# Synthesis, Characterization, and Sorption Capacity of Layered Double Hydroxides and Their Complexes with Polymerin

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Mg−Al layered double hydroxides (LDHs) containing chloride (LDH−Cl) or carbonate (LDH−CO$_3$) in the interlayer were obtained at room temperature and after calcitation at 450 °C (LDH−Cl-450 and LDH−CO$_3$-450) and were characterized by X-ray diffraction and Fourier transform infrared analyses. Sorption isotherms of a humic acidlike fraction naturally occurring in olive oil mill waste waters, named polymerin, on these LDH minerals were carried out. Because LDH−CO$_3$ showed the highest capacity to sorb polymerin among the four LDH minerals synthesized, two organo−mineral complexes named LDH−CO$_3$−LP (low polymerin) and LDH−CO$_3$−HP (high polymerin) were prepared by coprecipitation (LDH−CO$_3$−LP) and sorption onto a preformed LDH−CO$_3$ mineral (LDH−CO$_3$−HP). These complexes were characterized chemically and physicochemically, and their stability to pH and after thermal treatment at 80 °C were evaluated. The diffuse reflectance infrared Fourier transform and X-ray analysis of the complexes indicated that polymerin was sorbed only on the external surfaces of LDH−CO$_3$ and no intercalation occurred. The LDH−polymerin complexes appeared to be more stable than LDH−CO$_3$ at pH 4.0 and showed that they were able to sorb both As(V) and Zn. Because the waste waters are usually contaminated with mixtures of pollutants in cationic and anionic forms, the LDH−polymerin complexes appear more suitable than the sorbents in a potential water remediation process.

KEYWORDS: Layered double hydroxides; polymerin; sorption; XRD; DRIFT; Zn; As(V)

## INTRODUCTION

An urgent need exists to develop less expensive, simpler, and more efficient methods for removing trace contaminants from water. Sorption is one of the most relevant methods that has been successfully applied to remove heavy metals and organic chemicals from hazardous waste waters, because of its low maintenance costs, high efficiency, and ease of operation. An efficient sorbent to remove contaminants from solutions would consist of particles with a large surface area, small diffusion resistance, and high reactivity and affinity for the pollutants.

Layered double hydroxides (LDHs) or anionic clays are a class of synthetic two-dimensional lamellar compounds with positively charged layers and charge-balancing anions located in the interlayer region. They have the general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}$ $(A_{x/n}^{n-})\cdot mH_2O$ (1), where $M^{2+}$ and $M^{3+}$ are divalent and trivalent metal ions, $x$ is the metal ratio $M^{3+}/(M^{2+} + M^{3+})$, $A^{n-}$ is the anion in the interlamellar region, and $m$ is the amount of water present in the same region. LDHs are also widely known as hydrotalcite-like compounds due to their structural similarities to hydrotalcite, a mineral with the formula $Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$. The hydrotalcite structure results from the stacking of brucitelike layers $[Mg(OH)_2]$ containing a positive residual charge arising from the partial isomorphous substitution of $Mg^{2+}$ cations with $Al^{3+}$ cations. The anions present in the interlamellar spaces balance the positive excess charge (1).

LDHs have been synthesized by direct methods, of which the most frequently used is the coprecipitation method (2, 3), and indirect methods, such as anionic exchange using LDHs as precursors (4, 5). Advanced applications have sought to synthesize a large range of LDHs varying either the divalent and trivalent cations or the interlamellar anions, which can be of an inorganic or organic nature (6, 7).

Actually, there is an increasing interest in LDHs because they can be used for numerous applications, for example, catalysts and catalyst supports, trapping agents for anionic contaminants, ion exchangers, sorbents, and medical applications. In particular, LDHs can be efficient delivery vehicles of drug, nucleotides/genes, and biomedical and other functional molecules (8) because these compounds, intercalated in LDHs, are slowly released, thus reducing the frequency of dose. LDHs have also been proposed as supports for the preparation of slow release formulations of acid herbicides (9).

The large surface area, high anion exchange capacity, and good thermal stability (10) make LDHs interesting in environmental protection due to their capacity to remove from water organic compounds such as surfactants (11), phenolic compounds (12), pesticides (13), and inorganic oxyanions (14−17). In recent

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studies, LDHs were intercalated with anionic ligands (*6*, *18*−*22*), with the aim to also remove cationic heavy metals from contaminated waters.

Polymerin, humic acidlike fraction naturally occurring in olive oil mill waste waters (OMWW) (*23*), has been shown to be a good sorbent for the potential remediation of contaminated waters. Polymerin is effective in adsorbing heavy metals in either cationic (mainly) or anionic forms (e.g., $Cr_2O_7^{2-}$) (*24*, *25*), acidic and basic pesticides (*26*, *27*), and hydrophobic toxic organic compounds (*28*).

With the aim to increase the field of LDH applications in water remediation, we studied the sorption of polymerin onto LDH minerals synthesized under different conditions in the presence of carbonate (LDH−$CO_3$) or chloride (LDH−Cl) before and after preheating at 450 °C. Then, we prepared selected LDH−polymerin complexes as possible sorbents for the removal of heavy metals in both cationic and anionic forms from polluted waters. In particular, we studied (i) the physical and chemical properties and the stability of a LDH−$CO_3$ mineral and two organo−mineral complexes, namely, LDH−$CO_3$−low polymerin (LDH−$CO_3$−LP) and LDH−$CO_3$−high polymerin (LDH−$CO_3$−HP) and (ii) the capacity of these latter sorbents to remove Zn and As(V) from contaminated waters.

## MATERIALS AND METHODS

**Recovery of Polymerin.** OMWW were kept refrigerated at −20 °C in tightly closed PVC vessels, and polymerin was prepared when required. Polymerin was recovered from OMWW by a simplified procedure, which is also cheaper than that described by Capasso et al. (*23*). Briefly, 1 L of OMWW (year 2007) from a pressure processing system located in Monopoli (Italy) was precipitated with cold methanol; the suspension was centrifuged at 10000 g min$^{-1}$ for 30 min, and the solid precipitate was recovered and lyophilized, obtaining the solid residue known as polymerin (8.9 g), whose characteristics have been described in a previous work (*27*).

