



Letter to the Editor

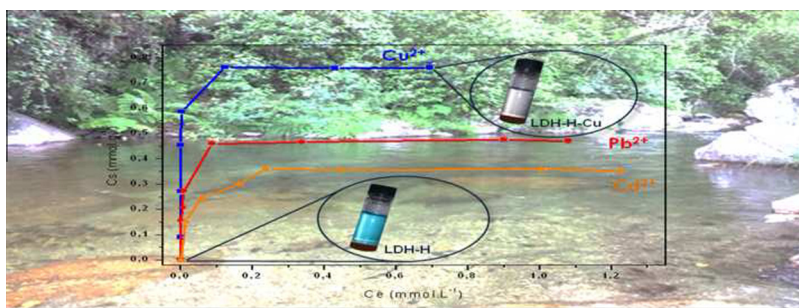
## Removal of $\text{Cu}^{2+}$ , $\text{Pb}^{2+}$ and $\text{Cd}^{2+}$ by layered double hydroxide–humate hybrid. Sorbate and sorbent comparative studies

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## HIGHLIGHTS

- Layered double hydroxide–humate hybrid was synthesized by ionic exchange method.
- Inorganic matrix was stabilized by humate incorporation.
- High capacity for the  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  removal by different mechanisms.
- The simultaneous heavy metal sorption increased the total metal amount sorbed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The synthesis of a layered double hydroxide–humate (LDH–H) hybrid was purposed for the removal of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  from aqueous solutions. This sorbent has been synthesized by incorporating humate anion into magnesium aluminum layered double hydroxide with chloride as an interlayer anion (LDH–Cl) via ion exchange. The effects of various physico-chemical factors such as pH influence, contact time, initial metal concentration and the simultaneous sorption of the three heavy metal ions onto LDH–H were investigated. The sorption capacities of humic acid (HA), LDH–Cl and LDH–H were compared under the same experimental conditions. The hybrid LDH–H presented better properties, such as greater stability and less pH increase throughout the sorption process. A high affinity and large removal capacity of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  were obtained by complexation and hydroxide precipitation mechanism, being this major for the case of  $\text{Cu}^{2+}$ , according to its low hydroxide solubility product value. The sorption isotherms were well described by the Langmuir equation. The metal removal efficiency was lower when the three cations were competing for the available adsorbent sites, compared to monocomponent solutions.

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## 1. Introduction

Heavy metals are important pollutants that reach the soils and waters due to natural processes and human activities such as

mining, metal plating, batteries and fertilizing industry among many others. They are not biodegradable and their toxicity lies in their bioaccumulativity. For humans, extended exposure to heavy metals can result in damage to mental and central nervous function, blood composition, lungs, liver and other vital organs. World Health Organization drinking water guideline values for Cu, Cd and Pb are 2, 0.003 and 0.01 mg/l respectively [1]. Therefore, there is a great interest in the development of processes for heavy metals removal from wastewater ground water and sediments. Methods

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applied in heavy metal removal from aquifers are chemical precipitation as sulfides or hydroxides, filtration, coagulation, inverse osmosis, electrolysis, etc. [2–5]. However, some of them are expensive or unsuitable and there is an increasing interest in the research of low-cost and non-toxic alternatives adsorbents such as zeolites [6], clays and clay minerals [7,8], as well as agricultural and municipal wastes [9].

Thus, heavy metals are immobilized by humic substances (HS), which are the product of decomposed organic matter in soils and waters. Their sorbent properties arise from the presence of humic acid (HA) which is the most abundant fraction of HS. HA are large colloidal molecules with variable composition, but they have a high content of oxygen-containing (carboxylic, phenolic) functional groups [10]. These functional groups exist in anionic form in a large pH range and in bond metal ions through electrostatic interactions and coordinate bonding [11–13]. HA could provoke problems in water treatments for many reasons such as the alteration of color, taste, odor, forming of carcinogenic by-products during the chlorination etc. Consequently, different materials such as activated carbon, alumina, zeolites, clays and clay minerals were proposed for the uptake of HA from waters [14–17]. Moreover, humic acids affect the removal capacity of pollutants such as heavy metal ions by other sorbents, such as carbon nanotubes and zero valent iron nanoparticles [18].

