



Organo/layered double hydroxide nanohybrids used to remove non ionic pesticides

D. Chaara^{a,1}, F. Bruna^b, M.A. Ulibarri^a, K. Draoui^c, C. Barriga^{a,*}, I. Pavlovic^a

^a Dpto de Química Inorgánica e Ingeniería Química, Instituto Universitario de Química Fina y Nanoquímica (IUQFN), Universidad de Córdoba, Campus de Rabanales, Campus de Excelencia Internacional Agroalimentario, Ceia3, Edificio Marie Curie, 14071 Córdoba, Spain

^b Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS), CSIC, Avenida Reina Mercedes 10, Apartado 1052, 41080, Sevilla, Spain

^c Department de Chimie, Laboratoire LPCIE, Faculté des Sciences, BP 2121, Tetouan, Morocco

ARTICLE INFO

Article history:

Received 15 July 2011

Received in revised form 7 September 2011

Accepted 9 September 2011

Available online 16 September 2011

Keywords:

Organo/layered double hydroxide

Nanohybrid

Pesticide

Adsorption

Controlled release

ABSTRACT

The preparation and characterization of organo/layered double hydroxide nanohybrids with dodecylsulfate and sebacate as interlayer anion were studied in detail. The aim of the modification of the layered double hydroxides (LDHs) was to change the hydrophilic character of the interlayer to hydrophobic to improve the ability of the nanohybrids to adsorb non-ionic pesticides such as alachlor and metolachlor from water. Adsorption tests were conducted on organo/LDHs using variable pH values, contact times and initial pesticide concentrations (adsorption isotherms) in order to identify the optimum conditions for the intended purpose. Adsorbents and adsorption products were characterized several physicochemical techniques. The adsorption test showed that a noticeable increase of the adsorption of the non-ionic herbicides was produced. Based on the results, the organo/LDHs could be good adsorbents to remove alachlor and metolachlor from water. Different organo/LDHs complexes were prepared by a mechanical mixture and by adsorption. The results show that HTSEB-based complex displays controlled release properties that reduce metolachlor leaching in soil columns compared to a technical product and the other formulations. The release was dependent on the nature of the adsorbent used to prepare the complexes. Thus, it can be concluded that organo/LDHs might act as suitable supports for the design of pesticide slow release formulations with the aim of reducing the adverse effects derived from rapid transport losses of the chemical once applied to soils.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Agricultural pesticides are often detected in natural waters, and this has raised concerns regarding the protection of health and the environment. They are an important group of organic pollutants which production and uses are still increasing but must be controlled to minimize contamination problems [1,2]

The research of new adsorbent is a strategy to remediate the contamination of water produced by an increase in the use of pesticides to improve agriculture production.

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, consist of brucite-like layers which contain the hydroxides of divalent (M^{II}) and trivalent (M^{III}) metal ions and have an overall positive charge balanced by hydrated anion

between layers. These compounds present a general formula $[M^{II}_{(1-x)}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$ where A^{n-} is the intercalated anion. Because of the strong hydration of these inorganic ions the interlayer spaces have hydrophilic nature they resemble clay minerals. As a result, the natural clay minerals as well as LDHs show rather weak affinity to most of the non ionic organic compounds and are seldom by use as sorbents for organic compounds [3,4]

Under suitable conditions, the inorganic ions on clay minerals and layered double hydroxides can be replaced by organic ions which make the interlayer spaces become hydrophobic, [5–9]. Therefore, the adsorption ability of clay minerals and LDHs for organic pollutants can be significantly improved by modifying the interlayer. These organoclays and organo/LDHs have applications in a wide range of organic pollution control fields [10–14]

To date, there are few studies of LDHs modified with organic anions and in particular of their adsorption properties. The number of publications of organoclay (more than 2000) is much higher than organo/LDH (approx. 50) over the last 10 years (source: Citation Report of Web of Science in June 2011). However, recently the scientific interest in organo/LDH is increasing. This gives rise

* Corresponding author. Tel.: +34 957 218648; fax: +34 957 218621.

E-mail address: cbarriga@uco.es (C. Barriga).

¹ Permanent address: Department de Chimie, Laboratoire LPCIE, Faculté des Sciences, BP 2121, Tetouan, Morocco.

to an emerging research field of the hydrotalcites since the results obtained regarding its application as adsorbents of pesticides are very promising.

The organo/LDHs with suitable anion can provide interlayer spaces between 2 and 4 nm and might be considered as nanohybrids with hydrophobic characteristics in the interlayer space and external surface.

The aim of this work was to prepare different nanohybrid intercalated hydrotalcites with two organic anions: dodecylsulfate (DDS) and sebacate (SEB) and with different ratio Mg/Al = 3 and 2, to increase the charge density of the layers and consequently to increase the content of interlayer sebacate anions. These nanohybrids were used to assess the removal of alachlor and metolachlor from water, two widely used herbicides with hydrophobic characteristic. Additionally, the metolachlor has been selected to explore the release behavior from the formulation with organo/LDH nanohybrids.

2. Materials and methods

2.1. Organic anions, pesticides and soil

The organic anions used for the preparation of the organo/LDH nanohybrids containing DDS and SEB, were supplied as soluble sodium salt and acid form, respectively, by Sigma–Aldrich. The log K_{ow} values are 5.4 and 1.86 for dodecylsulfate and sebacate acid respectively.

Alachlor (2-chloro-2',6'-diethyl-N-(methoxymethyl)) and metolachlor (2-chloro-N-(6-ethyl-o-tolyl)-N-[(1RS)-2-methoxy-1-methylethyl]acetamide) are selective pre-emergence herbicides which belong to aniline herbicides. Analytical standard alachlor and metolachlor was purchased from Sigma–Aldrich. The water solubility values of alachlor and metolachlor at 25 °C are 0.110 g/L and 0.120 g/L and their log K_{ow} values are 2.9 and 3.45 respectively (data obtained from Scifinder Scholar). The molecular structures of the herbicides and organic anions used are shown in Fig. 1.

The soil used in the leaching experiments was fluvisol from the terraces of the Guadalquivir River, Córdoba (Spain). The soil was sampled (0–20 cm), air-dried, and sieved (2 mm) prior to use. It had 660 mg/kg sand, 150 mg/kg silt, 190 mg/kg clay, and 3.6 mg/kg organic matter. Soil pH was 8.7 in a 1:2 (w:w) soil:deionized water mixture.

2.2. Synthesis of the organo/LDH nanohybrids

The organo/LDHs containing DDS and SEB anions and Mg/Al = 3 and 2 respectively, were obtained by the coprecipitation method [15] using N₂ atmosphere and CO₂-free water. The samples were figured as HTDDS1 and HTSEB. For comparison purposes another organo/LDH with DDS was obtained under the same experimental conditions but without washing the precipitate. After removing the supernatant the tube containing the solid was dried. This organo/LDH was named HTDDS2. A carbonate–Mg/Al hydrotalcite (HTCO₃) was also prepared by the coprecipitation method [16] for the same purpose.

2.3. Adsorption and desorption experiments

Alachlor and metolachlor adsorption isotherms on HTDDS1, HTDDS2 and HTSEB were obtained by the batch equilibration procedure. Triplicate 20 mg adsorbent samples were equilibrated through shaking for 24 h at room temperature with 30 mL of herbicide solutions with initial herbicide concentrations (C_0) ranging between 0.1 and 0.35 mmol/L. After equilibration, the supernatants were centrifuged and separated to determine the concentration of herbicides by UV–visible spectrophotometry at 265 nm and 220 nm

for alachlor and metolachlor respectively. The amount of herbicide adsorbed (C_s) was calculated from the difference between the initial (C_0) and equilibrium (C_e) solution concentrations.

Desorption was realized immediately after adsorption from the highest equilibrium point of the adsorption isotherm and was repeated three times.

