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RETENTION OF METAMITRON BY MODEL AND NATURAL PARTICULATE MATTER

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Adsorption isotherms of metamitron on model soil colloidal components: kaolinite, illite, montmorillonite, iron oxide and humic acid, and their binary associations were obtained using a batch equilibration procedure. Sorption parameters, K_f and n_f , were calculated by fitting the sorption data to the Freundlich equation and results obtained for binary associations were compared with those obtained for the individual model components. The sorption efficiency of the humic acids and their binary associations was measured as K_{oc} . The adsorption behaviour of the $< 2 \mu\text{m}$ fraction of two soils from Southern Spain was also studied as natural particulate matter. Montmorillonite and humic acids were found to be the most important components responsible for metamitron retention by the model adsorbents studied. On the contrary, metamitron showed little interaction with kaolinite, illite or iron oxide. These individual adsorption behaviours were reproduced in the montmorillonite-iron oxide-humic acid binary systems, but with differences suggesting changes on the surface properties upon association. Differences in K_{oc} values of isolated humic acids and their associations indicate that the interaction transforms the humic acid surfaces and suggest different types of bonding between colloids and metamitron. The results obtained with model adsorbents and their associations were in agreement with the highest adsorption of metamitron found for the natural clay fraction of two soils which displayed the largest adsorption in that with the highest content in montmorillonite and organic carbon. The importance of organic matter and montmorillonite in metamitron adsorption by colloidal components was also shown by the decrease in K_f and the increase in K_{oc} observed after removal of organic matter from the soil clay fraction with the highest organic carbon content.

KEY WORDS: Clays, herbicides, model soil components, sorption.

INTRODUCTION

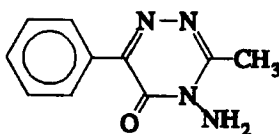
Although most non-ionic pesticides tend to adsorb on the organic fraction in particulate matter^{1,2}, in the case of polar uncharged pesticides (the condition of water solubility $> 10^{-3}$ M can be useful) or when the organic carbon content is low relative to the clay mineral content, the contribution of clay to sorption may become more evident^{3,4}. Whereas much research work has been devoted to study the sorption of low polarity organic contaminants in sediments and particulate matter as related to their water transport, much less information can be found dealing with high solubility organic compounds. We have found studying the behaviour of polar, ionic or ionizable pesticides in soils that the sorption of these compounds by soils is much more closely related to the clay content than to the organic matter content⁵⁻¹⁰. Moreover, the clay fraction of soils and sediments is also very important in contaminant transport by runoff, surface, and even ground water^{11,12}.

Metamitron (4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4H)-one) is a triazinone herbicide of water solubility as high as 1.7 g/kg at 20°C¹³. Organic matter has been found to be the most important soil component in the adsorption of metamitron by particulate matter¹⁴, but adsorption studies on different soils and model adsorbents¹⁵ have also shown the importance of clays in sorption of this herbicide. However, even though model sorbents can be very helpful in predicting the retention of pesticides by natural systems, the intimate association between the individual constituents may cause some modification of their adsorptive properties^{16,17}. Thus, the aim of this paper was to investigate the adsorption of metamitron by binary associations between model colloidal components: clay minerals, iron oxide and humic acid, and to compare the results with those for the isolated constituents. To complement the results, the adsorption behaviour of the < 2 µm fraction isolated from two soils from Southern Spain was also studied.

MATERIALS AND METHODS

Herbicide and sorbents

The herbicide metamitron used in this study was the high purity compound purchased from Riedel-deHaën. This herbicide is a crystalline solid of melting point 166.6°C, v.p. 86 µPa at 20°C and water solubility at 20°C 1.7 g/kg¹³. Metamitron is a selective herbicide due to detoxification reactions which occur at the 4-amino group in tolerant plants¹⁸ such as sugar and fodder beets.



Metamitron

The clay minerals used in this work were IMt-1 illite, KGa-1 kaolinite and SWy-1 montmorillonite, supplied by the Clay Minerals Repository of the Clay Minerals Society. The < 2 µm fraction of SWy1, used to obtain the clay-iron oxide and clay-humic acid binary associations, was saturated with Ca²⁺ and Fe³⁺ by five successive treatments with solutions of the corresponding chloride, washed with deionized water until Cl⁻ free and freeze-dried.

Poorly crystallized ferrihydrite was prepared following the procedure of Murad and Schwertmann¹⁹: a 0.5 M Fe(NO₃)₃ solution was neutralized with NH₄OH to a pH of 7.5, washed until NO₃⁻ free and freeze-dried.

The humic substances (HA) used in the present study were a commercial humic acid (Fluka) and a natural humic acid extracted from the A horizon of a Typic Xerochrept soil on a shale parent rock. The extraction procedure and characteristics of the soil humic acid have been reported previously by Saiz-Jimenez *et al.*²⁰

The clay fractions (< 2 µm particle size fraction) of a Fragixeralf soil and Entic Chromoxerert soil were obtained by sedimentation using the pipette method after previous carbonate elimination²¹. The soil clay of the Entic Chromoxerert soil was

treated with 30% hydrogen peroxide for removal of organic matter and then washed with 0.5 M CaCl_2 .

Synthesis of binary colloidal associations

Clay-iron oxide associations Aqueous solutions with two different concentrations of $\text{Fe}(\text{NO}_3)_3$ (7.5 and 15 mM) were stirred for 10 min in the presence of 2 g CaSWy/ 100 ml solution. A blank without $\text{Fe}(\text{NO}_3)_3$ but containing an appropriate amount of HNO_3 in order to achieve the same pH as the Fe^{3+} solutions was also prepared. All suspensions were neutralized with NH_4OH to a pH of 7.5. "Amorphous iron oxide" coated clays and blanks were washed, freeze-dried and stored in open air until used.

