and DMA cation), ODTMA (18C alkyl chain and TMA cation) and HDPY (16C alkyl chain and pyridinium cation) was compared through the linear sorption distribution coefficients K_d . This parameter called also partitioning or hydrophobic sorption constant was used because it is more commonly used in the literature for comparative studies than the Freundlich sorption constant [6,9], when the sorption of organic compounds is highly correlated to the OC. Data from sorption isotherms from this work, and from our previous studies [7,28] were re-calculated and K_d values were determined by fitting sorption isotherms to linear regression forced through the joint axis origin (0,0) according to equation $C_s = K_d C_e$. K_d values, correlation coefficients r^2 , and K_d values normalised to 100% OC ($K_{d_{oc}} = 100 K_d / \% \text{ OC}$) are included in Table 3.

K_d values indicate that the highest sorption is always for the fungicide penconazole, which has a higher hydrophobic character ($\log K_{ow} = 3.72$). Furthermore, the greatest sorption of both fungicides occurs for the clay minerals with the highest CEC and saturated with the greatest size organic cation (DHDDMA), i.e. organo clays with high OC content. According to this, a statistically significant linear relationship was found between the K_d values for each fungicide and the OC content of organo clays considered all together ($n = 18$ values) for a confidence level of 99%. The statistical r^2 indicates that the model explains 90% of the variability of K_d for penconazole and 80% for metalaxyl (Fig. 3), and the correlation coefficients r (0.94 for penconazole and 0.89 for metalaxyl, $p < 0.001$) indicate a relatively or moderately strong relationship between the variables K_d and OC for penconazole and metalaxyl, respectively. These results could suggest the sorption of fungicides by partition between the aqueous solution and the organic medium created by the alkyl chains of the exchanged ammonium cations regardless of the type and structure of these cations. The higher correlation coefficient for penconazole (more hydrophobic than metalaxyl) points to a more effective partition of this compound in the organic phase.

However, the correlation coefficients from the relationships between the K_d values and the OC contents of the organo clays

Table 4

Linear regression equations for the relationships between the distribution coefficient values (K_d) of penconazole and metalaxyl by organo clays and the organic carbon contents of HDPY-clays, ODTMA-clays and DHDDMA-clays

Organo clays	Penconazole	Metalaxyl
HDPY-clays	$K_d = 563 \text{ OC} - 1430$ ($r^2 = 0.87$)	$K_d = 4.36 \text{ OC} - 2.31$ ($r^2 = 0.80$)
ODTMA-clays	$K_d = 409 \text{ OC} - 1032$ ($r^2 = 0.91$)	$K_d = 6.99 \text{ OC} - 7.89$ ($r^2 = 0.87$)
DHDDMA-clays	$K_d = 467 \text{ OC} - 1596$ ($r^2 = 0.94$)	$K_d = 4.52 \text{ OC} - 13.5$ ($r^2 = 0.92$)

for the sorption of each fungicide by all three organo clays studied indicate that this relationship is not completely linear. This means that the sorption capacity of the OC that is adsorbed by the different organo clays (i.e. DHDDMA, ODTMA and HDPY cations) is not the same. In this sense, the different $\log K_{d_{oc}}$ values for the sorption of the same fungicide by the organo clays (Table 3) also indicate that the sorption capacity of the organic phases derived from the different organic cations is not only a function of the increased OC of the clay.

A statistical approach was used to study the influence of organic cation structure on the sorption of fungicides by the organo clays. The linear relationship between the distribution coefficients K_d and the OC contents for the sorption of penconazole or metalaxyl by each organo clays, DHDDMA-clays, ODTMA-clays and HDPY-clays, was obtained (Table 4). The linear regressions obtained for penconazole ($r^2 \geq 0.87$, $p < 0.05$) indicate a similar increase in the sorption for the clays saturated with the organic cations ODTMA and DHDDMA when the OC content of these samples is increased. However, a greater increase in penconazole sorption by the clays saturated with the organic cation HDPY was observed when the OC content is increased. For metalaxyl, the linear regressions obtained ($r^2 \geq 0.80$, $p < 0.05$) indicate a similar increase in the sorption for the clays saturated with the organic cations HDPY and DHDDMA when the OC content is increased and there was a greater sorption by the clays saturated with the organic cation ODTMA.