**Chemical, Physicochemical, and Spectroscopic Methods.** Protein, carbohydrate, and phenol concentrations of polymerin were determined by colorimetric methods. The protein amount was estimated by the Bradford method (*30*) using bovine serum albumin as a standard. Carbohydrates were analyzed by means of an anthrone reagent (*31*) using D-mannose and D-galactose as standards. The total phenols were determined by the Folin−Ciocalteu method (*32*) using gallic acid as the reference standard and reading the absorbance at 760 nm. Carbon elemental analyses were performed using a Fisons EA 1108 elemental analyzer for hydrogen, carbon, nitrogen, and sulfur (CHNS). The $E_4/E_6$ ratio, calculated by the absorbance ratio between 465 and 665 nm, was registered using a Perkin-Elmer UV−visible spectrophotometer. The specific surface area was calculated by nitrogen adsorption isotherms data at 77 K using the Brunnauer−Emmett−Teller (BET) method. The point of zero charge (PZC) of raw polymerin was determined according to the method reported by Tsai et al. (*33*) using the potentiometric titration curve (TIM 856 Titration Manager automatic titrator) as a function of pH at different ionic strengths. Briefly, dry samples (250 mg) of raw polymerin were dissolved in 100 mL of 0.1, 0.01, and 0.001 mol L$^{-1}$ NaCl solutions, brought to pH 9.0 with 2.0 mol L$^{-1}$ NaOH and successively brought to pH 2.0 with 0.05 mol L$^{-1}$ HCl. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy analysis was performed using a Perkin-Elmer Spectrum One FT-IR with a resolution of 1 cm$^{-1}$. For sample preparation, 0.2 mg of sample was mixed with 200 mg of KBr (FT-IR grade, Aldrich, Chemical Co., Milwaukee, WI). The mixture was finely ground in an agate mortar and transferred to a sample holder. The surface was smoothed with a microscope glass slide, and DRIFT spectra were recorded.

**Synthesis of LDH−$CO_3$ and LDH−Cl Minerals.** LDHs with carbonate in the interlayers (LDH−$CO_3$) were prepared by direct coprecipitation at room temperature, following the procedure of Ulibarri et al. (*29*). Briefly, a solution containing Mg(NO$_3$)$_2$·6H$_2$O (0.25 mol L$^{-1}$) and Al(NO$_3$)$_3$·9H$_2$O (0.125 mol L$^{-1}$) was added dropwise to an aqueous solution containing KOH (3.4 mol L$^{-1}$) and Na$_2$CO$_3$ (1.0 mol L$^{-1}$) under vigorous stirring. After complete addition, the resulting slurry was aged for

20 h at room temperature in the mother liquid. The precipitate was recovered by centrifugation at 7000 g min$^{-1}$ for 30 min, washed five times with deionized water, dialyzed in membrane with cutoff of 12−14 kDa, freeze-dried, and lightly ground to pass through a 0.315 mm sieve.

LDHs with chloride in the interlayers (LDH−Cl) were prepared by coprecipitation method, as described by Constantino and Pinnavaia (*2*). A solution containing MgCl$_2$·6H$_2$O (0.25 mol L$^{-1}$) and AlCl$_3$·9H$_2$O (0.125 mol L$^{-1}$) was added dropwise under vigorous stirring at room temperature to a KOH solution at pH 10.0. The suspension was kept at this pH by adding 2 mol L$^{-1}$ NaOH. The final suspension, aged for 20 h at room temperature, was treated as described above for LDH−$CO_3$.

Subsamples of LDH−$CO_3$ and LDH−Cl were calcined in a oven at 450 °C for 4 h, obtaining two sorbents named LDH−$CO_3$-450 and LDH−Cl-450. Before each experiment, all of the materials were ground in a planetary ball mill (Retsch, PM 200).

**Sorption Isotherms of Polymerin onto LDH Minerals.** The sorption of polymerin onto LDH−$CO_3$, LDH−Cl, LDH−$CO_3$-450, and LDH−Cl-450 was carried out at room temperature by diluting a 10 g L$^{-1}$ stock solution of polymerin, in a range from 0.01 to 2.5 g L$^{-1}$, in 4 mL screw cap vials containing 10 mg of sorbent. The experiments were conducted in 0.03 mol L$^{-1}$ NaNO$_3$ at native pH using an end-over-end shaker. After 3 days of equilibration, vials containing samples and blanks (LDHs and polymerin) were centrifuged at 7000 g min$^{-1}$ for 30 min, and supernatants were analyzed by UV−vis spectrophotometry at 254 nm. This wavelength has been chosen because it is characteristic of natural substances such as HAs, aromatic compounds, tannins, and lignin. The detection limit was 0.5 mg L$^{-1}$. The sorption of polymerin by the sorbents was obtained by mass balance, using the corresponding calibration curve.

**Preparation of LDH−Polymerin Complexes.** Two different methods have been used for the preparation of LDH−polymerin complexes: direct synthesis or coprecipitation and indirect synthesis or sorption. In the first case, the same procedure used for the preparation of LDH−$CO_3$ was adopted, except that 2 g of polymerin was added in the basic solution. The complex so obtained was called LDH−$CO_3$−LP. In the second case, 1.0 g of polymerin was added to a suspension containing 4.0 g of LDH−$CO_3$ in 1.6 L of deionized water, under vigorous stirring. After 72 h, the precipitate was washed, dialyzed, and freeze-dried. The matrix so obtained was called LDH−$CO_3$−HP. Both of the experiments were carried out in duplicate.

PZC was performed according to the method described by Mustafa et al. (*34*). Dry samples (100 mg) were suspended in 40 mL of 0.001 mol L$^{-1}$ KCl solution as a background electrolyte and equilibrated for 30 min under magnetic stirring. The initial pH of the solution was adjusted to pH 4.0 by the addition of either 0.1 mol L$^{-1}$ HCl or 0.1 mol L$^{-1}$ KOH. The suspensions were equilibrated for a further 10 min, and the pH was then measured. The suspension pH was recorded every 2 min as a function of volume of titrant added until pH 11.0 was reached. The PZC of the sorbents was determined from the variation of the surface charge density as a function of pH.