A class of minerals, which are also reported to be good sorbents of both heavy metals and HA, are the layered double hydroxides (LDHs) [16,19]. The structure of LDHs, also known as hydrotalcite-like compounds, are derived from that of brucite ( $\text{Mg}(\text{OH})_2$ ) by isomorphic substitution of  $\text{Mg}^{2+}$  by  $\text{Al}^{3+}$  ions. The charge excess generated is balanced by intercalation of anions between the layers [20]. The general LDH formula can be represented as  $[\text{M}_1^{II-x}\text{M}_x^{III}(\text{OH})_2]\text{X}^{n-x/n}\cdot m\text{H}_2\text{O}$  where  $\text{M}^{II}$ ,  $\text{M}^{III}$ , and X represent a divalent and trivalent cation and the interlayer anion, respectively. All of them may vary over a wide range and X is quite easy to exchange with other anions [21,22]. These materials are receiving increasing attention due to interesting specific properties such as anion exchange capacity, acid–base buffering capacity, reconstruction from their calcination products, and high customization possibilities. Therefore, LDHs have been studied for their potential applications in diverse areas [23–25], their low toxicity making them suitable for environmental applications [26–30]. Thus, LDHs were used to remove heavy metal by precipitation of the corresponding hydroxides due to their pH buffering capacity and when LDHs are functionalized with chelating ligands such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetate or meso-(2,3)-dimercaptosuccinate etc., the solids thus obtained showed sorption capacity for heavy metal cations such as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  [31–33]. The objective of this work was to obtain a layered double hydroxide–humate hybrid (LDH–H) and explore its capacity to remove  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  from water. Firstly, the sorption capacity of this hybrid was compared to those of chloride intercalated LDH and humic acid. Afterwards, the effect of pH, the contact time and initial metal concentration on LDH–H sorption capacity was assessed and the competition between the three heavy metal ions was evaluated.

## 2. Experimental

All reagents were reagent grade and purchased from Aldrich. Water was distilled and previously boiled and purged with  $\text{N}_2$  to prevent  $\text{CO}_2$  presence.

### 2.1. Synthesis and characterization

The synthesis of the layered double hydroxide–humate hybrid (LDH–H) was carried out in two steps: the preparation of a chloride

intercalated precursor (LDH–Cl), obtained by the coprecipitation method [21], which was afterwards dispersed in a sodium humate solution.

LDH–Cl was prepared by drop-wise addition of a 200 mL aqueous solution of 0.75 M of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and 0.25 M of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  to a 0.25 M of NaCl solution under vigorous agitation and constant pH = 8, set by addition of 1 M NaOH solution. The synthesis was performed in  $\text{N}_2$  atmosphere in order to avoid atmospheric  $\text{CO}_2$  dissolution and consequently carbonate incorporation to the solid. The suspension obtained was hydrothermally treated at 80 °C for 24 h, separated by centrifugation and washed. A portion of the precipitate was dried at 60 °C to obtain LDH–Cl, while the remaining slurry was suspended in a 0.13 M sodium humate solution under vigorous stirring and a constant pH = 8 for 24 h. The resulting dispersion (LDH–H) was separated by centrifugation, washed and dried as previously described.

Mg and Al elemental chemical analyses were performed by Inductively Coupled Plasma Mass Spectrometry (ICP–MS) in a Perkin Elmer ELAN DRC–e instrument. The samples were dissolved in concentrated  $\text{HNO}_3$  and diluted to meet the calibration range. Powder X-ray diffraction (PXRD) patterns were recorded using a Siemens D-5000 diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54050$ ). Fourier-transform infrared (FT–IR) spectra were registered using the KBr disk method on a Perkin Elmer Spectrum One spectrophotometer. TG and DTA curves were recorded on a Setaram Setsys Evolution 16/18 apparatus in an oxidizing atmosphere and at the heating rate of 5 °C/min. Finally, SEM images were recorded in a JEOL JSM 6300 instrument on samples covered with an Au layer.

### 2.2. Sorption experiments

The optimal sorption conditions (initial pH, contact time) were determined in the sorption experiments performed. 0.05 g of the adsorbent (LDH–Cl or LDH–H) was dispersed in 30 mL, 1 mM aqueous solutions of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  nitrate salts. Sorption isotherms were performed in 30 mL dispersions containing 0.05 g sorbent with increasing initial concentration ( $C_0$ ) of the corresponding heavy metal ion ( $C_0 = 0\text{--}2$  mM). Finally, the competence between the three heavy metals for LDH–H sorbent was studied by dispersing 0.05 g of sorbent in 30 mL solutions containing all three heavy metal ions ( $C_0 = 1$  mM and initial pH 5, each). The initial pH 5 was selected to be sure that the all of the metal ions were dissolved in all cases.

The experiments were performed by duplicate in all cases. The dispersions were shaken at 52 rpm at room temperature, centrifuged and finally filtered on Nylon filters (pore size 0.22  $\mu\text{m}$ ). The heavy metal concentration of the resulting supernatants was determined by atomic absorption spectrometry (AAS) in a Perkin Elmer AAnalyst400 instrument, the samples being dissolved in concentrated  $\text{HNO}_3$  and diluted to meet the calibration range. These concentrations were used to determine the amount of each metal adsorbed by the sorbents ( $C_s$ ,  $\text{mmol g}^{-1}$ ):

$$C_s = (C_0 - C_e)V/W \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium solution concentrations ( $\text{mmol L}^{-1}$ ),  $W$  is the weight of solid (g) and  $V$  is the solution volume (L).