Adsorption–desorption data were fitted to the Langmuir equation:

$$\frac{C_e}{C_s} = \left(\frac{C_e}{C_m} \right) + \left(\frac{1}{C_m L} \right) \quad (1)$$

and the logarithmic form of Freundlich equation:

$$\log C_s = \log K_f + n_f \log C_e \quad (2)$$

where C_m is the maximum adsorption capacity at the monolayer coverage (mmol/g), L (L/mmol) is a constant related to the adsorption energy and K_f (mmol^{1-n_f} L^{n_f} g⁻¹) and n_f are the Freundlich constants.

2.4. Characterization of the adsorbents and adsorption products

The adsorbents HTSDS1, HTSDS2 and HTSEB and the adsorption products were characterized by different physical chemical techniques. Powder X-ray diffraction (PXRD) patterns were recorded on powder samples at room temperature under air conditions, using a Siemens D-5000 instrument with Cu K α radiation. FT-IR spectra were recorded by using the KBr disk method on a Perkin Elmer Spectrum One spectrophotometer and the ATR-FT-IR method was used for alachlor. Elemental chemical analyses for Mg and Al were carried out by atomic absorption spectrometry on a Perkin Elmer AA-3100 instrument.

DDS and SEB amounts were calculated from elemental analysis of S and C respectively, carried out on Elemental Analyse Eurovector EA 3000 instrument. The interlayer water amount was obtained from TG-curves recorded on a Setaram Setsys Evolution 16/18 apparatus, in air at the heating rate of 5 °C/min.

Scanning electron microscopy (SEM) micrographs were obtained using a JEOL JSM 6300 instrument; the samples were prepared by deposition of a drop of sample suspension on a Cu sample holder and covered with an Au layer by sputtering in a Baltec SCD005 apparatus.

2.5. Preparation of organo/LDH–metolachlor complexes

Four complexes were prepared with HTDDS1 and HTSEB and metolachlor. Two of them were based on the adsorption isotherms, figured as HTDDS1–Meto_{Ads} and HTSEB–Meto_{Ads}, and loaded with a 3% of the herbicides. The other two were prepared by mechanical mixture of the components by soft grinding of the adsorbents and the herbicides (in the same proportion as the adsorption complexes) dissolved in acetone and then were let the solvent evaporate. These figured as HTDDS1–Meto_M and HTSEB–Meto_M.

2.6. Bath release experiments

The release of metolachlor into water from the organo/LDH–herbicide complexes was compared with the release of the herbicides as a free (technical) product. For this purpose, 0.18 mg of metolachlor as organo/LDHs–herbicide complexes or as a technical product was added to 500 mL of distilled water. The experiments were conducted as described by Bruna et al. [17]. The herbicide concentration was determined by HPLC using a Waters 1525 chromatograph coupled to a Waters 2996 diode-array detector and UV detection at 220 nm for metolachlor.

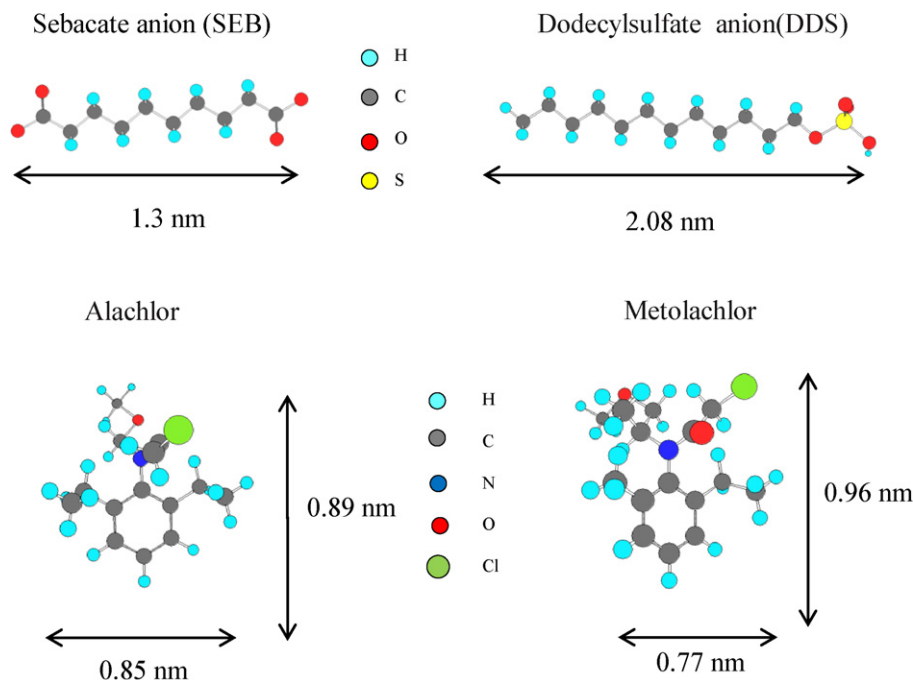


Fig. 1. The molecular structure of organic anions and herbicides.

2.7. Soil-column leaching experiments

Leaching experiments were conducted as described by Bruna et al. [17]. The calculated pore volume of the columns after saturation was 68 ± 2 mL. The leaching experiment was conducted in triplicate and the concentrations of metolachlor were analysed by HPLC.

3. Results and discussion

3.1. Characterization of organo/LDH nanohybrid sorbents

3.1.1. Elemental analysis

The results of elemental analysis for the nanohybrids used as adsorbents are shown in Table 1 together with other characteristics.

The organic anion was determined from the ratio S/Al for the samples HTDDS1 and HTDDS2, and from C/Al for the HTSEB sample. The content of S indicates that the layer charge in HTDDS1 is not balanced only by the organic anion. The exchange percentage in the product was 92% based upon anion exchange capacity (AEC). However, in HTDDS2 it was 100% and the amount of S was higher than required to compensate the layer charge suggesting the precipitation of sodium dodecylsulfate, as it is indicated in Table 1. The elemental analysis of C for the HTSEB sample indicated a small excess of sebacate to compensate the layer charge which could be considered as precipitated salt as has been shown in Table 1. The proposed formulae were obtained from the elemental analysis, assuming that all the positive charge is compensated by the maximum amount possible of dodecylsulfate and sebacate anions for HTDDS and HTSEB respectively. The amount of water was attained from TG data (not included) and metal content analysis.

3.1.2. X-ray diffraction

The PXRD patterns of the organo/LDHs included in Fig. 2 together with HTCO_3 show that they are typical hydroxylaluminum-like compounds. The reflections for HTCO_3 were indexed on the basis of a hexagonal unit cell with a and c parameters 0.304 nm and 2.34 nm respectively. The corresponding values of the basal

spacing $d_{(003)}$ for the organo/LDH adsorbents are also included in Table 1. As expected, the positions of the basal reflections of all the prepared organo/LDHs are shifted to smaller 2θ reflection angles regarding carbonate hydroxylaluminum, which reveals expansion in the interlayer distances, moreover several harmonics are also observed indicating well ordered structure. The van der Waals end-to-end length of dodecylsulfate anion estimated was 2.08 nm taking into account that the LDH layer thickness is 0.48 nm so the dodecylsulfate chains can fit perfectly in the perpendicular direction and

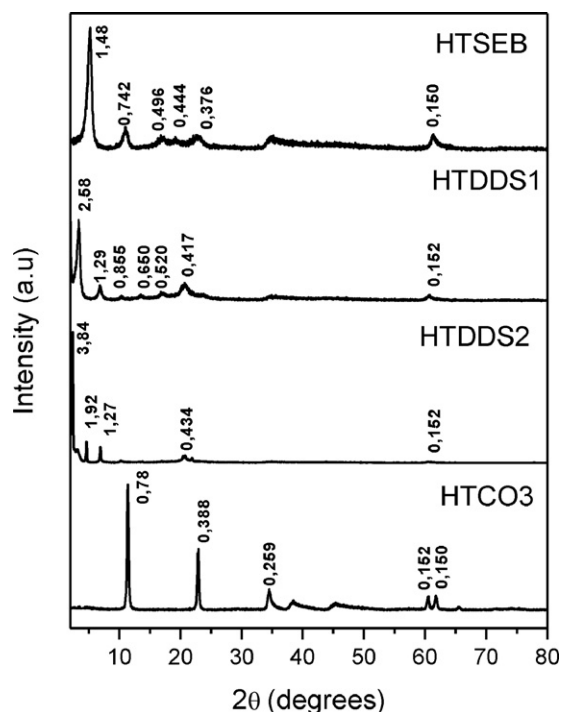


Fig. 2. PXRD patterns for the samples HTDDS1, HTDDS2, HTSEB and HTCO_3 .