Clay-humic acid associations CaSWy-Fluka humic acid and CaSWy-Soil humic acid complexes were obtained by adding 2.5 g of clay to a solution (pH 6.5) of 500 ml of 500 mg/l humic acid previously dissolved using 1 M NaOH. To maintain a constant ionic strength, 0.01 M NaCl was used as background electrolyte. After shaking for 24 h, clay-humic acid associations and a corresponding blank were dialyzed, lyophilized and stored in open air until used.

Amorphous iron oxide-humic acid associations Poorly crystallized ferrihydrite was used to obtain the amorphous iron oxide-humic acid complexes following the same steps as those for the synthesis of clay-humic acid associations.

Physicochemical properties of the sorbents

Fe content of clay-iron oxide associations was determined by oxalate extraction using the procedure of McKeague and Day²²: samples of 50 mg of clay were treated with a solution of 10 ml of 0.2 M ammonium oxalate/oxalic acid, shaken in complete darkness for 4 h and centrifuged. The iron(III) in the supernatants was estimated by atomic absorption spectroscopy.

Total C of the clay- and iron oxide- humic acid complexes and soil clays was determined in a total elemental carbon analyzer. In order to estimate the fraction of humic acid "actually bound" to the clay or iron oxide in the complexes, U.V. absorption (285 nm) was measured for the humic acid solutions before and after shaking for 24 h in combination with the clay or iron oxide. Differences were assumed to be the amounts of humic acid bound to the clay or iron oxide.

The pH of the samples was measured in 1:200 solid to 0.01 M CaCl_2 . For the pH measurements, suspensions were equilibrated for 4 h, centrifuged, and pH of the supernatant measured using a combination glass electrode.

BET specific surface areas were obtained by nitrogen adsorption at 77°K using a Carlo Erba Sorptomatic 1900. Samples were outgassed at 80°C and equilibrated under vacuum for 15 h before measuring the nitrogen adsorption isotherm.

X-ray diffractograms of the air-dried SWy samples and its complexes with iron oxide and humic acid were obtained on oriented specimens with a Siemens D-500 diffractometer using CuK_α radiations

The clay mineralogy of the soil clay fractions were obtained by X-ray diffraction of oriented samples previous saturation in Mg and K cations, and ethylene-glycol and 500°C treatments²³. Iron content was determined by cold extraction with citrate-dithionite solution²⁴.

Adsorption experiments

Adsorption studies were performed using a batch equilibration procedure. 200 mg of the model adsorbents studied and their associations were treated with 10 ml of solutions with different metamitron initial concentrations in the mM range (C_i). To minimize ionic strength changes and to promote flocculation, 0.01 M CaCl_2 was used as background electrolyte. Suspensions were shaken at $20 \pm 2^\circ\text{C}$ for 24 hours in 50 ml polypropylene centrifuge tubes and then centrifuged at 18000 r.p.m. at the same temperature. All samples were run in duplicates. It was checked that no significant sorption of metamitron took place on the walls of the tubes. Equilibrium concentration (C_e) was determined in the supernatants by liquid chromatography. The following conditions were used: Nova-Pack column of 150 mm length \times 3.9 mm i.d.; column packing, C18; flow rate, 1 ml/min; eluent system, 70:30 (v:v) water-methanol; UV detection, 300 nm. Differences between C_i and C_e were assumed to be metamitron adsorbed.

Adsorption isotherms were fitted to the logarithmic form of the Freundlich empirical equation:

$$\text{Log}(C_s) = \text{Log}(K_f) + n_f \text{Log}(C_e) \quad (\text{Eq. 1})$$

where C_s (mmol/kg) is the amount of metamitron adsorbed at the equilibrium concentration C_e (mmol/l), and K_f and n_f are the adsorption capacity and intensity factor, respectively, which can be calculated from the logarithmic plot of C_s vs C_e .

In the case of the ferrihydrite-humic acid associations, since the amounts of herbicide adsorbed were very low, a distribution coefficient, K_d (l/kg), was obtained ($K_d = C_s/C_e$) using initial concentration $C_i = 1$ mM and increasing solid:solution ratio to 0.5 g: 10 ml, thus improving the precision of herbicide adsorption measurements²⁵. A distribution coefficient at $C_i = 1$ mM was also calculated in the case of CaSWy, FeSWy and Fluka HA varying the initial pH of the solutions.

The adsorption on soil clays was performed at two solid/solution ratios: 1/10, in order to compare the adsorption capacity of the two soil clays, and 1/50, in order to study the influence of the removal of organic matter by H_2O_2 treatment on metamitron sorption; this last solid/solution ratio was the same as that used for model sorbents.

For humic acids and its binary associations, a K_{oc} was calculated from Freundlich K_f values as follows:

$$K_{oc} = \frac{K_f}{\%OC} \times 100$$

as a measure of sorption capacity or efficiency of the organic matter of these model and natural sorbents.

RESULTS

Physicochemical properties of the samples

Table 1 shows some physicochemical properties of the model adsorbents used in this study. It should be noticed the very low pH and the lower basal spacing (d_{001}) of the FeSWy montmorillonite when compared with the CaSWy montmorillonite, the last used

Table 1 Physicochemical properties of the model adsorbents.

Sample	S_{BET} (m^2/g)	% O.C.	pH	d_{001} (\AA)
CaSWy	23	–	7.9	15.1
FeSWy	36	–	2.9	12.8
IMt-1	33	–	7.9	10.1
KGa-2	24	–	4.6	7.2
Ferrihydrite	315	–	5.6	–
Soil humic acid	–	42.6	2.9	–
Fluka humic acid	–	41.0	4.6	–

in the synthesis of the clay-humic acid and clay-iron oxide binary associations. The soil humic acid gives also lower pH than the commercial one, indicating a major presence of the functional acidic groups, -COOH and -OH, in the former.

