Uptake of Cu^{2+}, Cd^{2+} and Pb^{2+} on Zn–Al layered double hydroxide intercalated with edta

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Abstract

Hydrotalcite-like compound $[Zn_2Al(OH)_6]_2edta \cdot nH_2O(ZnAl\text{-}edta)$ was obtained from the precursor $[Zn_2Al(OH)_6]NO_3 \cdot nH_2O$ (ZnAl-NO₃), by the anion exchange method, with the aim of uptake Cu^{2+}, Cd^{2+} and Pb^{2+} from the aqueous solutions by chelating process between edta and metal cations. The amount of Cu^{2+}, Cd^{2+} and Pb^{2+} adsorbed was monitorized by atomic absorption technique at different contact time, pH and metal concentrations. The results indicate the very fast adsorption of the metal cations by ZnAl-edta reaching the equilibrium of the uptake reaction in two hours for Cu and Pb and 24 h for Cd. The shape of the adsorption isotherms suggests specific interaction and high *host–guest affinity*. At pH 5.5 and initial concentration $C_i = 10$ mM, the amount adsorbed was $C_s = 1117$, 375 and 871 μmol/g for Cu^{2+}, Cd^{2+} and Pb^{2+}, respectively.
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1. Introduction

Layered double hydroxides (LDH) or anionic clays are lamellar ionic compounds, containing a positively charged layer and exchangeable anions in the interlayer (Cavani et al., 1991). They consist of brucite-like layers, with a partial M^{II} for M^{III} substitution, leading to an excess of positive charge compensated with anions situated in the interlayer together with water molecules. These materials can be represented by the general formula

$$[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[X^{m-}_{x/m}] \cdot nH_2O^{x-},$$
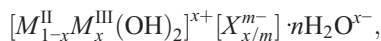
abbreviated as $[M^{II}M^{III}-X]$,

where $M^{II} = Mg^{2+}$, Mn^{2+}, Zn^{2+}... $M^{III} = Al^{3+}$, Fe^{3+}, Cr^{3+}... and $X^- = CO_3^{2-}$, Cl^-, NO_3^-....

The structure of these materials as well as their high anionic exchange capacity (AEC, ∼3 meq/g) make them suitable for many applications (Vaccari, 1999, Rives and Ulibarri, 1999), such as the sorption of many inorganic (Amin and Jayson, 1996; Fetter et al., 1997; Houri et al.,

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1998; Kovanda et al., 1999) and organic (Hermosın et al., 1993, 1996; Pavlovic et al., 1997; Ulibarri et al., 2001; You et al., 2002a,b; Pavlovic et al., 2005) anions, potential contaminants of waters. Recently, some authors reported about LDH containing chelating agents such as etilendiaminetetraacetate, edta (Tsyganok et al., 2001) and nitrilotriacetate, NTA, (Kaneyoshi and Jones, 1999), as well as the metal cations uptake by these materials (Gutmann et al., 2000; Tarasov et al., 2003; Li et al., 2004).

Our previous study of ZnAl-LDH structure (Crespo et al., 1997; Barriga et al., 1998) suggested that this compound could be functionalzed with edta and thus used for the uptake of the metal cations from the solutions. Although high concentrations of Zn^{2+} could result harmful for the environment, it is the second more abundant trace metal in the human body (Dunnick and Fowler, 1988) and can be considered as no toxic to humans (Nac. Res. Con., 1979). The achieving of the optimal conditions and control of Zn dissolution permit the use of this material as a heavy metal adsorbent from waters. The aim of this work is to obtain the hydrotalcite $[Zn_2Al(OH)_6]_2edta \cdot nH_2O$ (ZnAl-edta) and to study its potential capacity for the uptake of metallic cations (Cu^{2+}, Cd^{2+} and Pb^{2+}) from water solutions, based on the stability of the chelates formed between edta and many metals.

2. Experimental

2.1. Synthesis

All the reagents used for synthesis were of 98–99% purity.

The synthesis of ZnAl-edta include two steps: the preparation of the precursor, $[Zn_2Al(OH)_6]NO_3 \cdot nH_2O$ (ZnAl-NO_3) and the anion-exchange reaction of this compound with Na_2-edta, to obtain $[Zn_2Al(OH)_6]_2edta \cdot nH_2O$.