X-ray diffraction (XRD) patterns of randomly oriented specimens were recorded with a Rigaku Geigerflex D/Max IIIC diffractometer using iron-filtered Cu Kα radiation generated at 40 kV and 30 mA, at a scan speed of 1° 2θ min$^{-1}$. The oriented specimens were stored for 24 h at 20 °C in a desiccator containing CaCl$_2$ before XRD analysis. The XRD intensities of the mineralogical entities were enhanced by summing eight times the signal. In adding, characterization of LDH−$CO_3$ and complexes was also performed using the same methods reported for polymerin.

**Methods for Assessing the Stability of LDH and LDH−Polymerin Complexes.** The stability was evaluated by equilibrating 400 mg of LDH−$CO_3$, LDH−$CO_3$−LP, and LDH−$CO_3$−HP in 160 mL of 0.03 mol L$^{-1}$ NaNO$_3$ at pH 4.0, 6.0, and native pH (8.5−9.0). The pH of the complexes was kept constant by adding HCl or NaOH while no adjustment was necessary for LDH−$CO_3$. After 48 h, samples were centrifuged, freeze-dried, and weighed to determine the residual solid materials. All of the samples were analyzed by XRD and DRIFT.

Subsamples of LDH−$CO_3$−LP were kept in mother waters in an oven at 80 °C for 7, 15, 30, 60, 90, 120, and 180 days and then washed, centrifuged, freeze-dried, and weighed to estimate the degree of stability of the complex. The dry powder samples were also analyzed by CHNS, XRD, and DRIFT.

**Sorption of Zn or As(V) onto LDH−$CO_3$ and LDH−$CO_3$−Polymerin Complexes.** Sorption experiments of Zn or As(V) were

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**Table 1.** Chemical Composition and Physicochemical Properties of Polymerin[a]

| | |
|---|---|
| polysaccharide (% w:w) | 36.7 |
| protein (% w:w) | 32.5 |
| melanin (% w:w) | 24.4 |
| metals (% w:w) | 3.4 |
| carbon (% w:w) | 45.8 |
| $E_4/E_6$ ratio | 3.8 |
| PZC | 2.2 |
| COOH acidity (mequiv g$^{-1}$) | 3.9 |
| phenolic OH acidity (mequiv g$^{-1}$) | 5.8 |
| surface area (m$^2$ g$^{-1}$) | 312.0 |

[a] The averages and standard deviations of three measurements were recorded for each sample. The standard deviation was lower than 4%.

carried out at room temperature on LDH−CO$_3$, and on LDH−CO$_3$−LP and LDH−CO$_3$−HP complexes. Stock solutions were prepared by dissolving 20 mmol L$^{-1}$ of Zn(NO$_3$)$_2$·6H$_2$O and 0.01 mol L$^{-1}$ of Na$_2$HAsO$_4$. Sorption experiments were conducted at a solid/liquid ratio of 1, obtained by adding 10 mg of sorbent (LDH−CO$_3$, LDH−CO$_3$−LP, and LDH−CO$_3$−HP) and dried at 100 °C for 1 h to 9.5 mL of 0.03 mol L$^{-1}$ NaNO$_3$, and the final volume was brought to 10 mL. Different volumes of stock solution were added to each sorbent to give an initial concentration of heavy metal ranging from 8.4 × 10$^{-3}$ to 15.3 mmol L$^{-1}$ for Zn and from 50 × 10$^{-3}$ to 7.5 mmol L$^{-1}$ for As(V), respectively. Each suspension was kept constant to pH 4.0 for 48 h by the addition of dilute solutions of HCl or KOH. Preliminary tests indicated that an apparent equilibrium was reached after 24−48 h of reaction. After sorption, the suspensions were centrifuged at 7000 g min$^{-1}$ for 30 min, and the supernatants were analyzed.

Zn was determined by atomic absorption spectrometry (AAS) utilizing a Perkin-Elmer 3030 B atomic absorption spectrometer equipped with deuterium-arc background correction. An air−acetylene flame was used as the atomization source. Arsenate was analyzed by ionic chromatography using a Dionex DX-300 Ionic Chromatograph (Dionex Co., Sunnyvale, CA), an Ion-Pac AS11 column (4.0 mm), an eluent of 0.05 mol L$^{-1}$ NaOH at a flow rate of 2.0 mL min$^{-1}$, and a CD20 Conductivity Detector combined with autosuppression. The amount of each metal retained on the sorbents was determined by the difference between the initial quantity of metal added and that present in the equilibrium solution. Experimental uncertainties were evaluated in vials without samples, which showed that total uncertainty was less than 4% of the initial concentrations. All of the experiments were performed in triplicate.

The sorption data were analyzed according to the Langmuir equation, which can be written as follows:

$$S = S_m KC_e/(1 + KC_e)$$

where $S$ is the amount of polymerin sorbed on LDHs (g kg$^{1-}$), $K$ is the Langmuir constant related to the binding energy, $S_m$ is the maximum amount of polymerin (g kg$^{1-}$) sorbed, and $C_e$ is the equilibrium concentration of polymerin (g L$^{-1}$).

## RESULTS AND DISCUSSION

**Characterization of Polymerin.** Chemical and physicochemical properties of polymerin, a humic acidlike polyelectrolyte, are shown in **Table 1**. Polymerin was composed of carbohydrates (36.7%, w/w), proteins (32.5%, w/w), melanin (24.4%, w/w), and metals (3.4%, w/w), naturally bound and chelated to the organic matrix (23). The anionic proprieties of this material were due to the high carboxylic and phenolic acidity corresponding to 3.9 and 5.8 mequiv g$^{-1}$ respectively. Polymerin showed a higher content in phenolic groups attributable to its catecholmelanine nature, as opposed to humic substances, which are characterized by a high content of carboxylic groups with respect to the phenolic ones [3.7 and 1.3 mequiv g$^{-1}$, respectively (35)].