Table 1
Chemical composition of adsorbents, structural data and proposed formulae.

Sample	wt.%					Atomic ratio			d_{003} (nm)	d_{110} (nm)	Proposed formulae
	Mg	Al	N	S	C	Mg/Al	S/Al	C/Al			
HTDDS1	11.1	3.9	–	4.2	27.1	3.2	0.9	15.7	2.58	0.152	$[\text{Mg}_{0.76}\text{Al}_{0.24}(\text{OH})_2](\text{C}_{12}\text{H}_{25}\text{SO}_4)_{0.22}(\text{CO}_3)_{0.01}\cdot 0.83\text{H}_2\text{O}$
HTDDS2	9.0	3.3	0.35	5.9	31.3	3.1	1.5	21.7	3.84	0.152	$[\text{Mg}_{0.76}\text{Al}_{0.24}(\text{OH})_2](\text{C}_{12}\text{H}_{25}\text{SO}_4)_{0.24}\cdot 0.79\text{H}_2\text{O}^a$
HTSEB	13.5	18.1	–	–	18.9	1.9	–	5.3	1.48	0.150	$[\text{Mg}_{0.65}\text{Al}_{0.35}(\text{OH})_2](\text{C}_{10}\text{H}_{16}\text{O}_4)_{0.175}\cdot 1.36\text{H}_2\text{O}^b$
HTCO ₃			–	–		2.7	–	–	0.78	0.152	$[\text{Mg}_{0.73}\text{Al}_{0.27}(\text{OH})_2](\text{CO}_3)_{0.135}\cdot 0.64\text{H}_2\text{O}$

The excess of S corresponds to

^a 0.122NaC₁₂H₂₅SO₄ per FW and the wt.% of N to 0.05NaNO₃.

^b The same for the sample HTSEB.

the chains could be in an all-trans conformation [6] in the HTDDS1 sample with a basal spacing of 2.58 nm (Table 1).

However, for the HTDDS2 sample a basal spacing of 3.84 nm was observed, similar to those obtained in previous studies [18,19], which could suggest that there is a bilayer arrangement with a slant angle $\alpha = 60.4^\circ$ between the chain of DDS and the surface of the layer [20,21]. A schematic arrangement of the anions on modified hydrotalcites (nanohybrids) is included in Fig. 3.

For the HTSEB sample a basal spacing 1.48 nm was observed. This lead to a gallery height of 1.0 nm so the anions could be considered as monolayer in a vertical position and tilted towards the brucite-like layers according to the length of sebacate (≈ 1.3 nm) [17], the slant angle required is $\sin^{-1}(1.0/1.3) = 50.3^\circ$. The basal spacing was lower than that obtained for an organohydrotalcite with a ratio Mg/Al = 3.2, $d_{003} = 1.58$ nm by Bruna et al. [17]. This can be due to the difference of the layer charge and/or the dried treatment in each case [18]. The value of spacing corresponding to (1 1 0) reflection, included in Table 1, agrees with the metal ratio, which increases slightly as charge density decreases.

3.1.3. FT-IR spectroscopy

Fig. 4 shows the FT-IR spectra of the organo/LDH samples (HTDDS1 is not included because it is almost equal to HTDDS2). The data reveal the LDH-like structure of all adsorbents with the corresponding interlayer anions (DDS and SEB) as reported previously [22–25]

3.1.4. Scanning electron microscopy

The SEM images, included in Fig. 5, showed that the HTCO₃ sample consisted of thin plate-like crystal with an irregular shape and size <10 μm (Fig. 5a) and that the HTDDS1 and HTSEB (Fig. 5b and d) are very similar. In contrast, the HTDDS2 (Fig. 5c) particles formed aggregated via hydrophobic interactions and the surfaces are more diffused. This suggests that an excess of DDS could coat the outer surfaces and gives rise to crystallized NaDDS (not observed by PXRD) when the sample were separated by centrifugation and dried as has been noted by other authors [18,26].

3.2. Study ofalachlor and metolachlor removal with HTDDS and HTSEB

3.2.1. Adsorption of herbicides by HTDDS1 and HTDDS2

Alachlor and metolachlor adsorption tests were carried out with the HTDDS1 and HTDDS2 sorbents and HTCO₃ for comparison purposes. The herbicides adsorption on the inorganic hydrotalcite, HTCO₃ was negligible (data not included) as has been observed for carbetamide [15]. This confirmed that the transformation of the hydrotalcite interlayer from hydrophilic to hydrophobic increases its affinity for non-ionic compounds such asalachlor and metolachlor.

The influence of pH onalachlor and metolachlor adsorption was examined at an initial value of 3, 11 and the pH value of the corresponding herbicide solution (~ 6 foralachlor and 7 for metolachlor). The final pH was tested for each experiment, and the maximum value obtained was 9.5, it was consistent with the buffering properties of hydrotalcites. The results (not shown) indicated that adsorption was not significantly affected by the initial pH. This led us to adopt an initial pH 6 and 7 foralachlor and metolachlor respectively for all adsorption tests.

The kinetic results are included in Fig. 6a for adsorption of herbicides in HTDDS1 and HTDDS2 showing that the adsorption process was quite fast in both cases and the equilibrium can be reached at 4 h foralachlor and 6 h for metolachlor, because of the higher hydrophobic character of metolachlor which has slower adsorption rates in water and the bulky molecules of the metolachlor makes its diffusion more difficult. Moreover, an increase of the herbicides concentration gives rise to an increase on the amount of adsorbed herbicides in all cases. The Cs values obtained by adsorption on HTDDS1 were slightly higher than those obtained for HTDDS2, in spite of that the interlayer space being lower for HTDDS1. However, different aggregated species can be formed according to the amount or concentration of DDS organic anion in the synthesis process of nanohybrid (admicelles, hemicelles or mixed hemicelles) [27]. As has been noted by Moyo et al. [28], intercalation of organic compounds creates diverse types of

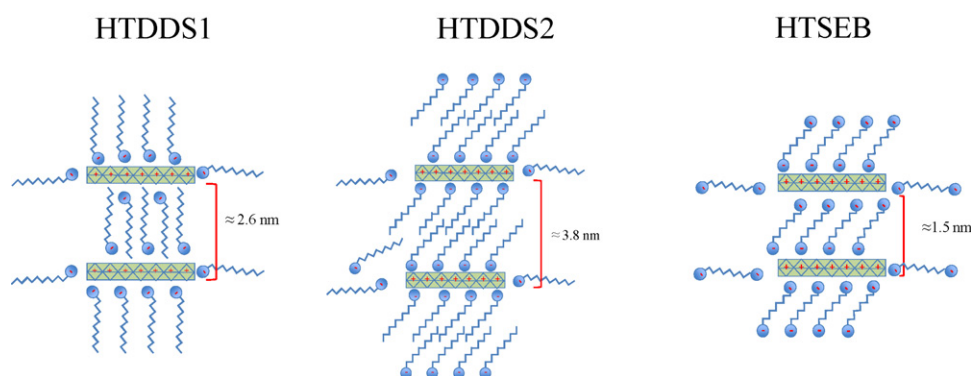


Fig. 3. Schematic arrangement of DDS and SEB anions on the prepared adsorbents.