The adsorption isotherm data were fitted to the Langmuir model (Eq. (2))

$$C_e/C_s = (1/C_m)C_e + 1/(C_m K_L) \quad (2)$$

where  $C_m$  is the maximum sorption capacity at the monolayer coverage ( $\text{mmol g}^{-1}$ ) and  $K_L$  ( $\text{L mmol}^{-1}$ ) is a constant related to the adsorption energy.

### 3. Results and discussion

#### 3.1. Characterization of the LDH–Cl and LDH–H

The XRD patterns of LDH–Cl and LDH–H (Fig. 1) portrayed characteristic peaks of hydroxylate-like compounds [34], sharp, high intensity (001) peaks at  $2\theta$  values below  $30^\circ$ , and broad, low intensity ( $hkl$ ) peaks above this value. The basal spacing obtained for LDH–Cl (7.7 Å) was typical of chloride-intercalated hydroxylates [34]. LDH–H basal spacing was slightly higher (7.9 Å) and similar to other HA containing LDHs previously reported. Thus, Seida and Nakano [35] suggest that LDH weathering provokes a coagulation of a part of humic acid which is adsorbed on LDH surface, while a small part is bonded by ionic exchange with LDHs interlayer carbonates. Also, Vreysen and Maes [16] propose a ligand exchange between HA and Al–OH groups of the brucite layers as a main mechanism of humic acid bonding to LDH. We consider that the incorporation of HA anions were produced mainly at the surface of the LDH particles, and that a partial intercalation of the humate near the LDH particle edges was concurrent. Humate anions were disposed in a parallel position to the layers, which could explain the slight basal spacing increase.

The FT-IR spectra of LDH–Cl (Fig. 2a) presented bands corresponding to the hydroxylated layers (below  $900\text{ cm}^{-1}$ ), hydroxyl stretching (above  $3000\text{ cm}^{-1}$ ), and bending mode of the interlayer water ( $1630\text{ cm}^{-1}$ ) while the bands at  $1358$  and  $1408\text{ cm}^{-1}$  were assigned to the presence of a small fraction of carbonate anions. On the other hand, LDH–H (Fig. 2b) presented characteristic bands of the humate anion (Fig. 2c):  $1603$  and  $1387\text{ cm}^{-1}$  were attributed to antisymmetric and symmetric carboxylate vibration while those at  $1105$  and  $1041\text{ cm}^{-1}$  were assigned to bending  $=\text{CH}$  vibration of HA [36].

The SEM images of LDH–Cl (Supplementary data, Fig. S1) showed that the sample consisted of well-shaped, regular particles (Fig. S1a and S1b) formed by aggregation of small plate-like units. LDH–H particles (Fig. S1c) presented a broader size range and more irregular edges (Fig. S1d). The increased particle size was assigned to a larger agglomeration of the LDHs platelets related to a higher hydrophobicity and lower particle charge expected for LDH–H particle surface due to the intercalation of an organic anion [37] thus increasing the particle–particle interactions. On the other hand, the irregular shape of LDH–H particles is similar to that obtained for other LDHs that incorporate organic anions at their surface [38].

DTA curves of LDH–Cl and LDH–H and HA are included in Fig. 3. Three endothermic effects at  $83$ ,  $371$  and  $421^\circ\text{C}$  were observed during the thermal treatment of LDH–Cl (Fig. 3a). These thermal

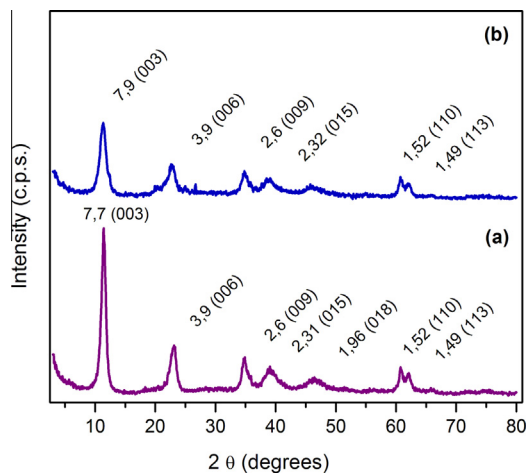


Fig. 1. XRD patterns of (a) LDH–Cl and (b) LDH–H.