Table 2 summarizes the physicochemical properties of the binary associations studied, together with the physicochemical properties of the blanks used in every case. The clay-iron oxide associations show a significant increase in S_{BET} when the amount of Fe in the complexes increases, due to the contribution of amorphous iron precipitated which has higher nitrogen surface area, than that of montmorillonite (Table 1). Table 2 also shows a decrease in d_{001} of the montmorillonite in the complex of higher Fe content when compared with the blank sample, which also shows a decrease with respect to the untreated sample (Table 1).

CaSWy complexes with humic acid (Table 2) show a reduction of S_{BET} when compared with the blank sample, which has been attributed to humic substances blocking the clay minerals surfaces and, thus, giving rise to a reduction of N_2 measurable surfaces^{16,26}, since surface area of humic substances cannot be measured by N_2 adsorption. The S_{BET} reduction in the clay-humic acid complexes is higher for the soil humic acid than for the commercial Fluka humic acid. Table 2 also shows a small increase in the basal spacing value d_{001} of the blank and humic treated montmorillonites. The complexes iron oxide-humic acid showed, as in the case of the clay-humic acid complexes, a reduction in S_{BET} when compared with the blank sample, but there are no significant differences between the two different humic substances.

Table 2 Physicochemical properties of the clay-iron oxide-humic acid binary associations.

Complex	mg Fe/g complex	% C	S_{BET} (m^2/g)	pH	d_{001} (\AA)
CaSWy-Ferrihydrite	21.0	–	45	5.8	–
	36.5	–	56	5.7	13.7
Blank	2.2	–	28	6.3	14.9
CaSWy-Soil HA	–	2.9	5	5.0	15.6
CaSWy-Fluka HA	–	3.3	9	5.2	15.4
Blank	–	–	24	7.1	15.3
Ferrihydrite-Soil HA	–	4.4	293	5.2	–
Ferrihydrite-Fluka HA	–	4.2	298	5.6	–
Blank	–	–	317	5.9	–

Table 3 shows the physicochemical properties and clay mineralogy of the two soil clay samples used in this study and of the clay fraction of the *Entic Chromoxerert* (soil clay 2) after treatment with H_2O_2 . This soil clay has higher organic carbon content when compared with the clay fraction of the *Fragixeralf* soil (soil clay 1) and similar specific surface area. When considering the clay mineralogy, soil clay 1 is predominantly illitic whereas soil clay 2 has a very high content in montmorillonite. Treatment of soil clay 2 with H_2O_2 gave rise to a reduction in organic carbon content and, hence, to an increase in S_{BET} .

Adsorption on model adsorbents

Figure 1 shows the adsorption isotherms of metamitron on CaSWy, FeSWy, soil HA and Fluka HA. Adsorption isotherms on IMt-1 illite, KGa-2 kaolinite and ferrihydrite are not shown in this figure because of the very low amounts of metamitron adsorbed. Adsorption isotherms are of the L type, according to Giles *et al.*²⁷ classification, indicating a reduction in adsorption sites when the concentration in solution increases. Systems showing this type of isotherms are those in which highly polar solutes are involved²⁸, in agreement with the high water solubility (1.7 g/l) of metamitron³. However the isotherms on HAs are also close to the C or constant partitioning type, which generally occur due to hydrophobic interactions between organic molecules and organic surfaces. Table 4 shows adsorption coefficients after fitting adsorption isotherms to the Freundlich equation. The values for n_f were found lower than unity as corresponds to L isotherms, but for HAs were closer to the unity as corresponds to the partial C-type isotherm character. Adsorption of metamitron is much higher in the case of the FeSWy montmorillonite than in the CaSWy, whereas no significant differences were observed between adsorption of metamitron on soil humic acid and commercial humic acid. However, the K_{oc} value for commercial HA was found slightly higher than that for the soil one.

Table 3 Physicochemical properties and clay mineralogy of the clay fraction of a *Fragixeralf* soil (soil clay 1) and of a *Entic Chromoxerert* soil (soil clay 2).

Parameter	Soil clay 1	Soil clay 2
% Organic carbon		
untreated sample	1.22	2.84
H_2O_2 treated	–	0.91
mg Fe/g clay	14.0	21.8
pH	5.2	5.8
C.E.C. (meq/100 g)	26	55
Clay Mineralogy (%)		
Illite	85	45
Kaolinite	10	0
Montmorillonite	5	55
S_{BET} (m^2/g)		
untreated sample	56.0	53.2
H_2O_2 treated	–	78.0