#### 2.1.1. Synthesis of ZnAl-NO_3

The hydrotalcite $[Zn_2Al(OH)_6]NO_3 \cdot nH_2O$ was prepared by coprecipitation method (Reichle, 1986) at room temperature. 200 mL of 0.2 M $Zn(NO_3)_2 \cdot 6H_2O$ and 0.1 M $Al(NO_3)_3 \cdot 9H_2O$ were slowly dropped to 200 mL of 1 M $NaNO_3$ solution, under vigorous agitation, using distilled, CO_2-free water and maintaining the pH at 8. The solution was purged by N_2 to avoid CO_2 uptake by hydrotalcite. The resulting slurry (ZnAl-NO_3) was filtered and washed, and then suspended at 150 mL of distilled and CO_2-free water.

2.1.2. Synthesis of ZnAl-edta

150 mL of previous hydrotalcite suspension was added to a 0.015 mol of Na_2H_2Y (where Y is edta^{2-} anion), under N_2 flow

at 75 °C. Since edta exhibits the following aqueous dissociation constants: $pK_1 = 2.00$, $pK_2 = 2.66$, $pK_3 = 6.16$ and $pK_4 = 10.24$, pH during the synthesis was maintained at 5.5 when the ligand exists mainly as $[H_2Y]^{2-}$, adequate for the anion-exchange reaction with LDH:

$$2[Zn_2Al(OH)_6]NO_3 + [H_2Y]^{2-} \rightarrow [Zn_2Al(OH)_6]_2[H_2Y] + 2NO_3- \quad (1)$$
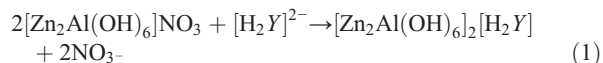
The product of the interchange has been named as ZnAl-edta.

2.2. Adsorption experiments

The adsorption experiments of Cu^{2+}, Cd^{2+} and Pb^{2+} on ZnAl-edta were carried out suspending duplicate samples of 0.1 g of ZnAl-edta in 30 mL of aqueous solution of Cu, Cd and Pb nitrate salts. It was determined the optimum initial pH, contact time and concentration of metal salts for the metal intercalation on ZnAl-edta. The pH conditions studied were limited by the solubility product of the metal hydroxides: $Ps_{Cu(OH)_2} = 1 \cdot 10^{-20}$, $Ps_{Cd(OH)_2} = 3.2 \cdot 10^{-14}$ and $Ps_{Pb(OH)_2} = 2.5 \cdot 10^{-16}$. The suspensions were agitated at 50 rpm at room temperature. The supernatants were separated to determine the amount of metal adsorbed by ZnAl-edta by atomic absorption method. This amount was determined from the difference between initial and final concentration of the metal ion in the supernatant solutions. Metal solutions without adsorbent (blank samples) were also shaken under the same experimental conditions, with the aim to identify potential losses of heavy metals by processes such as precipitation, adsorption to tubes etc. The adsorption isotherms were measured by batch equilibration technique as described elsewhere (Hermosın et al., 1993; Pavlovic et al., 1997).

2.3. Characterization of the adsorbents and adsorption products

The final product ZnAl-edta was separated by centrifugation, then washed and dried at 60 °C and studied by XRD and TG-DTA techniques and FT-IR spectroscopy.

X-ray diffraction patterns (XRD) of powder samples were recorded at room temperature under air conditions on a Siemens D-5000 instrument, using Cu K_α radiation ($\lambda = 1.54050$ Å).

The infrared spectra were obtained with a Perkin Elmer Spectrum One spectrophotometer using KBr disc method.

Elemental chemical analyses for Zn, Al, Cd, Cu and Pb were determined by atomic absorption spectrometry in an Perkin Elmer AA-3100 instrument. Samples were dissolved in concentrated HCl. Elemental chemical analyses of C and N were carried out on Euro Elemental Analyze Eurovector instrument.

3. Results and discussion

3.1. Synthesis and characterization of ZnAl-NO₃ and ZnAl-edta

The chemical analysis of the original ZnAl-NO$_3$ and modified ZnAl-edta hydrotalcites are shown in the Table 1. The results indicate that the molar ratio Zn : Al of LDH-NO$_3$ is very close to the value in the starting solution, whereas in the ZnAl-edta is lower. This is probably due to the partial dissolution of the hydroxyl layers during the anionic exchange, realized at pH 5.5.

The results of the analysis also suggest that the edta compensate the 86% of the total charge in the layer (0.22 moles of edta), and the rest is probably compensated with chloride and/or hydroxyl anions (14% of the interlayer charge) which compete with edta during the anionic exchange. The amount of interlayer water was determined by the thermogravimetric curves, from the weight loss between room temperature and 150 °C (not shown).