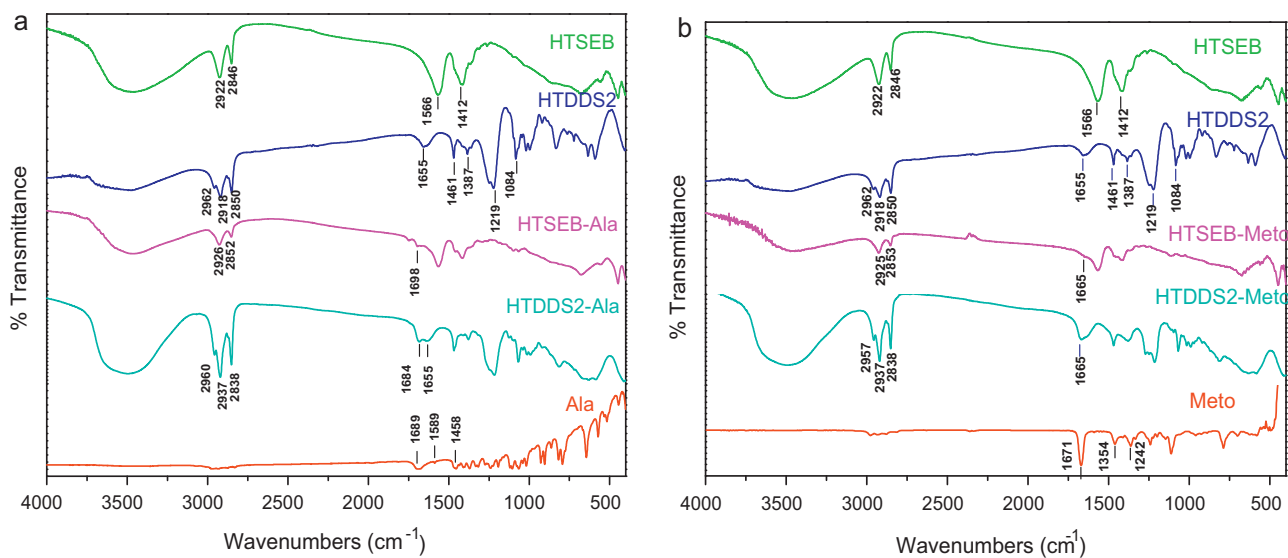


Fig. 4. FT-IR spectra of the adsorption products of (a) alachlor and (b) metolachlor on the HTDDS2 and the HTSEB adsorbents. The sodium dodecylsulfate, sebacic acid and the herbicides spectra are also included.

supramolecular structures in the clay interlayer. The intercalation of surfactants such as DDS from aqueous solution can be considered as a change in the nature of the micelle structure from spherical to lamellar [29]. Under suitable experimental conditions the

formation of double layers over the surface of the solid is favoured. The formation of double layer of surfactant in the interlayer space of HTDDS2 adsorbent, as has been confirmed by X-ray diffraction, gives rise to negative charges on the surface of organic/LDH [18,30]

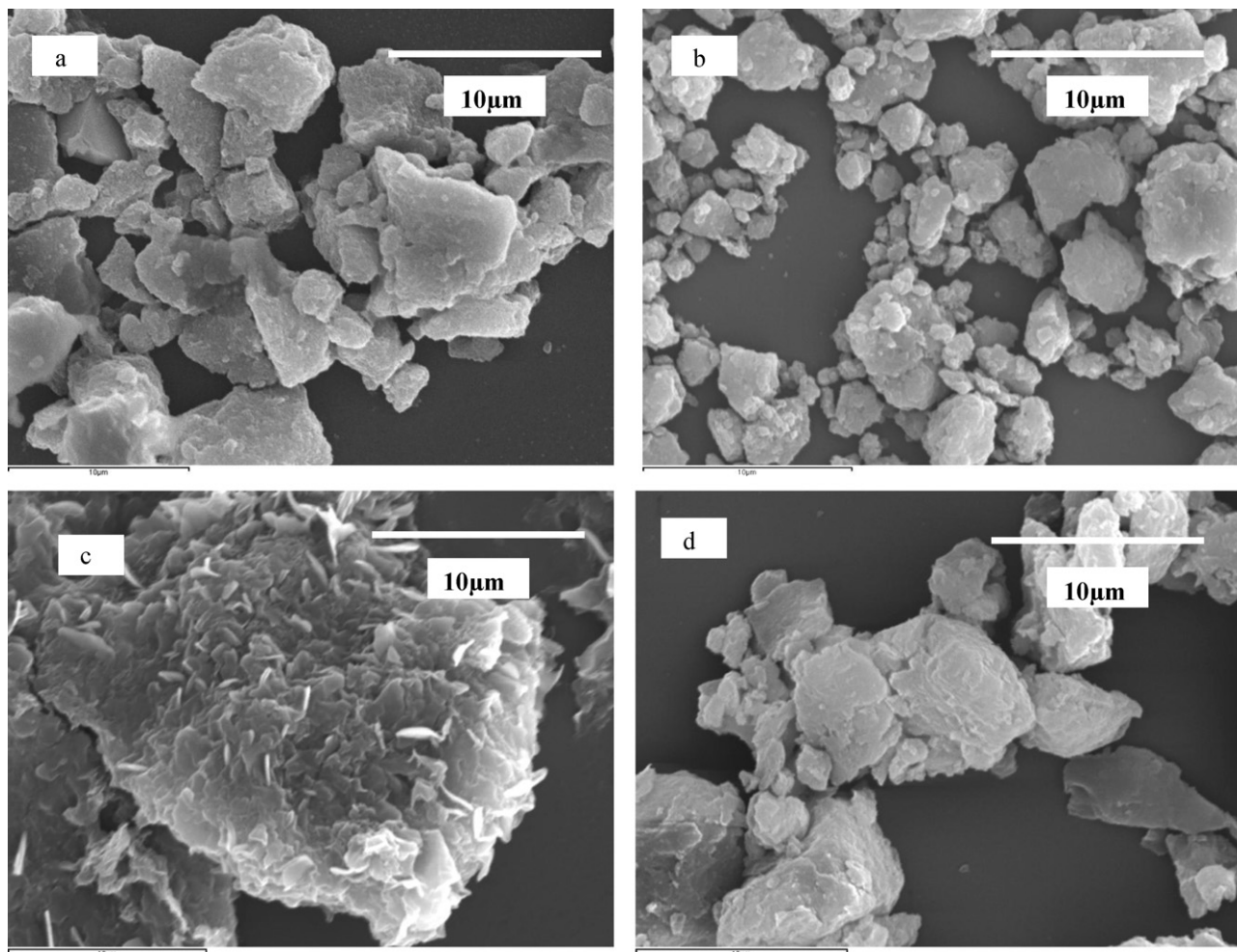


Fig. 5. SEM images of the (a) HTCO_3 , (b) HTDDS1, (c) HTDDS2 and (d) HTSEB samples.