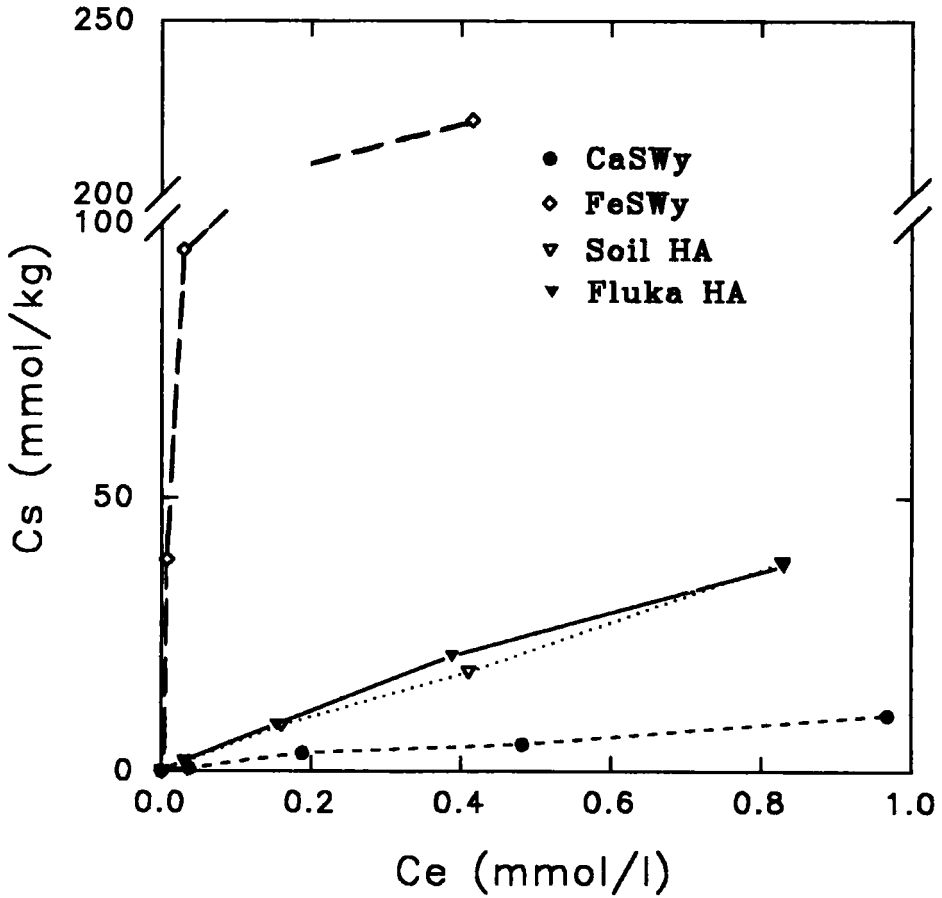


Figure 1 Adsorption isotherms of metamitron on selected primary model adsorbent.

Table 4 Adsorption coefficients of metamitron on model adsorbents calculated from Freundlich equation (K_f , K_{oc} , and n_f) and correlation coefficients (r). K_{oc} values for the humic acid samples.

Sample	K_f	K_{oc}	n_f	r
CaSWy	10.8	—	0.85	0.989
FeSWy	339.3	—	0.41	0.983
IMt-1	1.2	—	0.76	0.988
KGa-2	—	—	—	—
Ferrihydrite	—	—	—	—
Soil HA	43.9	103	0.92	0.999
Fluka HA	46.4	113	0.89	0.999

Distribution coefficients, K_d , for metamitron at different initial pH were also calculated in the case of the CaSWy and FeSWy montmorillonites and Fluka HA and are given in Table 5. The decrease in the initial pH of the metamitron solution gives rise to an increase in adsorption of metamitron on montmorillonite, specially in the case of CaSWy. No significant changes in adsorption are observed in the case of the Fluka HA when varying the initial pH of metamitron solution.

Adsorption on clay-iron oxide-humic acid binary associations

Figure 2 shows metamitron adsorption isotherms on CaSWy-ferrihydrate complexes with 21.0 and 36.5 g Fe/g of complex, together with the adsorption isotherm of the blank sample, and Table 6 gives the adsorption coefficients obtained from the Freundlich equation. Adsorption isotherms were now closer to C-type and hence they show n_f values close to unity. Adsorption of metamitron on the complexes increases when compared with the blank sample, and is higher in the complex of higher amount of Fe, although very low adsorption of metamitron on ferrihydrate was observed. The blank sample CaSWy (Table 6) was found to adsorb more metamitron than the untreated one (Table 4).

The adsorption isotherms of metamitron on the clay-HA complexes are shown in Figure 3, together with the adsorption isotherm of the blank; and Freundlich adsorption coefficients are summarized in Table 6. Again, the blank CaSWy sample shows higher adsorption than the untreated sample (Table 4). The n_f values of the blank and complexes were closer and even higher than unity, indicating certain C-type character of these isotherms and higher intensity of sorption than corresponding to isolated model sorbents (Table 4). In both complexes, CaSWy-Soil HA and CaSWy-Fluka HA, adsorption increases when compared with the blank sample, although this increase is more significant in the case of the commercial humic acid (Table 6, Figure 3).

The K_{oc} of CaSWy-HA and ferrihydrate-HA are summarized in Table 6. For CaSWy-HA associations, two K_{oc} were obtained: a) $K_{oc\ tot}$, from the K_f values of the those binary associations and b) $K_{oc\ dif}$, from the difference between K_f values for the CaSWy-HA associations and that of the corresponding blank, which should give the contribution of HA to the adsorption of metamitron by the clay-HA association. $K_{oc\ tot}$ of the complexes (Table 6) are much higher than those corresponding to the isolated HAs ($K_{oc\ HA}$, Table 4), as they include the contribution of clay to metamitron sorption. $K_{oc\ dif}$ values are more similar to the $K_{oc\ HA}$ values, although they are still higher than those corresponding to the HAs.

Table 5 Distribution coefficients (l/kg) of metamitron on CaSWy, FeSWy and Fluka humic acid varying the pH of the initial metamitron solution concentration ($C_i = 1$ mM) and pH of the suspensions after 24 hours of interaction time.

