

Layered Double Hydroxides as Supports for the Slow Release of Acid Herbicides

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A Mg/Al layered double hydroxide (LDH) was intercalated with the anionic herbicides 2,4-D, MCPA, and picloram by using three different methodologies: (i) direct synthesis (DS), (ii) regeneration (RE), and (iii) ion exchange (IE). The resulting complexes were characterized and assayed by batch release and column leaching tests, aiming at the controlled release of these herbicides. All the tested LDH–herbicide complexes displayed similar slow herbicide release properties in water, although the IE method seemed to result in complexes with a greater fraction of herbicide in a readily available form. Apparently, the LDH–herbicide complexes released most of the active ingredient present in the complexes at the end of the batch release experiment. This was attributed to the replacement of the intercalated herbicide by carbonate and hydroxyl anions from the aqueous solution. Compared to the free herbicides, the application of the three LDH–herbicide complexes (RE) to soil columns resulted in reduction in the maximum herbicide concentration in leachates and led to the retardation of herbicide leaching through the soil. All LDH–herbicide complexes presented an herbicidal efficacy similar to that of the free (technical) herbicides. Our results indicated the potential applicability of LDHs as supports for the preparation of slow release formulations of acid herbicides such as 2,4-D, MCPA, or picloram.

KEYWORDS: Layered double hydroxides; slow release; acid herbicides; 2,4-D; MCPA; picloram

INTRODUCTION

The presence of pesticides in surface and groundwater is a consequence of the increasing use of these chemicals in agricultural activities. Pesticide run-off and their leaching down through the soil profile are the main processes leading to water contamination, which have made them a serious environmental problem and a primary source of water pollution. The risk of ground and surface water contamination is particularly high for acid pesticides whose anionic forms predominate under pH conditions encountered in the soil and water environments, because anionic pesticides are mostly very weakly retained by the soil particles (1, 2). Pesticide movement through the soil profile is also highly dependent on the soil characteristics, such as its structure, organic matter content, pH, and biological activity. Pesticide movement is also influenced by tillage, the amount and timing of rainfall or irrigation, and the form in which the pesticide is applied to the soil (3). One approach to minimize pesticide transport losses is to use controlled release formulations, in which the pesticide is incorporated or sorbed into a

matrix or a carrier before application, thereby limiting the amount of chemical immediately available for unwanted transport losses.

Numerous natural and synthetic materials have been proposed for use in pesticide controlled-release formulations, in which only part of the active ingredient is in an immediately available form; the bulk of the pesticide is trapped or sorbed in an inert support and is gradually released over time. Beneficial effects related to the use of controlled release formulations include reduction in the amount of chemical required for pest control, decrease in the risk of environmental pollution, and a general decrease in nontarget effects (4, 5). Clay minerals have been widely used for this purpose. Inorganic clays and organically modified clays have been largely tested as supports for the controlled release of herbicides, such as fenuron, picloram, hexazinone, simazine, alachlor, metolachlor, and 2,4-D (4, 6–9). Nevertheless, the anionic character of clay minerals limits their usefulness as sorbents of acid herbicides when the latter are present in their anionic forms.

The high affinity of layered double hydroxides (LDHs) or hydroxalite-like materials for organic anions, including anionic pesticides, has been widely demonstrated (10–19). LDHs can be easily synthesized by reacting a dilute aqueous solution of

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magnesium and aluminum chlorides with sodium carbonate (20). Their general formula may be represented as $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]A_{x/m}^{m-} \cdot n\text{H}_2\text{O}$, where M(II) and M(III) are divalent and trivalent cations that occupy octahedral positions in the brucite-like layer, which is positively charged and requires the presence of interlayer anions (A^{m-}) to maintain overall charge neutrality (21). Intercalation of organic anions within the layered structure of LDHs can take place by different mechanisms, such as coprecipitation, ion exchange, or regeneration (11, 17, 22). Investigations concerning the applications of LDHs are mostly related to the field of catalysis, ion exchangers, and wastewater treatment (20, 23). The use of LDHs as support for controlled release formulations of pharmaceuticals such as ibuprofen, citrate, salicylate, and aspartic and glutamic acids has been reported (22, 24, 25). However, very little work has been conducted to assess the applicability of LDHs in the preparation of pesticide controlled release formulations (26–28).

The present work was designed to investigate the usefulness of a Mg/Al LDH (Mg-to-Al ratio = 2) as a support for the herbicides 2,4-D, MCPA, and picloram, in an attempt to slow herbicide release and reduce their leaching. LDH–herbicide complexes were prepared following different synthesis methods. Their ability to act as slow release formulations of the herbicides was evaluated through batch release and column leaching tests. Bioassays were also performed to determine the herbicidal activity of the proposed LDH-based formulations.

MATERIALS AND METHODS

Herbicides, Reagents, and Soil. Analytical-grade 2,4-D, MCPA, and picloram (purity > 97%) were purchased from Sigma. 2,4-D (2,4-dichlorophenoxyacetic acid) has water solubility 620 mg L⁻¹ and pK_a = 2.6. MCPA (4-chloro-2-methylphenoxyacetic acid) has water solubility 825 mg L⁻¹ and pK_a = 3.1. Picloram (4-amino-3,5,6-trichloropyridine-2-carboxylic acid) has water solubility 430 mg L⁻¹ and pK_a = 2.3. The reagents used to prepare the Mg/Al LDH were of analytical grade. The soil used in the column leaching tests and in the bioassays was a sandy clay loam soil from Seville (Spain), classified as Typic Rhodoxeralf. The soil was sampled (0–20 cm), air-dried, sieved (2 mm), and stored at 4 °C before use. Soil texture (20% clay, 10% silt, and 70% sand) was determined by sedimentation and the organic matter content (0.99%) by the Walkley-Black method (29). Soil pH was 7.9 in a 1:2 (w:w) soil:deionized water mixture.