The DRIFT spectrum of polymerin (**Figure 1**) showed a band characteristic of −OH groups (3316 cm$^{-1}$), four weak albeit correlated bands corresponding, respectively, to the stretching of methylester groups (1726 and 1288 cm$^{-1}$) and the symmetric and
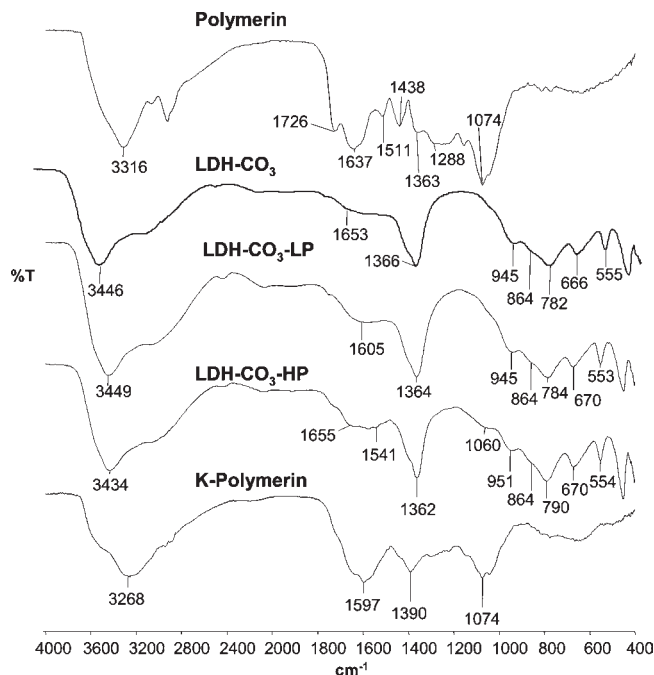


**Figure 1.** DRIFT spectra of LDH−CO$_3$, LDH−CO$_3$−LP, LDH−CO$_3$−HP, polymerin, and K−polymerin, which form at high pH values (see the text for an explanation).

asymmetric stretching of the corresponding CH$_3$ groups (1438 and 1363 cm$^{-1}$). In addition, the spectrum showed the band due to the stretching of aromatic rings and C=O peptide groups (1637 cm$^{-1}$) and the band corresponding to the stretching of C−OH bonds of the polysaccharide component (1074 cm$^{-1}$). The absorption at 1511 cm$^{-1}$ was also assignable to the aromatic ring stretching. Finally, the bands at 1637 and 1438 cm$^{-1}$ were also ascribable to the symmetric and asymmetric stretching of COO$^-$ groups (23).

It is well-known that a low $E_4/E6$ ratio indicates a high degree of condensation of aromatic constituents (36). $E_4/E_6$ is <5 for small molecular weight compounds and >5 for larger molecular weight ones (36). Polymerin presented an $E_4/E_6$ ratio of 3.82 (**Table 1**), which indicates the presence in solution of fraction with relatively small molecular weights. Finally, polymerin showed a surface area of 312 m$^2$ g$^{-1}$ (**Table 1**).

**Nature of LDH−CO$_3$ and LDH−Cl and Their Complexes with Polymerin.** XRD patterns of LDH−CO$_3$ and LDH−Cl (**Figure 2**) showed the characteristic pattern of a crystalline hydrotalcite-like material with sharp and symmetrical peaks. Basal spacings calculated from the $d_{003}$ reflection were 7.60 and 7.58 Å, which correspond to the carbonate and the chloride anions in the interlayer domains (2, 29, 37, 38). The uncalcined materials showed a well-crystallized structure with respect to the calcined ones. In fact, XRD patterns of LDH−CO$_3$-450 and LDH−Cl-450 showed the disappearance of the hydrotalcite-like peaks and the appearance of broad peaks centered at 2.55, 2.10, and 1.49 Å (not shown). After calcination, LDH−CO$_3$ and LDH−Cl lost the crystalline structure because of the dehydration of the same structure and the formation of mixed Mg−Al oxides (39, 40).

The DRIFT spectrum of LDH−CO$_3$ (**Figure 1**) presented the characteristic bands of hydrotalcite. It showed a broad peak at 3446 cm$^{-1}$ corresponding to the stretching of the −OH attached to Al and Mg and −OH of water; a signal at 1653 cm$^{-1}$, assignable to the bending vibration of the interlayer water; and three peaks at 945, 782, and 555 cm$^{-1}$, corresponding to the stretching of Al−O and Mg−O. The presence of CO$_3^{2-}$ in the
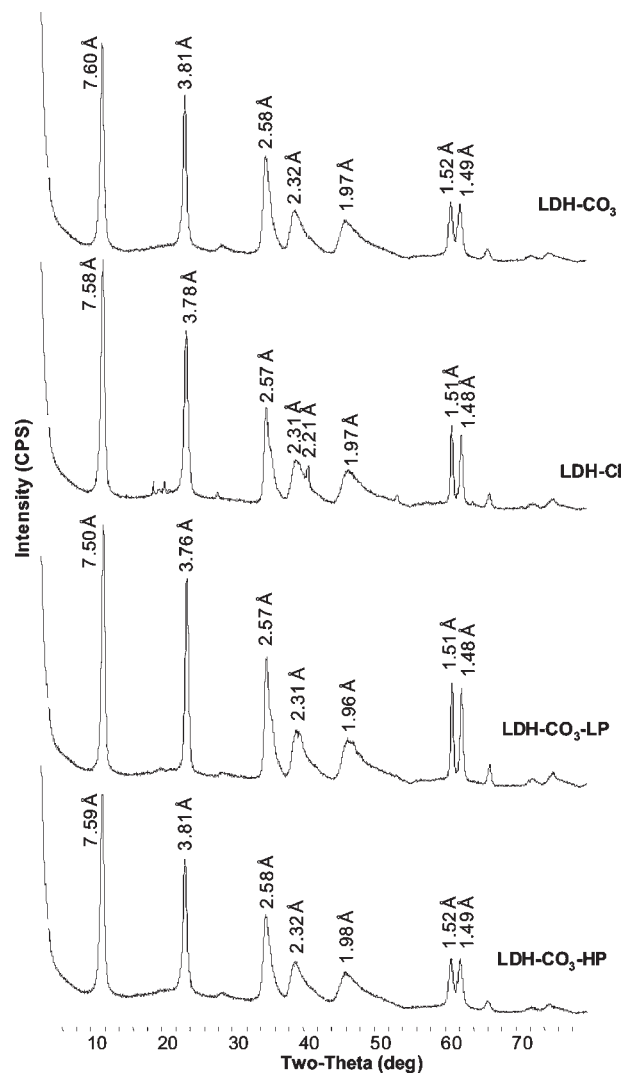
**Figure 2.** XRD of LDH−CO$_3$, LDH−Cl, LDH−CO$_3$−LP, and LDH−CO$_3$−HP.



