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SORPTION CAPACITY OF ORGANO-CLAYS FOR ANIONIC AND POLAR ORGANIC CONTAMINANTS

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SUMMARY

Distribution coefficients of two organic contaminants, the anionic herbicide alloxydim and the polar compound nitrophenol, showed that organic clays are good sorbents from water, through combination of both hydrophobic and polar interactions between organic contaminants and interlayer alkylammonium. Primary alkylammonium showed better efficiency than quaternary one, suggesting H-bonds between -NH and polar contaminants.

Key words: adsorption, alkylammonium, hydrophobic interactions, organo-clays, organic contaminants, polar interactions.

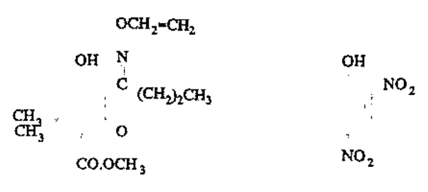
INTRODUCTION

The study of possible adsorbents to eliminate the toxics from water or to prevent or decrease their movement far from the source is a field of increasing interest. Activated carbon is one of the most effective adsorbents for organic contaminants but, in the past few years, there has been an increasing interest for designing and studying clay-based sorbents (1-8). Although organic clays has been shown mainly as good sorbents for non polar organic contaminant (1,2,4), we have reported a study of the adsorption of the acidic pesticide 2,4-dichlorophenoxy acetic acid by several organic clays (7-9) showing the potential use of these materials as sorbent for anionic or polar contaminants.

The objective of this work was to assess the adsorbent power of some organo-clays as a function of their surface properties and to relate this adsorption power with the properties of an anionic contaminant (alloxydim, herbicide) and a polar contaminant (dinitrophenol), dealing also with the adsorption mechanisms.

MATERIALS AND METHODS

Contaminants:



Alloxydim Dinitrophenol

Alloxydim is an herbicide which, due to its anionic nature, is weakly retained by soils and thus it has great risk to contaminate surface and ground waters This herbicide was used as the sodium salt of the technical product, as kindly suplied by Nippon Soda Co., Ltd.. Dinitrophenol can be found in soils and waters coming from the industry (pesticide synthesis) and from pesticide degradation. The pure compound was purchased from Aldrich.

Organo-clays:

The organic clays were prepared by treating the clay with a ethanol/water solution of the alkylammonium chloride, washing with ethanol/water and distilled water until chloride test was negative and finally freezing-dried. The organic carbon content were determined in a Hewlett-Packard microanalyzer and the basal spacings (d_{001}) by X-ray diffraction on oriented specimen obtained by drying a 2% water suspension in a glass slide. The surface properties of the clays used in this study are summarized in Table 1.

Adsorption Experiments:

Batch of 0.02 or 0.05g of clays were equilibrated with 10ml of 1mM alloxydim or DNP solutions in aqueous $CaCl_2$ 0.01 M.. Adsorption capacity (Kf) was measured by calculating the distribution coefficient, Kd, at 1mM solution concentration and the distribution coefficient in organic carbon basis, Koc, was also calculated, according to the expressions [1] and [2] respectively:

$$Kd = Cs(mmol/kg)/Ce(mM) \quad [1] \qquad \text{and} \qquad Koc = Kd \times 100/\%OC \quad [2]$$

where Cs is the amount of contaminant adsorbed by the clay as calculated from the difference between initial and final concentration (Ce) in solution.

Alloxydim and DNP concentrations in solutions were monitored by UV(290nm) and VIS (360nm) spectroscopy, respectively. The results corresponds to mean values of triplicates which were corrected by using two blank or control samples: clay in 0.01 M

$CaCl_2$ and organic contaminant in 0.01mM $CaCl_2$.

Table 1. Surface Properties of organic clays.