Preparation of LDH–Herbicide Complexes. LDH–herbicide complexes containing 2,4-D, MCPA, or picloram were prepared following three different methodologies: (i) direct synthesis using the coprecipitation method (DS), (ii) indirect synthesis using the regeneration method (RE), and (iii) indirect synthesis using the ion exchange method (IE). To obtain the DS complexes, a solution containing 1.0·10⁻² mol of Mg(NO₃)₂ and 5.0·10⁻³ mol of Al(NO₃)₃ was added dropwise under vigorous stirring and nitrogen flux to an aqueous solution containing 5.0·10⁻² mol of the pesticide, i.e., 10 times higher than the amount of Al³⁺ to be added, on a molar basis. The addition was carried out keeping the resulting mixture at 80, 70, or 55 °C for 2,4-D, MCPA, and picloram, respectively. The pH was maintained at 10.0 ± 0.1 by addition of a 2 mol L⁻¹ NaOH solution. The resulting slurries were aged for 72 h at temperatures that were 10 °C higher than the coprecipitation temperature. The resulting materials were separated by vacuum filtration, washed with water, and dried under vacuum at room temperature in the presence of silica gel. The samples obtained by this method will be hereafter referred to as 2,4-D-DS, MCPA-DS, and Picloram-DS. To obtain the RE complexes, 250 mL of an aqueous solution containing 1.5·10⁻² mol of the desired herbicide was added to 1.0 g of calcined Mg–Al–CO₃, (i.e., LDH sample calcined at 500 °C for 4 h), previously synthesized according to Crepaldi (13). The amount of herbicide corresponded to the expected amount of anion exchange sites, based on the uncalcined LDH sample. The suspension was kept under vigorous stirring at 25 °C for 72 h. The resulting material was separated by centrifugation and dried under

vacuum at room temperature in the presence of silica gel. The obtained samples were named 2,4-D-RE, MCPA-RE, and Picloram-RE. To obtain the IE complexes, 250 mL of an aqueous solution containing 1.5·10⁻² mol of the herbicide was added to 1.0 g of Mg–Al–Cl LDH, previously synthesized according to Miyata (30). The herbicide to Al molar ratio in the exchange mixture was 4:1. The suspensions were kept at 25 °C for 72 h under vigorous stirring. The resulting materials were separated by centrifugation and dried under vacuum at room temperature in the presence of silica gel. The samples obtained by this method were named 2,4-D-IE, MCPA-IE, and Picloram-IE. On the basis of the Mg/Al ratio used during the syntheses and assuming absence of carbonate and hydroxyl anions in the samples, the theoretical composition of the complexes prepared can be written as Mg₂Al(OH)₆Y·nH₂O, where Y is the herbicide (2,4-D, MCPA or picloram) in its anionic form.

Characterization of LDH–Herbicide Complexes. All LDH–herbicide complexes were analyzed by powder X-ray diffraction (PXRD) using a Siemens D5005 X-ray diffractometer with a graphite crystal monochromator for selecting the Cu K_{α1} radiation (1.5405 Å). X-ray diffraction patterns were obtained at a 0.02° s⁻¹ rate. Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets samples (2.5% solid solution) using an ABB Bomem MB 100 instrument, with 60 scans per sample. The herbicide content in the LDH–herbicide complexes (10 mg) was determined after dissolution of the LDH sample using 1 mL of concentrated HNO₃ (65%). Following the destruction of the complexes, 10 mL of methanol was added, the volume was completed to 50 mL with deionized water, and the resulting solutions were filtered and analyzed by high-performance liquid chromatography (HPLC) to determine the herbicide concentration.

Batch Release Study. Herbicide release from the LDH–herbicide complexes into water was monitored using a batch method. To this end, 10 milligrams of LDH–herbicide complex were added to 200 mL of distilled water in glass bottles closed with screw caps. At selected times after addition of the complexes, the bottles were hand-shaken, and allowed to settle for 10 min. Then 2 mL of the supernatant solution was sampled and filtered, and the herbicide concentration was determined by HPLC. The periodical removal of such a small amount of supernatant (2 mL) was assumed to have no influence on the release pattern. The herbicide release kinetic experiment was carried out in duplicate.

Column Leaching Experiment. For the leaching study, we used methacrylate columns of 30 cm length x 5 cm internal diameter made up of six 5 cm-long sections sealed with silicon, which also helped minimize the preferential flow along the column walls. The top ring was filled with sea sand and the bottom ring with sea sand plus glass wool, to prevent loss of soil and contamination of leachates with soil particles. The other four rings were hand-packed with 490 g of air-dried soil, then saturated with 300 mL of water and allowed to drain for 24 h. The calculated pore volume of the columns after saturation was 200 ± 20 mL. Samples of 2,4-D, MCPA, or picloram were added to the top of duplicate columns at an application rate of 5 kg ha⁻¹ (1 mg active ingredient) either as free (technical) herbicide dissolved in 10 mL water or as the LDH–herbicide complex (RE). This application rate fell within the range of 2.2–9.5 kg ha⁻¹ recommended for the field application of picloram, and was just slightly higher than the application rates recommended for 2,4-D and MCPA (0.3–2.3 kg ha⁻¹) (31). The amount of complex containing 1 mg of active ingredient was calculated from the herbicide contents in the LDH–herbicide complex, determined by HPLC after the acid destruction of the complexes. The columns were leached with water at a rate of 50 mL day⁻¹. The leachates were collected daily and the concentration of 2,4-D, MCPA, or picloram was determined by HPLC until the herbicide concentration was lower than 0.2 mg L⁻¹.