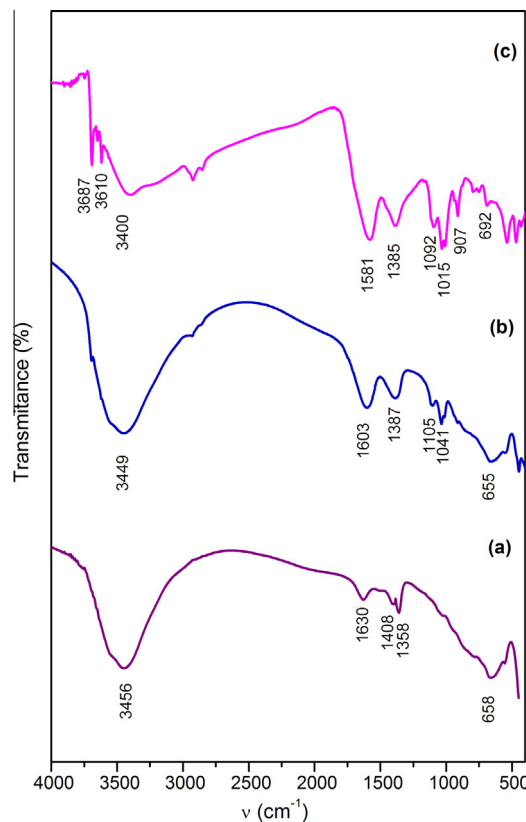


Fig. 2. FT-IR spectra of (a) LDH–Cl, (b) LDH–H and (c) sodium humate (NaH).

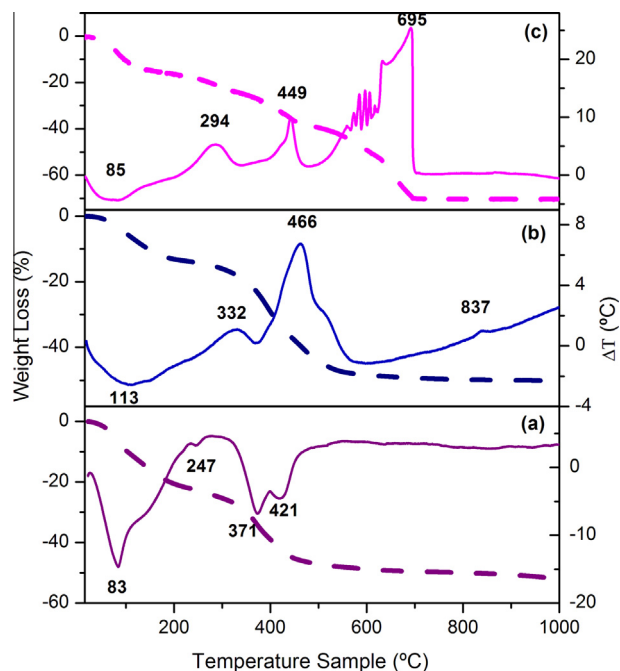


Fig. 3. TG and DTA curves of (a) LDH–Cl, (b) LDH–H and (c) NaH.

effects and their corresponding weight losses were assigned to (1) interlayer water loss, (2) dehydroxylation of the layers and (3) interlayer chloride loss [34]. The DTA curve of the LDH–H hybrid (Fig. 3b) showed the endothermic peak corresponding to the interlayer water, while the endothermic peaks corresponding to the last two effects were overlapped by an exothermic process

**Table 1**  
Chemical analysis results of LDH–Cl and LDH–H.

	% wt		Atomic ratio Mg/Al	Proposed formula
	Mg	Al		
LDH–Cl	20	8	2.8	$[Mg_{0.74}Al_{0.26}(OH)_2](Cl)_{0.26} \cdot 0.83H_2O$
LDH–H	15	7	2.4	$[Mg_{0.71}Al_{0.29}(OH)_2](X)_{0.29/n} \cdot mH_2O$

X = Cl and/or H ( $n = 1$  and/or  $2$ ;  $m = 0.58$ – $0.71$ ).

of HA oxidation (Fig. 3c). The metal analysis of the LDH–Cl and LDH–H and their proposed formulae are represented in the Table 1.

The results indicated that the molar ratio Mg:Al of the sample LDH–Cl was very close to that in the starting solution, while a decrease had been observed on the sample LDH–H because of a Mg partial dissolution during the HA exchange. According to the Mg/Al ratio and considering that the charge of the layer is only balanced by humate or chloride anion, a formula with a range of substitution was proposed for the LDH–H sample. The number of water molecules has been calculated from the first weight loss in the TG curve and the range has been obtained in accordance to the degree of the anionic substitution. The total weight loss for the proposed formula is consistent with the experimental value obtained by the TG curve, which is ~50% considering a total substitution of chloride by humate. This result confirmed that the HA incorporation was probably produced at the surface of LDH particles along with an important intercalation at the edges of the particles.