Origin and type	Alkyl chain[a]	CEC[b] (meq/100g)	%Organic carbon	d_{001}[c] nm
Wyoming Smectite(SWy-1)		76		
SWC18$_1$	1C18		11.4	1.61
SWC18$_2$	1C18		17.6	2.21
SWHDTM	1C16-3C1		13.6	1.76
SWTB	4C4		13.5	1.76
Arizona Smectite (SAz)		120		
SAC18$_1$	1C18		11.9	1.80
SAC18$_2$	1C18		41.1	3.68
California Hectorite(SHCa-1)		64		
HC18	1C18		19.2	1.68
Santa Olalla Vermiculite(V)		140		
VC18	1C18		16.9	1.69

[a] 1C18=Octadecylammonium, 1C16-3C1=Hexadeciltrimethylammonium, and C4=tetrabutylammonium; [b] CEC=Cation exchange capacity: a measure of the layer charge; [c] d001=basal spacing=interlayer distance of the organoclays by X-ray diffraction

RESULTS AND DISCUSSION

The results of the adsorption capacity expressed as distribution coefficients for alloxydim and DNP in the organo-clays, Kd, and in organic carbon basis, Koc, studied in each case, are shown in Table 2. This Table also summarizes the organic carbon content and the basal spacings of these clays from X-ray diffraction measurements as properties related to the sorption capacity. Figure 1 shows the diverse alkylammonium distribution in the clay interlayer, which depends on the layer charge and the alkyl chain length, as giving by the basal spacing value after Lagaly (10). As the layer charge (or CEC, Table 1) of the clay increased, for a given alkylchain, the organo-clay tends to shift from *a* to *c* structure. These cations has been shown to act as lipophilic medium trough their alkylchains (1,2,4) and as polar or ionic medium through their ammonium groups (7-9).

Table 2. Distribution coefficient Kd and distribution coefficient in organic carbon basis Koc for alloxydim and 2,4-dinitrophenol in organic clays.

Sample	%OC	d_{001} nm	Kd mmol/kg	Koc mmol/kg
Alloxydim(0.05g clay)				
$SWC18_1$	11.4	1.61	52	456
$SWC18_2$	17.6	2.21	484	2750
$SAC18_2$	41.1	3.68	16	3
VC18	15.9	1.69	8	50
DNP(0.02g of clay)				
$SWC18_2$	17.6	2.21	993	5600
$SAC18_2$	41.1	3.68	3585	8722
DNP(0.05g of clay)				
VC18	15.9	1.69	117	736
HC18	19.2	1.69	150	781
$SAC18_1$	11.9	1.80	2463	20697
SWHTDM	13.6	1.76	380	2800
SWTB	13.6	1.56	0	0

The anionic compound alloxydim is highly adsorbed by the lower layer charge, $SWC18_2$ montmorillonite, even having lower carbon content than higher charge, $SAC18_2$ montmorillonite and VC18 vermiculite. This fact indicates that the polar or ionic attraction plays a major role in the interaction as compared to the hydrophobic or non ionic interactions. Indeed, the maximum effectivity of the organic carbon content (Koc for $SWC18_2$) is obtained when alkylammonium ions are in the interlayer spaces of the montmorillonite $SWC18_2$ in pseudotrimolecular layer. These ionic interactions between alkylammonium cations and alloxydim anions should occur in the interlayer spacings since they were favoured for lower layer charge SWy-1, where the opening of the layer is easier, than in high layer charge SAz. However some hydrophobic forces contributions are also suggested by the highest Kd and Koc values obtained for $SWC18_2$ which had the higher carbon content than $SWC18_1$. This