Initial pH	CaSWy		FeSWy		Fluka HA	
	Final pH	K_d	Final pH	K_d	Final pH	K_d
3.0	4.3	135.3	2.7	3.6×10^3	4.4	43.6
5.3	7.3	15.9	2.8	2.3×10^3	4.6	43.4
7.3	7.3	15.7	2.9	2.2×10^3	4.6	45.5

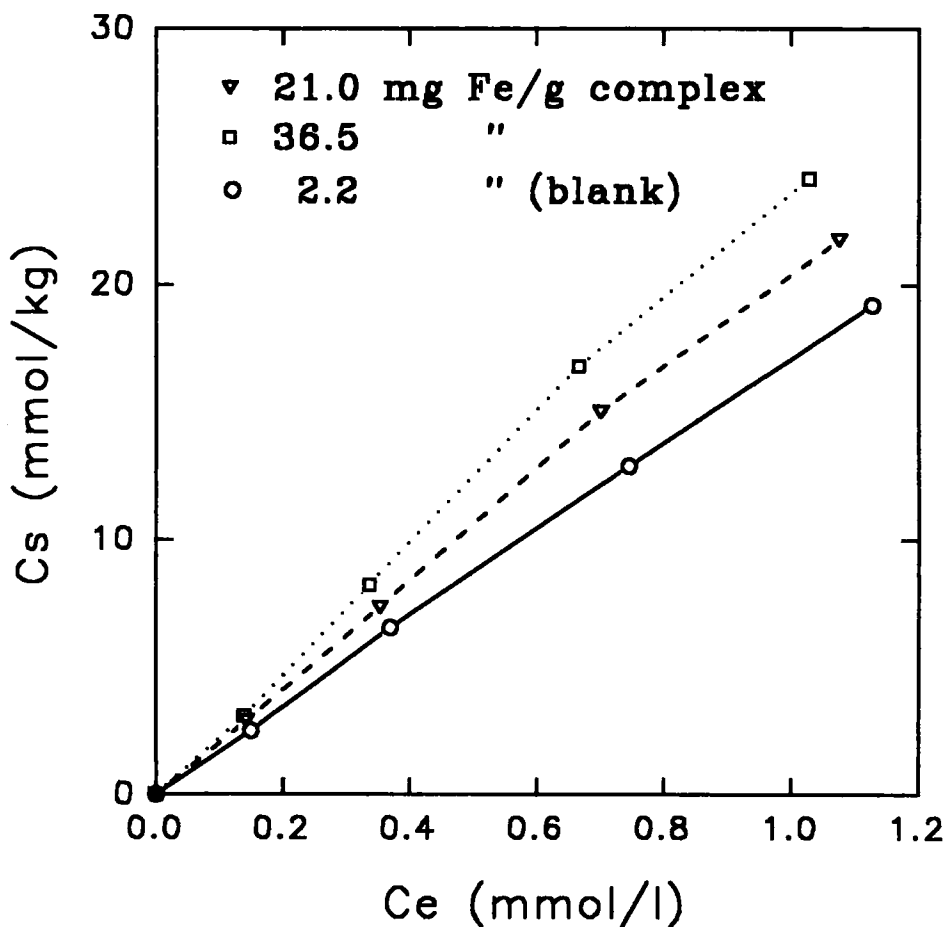


Figure 2 Adsorption isotherms of metamitron on CaSWy-ferrihydrate associations.

Table 6 Adsorption coefficients of metamitron on clay-ferrihydrate-humic acid binary complexes calculated from Freundlich equation (K_f and n_f) and distribution coefficients K_d for the ferrihydrate-humic acid complexes ($C_i = 1$ nM). K_{oc} obtained from K_f values of the CaSWy-HA and ferrihydrate-HA complexes, $K_{oc-total}$ and K_{oc} calculated from the difference between K_f of the complexes and the blank samples, K_{oc-dif}

Complex	mg Fe/g complex	K_f	n_f	K_d	$K_{oc-total}$	K_{oc-dif}
CaSWy-Ferrihydrate	21.0	20.8	1.01	—	—	—
	36.5	24.6	1.04	—	—	—
Blank	2.2	17.3	1.01	—	—	—
CaSWy-Soil HA	—	16.7	0.99	—	576	113
CaSWy-HA Fluka	—	20.8	1.14	—	630	224
Blank	—	13.4	1.05	—	—	—
Ferrihydrate-Soil HA	—	2.4	1.26	2.01	54	—
Ferrihydrate-HA Fluka	—	2.8	1.09	2.92	66	—
Blank	—	—	—	0.91	—	—