**Figure 3.** Sorption isotherms of polymerin on LDH−CO$_3$, LDH−Cl, LDH−CO$_3$-450, and LDH−Cl-450.

**Table 2.** Langmuir Parameters for the Sorption of Polymerin on LDH−CO$_3$, LDH−CO$_3$-450, LDH−Cl, and LDH−Cl-450

| | Langmuir parameters | | |
| --- | --- | --- | --- |
| | $S_m$ | $K$ | $R^2$ |
| LDH−CO$_3$ | 83 ± 3.2[a] | 5.5 ± 0.61[b] | 0.99 |
| LDH−CO$_3$-450 | 57 ± 5.4 | 13.7 ± 5.8 | 0.98 |
| LDH−Cl | 67 ± 6.7 | 2.71 ± 0.5 | 0.94 |
| LDH−Cl-450 | 76 ± 21 | 1.2 ± 0.56 | 0.97 |

[a] Standard error of $S_m$. [b] Standard error of K.

interlayer was demonstrated by three characteristic peaks at about 1366, 864, and 666 cm$^{-1}$. The spectrum of LDH−Cl (not shown) was very similar to the spectrum of LDH−CO$_3$, with a slight shift of the signals. Moreover, the signal at about 1366 cm$^{-1}$ was particularly weak, indicating that carbonate was present only as an impurity. The DRIFT spectrum of LDH−Cl-450 and LDH−CO$_3$-450 (not shown) presented a strong decrease of the peak at about 1366 cm$^{-1}$ (mainly in LDH−CO$_3$-450).

LDH−Cl and LDH−CO$_3$ showed a surface area of 421 and 396 m$^2$ g$^{-1}$, respectively. After heating at 450 °C, the surface area of LDH−Cl decreased to 395 m$^2$ g$^{-1}$, whereas the surface area of LDH−CO$_3$ increased to 515 m$^2$ g$^{-1}$, attributable to the removal of CO$_2$ and H$_2$O after heating, which promoted the formation of channels and a particularly porous and reactive material (*3, 37*).

With the aim to obtain polyvalent organo−mineral complexes, able to sorb cationic and anionic pollutants, sorption studies of polymerin on calcined and uncalcined matrices were carried out. Sorption isotherms are shown in **Figure 3**, while the Langmuir parameters are listed in **Table 2**. Vreysen and Maes (*41*) reported a contact time of 40 h for the sorption of HAs on LDHs. Thus, a contact time of 72 h used in this work was sufficient to ensure sorption equilibrium conditions. LDH−CO$_3$ showed a greater capacity to sorb polymerin than the other sorbents. The $S_m$ values of the Langmuir equation (**Table 2**) are evidence that the
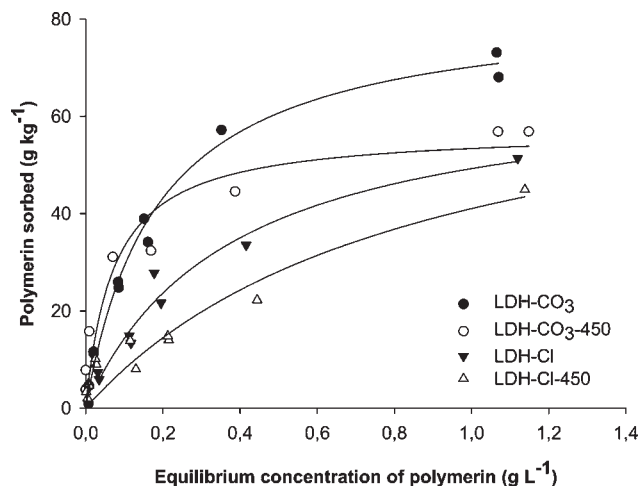
quantities of polymerin sorbed on the materials under investigation decreased according to the following order: LDH−CO$_3$ > LDH−Cl-450 > LDH−Cl > LDH−CO$_3$-450.

We have ascertained that the $E_4/E_6$ ratio of the polymerin, which remained in the supernatants after sorption onto LDH−CO$_3$ and LDH−Cl, increased from 3.82 to 6.07 and 7.16, respectively, revealing high concentrations of higher molecular weight substances in solution. These data indicate that the small molecules present in the polymerin were more easily sorbed than the larger ones. In fact, LDHs are mesoporous sorbents, and consequently, small molecules can easily enter these spaces. The same results were obtained by Vreysen and Maes (*41*) for sorption of HA and FA on LDHs.

**Nature of the LDH−CO$_3$−LP and LDH−CO$_3$−HP Samples.** LDH−CO$_3$ showed the highest capacity to retain polymerin if compared to the other sorbents used in this work. Therefore, it was chosen for the preparation (see the Materials and Methods) of complexes with polymerin, to carry out experiments on the sorption of heavy metals.