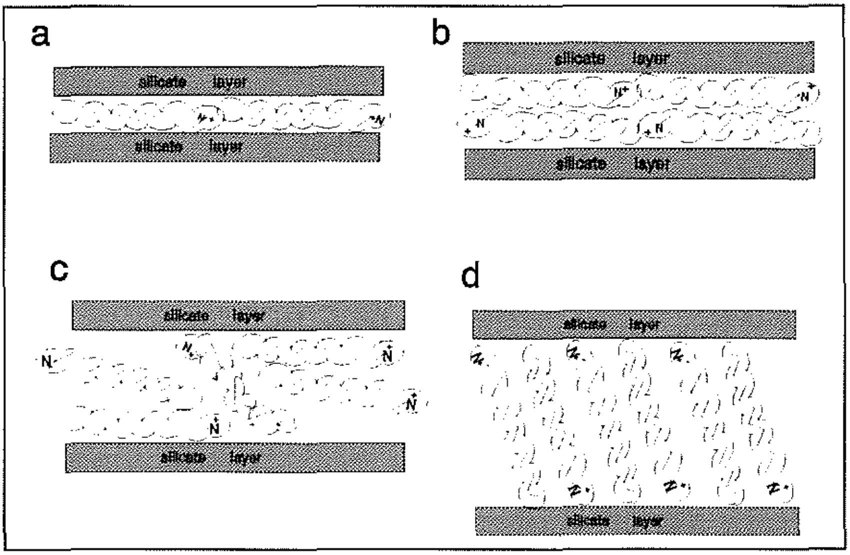


Figure 1. Alkylammonium interlayer distribution depending of the basal spacing value (d001) after Lagaly (11): a)monolayer (1.4nm), b)bilayer (1.8nm), c)pseudotrilayer (2.2nm) and d)paraffin (>2.2nm).

combined ionic and hydrophobic adsorption mechanism had been previously reported for acidic 2,4-D herbicide in organic clays (7-9). The lowest Kd and Koc obtained for $SAC18_2$ sample having the highest carbon content and the paraffinic interlayer distribution, as given by its d_{001}, suggest that in this case the ionic attraction is more important that the hydrophobic one.

The adsorption of the polar organic dinitrophenol was measured at different solid/solution ratios for the diverse organic clays (Table 3) because of the low disponibility of the clays $SWC18_2$ and $SAC18_2$ and the high adsorption detected on these samples in previous experiments. The Kd and Koc of DNP in $SWC18_2$ and $SAC18_2$ samples seem to indicate that hydrophobic forces contribute highly to this adsorption, since the highest value were found for $SAC18_2$ sample, having the maximum carbon content and the paraffinic structure of the interlayer. However the high Koc obtained for $SWC18_2$, with pseudotrilayer distribution, suggests possible contribution of polar bonds. The contribution of hydrophobic and polar bonds to DNP adsorption in organo-clays is also suggested by the Kd and Koc values obtained for the other organic clays studied at higher solid/solution ratio (0.05g/10ml).

The lower Koc found for VC18 and HC18 were possibly due to the low interlayer spacings corresponding to a bilayer and monolayer structure (Figure 1) which does not help, as pseudotrilayer or paraffinic distributions, to hydrophobic interactions between DNP molecules and the alkylchains. The highest Koc found for $SAC18_1$ seems to indicate that pseudotrimolecular layer is more effective than paraffinic one ($SAC18_2$), because DNP adsorption should not be due only to hydrophobic interactions. The contribution of polar bonds seems to be confirmed with the low value obtained for Kd in SWHDTM as compared to those of $SAC18_1$ and $SWC18_2$ of similar carbon content, even the no sorption observed in SWTB. These quaternary alkylammonium cations have not the possibility to form H-bonds, through the amino group, with the oxigen of $-NO_2$ groups of DNP .

CONCLUSIONS

This study shows that organic alkylammonium clays has good sorbents properties for the anionic herbicide alloxydim, specially low charge smectites and for dinitrophenol, specially high charge smectites. The use of proper organo-clays as filter for alloxydim and DNP contaminated water could be suggested. The adsorption of both contaminants occurs by ionic or polar and hydrophobic interactions prevailing the first for alloxydim and the second for DNP. Primary alkylammonium ions are more effective in attracting DNP than quaternary one, because the first have the possibility to H-bond amino group with nitro groups.

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