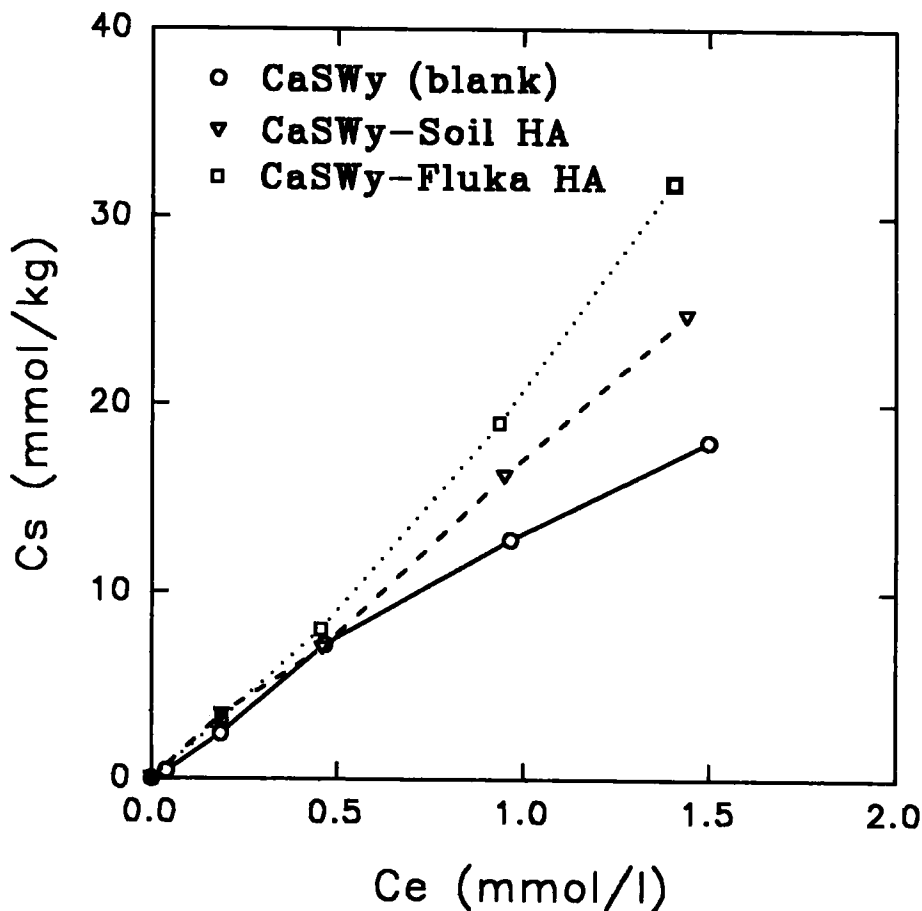


Figure 3 Adsorption isotherms of metamitron on CaSWy-Humic acid associations.

Freundlich adsorption coefficients for metamitron on ferrihydrite-HA complexes are given in Table 6. In this table are also given the distribution coefficients K_d calculated at high solid/solution ratio, since the amounts adsorbed were very low. Metamitron adsorption on the ferrihydrite-HA complexes increases when compared with the blank samples, and both adsorption coefficients, K_f and K_d , are higher in the case of the commercial HA complex than in the soil HA complex (Table 6) whereas the HAs do not show significant differences in adsorption (Table 4). Unlike for the clay-HA associations, the K_{oc} values obtained for ferrihydrite-HA associations shown on Table 6 are slightly lower than those corresponding to the isolated HAs (Table 4).

Adsorption on soil clays

Figure 4a shows adsorption isotherms of metamitron on soil clays, using a solid/solution ratio of 1 g/10 ml, and Figure 4b the adsorption isotherms on soil clay 2 before and after

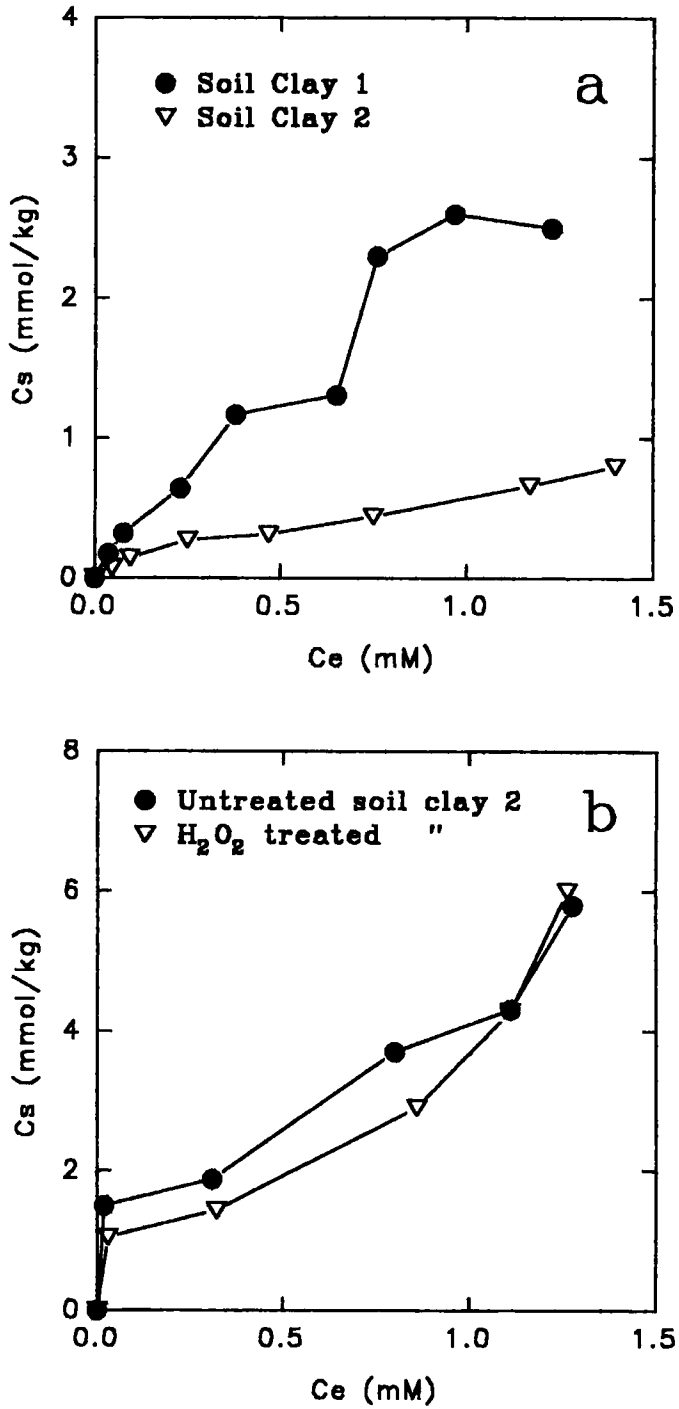


Figure 4 Adsorption isotherms of metamitron on a) soil clays 1 and 2 (1/10 soil-solution ratio) b) soil clay 2 before and after H₂O₂ treatment (1/50 soil-solution ratio).

treatment with H_2O_2 and decreasing solid/solution ratio to 200 mg/ 10 ml. Adsorption coefficients are summarized in Table 7. Adsorption is much higher in the case of the montmorillonitic clay fraction 2. Figure 4b and Table 7 show that treatment of the soil clay 2 with H_2O_2 gave rise to a slight decrease in adsorption capacity (K_f) and an increase in adsorption intensity (n_f) of the soil clay. However, at higher concentrations (Figure 4b), adsorption of metamitron on both samples seems to reach the same value. It is worth to note in this figure and table the increment in adsorption capacity (K_f) of metamitron when the solid/solution ratio is decreased, as more surface sites are being available, whereas the intensity n_f values accordingly decreases.