### 3.2. Sorbents comparison

The sorption capacity of LDH–Cl, LDH–H (0.05 g/30 mL,  $C_i = 1$  mM, pH initial = 5, 48 h.) and HA (0.014 g/30 mL, amount equivalent to the total amount of humate adsorbed on 0.05 g of the LDH) was compared and the results are shown in Table 2. Copper was completely removed by LDH–Cl and LDH–H, both sorbents being more effective than HA. In the case of  $Pb^{2+}$ , LDH–Cl and LDH–H were capable of producing an almost complete removal, while HA presented lower sorption values. Finally, HA produced the highest  $Cd^{2+}$  removal, followed by LDH–H and LDH–Cl, respectively. On the other hand, equilibrium (final) pH values ( $pH_f$ ) were highly dependent on the sorbent. The buffering capacity of LDH–Cl [39] produced the highest pH values, while the least important pH variation with respect to  $pH_i$  was produced for HA. The amounts of Mg and Al released from the solids after metal sorption experiments were also determined.  $Al^{3+}$  concentration was negligible in all cases, which was consistent with the low solubility of  $Al(OH)_3$  ( $K_{SP}(Al(OH)_3) = 5 \times 10^{-33}$ ). On the other hand, the Mg was detected in all supernatants and it increased upon heavy metal sorption. These results were related to the different sorption mechanisms of the sorbents: in the case of HA heavy metals were bounded by

**Table 2**  
pH final and percentages of Mg in the supernatants and heavy metals sorbed on different sorbents.

Sample	Metal	pH <sub>final</sub>	% Mg	% Sorbed
AH	$Cu^{2+}$	5.4	–	78
	$Pb^{2+}$	5.0	–	79
	$Cd^{2+}$	6.8	–	64
LDH–Cl	–	9.3	5.9	–
	$Cu^{2+}$	9.0	10.0	100
	$Pb^{2+}$	9.1	9.4	87
	$Cd^{2+}$	8.2	6.7	37
LDH–H	–	8.9	5.7	–
	$Cu^{2+}$	8.3	8.9	100
	$Pb^{2+}$	7.6	7.8	95
	$Cd^{2+}$	7.8	7.4	56

complex formation. Consequently, the heavy metals affinity for HA being determined by the stability of these complexes and the sorption process produced only minor pH variations. In the case of LDH–Cl, its buffering capacity led to an important pH increase and heavy metal precipitation as hydroxides was the main sorption mechanism [40]. These hydroxides precipitate either as part of a LDH structure, in a mechanism known as “diadochy” [41] or in a separate phase [42,43]. LDH–Cl affinity for heavy metal was then determined by the solubility products of the their hydroxides ( $K_{SP}(Cu(OH)_2) = 1 \times 10^{-20}$ ,  $K_{SP}(Cd(OH)_2) = 3.2 \times 10^{-14}$  and  $K_{SP}(Pb(OH)_2) = 2.5 \times 10^{-16}$ ). Finally, both mechanisms were concurrent in the LDH–H hybrid, humate anions stabilizing and adding complexation capacity to the inorganic matrix. All  $pH_f$  values for the heavy metal sorption on LDH–H were lower compared to those of LDH–Cl (Table 2) due to the stabilizing effect of humate anions [44]. Although the  $pH_f$  was sufficient to produce an almost complete precipitation of  $Cu(OH)_2$ , they were not enough for  $Pb^{2+}$  and  $Cd^{2+}$  due to the higher solubility of the corresponding hydroxides. Nevertheless, LDH–H showed higher  $Cd^{2+}$  sorption than LDH–Cl, which confirmed the contribution of the HA complexation mechanism [45].

According to the results obtained, LDH–H presents interesting properties due to (1) the stabilization of LDH matrix, diminishing the layers weathering and the final pH of the supernatants, which in turn, also decrease the environmental impact of the treated effluents and (2) the addition of a complexation mechanism, extending LDH functionalities. Also, due to the recurring presence of HA in the effluents, their interactions with LDHs and the effect on their sorptive behavior are of primary importance. As a consequence, the sorption behavior of the hybrid will be studied in the next section.