Bioassay. The herbicidal activity of the different LDH–herbicide complexes was determined using garden watercress (*Lepidium sativum*) seeds. Duplicate 8 cm-diameter pots were filled with 220 g soil, saturated with water, and allowed to drain for 24 h. Fifteen seeds of garden watercress were gently distributed on the surface of each pot, and 1 day after sowing, the free (dissolved) or LDH–based formulations of each herbicide were applied preemergence at an application rate of 2.5 kg ha⁻¹ for 2,4-D and MCPA, and at a rate of 5 kg ha⁻¹ for

picloram. The pots were watered daily with 10 mL distilled water. Herbicidal efficacy was determined 1 week after herbicide application by visual evaluation of the weed control efficacy.

Herbicide Analysis. Herbicide analysis was performed by HPLC using a Waters 1525 chromatograph coupled to a Waters 2996 diode-array detector. The following conditions were used: Novapack C18 column (150 mm length \times 3.9 mm i.d.); eluent mixture, 60:40 methanol: H_3PO_4 (pH = 2) for 2,4-D and MCPA, and 75:25 methanol: H_3PO_4 (pH = 2) for picloram at a flow rate of 1 mL min^{-1} , 25 μL injection volume, and UV detector at 230 nm for 2,4-D and MCPA, and 225 nm for picloram. External calibration curves with standard solutions between 0.1 and 50 mg L^{-1} were used in the calculations.

RESULTS AND DISCUSSION

Characterization of the LDH–Herbicide Complexes. The PXRD patterns of the LDH–herbicide complexes prepared by the three different methods are presented in **Figure 1**. The basal spacing of each sample was calculated from the average of the (00 l) peaks and is listed in **Table 1**. These basal spacings indicate the intercalation of the herbicide anions between the layers in a vertical position, with formation of an organic bilayer in the interlayer region (18, 33). The basal spacing values reported in **Table 1** are greater than those recently reported by Pavlovic et al. (17) for picloram- and 2,4-D-LDH complexes, but it should be noted that we used a Mg/Al ratio lower than that used by Pavlovic et al. (17) during the synthesis of their complexes, which should have resulted in greater surface charge density. The basal spacing values reported by Pavlovic et al. (17) were associated with a flat position of the anions within the LDH structure, which was probably favored by the lower surface charge density of their samples. The samples obtained by the indirect synthesis methods (RE and IE) display broadened peaks of low intensity (**Figure 1**). This behavior is not observed for the samples obtained by direct synthesis, which display well defined peaks of higher intensity, typical of well organized materials. This better organization of the LDH materials can be attributed to the hydrothermal treatment, which was carried out only in the case of the samples obtained by direct synthesis. The strong (0015) reflection found for some samples, such as the 2,4-D-IE complex, could be an indication of the presence of some unexchanged layers, i.e., containing chloride as interlayer anion, since the (006) reflection of the precursor, Mg–Al–Cl, is located at the same value of 2θ as the (0015) reflection of the 2,4-D-LDH complex. For the complexes containing MCPA and 2,4-D, the salt phase of the organic anions was also identified in the diffractograms (\blacklozenge).

The presence of herbicide anions in the LDH–herbicide complexes was confirmed by FT-IR spectroscopy (**Figure 2**). All the organic anions stretching and bending vibration modes can be observed in the spectra, besides the absorption bands of the LDH hydroxylated layers. One of the most distinct features of all spectra is the absence of the C=O stretching vibration of protonated carboxylic groups of the herbicides (near 1700 cm^{-1}) and the presence of a strong absorption band at about 1600 cm^{-1} , which can be assigned to the antisymmetric stretching vibration of ionized COO^- groups, together with a weaker symmetric stretching band near 1400 cm^{-1} (17). This result confirms the presence of the herbicides as anionic species in the complexes. For the 2,4-D-LDH samples, the bands observed around 1490 and 1420 cm^{-1} correspond to the C=C bond vibrations of the aromatic ring of 2,4-D. The herbicide's C–O–C antisymmetric and symmetric stretching bands appear at 1285 and 1069 cm^{-1} , respectively. The band at 860 cm^{-1} can be assigned to the C–Cl vibration (32). For the MCPA-LDH samples, a band at 2926 cm^{-1} can be attributed to the