Chemical and physicochemical properties of LDH−CO$_3$−LP and LDH−CO$_3$−HP are listed in **Table 3**. Chemical analysis demonstrated that LDH−CO$_3$−LP and LDH−CO$_3$−HP contained 8.5 and 18.9% of polymerin for dry weight of the complex, respectively. Both of the complexes sorbed prevalently the polysaccharidic component of polymerin, while protein and melanin were retained in similar amounts. However, it appears evident that LDH−CO$_3$ more selectively sorbed melanin than protein. In fact, in polymerin, the organic fraction constituted (% in weight) 36.7% polysaccharides, 32.5% protein, and 24.4% melanin, whereas in LDH−CO$_3$−LP and LDH−CO$_3$−HP, the organic material constituted 41.6−45.9% polysaccharides, 28.8−29.5% protein, and 24.6−29.5% melanin (**Tables 1** and **3**).

The PZCs of LDH−CO$_3$ and polymerin were about 10.2 and 2.2, respectively (**Tables 3** and **1**). Nevertheless, given that the

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**Table 3.** Chemical and Physical Properties of LDH−CO₃, LDH−CO₃−LP, and LDH−CO₃−HP

| | PZC | polymerin (%) | surface area (m² g⁻¹) | polysaccharide (%) | melanin (%) | protein (%) |
|---|---|---|---|---|---|---|
| LDH−CO₃ | 10.2 | | 396 ± 21 | | | |
| LDH−CO₃−LP | 9.9 | 8.5 ± 0.27[a] | 403 ± 12.6 | 3.3 ± 0.01 | 2.3 ± 0.18 | 2.3 ± 0.06 |
| LDH−CO₃−HP | 9.7 | 18.9 ± 0.45 | 349 ± 14.3 | 8.2 ± 0.31 | 4.4 ± 0.03 | 5.3 ± 0.17 |

[a] Standard deviation.
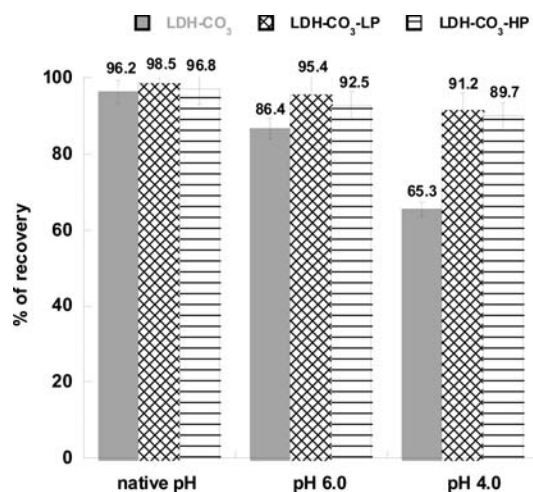


**Figure 4.** Percentage of recovery of LDH−CO₃ and LDH−CO₃−polymerin complexes in native condition and at pH 4.0 and 6.0 after acidic treatment.



**Figure 5.** DRIFT spectra of LDH−CO₃, LDH−LP, and LDH−CO₃−HP after treatment at pH 4.0.

surfaces of LDHs were only partially covered by polymerin, only a low decrease of the PZC was observed in the organo−mineral complexes (**Table 3**).

The DRIFT spectra of the two complexes (**Figure 1**) showed the characteristic signals of LDH−CO₃ with small bands at 1060 and 1541 cm⁻¹ of polymerin (LDH−CO₃−HP) or at 1605 and 1364 cm⁻¹ of K−polymerin (LDH−CO₃−LP). This latter material, reported by Capasso et al., (*24*), was a derivative of polymerin saturated with potassium with a molecular weight in the range of 3500−10000 Da, generated by the elevated pH of solution of KOH used during the preparation of the complex as a consequence of the broken linkages between the polymerin components and the hydrolysis of the ester groups.

The DRIFT spectra of the complexes also presented the characteristic bands of the carbonate anion indicating that neither polymerin nor K−polymerin were able to intercalate in the layer structure of LDH−CO₃. The XRD patterns of LDH−LP and LDH−HP were very similar to those of LDH−CO₃ (**Figure 2**), indicating that K−polymerin or polymerin was sorbed exclusively onto the external surfaces of the mineral matrix and that no intercalation occurred, due clearly to their high hindrance. Analogously, Vreysen and Maes (*41*) demonstrated that HA and FA sorption on LDHs occurred mainly by ion exchange ligand reaction with surface groups, but no intercalation was observed.

**Influence of pH and Hydrothermal Treatment on the Stability of LDH−CO₃, LDH−CO₃−LP, and LDH−CO₃−HP Samples.** With the aim to investigate the structural change and the stability of LDH−polymerin complexes, LDH−CO₃−LP and LDH−CO₃−HP were treated with HCl at pH 4.0 and 6.0 and compared with those at native pH (8.5−9.0) (**Figure 4**). All of the matrices showed a partial dissolution of the layer structure when the pH decreased. This process was less evident for the organo−mineral complexes than LDH−CO₃ (**Figure 4**). Santosa et al. (*42*) showed a progressive dissolution of LDH, by decreasing the pH of the suspension, as a consequence of the broken of the linkage between
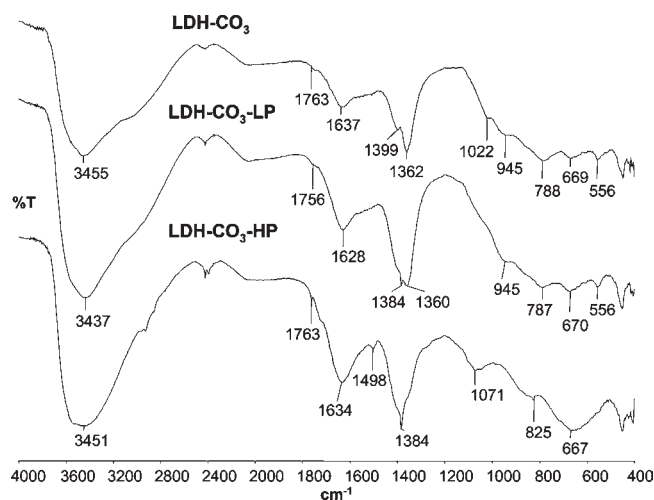
the protonated hydroxide groups and the Mg and Al of layer structure.