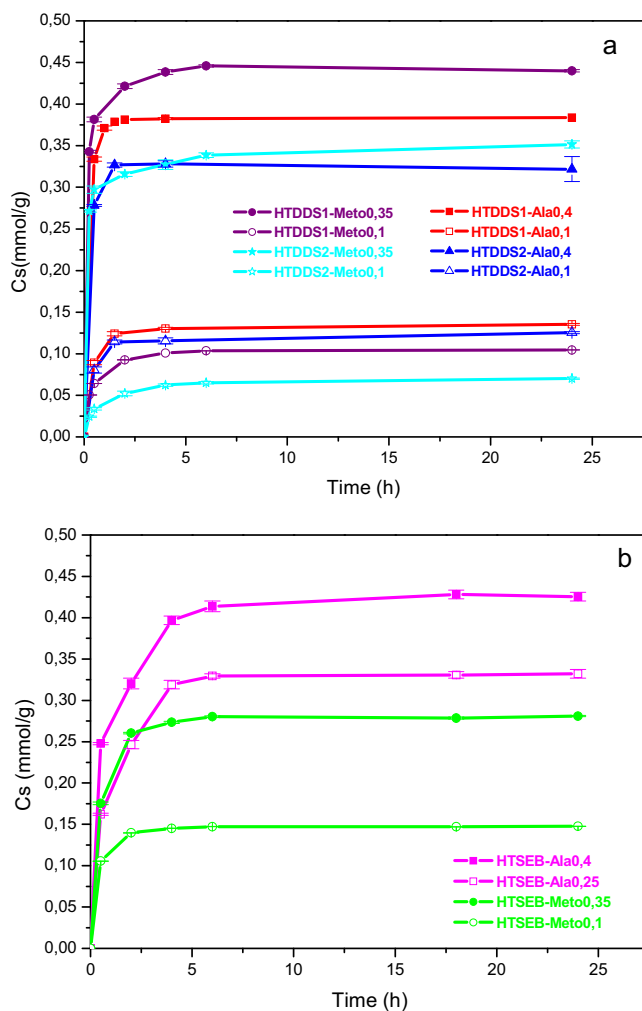


Fig. 6. The kinetic results for the adsorption process for (a) alachlor and (b) metolachlor on HTDDS1, HTDDS2 and HTSEB adsorbents.

and consequently a decrease of the adsorption of the low polar herbicides will be observed. On the other hand, the formation of monolayer hemicelles favours the herbicide adsorption on the alkyl chain, which is oriented towards the interphase solid–water as in the HTDDS1. The results of Fig. 6a show that the amount of herbicide adsorbed was higher for metolachlor than alachlor by HTDDS. This is likely due to the higher similarity of hydrophobic character of metolachlor and the organic anion DDS, which favour the hydrophobic interactions.

The adsorption isotherms are shown in Fig. 7 and the experimental adsorption data were fitted to the Freundlich and Langmuir adsorption models (Table 2). The correlation coefficients (R^2) for the Freundlich equation ranged from 0.91 to 0.98 and for Langmuir from 0.97 to 0.99. Therefore the adsorption isotherm will be discussed in function of the Langmuir equation which best described the observed data.

The isotherms for alachlor on HTDDS1 and HTDDS2 included in Fig. 7a correspond to the L-type [31]. The adsorption processes for metolachlor on HTDDS1 and HTDDS2 (Fig. 7b) are similar and the isotherms correspond to C-type indicating a partition mechanism between the aqueous solution and the organo/LDH. This type of isotherm is very common when the increase of the concentration is limited by the low solubility of the herbicide. A similar behavior was observed for adsorption of metolachlor on berberine-montmorillonite by Rytwo et al. [32]. The amounts adsorbed of alachlor ($C_s = 0.39$ mmol/L) and metolachlor ($C_s = 0.38$ mmol/L) on

HTDDS1 were slightly higher than on HTDDS2 ($C_s = 0.31$ mmol/L for alachlor and $C_s = 0.36$ mmol/L for metolachlor), which is in accordance with the orientation of the DDS molecules in the solid water interphase as was previously mentioned. The HTDDS2 adsorbent, with the bilayers of DDS anions, presents its negative charges towards the solution, so the hydrophobic interaction is less favoured in this case while for HTDDS1 the aliphatic chains oriented towards the solution enable its interaction with the non-ionic molecules of the herbicides (alachlor and metolachlor).

3.2.2. Adsorption of herbicides by HTSEB

Alachlor and metolachlor adsorption tests were carried out with the HTSEB nano-hybrid. The influence of pH was studied in the same way as in the case of HTDDS in the previous section and similar results were obtained. The adsorption process was carried out at initial pH 6 and 7 for alachlor and metolachlor respectively. The kinetic results showed that the adsorption was very fast in both cases (Fig. 6b); there was no appreciable influence of the size of the herbicide molecules to reach equilibrium. An increase of the herbicides concentration gives rise to an increase in the amount of adsorbed pesticides.

The isotherms of alachlor and metolachlor on HTSEB (Fig. 7c) correspond to L-type, this indicates that the adsorption occurs at the specific sites of the adsorbents. However, it could be observed that in the case of HTSEB–Meto the adsorbed amount ($C_s = 0.28$ mmol/L) was the lowest, but the shape of the adsorption isotherm according to Giles et al. [32] was the H-type (special L-type) indicating high affinity between the adsorptive and adsorbent, thus the metolachlor at low concentrations (0.1 and 0.15) was totally adsorbed.

The maximum amount of adsorbed alachlor ($C_s = 0.43$ mmol/L) was higher than for metolachlor ($C_s = 0.28$ mmol/L) on HTSEB. That can be due to the bulky molecules of metolachlor herbicide in respect to the lower interlayer space of adsorbent HTSEB makes its diffusion more difficult.

3.2.3. Desorption experiments of herbicides by the organo/LDH nano-hybrids

Desorption processes for both herbicides by HTDDS1 and HTDDS2 are included in Fig. 7a and b, which show that they are reversible for metolachlor according to similar hydrophobic character of pesticide and organic anions DDS. However, the desorption processes were highly reversible for HTSEB, according to the isotherm included in Fig. 7c, the negative hysteresis observed could be explained like an experimental artefact [33]. These results agreed with relative weak hydrophobic-type interaction of the herbicides molecules on the interlayer organic phase of the adsorbents and a similar behavior has been observed by terbutylazine in adsorbents alike and by modified montmorillonites [34].

3.3. Characterization of the adsorption products

The PXRD patterns of the adsorption products are included in Fig. 8. The interaction with the herbicides did not modify significantly the interlayer space for HTDDS1 (PXRD pattern not included) however for HTDDS2 the interlayer decreased to the value ($d_{003} = 2.53$ nm) close to a phase with the monolayer of the DDS anion. The contact time (24 h) between the herbicide solutions and the solid adsorbents in the adsorption test is enough to reorganize the interlayer space together with a decrease of the surfactant concentration. The decrease of the surfactant concentration produces the transformation of the bilayer into a monolayer of surfactant on the external surface of LDH (as hemicelles) [26,27] and the presence of monolayer of this surfactant in the interlayer space was confirmed by PXRD. These conditions acted as a washing process, part of dodecylsulfate was dragged by the aqueous

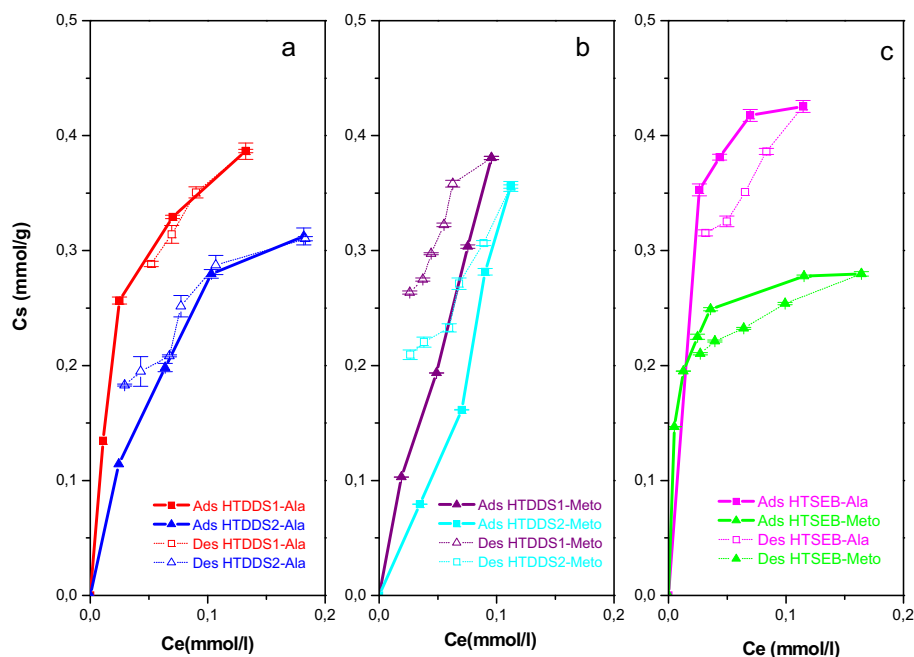


Fig. 7. The isotherms of alachlor and metolachlor on HTDSD1, HTDSD2 and HTSEB adsorbents.

solution and meant that both adsorption products became similar for the two sorbents (HTDSD1 and HTDSD2).