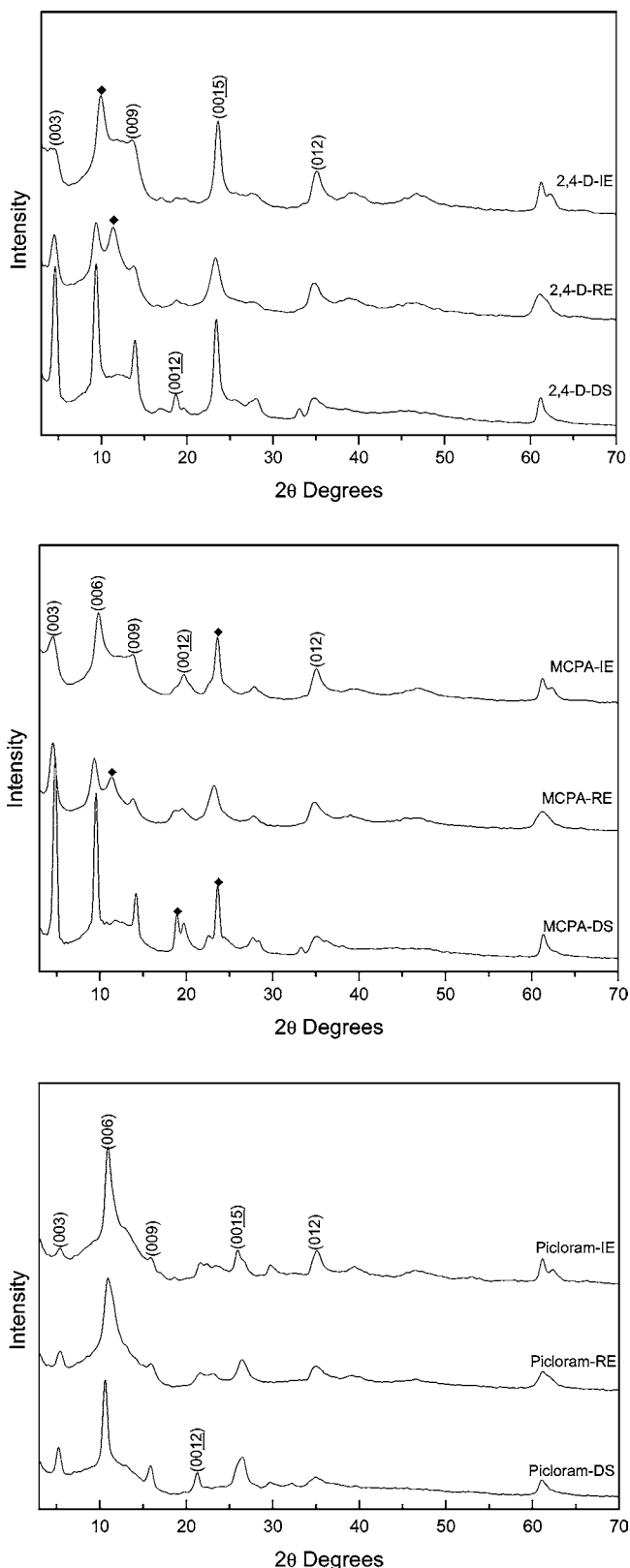


Figure 1. Powder X-ray diffraction (PXRD) patterns of LDH–herbicide complexes.

aliphatic C–H stretching vibrations. The bands observed around 1242 and 1054 cm^{-1} can be assigned to the phenyl–alkyl–ether groups present in MCPA. For the Picloram-LDH samples, the band at 1610 cm^{-1} can be partly attributed to the water molecules present in the interlayer region and to the herbicide's aromatic ring C=C bond vibration, whereas the band at 1360 cm^{-1} can be assigned to the C–N stretching of aromatic amines.

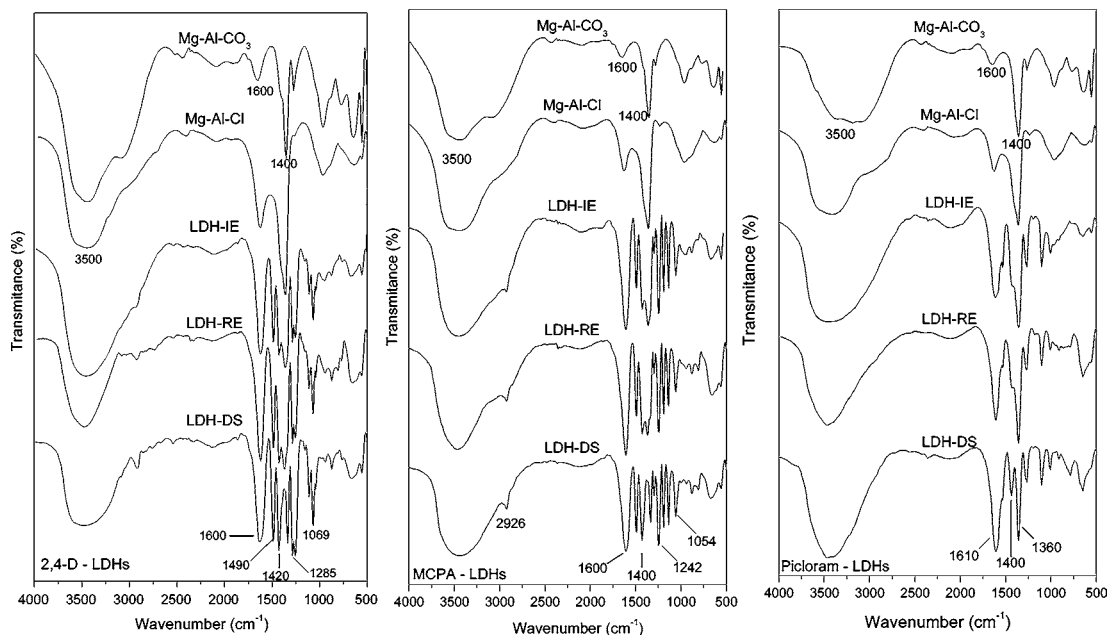


Figure 2. Fourier transform infrared (FT-IR) spectra of the LDH-herbicide complexes and the precursors, Mg-Al-CO₃ and Mg-Al-Cl, used for the synthesis of the complexes.