The DRIFT spectrum of LDH−CO₃ at pH 4.0 (**Figure 5**) showed the band at 1637 cm⁻¹ shifted with respect to the weak band observed at 1653 cm⁻¹ in the spectrum of LDH−CO₃ at native pH (**Figure 1**), due to the removal of carbonate by water molecules. Moreover, a decrease of metal−oxygen bands at 788 and 556 cm⁻¹ was attributable to the broken linkage between hydroxide groups linked to Mg and Al. In native conditions, the organo−mineral complexes showed an almost total recovery after 48 h under stirring (**Figure 4**). At pH 6.0 and pH 4.0, the percentage of recovery of the complexes was higher than that observed for LDH−CO₃ in the same conditions. The higher stability of the organo−mineral complexes may be attributed to polymerin molecules that covered and protected the surfaces of the mineral. The XRD analysis of LDH−CO₃ at pH 4.0 (**Figure 6**) showed a decrease of the peaks intensity previously observed at native pH and the appearance of new peaks ascribable to the formation of MgCO₃ formed by carbonate of LDH−CO₃ with Mg released in solution.

The stability of LDH−CO₃−LP was also evaluated by using a prolonged hydrothermal treatment. A temperature of 80 °C was chosen because it was low enough to avoid the loss of carbonate in the form of CO₂ and high enough to increase the degree of crystallinity (*3*). The data showed that a weak release of polymerin (from 3.9 to 3.4% of organic carbon) corresponding to 13.6% of polymerin occurred during the first week of hydrothermal treatment, and no significant variation in the organic carbon occurred after this period. The XRD and DRIFT analysis (no shown) of the treated samples showed the same pattern as the untreated ones.

**Sorption of As(V) or Zn on LDH−CO₃ and on LDH−CO₃−Polymerin Complexes.** Sorption isotherms at pH 4.0 of As(V) added to LDH−CO₃, LDH−CO₃−LP, and LDH−CO₃−HP are shown in **Figure 7**. The shape of the isotherm of As(V) on LDH−CO₃ indicated high affinity behavior, such that the

**Table 4.** Langmuir Parameters of As(V) and Zn on LDH–CO$_3$, LDH–CO$_3$–HP, and LDH–CO$_3$–LP

| | As(V) | | | Zn | | |
|---|---|---|---|---|---|---|
| | $S_m$ | $K$ | $R^2$ | $S_m$ | $K$ | $R^2$ |
| LDH–CO$_3$ | 1860 ± 293[a] | 4.76 ± 3.6[b] | 0.87 | 824 ± 68[a] | 0.2 ± 0.04[b] | 0.97 |
| LDH–CO$_3$–LP | 1180 ± 296 | 1 ± 0.61 | 0.81 | 1097 ± 75 | 0.13 ± 0.02 | 0.96 |
| LDH–CO$_3$–HP | 781 ± 114 | 1.22 ± 0.56 | 0.92 | 1493 ± 59 | 0.11 ± 0.01 | 0.97 |

[a] Standard error of $S_m$. [b] Standard error of $K$.
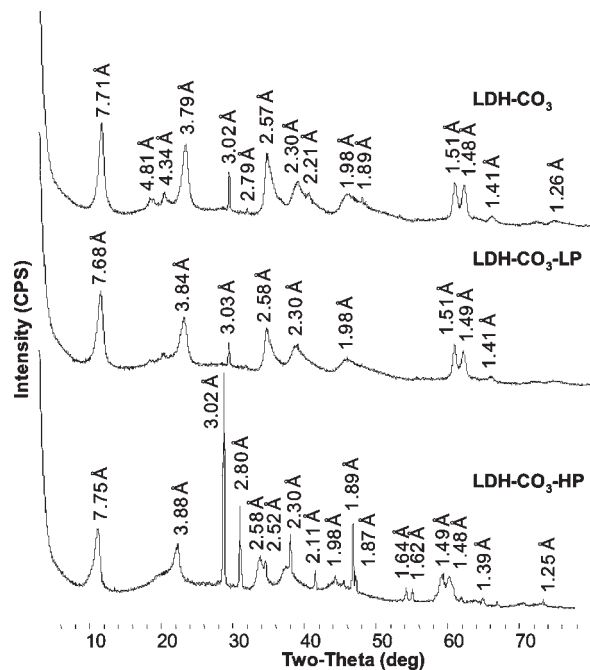


**Figure 6.** XRD patterns of LDH–CO$_3$, LDH–CO$_3$–LP, and LDH–CO$_3$–HP after treatment at pH 4.0.
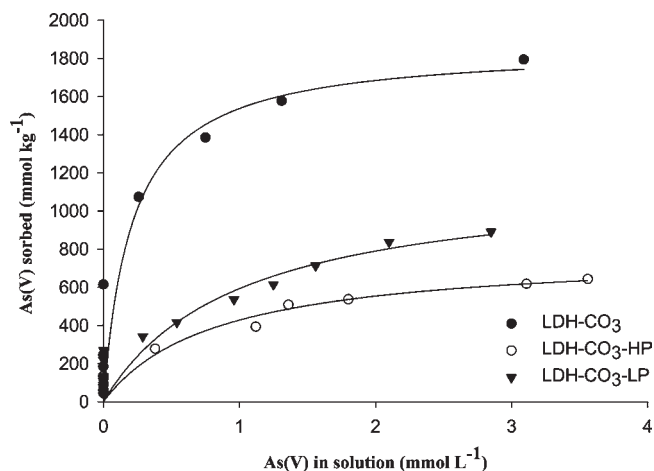