The XRD and TG-DTA techniques and FT-IR spectroscopy were applied to characterize the synthesis products and confirm that edta is intercalated into ZnAl-NO$_3$ through the anion exchange reaction (Eq. (1)). The XRD pattern of ZnAl-edta is represented in Fig. 1b and is different from that of sample with nitrate anion in the interlayer (Fig. 1a), but both are characteristic of a layered phase with the basal diffractions due to planes (003), (006) and (009). These patterns also indicate that the intercalation of edta in ZnAl-NO$_3$ gives rise to an increase in basal spacing from $d=7.9$ Å to $d=13.9$ Å. The substraction of 4.8 Å as the hydrotalcite-layer thickness from the $d=13.9$ Å, gives 9.1 Å as interlayer space occupied by edta, coinciding with the van der Waals end-to-end length of edta (9.1 Å) (CS Chem 3D 5.0 program). On the other hand, the value of $d_{110}=1.53$ Å for ZnAl-NO$_3$ decreases slightly for ZnAl-edta ($d_{110}=1.52$ Å) which agrees with the decrease of molar ratio Zn/Al.

This suggests that the ligand is probably accommodated in vertical position in the interlayer space of hydrotalcite, as we propose at the Fig. 2.
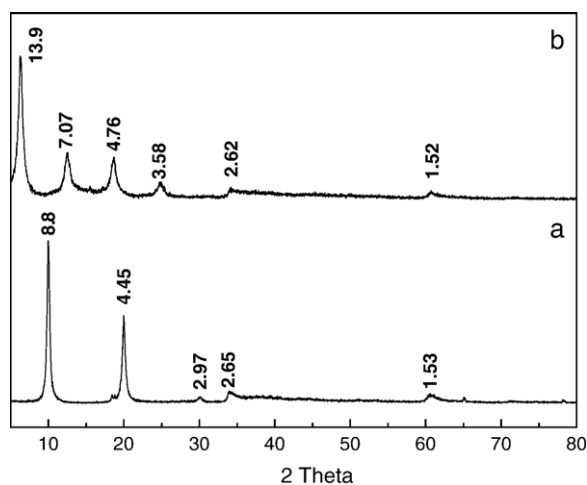

Fig. 1. XRD patterns of (a) ZnAl-NO$_3$ and (b) ZnAl-edta.

The Fig. 3 compares the FT-IR spectra of original ZnAl-NO$_3$ (3a), its anionexchange product with edta, ZnAl-edta (3b) and Na$_2$edta (3c). The FT-IR spectrum of ZnAl-NO$_3$ is similar to the reported by Cavani et al. (1991). The wide band at ~3450 cm^{-1} is attributed to the H-bonding stretching vibrations of OH-groups in the brucitelike layers and water molecules, as well as water bending vibration at 1620 cm^{-1}. The very sharp peak at 1385 cm^{-1} is attributed to the stretching vibration of NO$_3^-$ group, and it is not registered in the spectrum of anion exchange product, ZnAl-edta. The most interesting features in the Na$_2$-edta spectrum (3c) are the bands at 1394 and 1620 cm^{-1} attributed to the symmetrical and asymmetrical vibration of COO$^-$; the band at 1681 cm^{-1} corresponding to the stretching vibration of un-ionized COOH, and the band at 3027 cm^{-1} attributed to ν_{C-H} of alkyl groups (Bellamy, 1975). In the FT-IR spectrum of the ZnAl-edta (Fig. 3b) the band close to 1681 cm^{-1} is not observed probably due to its weakness in the pure compound. The monodentate coordination of carboxylate groups of edta is suggested by the difference in wave number ($\Delta\nu \geq 200$ cm^{-1}) between ν_{as} and ν_s of COO$^-$ (Deacon and Philips, 1980). This value is $\Delta\nu = 226$ cm^{-1} in