Table 1. Basal Spacing (Å) of LDH-Herbicide Complexes Prepared by Three Different Methods

sample	synthesis method		
	direct synthesis (DS)	regeneration (RE)	ion exchange (IE)
2,4-D-LDH	19.02	19.36	19.42
MCPA-LDH	18.43	19.19	19.24
Picloram-LDH	16.72	16.44	16.35

Table 2. Herbicide Content of the Different LDH-Herbicide Complexes and Total Amount of Herbicide Released from the Complexes into Water during the Batch Release Experiment

complex	synthesis method	herbicide content (mg herbicide/mg complex)	herbicide released into water (mg herbicide/mg complex)
2,4-D-LDH	DS	0.39	0.42
	RE	0.29	0.38
	IE	0.30	0.33
MCPA-LDH	DS	0.62	0.37
	RE	0.32	0.40
	IE	0.31	0.34
Picloram-LDH	DS	0.47	0.51
	RE	0.34	0.36
	IE	0.34	0.38

All LDH samples display a very intense and broadened band around 3600 and 3400 cm⁻¹. Those bands are typical of hydroxyl groups present in the LDH layers. Samples obtained by direct synthesis (DS) display bands of enhanced intensity. This is an indication of the larger amount of organic anion present in these samples. So, direct synthesis seems to result in complexes with larger amounts of organic anion than would be obtained by indirect procedures. This is confirmed by the amount of herbicide determined for each sample by acid destruction of the LDH structure (**Table 2**). These herbicide contents, on the other hand, are very high (29–62%), reflecting the presence of herbicide anions not only on the external surface, but also inside the LDH layered structure (internal surface).

Batch Release Study. The release into water of picloram, MCPA, and 2,4-D from the LDH complexes prepared by the

three different methods are shown in **Figure 3**. All LDH complexes released the herbicides slowly during the 8-day monitoring. A general observation is that the release by the LDH-herbicide complexes at short sampling times ($t < 8$ h) decreases in the following order $IE \geq DS > RE$. Thus, despite the fact that IE complexes have herbicide contents that are lower than those of the DS complexes and similar to those of the RE complexes (**Table 2**), they release larger amounts of herbicides than the DS and RE complexes at short sampling times. This may reveal differences in the amount of herbicide present in a readily available form, depending on the methodology used to prepare the complexes. Interestingly, except for the MCPA-DS complex, the total amounts of picloram, MCPA, and 2,4-D released at the end of the release experiment ($t = 8$ days) are generally equal to or even slightly greater than the herbicide contents determined by acid destruction of the complexes (**Table 2**). Incomplete destruction of the complexes or some chemical degradation of the herbicides under strongly acidic conditions could have resulted in underestimation of the amount of herbicide present in the complexes as determined by acid treatment. Nevertheless, except for the large discrepancy observed for MCPA-DS, the general agreement between the herbicide contents determined by acid treatment and the amounts of herbicide released in the batch kinetic experiment strongly indicates that most of the herbicide in the complexes is ultimately in a desorbable form, which is a very interesting feature for the practical use of these complexes as slow release formulations of the assayed herbicides (4). The desorption of organic anions from LDH can be attributed to their replacement with hydroxyl and/or carbonate anions present in water (28). This is because the affinity of the latter inorganic anions for LDH is higher than the affinity of monovalent organic anions, which is a result of the ability of OH⁻ and CO₃²⁻ to stabilize the LDH layered structure (11, 33). Nevertheless, for all the three herbicides studied here in, the differences between the release patterns of complexes prepared by different methodologies (DS, RE, IE) are not large (**Figure 3**). The most distinct behavior can be observed for the picloram-DS complex, where the large amounts of released herbicide can be explained by taking into account the high herbicide content of this complex (**Table 2**).