**Figure 7.** Sorption isotherms of As(V) on LDH–CO$_3$, LDH–CO$_3$–LP, and LDH–HP at pH 4.0.

sorption was characterized by a rapid rise at a low As(V) equilibrium concentration. The high capacity of LDHs to remove As(V) from an aqueous medium has been previously demonstrated (*43*). Vice versa, the sorption of As(V) on LDH–CO$_3$–LP and LDH–CO$_3$–HP increased slowly when the ligand equilibrium concentration increased, due to a weaker affinity of the anions for these sorbents. The maximum amount of As(V) sorbed on LDH–CO$_3$, LDH–CO$_3$–LP and LDH–CO$_3$–HP was 1860, 1180, and 781 mmol kg$^{-1}$, respectively (**Table 4**). Polymerin
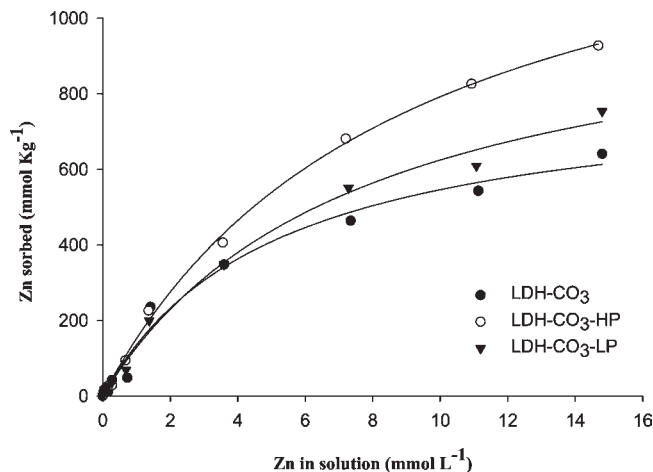


**Figure 8.** Sorption isotherms of Zn on LDH–CO$_3$, LDH–CO$_3$–LP, and LDH–HP at pH 4.0.

present in the organo–mineral complexes reduced by 37 (LDH–CO$_3$–LP) and 58% (LDH–CO$_3$–HP) the capacity of LDH–CO$_3$ to sorb As(V). The influence of biomolecules in preventing As(V) sorption on clay minerals, including LDHs, by competing for sorption sites has been widely studied [(*43*) and references therein].

Certainly, LDH–CO$_3$ appears to be the best sorbent for As(V), but LDH–CO$_3$ –LP (mainly) and LDH–CO$_3$ –HP also showed a relatively high capacity to sorb As(V) as well as a great capacity to sorb heavy metals in cationic form (as discussed below). Furthermore, organo–mineral complexes presented in this work showed a capacity to sorb As(V) comparable or greater than other sorbents studied in previous works. It was demonstrated that at pH 4.0 polymerin sorbed 384 mmol As(V) kg$^{-1}$ ($S_m$) through hydrogen bonds with alcoholic, phenol, and carboxymethyl groups, a polymerin–ferrihydrite complex was able to sorb up to 743 mmol As(V) kg$^{-1}$, whereas ferrihydrite showed a maximum sorbing capacity of 880 mmol kg$^{-1}$ (*25*). Therefore, among of all of the considered matrices, LDH–CO$_3$ proved to be the best sorbent for As(V) at pH 4, even if, at this pH, its chemical stability was the lowest in comparison to all of the other materials that we have studied.

The sorption isotherms of Zn on the three matrices and the respective parameters are shown in **Figure 8** and **Table 4**. As shown by the respective isotherms, the sorption followed the order LDH–CO$_3$–HP > LDH–CO$_3$–LP > LDH–CO$_3$ with a maximum amount of Zn sorbed corresponding to 1493, 1097, and 824 mmol kg$^{-1}$, respectively.

Park et al. (*20*) reported that reactions of Cu and Pb(II) with LDHs resulted in a process of surface precipitation of these heavy metals. Probably the same mechanism occurred when LDH–CO$_3$ reacted with Zn. The presence of polymerin in the organo–mineral complexes limited the precipitation, favoring the sorption process of Zn onto the negative sites of the organic material with a consequent greater amount of heavy metal removed from solution.

In conclusion, the sorption capacity of As(V) on LDH−CO$_3$, LDH−CO$_3$−LP, and LDH−CO$_3$−HP at pH 4.0 followed the order LDH−CO$_3$ > LDH−CO$_3$−LP > LDH−CO$_3$−HP (1860, 1180, and 781 mmol kg$^{1-}$, respectively). Therefore, among the three considered matrices, LDH−CO$_3$ appeared to be the most convenient for a possible application in the remediation of waters contaminated with arsenic or other anionic pollutants. However, because this sorbent showed at pH 4.0 a stability lower than that of the organo−mineral complexes (65.3 against 89.7% for LDH−CO$_3$−HP and 91.2% LDH−CO$_3$−LP of recovery), the choice of this sorbent as a possible treatment of waters individually contaminated with As(V) or other anionic pollutants appears possible at pH > 4.0 and must be evaluated on the cost−benefit ratio point of view. Anyhow, the employment of LDH−CO$_3$ or its corresponding complexes with polymerin appears much more convenient than that of ferrihydrite, polymerin, or their complex, as we recently published (*25*), by considering the maximum sorbing capacity of the latter (880, 384, and 743 mmol kg$^{-1}$, respectively).

On the contrary, the sorption capacities of Zn on LDH−CO$_3$−LP and LDH−CO$_3$−HP (1097 and 1493 mmol kg$^{-1}$, respectively) were higher than on LDH−CO$_3$ (824 mmol kg$^{1-}$), due to the presence of many negative charges on polymerin. Therefore, the two complexes could be more conveniently utilized for the decontamination of waters contaminated with heavy metals in cationic form. Even if the sorption capacity of Zn on the polymerin is much higher (*24*) than on the LDH complexes here considered, the potential decontamination process conducted on the latter sorbent is more simple and cheaper (only requiring a centrifugation procedure), whereas an ultrafiltration plant is necessary for the use of polymerin.

Finally, because the waste waters are usually contaminated with mixtures of pollutants in cationic and anionic form, the LDH−polymerin complexes appear more suitable than the sorbents in a potential water remediation process. In addition, a cyclic sorption process conducted on these matrices, renewed at each cycle, could be very efficient for the total removal of polluting metals from water, according to the methodology that we previously reported for the clean up of waters contaminated with mixtures of cationic heavy metals (*24*), anionic metalloids (*25*), or ionic herbicides (*26*, *27*).

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