The K_{oc} values of the soil clays in Table 7 are different to both HA isolated and associated at high solution ratio (Tables 4 and 6), but it may be due to the different solid/solution ratio used in model sorbents. In fact, Table 7 shows that K_{oc} values at the same solid/solution ratio as the model sorbents: a) for the untreated soil clay 2 is similar to $K_{oc\ dif}$ for CaSWy-Soil HA and b) for H_2O_2 -treated soil clay 2 is similar to $K_{oc\ tot}$ of CaSWy-Soil HA (Table 6).

DISCUSSION

The herbicide metamitron adsorbs on montmorillonite and humic acid to a much greater extent when compared with illite, kaolinite and ferrihydrite (Table 4). The higher adsorption on montmorillonite than on the other clay minerals is due to the internal surfaces of smectites (not measurable by N_2 adsorption), which can be accessible to water and organic molecules such as pesticides^{10,29-35}. Sanchez-Camazano and Sanchez-Martin³⁰ reported chloridazon, a herbicide similar to metamitron, adsorbing on montmorillonite forming interlayer complexes of well defined d_{001} values. Cox¹⁵ suggested also adsorption of metamitron in the interlayer of montmorillonites, increasing with decreasing the layer charge and the polarizing power of the interlayer cation. The higher adsorption observed in the FeSWy montmorillonite (Figure 1 and Table 4) could be due to the low pH of the FeSWy-metamitron solution suspensions which, as shown in Table 5, greatly affects metamitron adsorption. This suggests protonation of metamitron close to the montmorillonite surfaces and, thus, protonated metamitron can easily be adsorbed on the interlayer of montmorillonite by a cation exchange mechanism, as observed in the adsorption of other polar herbicides on montmorillonites^{10,33,34}. This higher adsorption can also be due to the higher polarizing power of the exchangeable cation in the case of FeSWy when compared with CaSWy, which can also give rise to protonation of the molecule in the interlayer space of the montmorillonite, where the pH would be lower³⁵, and, thereby, to an increase in adsorption^{10,33-35}. These mechanisms are

Table 7 Metamitron adsorption coefficients K_f , n_f and K_{oc} obtained from adsorption isotherms on soil clay 1 and 2 (1 g/10 ml solid/solution ratio) and on soil clay 2 before and after treatment with hydrogen peroxide (200 mg/10 ml solid/solution ratio).

Soil clay	solid/solution	K_f	n_f	K_{oc}
1	1/10	0.58	0.65	210
2	1/10	2.34	0.80	82
2	1/50	4.10	0.29	144
2 + H_2O_2	1/50	3.71	0.41	407

also favoured because the Fe-SWy is not usually obtained as homoionic (Fe^{3+}) form, since the low pH of the Fe_3Cl solutions promotes that some exchangeable sites become saturated by protons. This partial proton-saturation is also produced in the preparation of the "blank", as suggested by the decrease of d_{001} value of the blank (Table 6) as compared with the untreated CaSWy (Table 4), and also explains the increase in K_f value of this blank (Table 6) with respect the untreated sample (Table 4). This could be the reason for the increase in adsorption of the clay-iron oxide complexes when the amount of Fe in the complexes is increased (Figure 2 and Table 6). Metamitron does not adsorb on ferrihydrite (Table 4) and, as shown in Table 2, there are not significant differences between the pH of the two clay-iron oxide complexes suspensions and the blank sample that could explain this increase in adsorption. During the precipitation process in the synthesis of the complexes, exchangeable Ca could be substituted by Fe cations giving rise to non-homoionic SWy montmorillonite of d_{001} intermediate between CaSWy and FeSWy (Table 1) and, thus, to greater adsorption.

Metamitron adsorbs to a greater extent on humic acid than on CaSWy montmorillonite, since, beside polar groups ($\text{C}=\text{O}$ and NH_2) interacting with both mineral and organic colloidal surfaces through polar bonds^{29,36}, the phenolic and pyridazone ring of metamitron molecule can also interact with the aromatic nuclei of the humic substances through charge transfer mechanisms and hydrophobic interactions³⁶⁻³⁸. These two mechanisms, charge transfer and hydrophobic interactions, seem to be more important than the polar bonds in metamitron sorption, since no significant differences were found in adsorption at different initial pH (Table 5), which would affect polar interactions. According to this and Table 5 values, the polar interactions seems to play more important role in the soil humic acid than in the commercial one, which agrees with more functional groups than the commercial HA, as reported elsewhere³⁹.