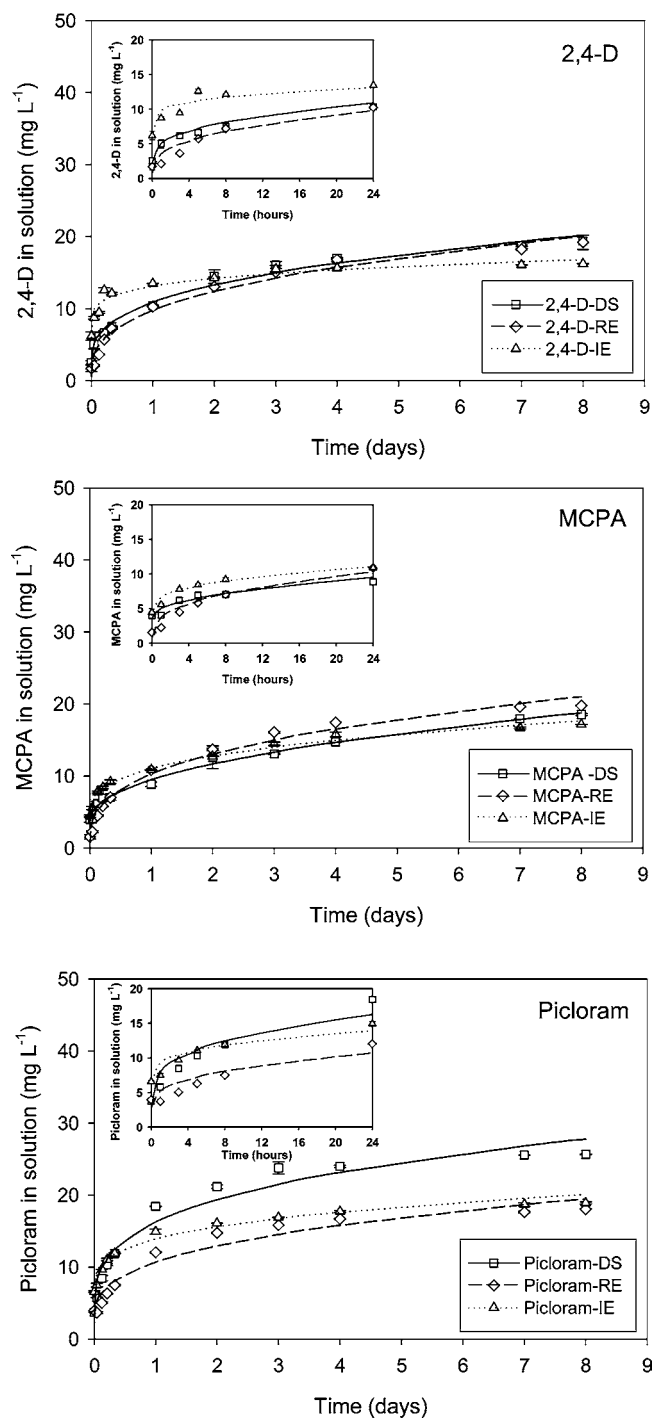


Figure 3. Herbicide release kinetics from LDH-herbicide complexes into water. Symbols are experimental data points, whereas lines are the fittings to the equation $C_t = k \cdot t^n + c'$.

In a previous study, Celis et al. (7) prepared different types of clay complexes containing herbicide picloram and determined their release behavior. For labile complexes consisting of mechanical clay-herbicide mixtures, the release equilibrium was reached after 1 day with nearly 100% herbicide release, whereas for strongly sorbed complexes, the release equilibrium was reached after 2–5 days with 80–100% herbicide release. In the present study, all herbicides were released from the LDH carriers into water at slower rates if compared with the clay complexes reported by Celis et al. (7), and presumably at much slower rates than would be expected from conventional formulations of the assayed herbicides, where the active ingredients

Table 3. Constants from Fitting the Herbicide Release Data to the Power Equation $C_t = k \cdot t^n + c'$

complex	synthesis method	c'	k	n	R^2
2,4-D-LDH	DS	2.1 ± 0.7^a	8.8 ± 0.9	0.34 ± 0.04	0.986
	RE	0.6 ± 0.9	9.2 ± 1.2	0.36 ± 0.05	0.979
	IE	6.0 ± 0.8	7.2 ± 0.9	0.20 ± 0.04	0.948
MCPA-LDH	DS	3.6 ± 0.5	5.9 ± 0.6	0.45 ± 0.04	0.990
	RE	0.5 ± 0.9	9.8 ± 1.1	0.35 ± 0.04	0.983
	IE	4.1 ± 0.5	7.0 ± 0.6	0.32 ± 0.03	0.987
Picloram-LDH	DS	2.4 ± 1.9	13.9 ± 2.2	0.29 ± 0.05	0.958
	RE	2.5 ± 1.4	8.2 ± 1.7	0.35 ± 0.07	0.946
	IE	5.9 ± 0.9	7.8 ± 1.0	0.27 ± 0.04	0.965

^a Value \pm standard error.

are present in an immediately available form (4, 7). We believe that the Coulombic attraction between the herbicide anions and the LDH's positively charged internal surfaces should contribute to strengthening the interaction between the herbicide and the sorbent, making the release slower when compared to previously assayed sorbents based on clay minerals.

Herbicide release data in water were analyzed by applying the power equation:

$$C_t = k \cdot t^n + c'$$

where C_t (mg L^{-1}) is the concentration of herbicide in solution at time t (days) and k , n , and c' are constants which are characteristic of the systems. This equation is similar to that previously used to describe pesticide release kinetics into water from different supports (4, 34). In general, there was a good fitting of the data to the equation with $R^2 > 0.94$ (Table 3). The increase in c' values in the order $\text{RE} \leq \text{DS} < \text{IE}$ indicates an increase in the initial or instantaneous release ($t = 0$) of the herbicides, whereas differences in k and n values indicate differences in the release rate. As mentioned above, despite the fact that IE complexes have herbicide contents that are lower than those of the DS complexes and similar to those of the RE complexes (Table 2), they release larger amounts of herbicides at $t = 0$ (i.e., they present greater c' values) than the DS and RE complexes, revealing that they contain a greater fraction of herbicide in a readily available form.

Column Leaching Study. For the column leaching test, we decided to use one type of LDH-herbicide complex (RE) only, considering that for all the three herbicides, the complexes prepared by different methodologies displayed similar release patterns (Figure 3). This type of complex (RE), prepared through reconstruction of the LDH layered structure from rehydration of its calcined product in the presence of organic anions (11, 12, 17), was easy to prepare. In addition, the ability of calcined LDH to remove anionic pesticides from water should permit the interesting application of this sorbent for decontamination of water contaminated with anionic herbicides, and subsequently recycle the LDH-herbicide complex to be used as a slow release formulation for agricultural application.