### 3.3. Heavy metal cations sorption by LDH–H

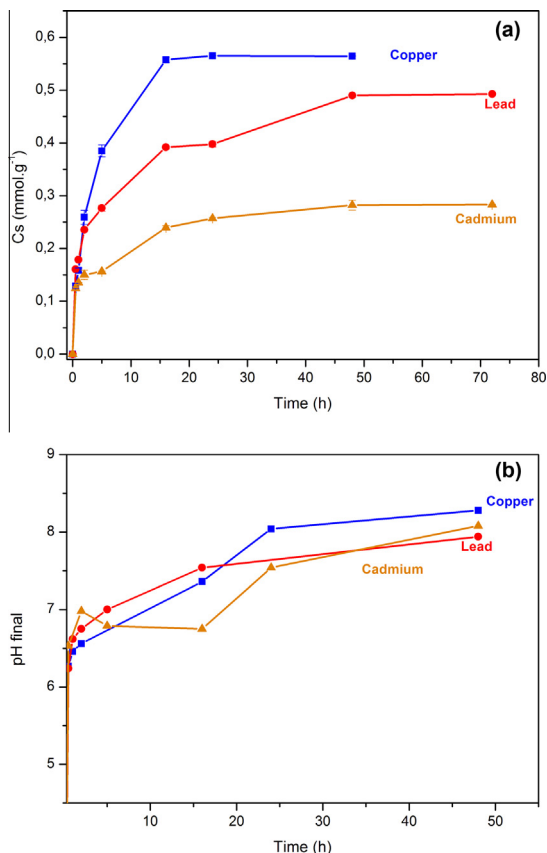
Table 3 shows the effect of pH on the heavy metal sorption capacity of LDH–H. Both  $C_s$  and  $pH_f$  slightly decreased with decreasing  $pH_i$ , as the buffering capacity of LDH–H is exhausted by both heavy metal sorption and proton consumption. It could be noted here that, as  $C_s$  decreases from  $Cu^{2+}$  to  $Cd^{2+}$ , the influence of  $pH_i$  in  $pH_f$  also decreased, which confirmed that the buffering capacity of LDHs was not consumed, i.e. lower pHs (higher acid concentrations) are necessary to displace the final pH from 7 to 8 range.

The kinetic study results (Fig. 4) showed that sorption was produced into two steps. The first step was fast and produced half of the final sorption within the first 2 h, and the second gradually approached to equilibrium, reaching it within 48 h in the cases of Pb and Cd, and 24 h for the case of Cu. 100%, 95% and 56% of the initial metal concentration were removed for Cu, Pb and Cd, respectively, and the time to reach equilibrium increased in the same sequence as well. A similar kinetic behavior was previously observed for  $Cu^{2+}$  on LDH modified by edta [46]: the first, fast step being assigned to the hydroxide precipitation mechanism and the

**Table 3**  
pH influence on the heavy metals sorption on LDH–H.

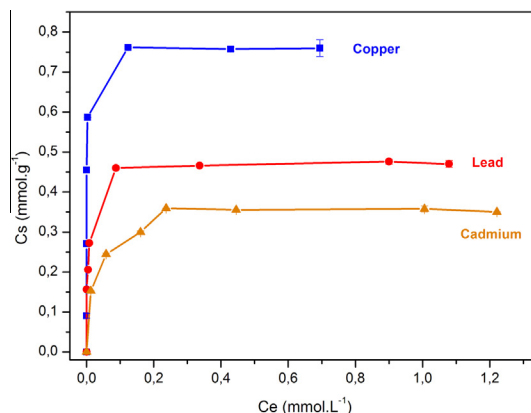
Sample	pH <sub>initial</sub>	pH <sub>final</sub>	$C_s$ (mmol g <sup>-1</sup> )
$Cu^{2+}$	3	6.1	0.51
	5	8.3	0.57
$Pb^{2+}$	3	7.4	0.34
	5	7.6	0.40
	7	8.0	0.36
$Cd^{2+}$	3	7.7	0.23
	5	7.8	0.26
	7	8.0	0.27





**Fig. 4.** The evolution of: (a) heavy metals uptake by LDH-H and (b) pH evolution ( $C_i = 1$  mM, pH initial 5).

second step to a cation exchange mechanism at edta complexes located at the interlayer. The only difference here was substitution of edta by HA. The presence of the second mechanism was