The adsorption of alachlor and metolachlor does not cause an important change in the interlayer spacing of the HTDSDs. The interlayer spacing of HTDSD1 and HTDSD2 is considerably larger than the pesticide molecules (see Fig. 1), therefore their incorporation can be considered in the edge of the particle tied to the alkyl chain of dodecylsulfate [19]. This has been observed in the adsorption of other non-ionic herbicides [15,17,35]

The PXRD patterns, included in Fig. 8, of the adsorption complexes with HTSEB showed a basal spacing of 1.87 nm and 1.84 nm for alachlor and metolachlor respectively, indicating that the adsorption of herbicides produced an increase in the interlayer space. This can be due to accommodation of the pesticide molecules between the HTSEB. Furthermore, the bigger interlayer space of HTDSD and/or the free hydrophobic chain enabled an easier interaction with the herbicides, without the modification of the interlayer, than in the case of HTSEB with a lower value of interlayer spacing. Instead, the HTSEB adsorbent has more free space in the interlayer between the organic anions. The number of mole per formula weight requests to balance the positive charges of the hydroxide layers is half for sebacate than dodecylsulfate due to the double charge of sebacate anion, considering the same layer charge density of the LDH. Therefore, the intercalation of the herbicide molecules in the free space between the sebacate anion [35] is favoured and gives rise to an increase of the interlayer space.

However, a high packing of the organic anion in HTDSD prevents the incorporation of the herbicide molecules into the interlayer space.

The FT-IR spectroscopy (Fig. 4) data show that characteristic bands corresponding to DDS and SEB anions are present in the adsorption products and that there is no noticeable change in respect to the adsorbents. Moreover, the herbicides are identified on the adsorbents in agreement with the presence of its characteristic bands as can be seen in Fig. 4. A light shift of the C=O vibration band from 1689 cm^{-1} and 1671 cm^{-1} in pure alachlor and metolachlor respectively to 1684 and 1665 cm^{-1} for the adsorption complex was observed on HTDSD-herbicide adsorption products. This could be due to the interactions between the pesticides and the organo/LDH similarly to the pesticides bounded to organoclay [34].

The intensity of the band corresponding to vibration mode C=O decreased for alachlor and metolachlor adsorbed by HTSEB and simultaneously the position of the band due to stretching vibrations of C-H bonds of aliphatic chains of sebacate is slightly shifted (from 2922 and 2846 cm^{-1} to 2926 and 2852 cm^{-1} for alachlor and 2925 and 2853 cm^{-1} for metolachlor which is indicative of the interactions between them.

These results confirm that the alachlor and metolachlor molecules has been adsorbed in the organo/LDHs studied, although the interlayer arrangement differed in the HTDSD and HTSEB adsorbents

Table 2
The parameters of Freundlich and Langmuir.

	Freundlich			Langmuir		
	$1/n_f$	K_f	R^2	C_m (mmol/L)	L	R^2
HTDSD1-Alachlor	0.40 ± 0.08	0.85–1.10	0.91	0.48 ± 0.02	36 ± 5	0.98
HTDSD2-Alachlor	0.52 ± 0.06	0.85–0.99	0.92	0.43 ± 0.01	14.5 ± 1.2	0.99
HTDSD1-Metolachlor	0.79 ± 0.06	1.33–1.58	0.98	0.8 ± 0.3	8 ± 5	0.98
HTDSD2-Metolachlor	0.86 ± 0.09	1.26–1.59	0.97	0.9 ± 0.3	4.5 ± 2.1	0.97
HTSEB-Alachlor	0.13 ± 0.02	0.76–0.81	0.94	0.4500 ± 0.0003	126 ± 11	0.97
HTSEB-Metolachlor	0.17 ± 0.02	0.65–0.71	0.92	0.2700 ± 0.0001	218 ± 15	0.98

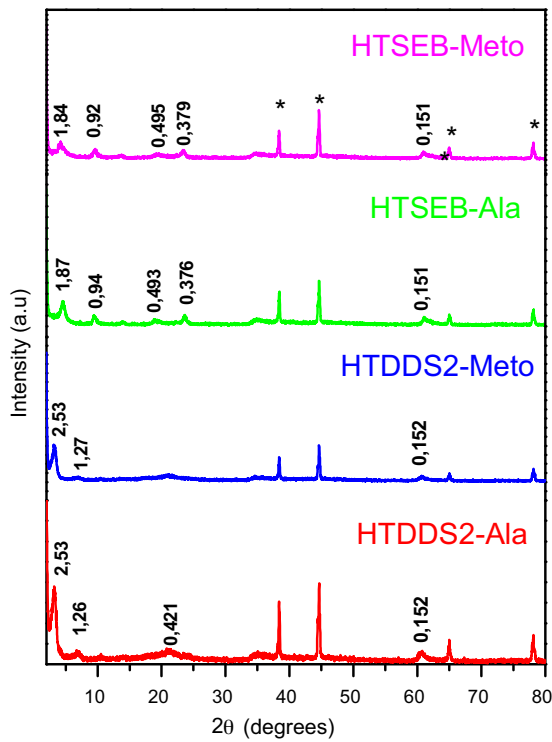


Fig. 8. PXRD patterns of the adsorption products of alachlor and metolachlor on HTDDS2 and HTSEB. (*) Al sample holder.

3.4. Desorption experiments in water and lixiviation in soil

The kinetic of release of metolachlor into water under static conditions from the complexes prepared HTDDS1-Meto_{Ads} and HTSEB-Meto_{Ads} is shown in Fig. 9a. Additionally, a free (technical) product and the mechanical mixture HTDDS1-Meto_M and HTSEB-Meto_M, which were used for comparison purpose, are also included in Fig. 9a. The release from free (technical) product was instantaneous but the evolution of the release was slower from the mechanical mixed complexes. The concentration of the herbicide for complex HTDDS1-Meto_M and HTSEB-Meto_M was similar for both and reaches 90% of the total load of metolachlor. The most prominent difference in the release kinetic was between HTDDS1-Meto_{Ads} and HTSEB-Meto_{Ads}, despite the same preparation method on these complexes. The HTSEB-Meto_{Ads} (8.5%) presents a slower release of the herbicide than HTDDS1-Meto_{Ads} (26%) in the first 12 h (see insert in Fig. 9a). 72% of metolachlor was released after 8 days from HTSEB-Meto_{Ads} against 99% from HTDDS1-Meto_{Ads}. This difference in the behavior of the herbicide release may be explained by the fact that the metolachlor molecules are trapped between the sebacate chains for the complex HTSEB-Meto_{Ads} as was indicated before while for the complex HTDDS1-Meto_{Ads} there is an adsolubilization [36] of the metolachlor on the external surface of the particles. These results are in agreement with the PXRD results that indicated a modification of the interlayer spacing for HTSEB-Meto_{Ads} but not for HTDDS1-Meto_{Ads}.