Breakthrough curves (BTCs) for 2,4-D, MCPA, and picloram applied to soil columns as free herbicides (dissolved in water) and as LDH-herbicide (RE) complexes are shown in Figure 4. The position of the maximum concentration peak, close to one pore volume ($V_0 = 200 \text{ mL}$), in the BTCs of the free herbicides indicates little retention of the compounds in the soil columns. At the pH of the soil used for our leaching test (pH 7.9), the anionic forms of picloram, MCPA, and 2,4-D predominate. Accordingly, little retardation of the herbicides

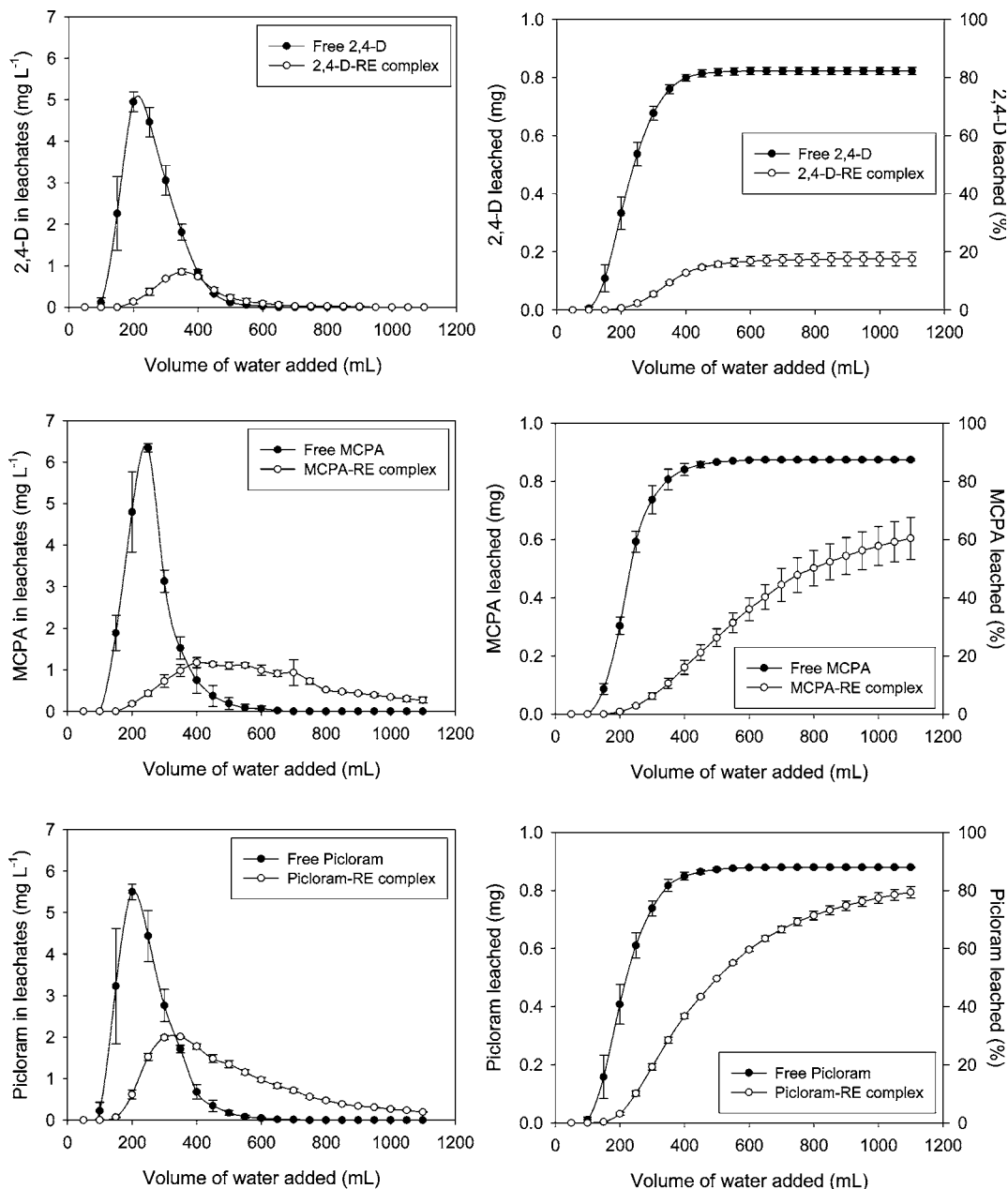


Figure 4. Breakthrough curves (BTCs) for 2,4-D, MCPA, and picloram after application to soil columns as free herbicides and as LDH–herbicide complexes: relative BTCs (left) and cumulative BTCs (right). Bars represent standard errors of duplicate experiments.

within the soil column is expected. Compared to the free herbicides, application of the herbicides as LDH complexes (RE) greatly reduce the maximum concentration peaks, flattening the BTCs and also shifting the maximum concentration peaks to larger volumes of added water, clearly indicating retarded leaching of the herbicides (**Figure 4** left). The maximum concentration decreases from 5.0 to 0.8 mg L⁻¹ for 2,4-D, from 6.3 to 1.2 mg L⁻¹ for MCPA and from 5.5 to 2.0 mg L⁻¹ for picloram. This maximum concentration of 2,4-D, MCPA, and picloram occurred in the leachates of LDH–RE 3 days (150 mL) later than in the case of the free herbicide. In addition, the presence of the herbicides in the leachates at moderate concentrations was extended up to >1000 mL of added water in the case of MCPA and picloram (**Figure 4** left). This is a very desirable feature of controlled release formulations, because the decrease in herbicide concentration in leachates without shifting of the maximum concentration peak can be due to the herbicide

irreversibly bound to the carrier, which is not available for leaching and could cause problems of carry-over effects for next crops (4).