DHDDMA and ODTMA are ammonium cations with two 16C alkyl chains or one 18C alkyl chain, respectively. These cations provide different OC contents to exchanged clays minerals (Table 3) but the OC provided has the same nature (aliphatic chain). Because this, their sorption capacity for penconazole must be similar. The greater sorption capacity of HDPY could be due to the higher hydrophobic character of pyridinium headgroup of this cation besides the 16C alkyl chain. In this sense, Gullick and Weber [6] also found greater K_{oc} values for the adsorption of 1,2,4-trichlorobenzene (TCB) ($K_{ow} 4.00$) by HDPY-bentonite than by HDTMA-bentonite.

However, the greater sorption capacity of ODTMA-clays for metalaxyl (less hydrophobic than penconazole, K_{ow} 1.75 and 3.72, respectively) could be explained considering that metalaxyl sorption by organo clays is due to partition and adsorption mechanisms. More polar aromatic compounds can be adsorbed by interaction with the alkyl chain ammonium headgroups as indicated by Witthuhn et al. [27] and Sheng and Boyd [5] and a greater interlayer expansion for the sorption of these compounds by HDTMA-montmorillonite is indicated by these authors. This possible interaction would be facilitated with the ODTMA cation since in the case of the DHDDMA could be impeded by a hindrance effect of the ammonium group by the two alkyl chains. Similarly, other authors have found a greater sorption of compounds with a low hydrophobic character such as methyl isobutyl ketone (MIBK) ($K_{ow} = 1.09$) by HDTMA-bentonite than by HDPY-bentonite [6].

$K_{d_{oc}}$ values varied in the same sense, they varied in the ranges: 3.97–4.73, 3.95–4.64 and 3.74–4.59 for penconazole sorption by HDPY-, DHDDMA- and ODTMA-clays, respectively, and in the ranges: 2.17–3.02, 2.20–2.86 and 1.90–2.63 for metalaxyl sorption by ODTMA-, HDPY- and DHDDMA-clays. These $K_{d_{oc}}$ values were

always greater for the sorption of penconazole than metalaxyl according to the linear relationship usually found between K_{oc} and K_{ow} values for various compounds on the long-chain organo clays [9].

Furthermore, $K_{d_{oc}}$ values of sorption of each fungicide by HDPY-, DHDDMA- and ODTMA-clays individually considered indicate that the sorption capacity of the OC derived from each organic cation is also depending on the native clay where it is supported. This could be due to differences in the surface charge density in organic cations of the clay minerals modified [7,19]. In this sense Sánchez-Martín et al. [7] found positive correlation between desorption constants $K_{des_{om}}$ values for the pesticide sorption by clay minerals and the surface charge density in ODTMA of the same clay minerals used in this work. The highest $K_{des_{om}}$ value corresponded to kaolinite and the lowest to montmorillonite for the pesticides penconazole, linuron, alachlor, atrazine and metalaxyl. These authors indicated that the highest charge density should give rise to the formation of a more effective or more accessible organic phase for partitioning pesticides in organo clays.

4. Conclusions

The results obtained showed that DHDDMA clays increased the sorption of the fungicides by clay, depending on the type of clay (higher for layered than for non-layered clays), and on the fungicide hydrophobicity (higher for penconazole with $K_{ow} = 3.72$ than for metalaxyl with $K_{ow} = 1.75$). The efficiency in sorption (after desorption) increased in relation to natural clays between 8.20–133 times (layered clays) and 22.8–36.8 times (non-layered clays) for the sorption of penconazole and between 2.85 and 87.4 times (layered clays) and 2.25–3.75 times (non-layered clays) for the sorption of metalaxyl. The comparative study on the sorption of the fungicides by exchanged clays with different structure organic cations, DHDDMA-clays, HDPY-clays, and ODTMA-clays, indicate a sorption increase of fungicides with the OC content of organo clays ($r^2 \geq 0.80$, $p < 0.001$) when they are considered together, suggesting sorption of fungicides by partition between the aqueous solution and the organic medium created by the alkyl chains of the exchanged ammonium cations regardless of the type and structure of these cations. However, the linear regressions between distribution coefficients (K_d) and the OC content derived of each organic cation, indicate a higher increase of sorption by HDPY-clays for penconazole and by ODTMA-clays for metalaxyl. These results and the $K_{d_{oc}}$ parameters, determining of sorption capacity of the organic phase, indicate that the effectiveness of OC provided by each organic cation is different. In the same sense, $K_{d_{oc}}$ values show different sorption capacity of both fungicides by organo clays prepared with different base clay minerals. The results obtained pointed out the importance of the organic cation structure of exchanged clays on the sorption process. They are of interest from an economic and environmental point of view, and must be taken into account when preparing more suitable organo clays, to be used as barriers as indicated by Rodríguez-Cruz et al. [37] to prevent the mobility of particular pesticides in soils coming from a point source of pollution.

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