Fig. 9b and c show the metolachlor breakthrough curves (BTCs) for HTDDS1-Meto_{Ads}, HTSEB-Meto_{Ads} and the free (technical) product. These formulations have been selected because they appeared to be those that released the herbicide more slowly in the batch release study, Fig. 9a. Metolachlor applied as organo/LDH complexes resulted in lower maximum concentrations in the leachates with respect to the application of the herbicide as free product (Fig. 9b). The maximum concentration of metolachlor in

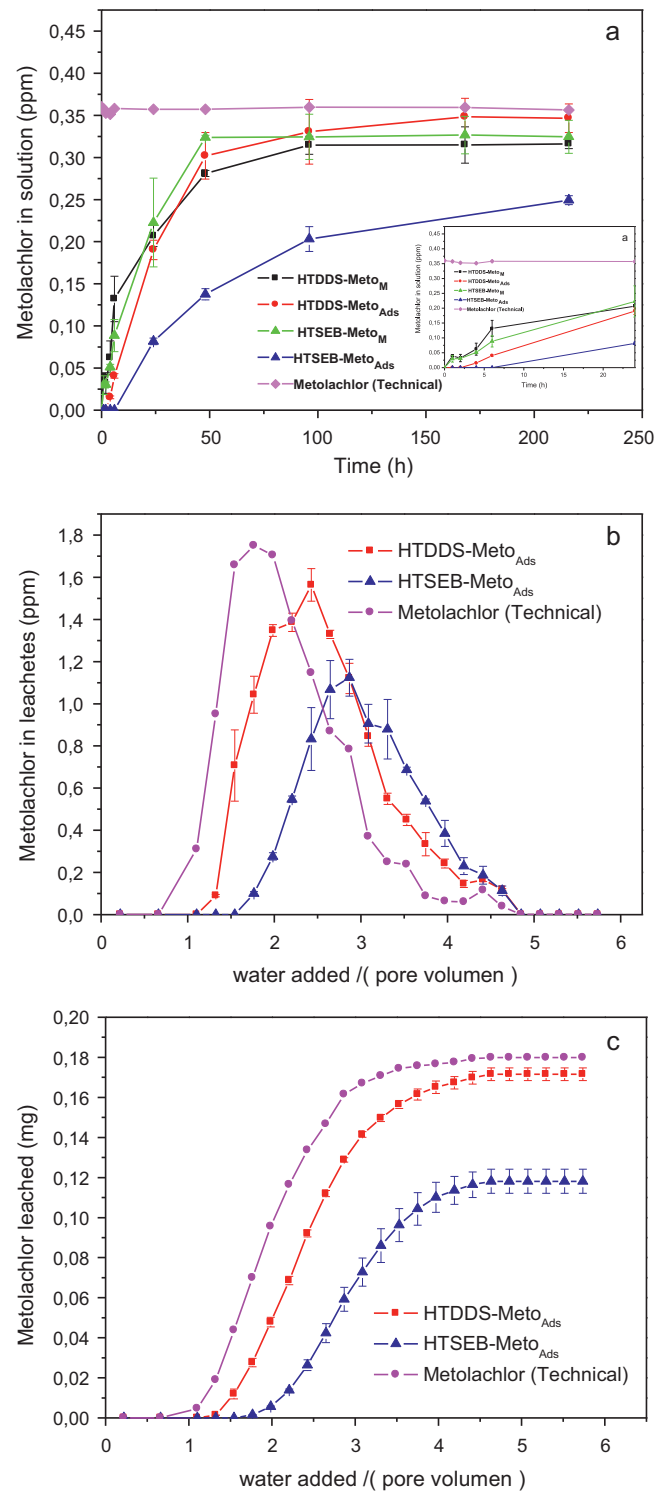


Fig. 9. (a) Metolachlor release kinetics into water from its complexes with HTDDS1 and HTSEB. (b) Metolachlor breakthrough curves (BTCs) after application to soil columns as a free (technical) product and as organo/LDH-metolachlor complex (c) cumulative BTCs.

leachates was reduced from 1.76 ppm, for the technical, to 1.56 ppm or 1.12 ppm for the HTDDS1-metolachlor and HTSEB-metolachlor complexes, respectively. Fig. 9b also shows that the maximum of the BTCs of the complexes is shifted towards larger volumes of added water, at 120 mL of added water in the commercial formulation, 165 mL in the HTDDS1-Meto_{Ads} and 195 mL in the HTSEB-Meto_{Ads}. This shift of the BTCs is an important feature,

because it indicates that the leaching of metolachlor was retarded by the application of the herbicide as organo/LDH complexes.

Cumulative BTCs (Fig. 9c) show that the amount of metolachlor accumulated in leachates was 99% of the amount applied to the soil as free (technical) product. This amount was a little less (95%) for HTDDS1–Meto_{Ads}, but reached only 66% when the complex applied was HTSEB–Meto_{Ads}. The amount leached was greater for HTDDS1–Meto_{Ads} than for HTSEB–Meto_{Ads}. This might be due to the type of interaction between the herbicide and the organo/LDH complex in each case. The metolachlor molecules could be trapped between the sebacate ions and a greater fraction of irreversibly adsorbed herbicide in HTSEB–Meto_{Ads} complex was retained compared to the HTDDS1–Meto_{Ads}. The amounts of metolachlor extracted from the soil columns at the end of the leaching experiments were less than 3% so the amount not recovered probably corresponded to the degradation of the herbicide within the soil column and/or the formation of strongly bound herbicide residues.

The results of the columns leaching test confirm that the sustained release of metolachlor from the formulation based on HTSEB–Meto_{Ads} retards the vertical movement of the herbicide through soil columns and reduce the total leaching losses of the herbicide.

4. Conclusions

The organo/LDH nanohybrids containing dodecylsulfate and sebacate were prepared and its structure confirmed by different characterization techniques. The interlayer spacing of organo/LDH nanohybrids range 1.5–3.8 nm presents suitable characteristics to remove alachlor and metolachlor. The adsorption tests conducted showed that a noticeable increase of the adsorption of the non-ionic herbicides by organo/LDH was produced with respect to inorganic LDHs. Two different arrangements of DDS ions on HTDDS1 and HTDDS2 were proposed (monolayer and bilayer) but finally after the adsorption process the products had the same arrangement of the interlayer anions.

The amount of herbicide adsorbed was higher for metolachlor than alachlor on HTDDS. This is likely due to the similar hydrophobic character of metolachlor and the organic DDS anions, which favour interactions between the pesticide and the organo/LDH. However, the adsorbed amount of metolachlor was lower than alachlor by HTSEB. The adsorbed amount of herbicides and the incorporation in the interlayer strongly depended on the herbicide structures and the properties of the organic anion which modifies the LDH, as well as the arrangement of the DDS and SEB in the organo/LDHs hybrid interlayers. On the other hand, the results obtained in the slow release experiments show that the HTSEB–Meto_{Ads} formulation has a controlled release behavior indicating potential applications as prolonged release vehicles for pesticide targeting.

The design and optimization of the chemical structure of organo/LDH nanohybrids could be considered very interesting as nanocarriers of non-ionic pesticides. Therefore, this research line is an open way to study the non-ionic pesticide interaction with the organo/LDH and design of formulations to improve the use of pesticide regarding agronomical and environmental issues.

Acknowledgements

This work was partially funded by MCI (AGL2008-04031-CO2-02) and J. Andalucía through Research Groups FQM-214 and RNM-124. D. Chaara acknowledges MAEC (Spain) a grant from AECID to research in Universidad de Córdoba (Spain). We appreciate the technical assistance received in the SCAI (Universidad de Córdoba) for Electron Microscopy and Elemental Analysis Units.