**Fig. 5.** Sorption isotherms of heavy metals on LDH-H at pH = 5.

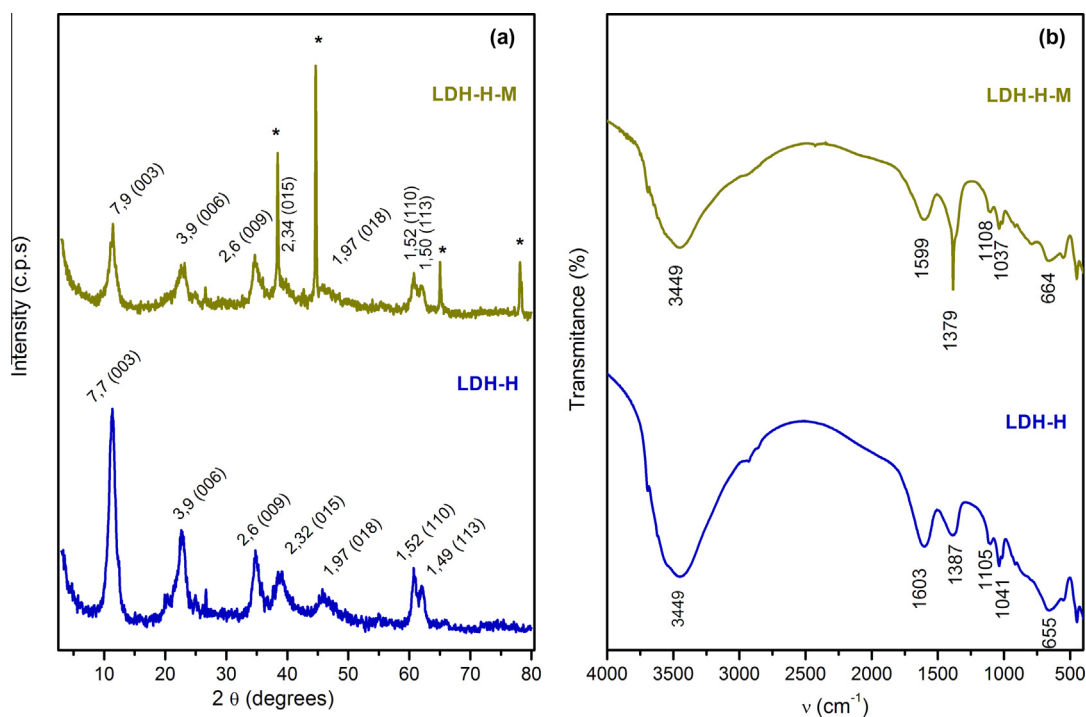
**Table 4**

Langmuir model parameters for heavy metals sorption on LDH-H.

Sample	$C_m$ (mmol g <sup>-1</sup> )	$K_L$	$R^2$
Cu <sup>2+</sup>	0.75	69	0.993
Pb <sup>2+</sup>	0.48	187	0.999
Cd <sup>2+</sup>	0.35	114	0.998

confirmed by Fig. 4b, which indicated that the main pH variation, associated with the hydroxide precipitation mechanism, was produced within the first minutes of the experiment in all cases.

The time of 48 h was considered enough to reach equilibrium for the sorption isotherm (Fig. 5). A steep Cs increase was registered in all cases, indicating the high effectiveness of LDH-H as sorbent, the metal ions being completely adsorbed at lower initial concentrations. As determined by the Langmuir model fitting (Table 4), the maximum sorption increased in the sequence Cd ( $C_m = 0.35$  mmol g<sup>-1</sup>) Pb ( $C_m = 0.48$  mmol g<sup>-1</sup>) and Cu ( $C_m = 0.75$  mmol g<sup>-1</sup>). These values were comparable to those obtained for similar



**Fig. 6.** XRD patterns (a) and FT-IR spectra (b) of the sorption products (M = Cu, Pb and Cd) corresponding to the last isotherm point (\*Al sample holder).

Mg–Al–LDHs: between 0.01 and 0.15 mmol g<sup>-1</sup> for Cd<sup>2+</sup> sorption by Mg–Al–LDHs containing carbonate and edta, respectively [47], 0.33 and 0.86 mmol g<sup>-1</sup> for Pb<sup>2+</sup> sorption by chloride-containing Mg–Al–LDHs [48,49] and between 0.78 and 2.50 mmol g<sup>-1</sup> for Cu<sup>2+</sup> sorption by chloride intercalated LDHs either [42,50]. In all cases sorption was assigned to a hydroxide precipitation mechanism, except for the case of Cd<sup>2+</sup>, which only reaches significant sorption capacity when complexation mechanism is incorporated by intercalating the solid with edta. Similarly, LDH–H showed higher sorption capacity than LDH–Cl or even than the edta intercalated Mg–Al–LDHs.

The sorption products were studied by PXRD and FT-IR (Fig. 6) and there were no important changes observed compared to the pure sorbent pattern (Fig. 1). PDRX of LDH–H–Metal complexes patterns (Fig. 6a) indicated that the crystallinity of the sorption product decreased but the LDH structure was maintained and there was no additional precipitates observed. This is probably due to the low mass of hydroxide formed respect the amount of sorbent in the experiments (less than 10% w/w in all cases, as calculated from C<sub>m</sub> values and the formula weight of the corresponding heavy metal hydroxide). The FT-IR spectrum (Fig. 6b) of sorbent after the sorption experiments showed slight displacements of the bands in the 1600–1000 cm<sup>-1</sup> zone, which is likely to be due to the interaction of the functional groups of the HA with metal ions.