Although no significant differences were observed in metamitron adsorption on the different humic acids in the primary systems, clay-HA associations showed higher adsorption of metamitron in the clay-Fluka HA system than in the clay-soil HA system. In both cases, adsorption was higher than in the corresponding to the blank sample (Figure 3 and Table 6), because of the contribution of HAs, which adsorb more herbicide than CaSWy (Table 4). The higher adsorption in the clay-Fluka HA system could be due to the higher organic carbon content of the association (Table 2). The larger reduction in S_{BET} in the clay-soil HA complex when compared with the clay-Fluka HA complex (Table 2), which can be attributed in both cases to a reduction in N_2 accessible surface areas due to interassociation of the two colloidal components^{16,40,41}, suggests different degrees of association of the clay with soil humic acid (with more functional groups) and commercial HA (with more aromatic nuclei)³⁹. When the CaSWy montmorillonite was shaken for 24 hours with the humic acid solutions and absorbance of the supernatants was measured before and after the interaction, the final absorbance was lower in the case of the soil HA, indicating a higher degree of association to the clay when compared with Fluka HA. The total amounts adsorbed in the complexes were 52 mg/g clay and 17.8 mg/g clay for the soil HA and Fluka HA, respectively. The K_{oc} values for clay-HA associations (Table 6), clearly show that $K_{\text{oc tot}}$ are not valid because of the contribution of the clay mineral. Even the $K_{\text{oc dif}}$ values were found higher than those corresponding to the isolated HAs (Table 4), indicating that clay-HA association enhances the sorption efficiency of HA, being this increase more pronounced in commercial HA because of the weaker interaction of this last one with clay surfaces when compared with soil HA. The enhanced sorption efficiency ($K_{\text{oc dif}}$) of the clay-associated HA may be attributed to, upon association, HA displays more opened or flat structures^{41,42} promoting hydrophobic interactions⁴².

Metamitron did not adsorb on ferrihydrite. At the pH of the iron oxide-metamitron solution suspensions, iron oxide surfaces would be positively charged, which would explain this behaviour. Although the high S_{BET} of the iron oxide could suggest binding sites for metamitron by H-bonds between surface ferrihydrite hydroxyls and the carbonyl group of the herbicide, metamitron molecules could find steric hindrance to reach the small micropores constituting the surface of this amorphous iron oxide⁴³. The iron oxide complexes with humic acid showed, as in the case of the clay-humic acid associations, greater adsorption on the complexes with Fluka HA, despite the lower OC content of this last one (Table 3). In this case, no significant differences were observed between the S_{BET} of the two complexes, which were greatly reduced when compared with the blank sample. Absorbance measurements before and after the interaction iron oxide-humic acid solution also indicated a higher degree of association of the soil humic acid to the iron oxide than the commercial one, and the amounts of humic acid adsorbed were 35.8 mg and 18.4 mg/g iron oxide for the soil HA and Fluka HA, respectively, in agreement with the high polar character of soil humic acid. Unlike the clay-HA associations, the K_{oc} values for ferrihydrite-HA are lower than those for HAs, and the lowest K_{oc} value was found for soil HA. This can be explained because the acidic phenol and carboxylic groups of the HAs can be tightly bound to surface iron ions on ferrihydrite surface^{42,44,45} and thus the sorption efficiency of HA for metamitron by these same groups is reduced. The greater content in acidic groups of soil humic acid, as suggested by the lowest pH of its suspension (Table 3), gives rise to a higher decrease in its K_{oc} value as compared to that of the commercial one (Table 3 and 6). This last fact suggests that an important type of bonding between metamitron and humic acid could be the ionic interaction between the protonated amino group and the carboxylic group of HA.

The results obtained with model adsorbents and their associations are in agreement with adsorption studies with soil clays, which indicated higher adsorption on the montmorillonitic soil clay of higher organic carbon content (Figure 4a and Table 7) than on the illitic soil clay. When the soil clay of higher organic matter content was treated with H_2O_2 for removal of organic matter, organic carbon was reduced from 2.84% to 0.91%, since the interaction of organic matter with clay minerals results in complexes resistant to peroxidation⁴⁶ and S_{BET} increased from 53.2 to 78.0 m^2/g (Table 3), due to the elimination of organic matter shielding clay minerals surfaces. Although this treatment gives rise to an increase in surface area which might become accessible for adsorption, metamitron adsorption slightly decreased, due to the reduction in organic matter. On the other hand, the increase in metamitron adsorption when the solid/solution ratio of the clay suspensions was decreased from 1:10 to 1:50 can be due to greater dispersion of the colloidal components of the clay fraction⁴⁷⁻⁴⁹, giving rise to an increase in adsorption on the interlamellar space of the smectites, which represent 45% of the silicate clay minerals of this soil clay fraction.

The K_{oc} values (Table 7) found for soil clays at higher soil/solution ratio ranged between the values corresponding to the clay-HA ($K_{\text{oc tot}}$ and $K_{\text{oc dif}}$) and to the ferrihydrite-HA associations. Even the lowest K_{oc} value found for soil clay 2 could be related with the higher iron oxide content of this natural colloidal association. At lower soil/solution ratio, the efficiency of the colloidal organic matter increases and falls in the same range as $K_{\text{oc dif}}$ values for CaSWy-Soil HA association, but after elimination of most of the interparticle colloidal OM the K_{oc} of this soil clay increased, falling in the range of $K_{\text{oc tot}}$ values of CaSWy-Soil HA associations, indicating an increase in the contribution to sorption of metamitron of the montmorillonitic component. The low K_{oc} value of the untreated soil clay 2 seems to indicate closer associations between colloidal components in natural systems than in the model systems.

CONCLUSIONS

Results of this work show the usefulness of studying sorption of pesticides on model pure colloidal sorbents and their associations besides natural colloidal mixtures (clay fraction of soil or sediments) to interpret the role of each component in the transport/sorption process and even the interaction mechanisms at molecular level. This work also shows the importance of the mineral components of the colloidal fraction in sorption of polar organic contaminants, such as metamitron, which sometimes may be obscured or confused with adsorption on organic matter.

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