Table 1
Chemical analysis results of compounds ZnAl-NO$_3$ and ZnAl-edta

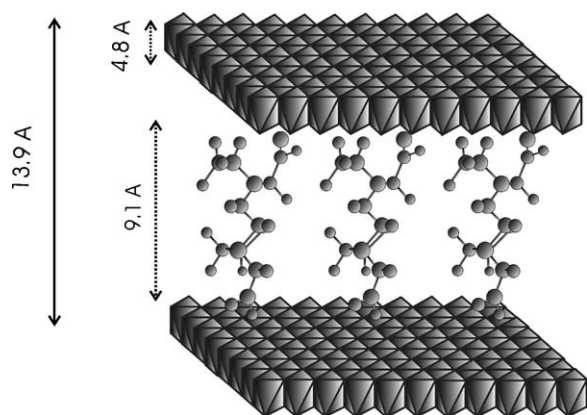|	% wt				Atomic ratios		Proposed formula
	Zn	Al	C	N	Zn/Al	Al/C	
ZnAl-NO$_3$	35.2	7.94	–	4.00	1.83	–	[Zn$_{0.65}$Al$_{0.35}$(OH)$_2$](NO$_3$)$_{0.35}$·0.4H$_2$O
ZnAl-edta	20.6	9.0	16.96	4.02	0.95	0.24	[Zn$_{0.49}$Al$_{0.51}$(OH)$_2$](H$_2$Y)$_{0.22}$X$_{0.07}$·0.7H$_2$O

X: Cl$^-$ and/or OH$^-$.

Fig. 2. Schematic representation of ZnAl-edta structure.

Na$_2$-edta (3c), and $\Delta v = 197$ cm^{-1} in the adsorption product (3b), indicating that the coordination mode of COO$^-$ groups is unchanged after intercalation of edta.

3.2. Adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} in ZnAl-edta

The effect of the initial pH and contact time on the uptake of Cu^{2+}, Cd^{2+} and Pb^{2+} from water are shown in Tables 2–4, respectively, where C_s is the amount of solute adsorbed in the solid at the equilibrium (expressed as µmol g^{-1}) being the initial concentrations of Cu(NO$_3$)$_2$·3H$_2$O, Cd(NO$_3$)$_2$·4H$_2$O and Pb(NO$_3$)$_2$ $C_i = 7$ mM. This adsorption is probably caused by the chelation process between the metal cations
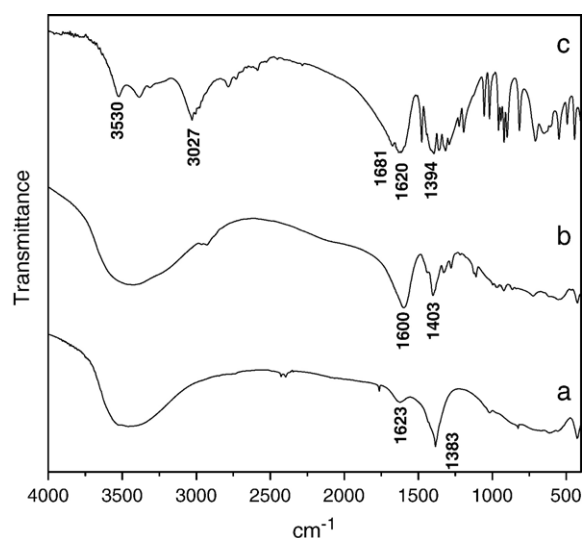

Fig. 3. FT-IR spectra of (a) original ZnAl-NO$_3$, (b) ZnAl-edta and (c) Na$_2$-edta.

Table 2
Effect of the initial pH and contact time on the uptake of Cu^{2+} by ZnAl-edta

Time (h)	pH initial	pH final	C_s (µmol/g)	% adsorbed
0.5	3	4.6	841±27	37±1.4
	6	5.1	906±18	46±0.9
2.0	3	5.7	877±16	40±0.8
	6	5.3	1114±3	52±0.3
24.0	3	4.7	918±4	42±0.3
	6	5.2	1187±2	56±0.3

and edta. In the case of Cu^{2+} the solution changes from blue to colorless while the solid becomes blue colored.

The results of Tables 2–4 indicate that the adsorption of Cu^{2+} on ZnAl-edta was higher than that of Cd^{2+} and Pb^{2+} at the same experimental conditions. In all cases the adsorption of metal cations was higher at pH 6 than at pH 3. It could be attributed to the fact that at pH 6 the liberation of the edta protons is favored, which is necessary for the chelating process. Also, the solubility of heavy metals increases with decreasing of pH improving their affinity for the aqueous phase and thus reducing the adsorption. The adsorption of Cu^{2+} at different pH was limited by the precipitation of this metal at pH 8. In the case of Cd^{2+} the adsorption at pH = 8 decreased again, probably because the intercalation of the hydroxyl anions compete with edta for the interlayer sites. From this reason, the adsorption of Pb^{2+} has not been studied at pH 8. When the initial pH is 3, an increase of pH of approximately 2 or 3 pH units is observed in all cases, due to the dissolution of the hydroxyl layers of hydrotalcites, also confirmed by the presence of Zn in the final solution by the atomic absorption technique. When the initial pH is 6 or 8, the final pH was always maintained around the value of 6. This agrees with the buffering properties of the hydrotalcite (Boclair and Braterman, 1999). Namely,