The simultaneous sorption of the three heavy metal ions is represented in Fig. 7. The sorption was slower and the amounts of metal uptaken were lower compared to the monocomponent solutions. The maximum amounts sorbed at the equilibrium time for the multicomponent system were C<sub>s</sub> = 0.46 mmol g<sup>-1</sup>, C<sub>s</sub> = 0.21 mmol g<sup>-1</sup>, C<sub>s</sub> = 0.00 mmol g<sup>-1</sup> for Cu, Pb and Cd respectively, vs. C<sub>s</sub> = 0.57 mmol g<sup>-1</sup>, C<sub>s</sub> = 0.49 mmol g<sup>-1</sup>, C<sub>s</sub> = 0.28 mmol g<sup>-1</sup> obtained for the corresponding experiments with a single heavy

metal ion. The highest amounts of the metal cations sorbed on LDH–H were reached for copper in both cases, while the sorption of Cd was completely inhibited by the presence of the other two cations probably due to sorption occupation sites by the species with more affinity and/or precipitation of the hydroxides. This behavior was concordant with the sequence of stability of the corresponding metal hydroxides (decreasing K<sub>ps</sub>) and correlated with the stability constants of M–humate complexes [45], decreasing in the order of Cu > Pb > Cd. Moreover, the sum of C<sub>s</sub> for the multicomponent system (0.67 mmol g<sup>-1</sup>) was larger than the maximum C<sub>s</sub> value obtained for the single metal experiments (Cu<sup>2+</sup> ion, 0.57 mmol g<sup>-1</sup>), indicating that both precipitation and complexation mechanisms are concurrent and that the different ions were incorporated to different sites. According to this result, Cd<sup>2+</sup> and Pb<sup>2+</sup> were competing preferentially for humate complexation sites.

#### 4. Conclusions

Layered double hydroxide–humate hybrid (LDH–H) was synthesized by dispersing chloride containing LDH in a humate solution. Humate incorporation was produced at the surface of the particles but also some intercalation at the particles edges was inferred. Humate incorporation produced a stabilization of the inorganic matrix and the resulting hybrid showed sorption capacity of Cu<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> due to precipitation and complexation mechanism. As a consequence, LDH–H presented an intermediate behavior compared to LDH–Cl and HA separately. Moreover, LDH–H presents a better stability, resulting in less pH increase during the experiments, which moderates the environmental impact of the sorption process. Also, LDH–H avoids the separation and dewatering problems associated with humic acids. The LDH–H sorption process was fast and was produced in two steps, the first fast step was exclusively associated with hydroxide precipitation, while in the second, slower step, the complexation mechanism was involved. LDH–H presented high affinity for heavy metal ions, leading to low pollutant concentrations at equilibrium while the sorption capacities were similar to other sorbents with similar characteristics. Finally, the presence of more than one heavy metal even increased the overall sorption capacity, indicating that different heavy metals were sorbed by different mechanisms, Pb<sup>2+</sup> and Cd<sup>2+</sup> competing for the humate complexation sites.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2014.05.132>.

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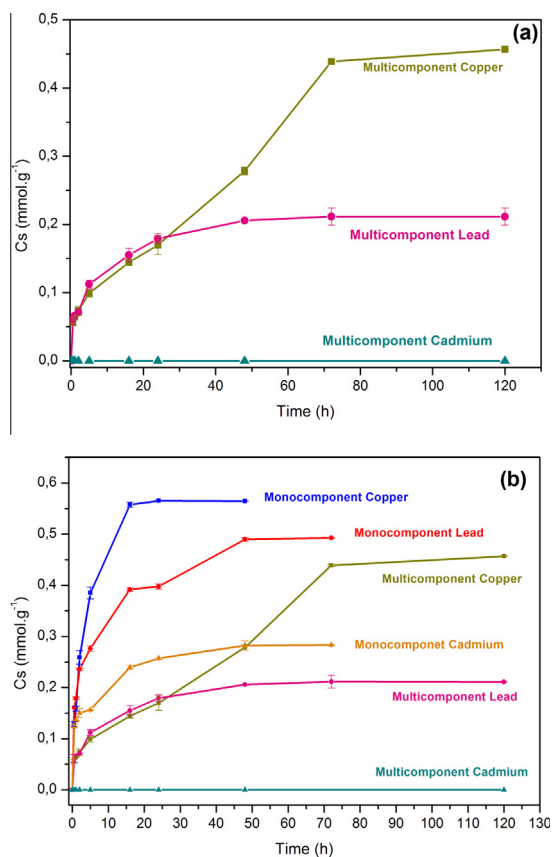


Fig. 7. The evolution of sorption of heavy metals on LDH–H: (a) metal cations coexisting in the solution (multicomponent) and (b) comparing with the monocomponent solution sorption behavior.

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