The total amounts of picloram, MCPA, and 2,4-D leached during the column experiment can be compared from the cumulative BTCs shown in **Figure 4** right. The total amount of 2,4-D accumulated in leachates after its application as an LDH–complex (18%) is much lower than the amount obtained after its application as free herbicide (82%). These results are similar to those found by Cox et al. (8) when they compared the leaching of 2,4-D applied to soil columns as free herbicide (methanolic solution) and as a clay–herbicide complex; the total amount of 2,4-D accumulated in leachates from the clay–herbicide complex (70%) was lower than the amount obtained in the case of free 2,4-D (80%). The larger leaching of 2,4-D from the complex used by Cox et al. (8) compared to the small leaching observed for our LDH complex can be attributed to

the fact that the Fe(III)-saturated montmorillonite used by Cox et al. (8) retained the herbicide only weakly, as a molecular species, and it was most likely retained on the external surface of the clay mineral only. In contrast, the large amounts of 2,4-D present in our LDH complexes is a result of the intercalation of the herbicide within the LDH structure, as demonstrated by PXRD analysis of the complexes. Coulombic attraction within the positively charged LDH layers should contribute to the strengthening of the interaction between the herbicide and the sorbent, making the release slower. On the basis of the short half-life of 2,4-D in most soils (<7 days) (31), we believe that the slow release of the herbicide from our LDH complexes increases the residence time of the herbicide within the soil column, thus increasing the chance for biodegradation. As a result, a small amount of 2,4-D is recovered in the leachates from the soil column when the herbicide is applied as a LDH complex (Figure 4).

The total amount of MCPA and picloram leached from soil columns after their application as LDH-herbicide complexes is larger than that measured for 2,4-D. It appears that degradation affects MCPA and picloram to a lesser extent if compared with 2,4-D, resulting in high recoveries in the leachates even when the herbicides are applied as LDH complexes. In fact, the differences between the total amounts of picloram (79%), MCPA (60%), and 2,4-D (18%) leached from our LDH-herbicide complexes can be related to the reported soil persistence of these herbicides (picloram > MCPA > 2,4-D). On the basis of their anionic character at the pH of the soil used here in, we believe that irreversible sorption to the soil is not likely to contribute to the amount of herbicide that is not leached from the soil columns. The extensive herbicide desorption from the LDH-herbicide (RE) complexes (Figure 3) observed in the batch release experiment also suggests that there is little contribution from irreversible sorption to the sorbent to the low herbicide recovery. Therefore, the differences in soil persistence of the acid herbicides, together with their residence time within the soil column, appear to be the major factors determining the total amount of 2,4-D, MCPA, and picloram leached during the column experiment. According to these results, LDH-herbicide complexes are expected to retain acid herbicides in soil surface layers for longer periods if compared with the application of the herbicides in an immediately available form. This increases the chance for degradation on one hand, and decreases the risk of groundwater contamination on the other.

Bioassay. The herbicidal activity of the LDH-RE complexes containing 2,4-D, MCPA, and picloram was compared with that of the free herbicides. Results indicate that all LDH-herbicide complexes (RE) applied preemergence are as effective as the free herbicide in preventing garden watercress (*Lepidium sativum*) growth; in contrast to the untreated pots, no seed germinated in the pots treated with either the free herbicides or the LDH-herbicide complexes (RE). The application rate of 2,4-D, MCPA, and picloram used in the bioassays was within the range recommended for the field application of these herbicides. These results demonstrate the efficiency of the LDH-herbicide complexes as controlled release formulations for 2,4-D, MCPA, and picloram, with the above-discussed advantage of minimizing rapid herbicide leaching losses.

In summary, intercalation of the acid herbicides 2,4-D, MCPA, and picloram within the layered structure of a Mg/Al layered double hydroxide (LDH) renders complexes with slow herbicide release properties. Carbonate and hydroxyl anions effectively replace the herbicide anions from the LDH complexes, promoting their slow release into the aqueous solution.

The release behavior is not highly dependent on the methodology used for intercalation of the herbicide anions within the LDH layers (direct synthesis, regeneration, or ionic exchange) or on the nature of the pesticide anions. Column leaching experiments demonstrate that the application of 2,4-D, MCPA, and picloram as LDH complexes flatten the BTCs of the herbicides, shifting their maximum concentration peaks to larger volumes of added water. Moreover, in the case of MCPA and picloram, the LDH complexes extend the presence of the herbicides in leachates at moderate concentrations up to larger volumes of added water if compared to the application of the free (dissolved) herbicides. The longer residence time of the herbicides within the soil column during the leaching test promotes degradation of the less persistent anions, in particular the degradation of 2,4-D, reducing the total amount of leached herbicide. MCPA and especially picloram persist longer without being degraded, resulting in larger amounts of leached herbicide when compared to 2,4-D. Nevertheless, leaching of MCPA and picloram occurs later and at lower concentrations when they are applied as LDH complexes. The LDH-herbicide complexes are as effective as the free herbicides in the control of garden watercress (*Lepidium sativum*) at application rates within the range of those recommended for the field application of these herbicides. Consequently, LDHs have interesting properties which show that they can be used as sorbents for the slow release of acid herbicides, such as picloram, MCPA, and 2,4-D, thus reducing the amount of herbicide immediately available for rapid transport losses while maintaining efficient weed control.

ABBREVIATIONS USED

MCPA, 4-chloro-2-methylphenoxyacetic acid; 2,4-D, 2,4-dichlorophenoxyacetic acid; DS, direct synthesis; RE, regeneration; IE, ion-exchange; LDH, layered double hydroxide; PXRD, powder X-ray diffraction; FT-IR, Fourier transform infrared; HPLC, high-performance liquid chromatography; BTC, breakthrough curve.

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