Table 3
Effect of the initial pH and contact time on the uptake of Cd^{2+} by ZnAl-edta

Time (h)	pH inital	pH final	C_s (µmol/g)	% adsorbed
0.5	3	4.8	306±8	16±0.4
	6	5.3	427±30	21±2.3
	8	5.5	282±16	15±0.9
2.0	3	5.9	379±9	20±2.8
	6	5.9	481±8	22±0.4
	8	5.9	330±9	18±0.4
24.0	3	6.2	409±19	22±1.2
	6	6.0	667±30	31±1.3
	8	5.9	374±70	21±4.5

Table 4
Effect of the initial pH and contact time on the uptake of Pb^{2+} by ZnAl-edta

Time (h)	pH initial	pH final	C_s (μmol/g)	% adsorbed
0.5	3	5.6	288±9	12±0.3
	6	5.4	457±10	22±0.3
2.0	3	4.8	389±24	16±1.0
	6	5.4	593±0.1	28±1.1
24.0	3	4.9	471±14	19±0.5
	6	5.5	629±3.5	29±0.0

the protons liberated from edta during the chelation of the cations at pH=8 decrease the pH of the media (Eq. (2)).

$$[Zn_2Al(OH)_6]_2[H_2Y]^{2-} + M^{2+} \rightarrow [Zn_2Al(OH)_6]_2[MY] + 2H^+ \quad (2)$$
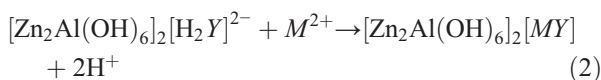
The higher adsorption of Cu^{2+} on ZnAl-edta than those of Cd^{2+} and Pb^{2+} in the above indicated conditions could be attributed to the stability constant of Cu-edta, greater than those of Cd-edta and Pb-edta (pKd=18.8, 16.5 and 18.0, respectively).

The kinetic results (Tables 2–4 and Fig. 4) indicate that the uptake of Cu^{2+} and Pb^{2+} cations by the ZnAl-edta was faster than that of Cd^{2+}. For Cu^{2+} and Pb^{2+}, the final concentrations of the metals in the solution decrease appreciably within two hours, and after that there are no important changes in the amount of these metal cations adsorbed. On the other hand, in the case of Cd^{2+} the main part of the metal amount is adsorbed on ZnAl-edta in 2 h, but after that time there is a slight increase of the adsorption until 24 h. This could be due to the great radium of Cd^{2+} which could cause steric hindrance and to the lower pKd
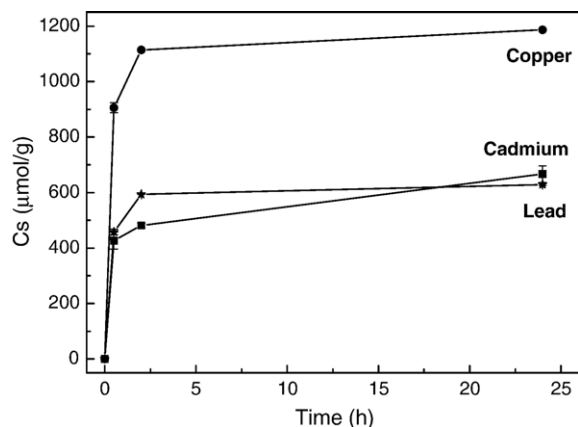
value than those corresponding to Pb^{2+} and Cu^{2+}. Although in the last case there is a slight increase of the adsorption from 2 h (22%) to 24 h (31%), in the order to optimize the adsorption process, the adsorption isotherms for the three metals were obtained in the time of 2 h.

The variation of the uptake of the Cu^{2+}, Cd^{2+} and Pb^{2+} by ZnAl-edta with initial metal concentration ranging from 2.5 to 40 mmol L^{-1} is shown in Fig. 5. The shape of the isotherms (Giles et al., 1960) suggests high affinity between the adsorbent and sorbate in all cases, mostly by electrostatic interaction, and reaching the" plateau" of the isotherm in the case of Cu^{2+} and Pb^{2+}.