References

- [1] J. Cornejo, R. Celis, L. Cox, M. Hermosin, Pesticide-clay interactions and formulations, in: F. Wypych, K. Satyanarayana (Eds.), *Clay Surfaces: Fundamentals and Applications*, Interface Science and Technology, Elsevier Academic Press, Amsterdam, 2004, pp. 247–266.
- [2] G. Lagaly, Pesticide-clay interactions and formulations, *Appl. Clay Sci.* 18 (2001) 205–209.
- [3] H. Zhao, G. Vance, Intercalation of carboxymethyl-beta-cyclodextrin into magnesium–aluminum layered double hydroxide, *J. Chem. Soc. Dalton Trans.* (1997) 1961–1965.
- [4] S. Yariv, H. Cross (Eds.), *Organo-clay Complexes and Interactions*, Marcel Dekker, New York, 2001.
- [5] M. Meyn, K. Beneke, Anion-exchange reactions of layered double hydroxides, *Inorg. Chem.* 29 (1990) 5201–5207.
- [6] A. Clearfield, M. Kieke, J. Kwan, J. Colon, R.C. Wang, Intercalation of dodecyl sulfate into layered double hydroxides, *J. Inclusion Phenom. Mol. Recognit. Chem.* 11 (1991) 361–378.
- [7] C. Wang, L. Juang, C. Lee, T. Hsu, J. Lee, H. Chao, Effects of exchanged surfactant cations on the pore structure and adsorption characteristics of montmorillonite, *J. Colloid Interface Sci.* 280 (2004) 27–35.
- [8] C. Volzone, J. Rinaldi, J. Ortega, Retention of gases by hexadecyltrimethylammonium-montmorillonite clays, *J. Environ. Manage.* 79 (2006) 247–252.
- [9] F.R. Costa, A. Leuteritz, U. Wagenknecht, D. Jehnichen, L. Haeussler, G. Heinrich, Intercalation of Mg–Al layered double hydroxide by anionic surfactants: Preparation and characterization, *Appl. Clay Sci.* 38 (2008) 153–164.
- [10] R. Celis, W. Koskinen, M. Hermosin, M. Ulibarri, J. Cornejo, Triadimefon interactions with organoclays and organohydrals, *Soil Sci. Soc. Am. J.* 64 (2000) 36–43.
- [11] R. Frost, Q. Zhou, H. He, Y. Xi, An infrared study of adsorption of para-nitrophenol on mono-, di- and tri-alkyl surfactant intercalated organoclays, *Spectrochim. Acta Part A* 69 (2008) 239–344.
- [12] Q. Zhou, Y. Xi, H. He, R.L. Frost, Application of near infrared spectroscopy for the determination of adsorbed p-nitrophenol on HDTMA organoclay-implications for the removal of organic pollutants from water, *Spectrochim. Acta Part A* 69 (2008) 835–841.
- [13] S. Laha, B. Tansel, A. Ussawarujikulchai, Surfactant-soil interactions during surfactant-amended remediation of contaminated soils by hydrophobic organic compounds: a review, *J. Environ. Manage.* 90 (2009) 95–100.
- [14] F. Bruna, R. Celis, I. Pavlovic, C. Barriga, Layered double hydroxides as adsorbents and carriers of the herbicide (4-chloro-2-methylphenoxy)acetic acid (MCPA): systems Mg–Al, Mg–Fe and Mg–Al–Fe, *J. Hazard. Mater.* 168 (2009).
- [15] F. Bruna, I. Pavlovic, C. Barriga, J. Cornejo, M.A. Ulibarri, Adsorption of pesticides carbetamide and metamitron on organohydrals, *Appl. Clay Sci.* 33 (2006) 116–124.
- [16] W. Reichle, Synthesis of anionic clay minerals (mixed metal hydroxides, hydroxalite), *Solid State Ionics* 22 (1986) 135–141.
- [17] F. Bruna, I. Pavlovic, R. Celis, C. Barriga, J. Cornejo, M.A. Ulibarri, Organohydrals as novel supports for the slow release of the herbicide terbutylazine, *Appl. Clay Sci.* 42 (2008) 194–200.
- [18] H. Zhao, K.L. Nagy, Dodecyl sulfate–hydroxalite nanocomposites for trapping chlorinated organic pollutants in water, *J. Colloid Interface Sci.* 274 (2004) 1–12.
- [19] T. Kameda, Y. Tsuchiya, T. Yamazaki, T. Yoshioka, Preparation of Mg–Al layered double hydroxides intercalated with alkyl sulfates and investigation of their capacity to take up N,N-dimethylaniline from aqueous solutions, *Solid State Sci.* 11 (2009) 2060–2064.
- [20] H. Kopka, K. Beneke, G. Lagaly, Anionic surfactants between double metal hydroxide layers, *J. Colloid Interface Sci.* 123 (1988) 427–436.
- [21] Y.-H. Chuang, C.-H. Liu, Y.-M. Tzou, J.-S. Chang, P.-N. Chiang, M.-K. Wang, Comparison and characterization of chemical surfactants and bio-surfactants intercalated with layered double hydroxides (LDHs) for removing naphthalene from contaminated aqueous solutions, *Colloids Surf., A* 366 (2010) 170–177.
- [22] V. Rives (Ed.), *Layered Double Hydroxides: Present and Future*, Nova Science Publishers Inc, New York, 2001.
- [23] H. Hongping, F. Ray, Z. Jianxi, Infrared study of HDTMA+ intercalated montmorillonite, *Spectrochim. Acta Part A* 60 (2004) 2853–2859.
- [24] J. Zhu, P. Yuan, H. He, R. Frost, Q. Tao, W. Shen, et al., In situ synthesis of surfactant/silane-modified hydroxalites, *J. Colloid Interface Sci.* 319 (2008) 498–504.
- [25] M. Bouraada, M. Lafjah, M.S. Ouali, L.-C. de Menorval, Basic dye removal from aqueous solution by dodecylsulfate- and dodecylbenzene sulfonate-intercalated by hydroxalite, *J. Hazard. Mater.* 153 (2008) 911–918.
- [26] P. Pavan, E. Crepaldi, G. Gomes, J. Valim, Adsorption of sodium dodecylsulfate on a hydroxalite-like compound. Effect of temperature, pH and ionic strength, *Colloids Surf. A* 154 (1999) 399–410.
- [27] L. Sun, C. Zhang, L. Chen, J. Liu, H. Jin, H. Xu, et al., Preparation of alumina-coated magnetite nanoparticle for extraction of trimethoprim from environmental water samples based on mixed hemimicelles solid-phase extraction, *Anal. Chim. Acta* 638 (2009) 162–168.
- [28] L. Moyo, N. Nhlapo, W.W. Focke, A critical assessment of the methods for intercalating anionic surfactants in layered double hydroxides, *J. Mater. Sci.* 43 (2008) 6144–6158.
- [29] E. Crepaldi, P. Pavan, J. Tronto, J. Valim, Chemical, structural, and thermal properties of Zn (II)–Cr (III) layered double hydroxides intercalated with sulfated and sulfonated surfactants, *J. Colloid Interface Sci.* 248 (2002) 429–442.

- [30] R. Rojas, F. Bruna, C. De Pauli, M. Ulibarri, C. Giacomelli, The effect of interlayer anion on the reactivity of Mg–Al layered double hydroxides: improving and extending the customization capacity of anionic clays, *J. Colloid Interface Sci.* 359 (2011) 136–141.
- [31] C.H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids, *J. Chem. Soc.* (1960) 3973–3993.
- [32] G. Rytwo, Y. Gonen, S. Afuta, Preparation of berberine-montmorillonite-metolachlor formulations from hydrophobic/hydrophilic mixtures, *Appl. Clay Sci.* 41 (2008) 47–60.
- [33] E. Barriuso, D.A. Laird, W.C. Koskinen, R.H. Dowdy, Atrazine desorption from smectites, *Soil Sci. Soc. Am. J.* 58 (6) (1994) 1632–1638.
- [34] M. Hermosin, R. Celis, G. Facenda, Bioavailability of the herbicide 2, 4-D formulated with organoclays, *Soil Biol. Biochem.* 38 (2006) 2117–2124.
- [35] B. Wang, H. Zhang, D. Evans, X. Duan, Surface modification of layered double hydroxides and incorporation of hydrophobic organic compounds, *Mater. Chem. Phys.* 92 (2005) 190–196.
- [36] K. Esumi, S. Yamamoto, Adsorption of sodium dodecyl sulfate on hydro-talcite and adsolubilization of 2-naphthol, *Colloids Surf. A* 137 (1998) 385–388.