Although the experiments of the pH influence on the adsorption were carried out at pH 6, the adsorption isotherms (Fig. 5) were obtained at pH 5.5, because Cu^{2+} precipitates at pH 6 at the highest concentrations, used to reach the isotherm "plateau". The amount of Cu^{2+} adsorbed by ZnAl-edta (C_s) at the initial concentration of Cu^{2+} C_i=10 mM, where the isotherm plateau is reached, was 1117 μmol per gram of adsorbent. In the case of Pb^{2+} the adsorption isotherm is very similar to the above mentioned, reaching the "plateau" in the point corresponding to the initial concentration of Pb^{2+} C_i=20 mM where the amount of Pb^{2+} adsorbed was C_s=1022 μmol per gram of adsorbent. However, in the adsorption isotherm of Cd^{2+} it was not possible to reach the plateau because of the very low reproducibility of the results using initial concentration $C_i \geq 40$ mM. Maximum adsorption obtained was C_s=834 μmol per gram of adsorbent for C_i=40 mM.

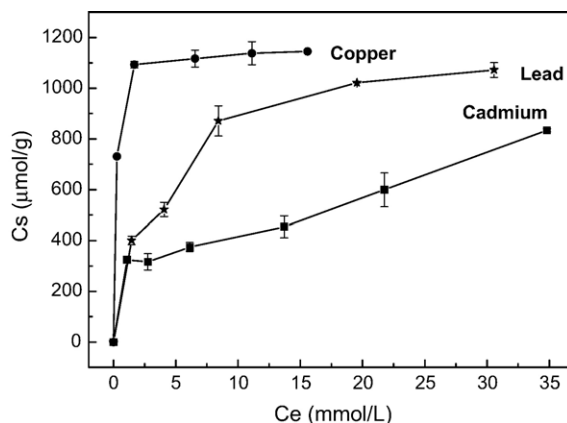Comparing the sorption capacity of ZnAl-edta for the metal cations with some sorbents of similar structure,

Fig. 4. Evolution of the adsorption of the metal cations on ZnAl-edta at pH=6.

Fig. 5. Adsorption isotherm of Cu^{2+}, Cd^{2+} and Pb^{2+} on ZnAl-edta (0.1 g/30 mL, pH 5.5, 2 h).

previously assayed, seem to be quite acceptable. Thus, the amount of Cu^{2+} uptaked by Li, Al-LDH intercalated by edta, reported by Tarasov et al. (2003) was $C_s = 750$ μmol per gram of sorbent. Mercier and Detellier (1995) and Celis et al. (2000) prepared clay minerals sepiolite and montmorillonite functionalized with ligands containing thiol groups as the sorbents of heavy metals. These authors found values of the amount of Pb^{2+} and Cd^{2+} adsorbed C_s ~350 μmol and for C_s ~260 per gram of adsorbent, respectively.

To confirm the chelation of metal cations in the interlayer, the XRD patterns of the isotherm products ZnAl-edta-M were obtained, but no change in the basal spacing of the adsorbent ($d_{003} = 13.9$ Å), was observed. Nevertheless, the basal spacing is very similar to that found by Pérez et al. (data not published) for ZnAl-(Cu-edta) and ZnAl-(Cd-edta), where the anions in the interlayer are the $Cu(edta)^{2-}$ $Cd(edta)^{2-}$ complexes ($d_{003} = 14.3$ Å and $d_{003} = 14.0$ Å, respectively).

Also for Mg–Al and Li–Al LDHs intercalated with M-edta complexes (M=Fe, Co, Ni, Cu, Eu) (Kaneyoshi and Jones, 2001; Lukashin et al., 2003; Li et al., 2004), the results suggest that the M-edta complexes are accommodate into the interlayer without apparent deformations.

4. Conclusions

Cu^{2+}, Cd^{2+} and Pb^{2+} cations are uptaked by ZnAl-edta hydrotalcite by their chelation with edta from the hydrotalcite interlayer. This process was monitored by atomic absorption technique at different contact time, pH and metal concentrations. The shape of the adsorption isotherms suggests in every case specific interaction and high affinity between the sorbent and sorbate corroborated by the corresponding kinetic study. From these results it is concluded that the adsorption of Cu^{2+} on ZnAl-edta was higher than those of Cd^{2+} and Pb^{2+} in the above indicated conditions. This could be attributed to the stability constant of Cu-edta, greater than those of Cd-edta and Pb-edta.

The XRD patterns also suggest that the Cu^{2+}, Cd^{2+} and Pb^{2+} are chelated by edta in ZnAl-edta and accommodate into the interlayer without apparent deformations.

Acknowledgements

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