



Removal of heavy metals from simulated wastewater by in situ formation of layered double hydroxides



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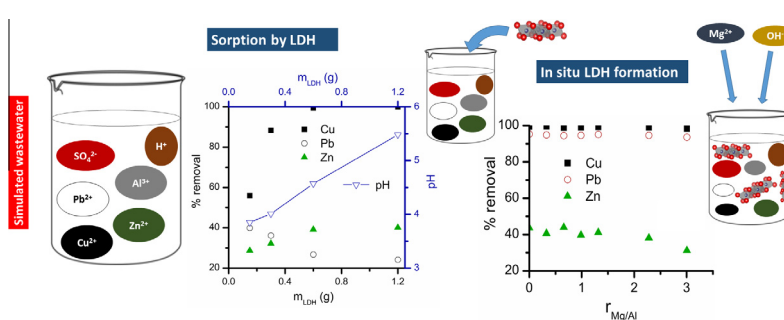
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HIGHLIGHTS

- Heavy metal sorption by LDHs based on dissolution/precipitation and diadochy.
- Hydroxide addition to solutions containing Al³⁺ and M²⁺ ions lead to in situ LDH formation.
- This process led to a complete Cu²⁺ and partial Zn²⁺ and Pb²⁺ removal.
- Addition of Mg²⁺ ions after pH increase led to competition with Zn²⁺ ions for LDH sites.
- Addition of Mg²⁺ ions before pH led to LDH formation and Zn²⁺ removal increase.

GRAPHICAL ABSTRACT



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ABSTRACT

Heavy metal removal from wastewater is an important environmental issue. Sorption by layered double hydroxides (LDHs) and precipitation in alkaline media are two of the main remediation techniques for these pollutants. Here, both processes are compared, with emphasis on the mechanisms involved and the solids obtained as residues. A heavy metal ion solution with high sulfate concentration was used as a simulated wastewater. It was treated with a carbonate-containing Mg–Al LDH to study sorption processes, while alkalization in the presence of Mg²⁺ ions was used to produce LDH in situ precipitation. The removal capacity of these processes was analyzed and the solids obtained upon remediation were characterized by PXRD patterns and FT-IR spectra. The obtained results were related to the removal mechanisms, the solubility products of heavy metal hydroxides and their capacity to produce LDH phases. High Cu²⁺ removal capacities were obtained in all cases, while those of Pb²⁺ and Zn²⁺ ions depended on the remediation procedure and factors such as Mg²⁺ ions concentration and final pH. Apart from Pb²⁺ ions, the heavy metal precipitated as LDH phases, which presented higher stability than simple heavy metal hydroxides and prevented Zn²⁺ mobilization in basic media.

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1. Introduction

Heavy metal pollution is one of the main environmental concerns due to the mobility and persistency of these pollutants [1]. Large volumes of wastewaters contaminated with these ions are produced by diverse activities, such as metallurgy, tanning and

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mining. Thus, pyrite ore processing produces acid wastewaters containing heavy metal ions (Zn^{2+} , Pb^{2+} and Cu^{2+} , among others) as well as a high sulfate concentration [2]. Huge volumes of these wastewaters are disposed in pits that poses high environmental risks of leaking, permeation or spoil.

Heavy metal remediation is performed by different techniques, the most important being chemical precipitation by hydroxides (usually lime) [3] or sulfides [4]. A large number of heavy metals precipitate in alkaline media to produce metal hydroxides and, if trivalent ions (Al^{3+} , Fe^{3+} , ...) are present, layered double hydroxides (LDHs) [5,6]. These are bidimensional solids with a structure similar to that of brucite ($\text{Mg}(\text{OH})_2$), where a portion of divalent ions are replaced by trivalent ones. Thus, their general formula can be written as $[\text{M}_x^{\text{II}}\text{M}_y^{\text{III}}(\text{OH})_z]^{x+y-3n}\text{X}_n^{\text{II}}\cdot m\text{H}_2\text{O}$, where M^{II} is the divalent ion (Mg^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , etc.), M^{III} the trivalent ion (Al^{3+} , Fe^{3+} , Cr^{3+} , etc.) and X^{II} is the interlayer anion (Cl^- , CO_3^{2-} , SO_4^{2-} , etc.) [7]. It is then possible to precipitate heavy metal ions such as Ni^{2+} , Zn^{2+} , Cu^{2+} , Cr^{3+} by simple alkalization of the wastewater and the formation of a heavy metal containing LDH. Moreover, the formation of the LDH phase produce the scavenging of the surrounding pollutant anions, which intercalate between the layers [5,8].

LDHs containing ions such as Mg^{2+} , Ca^{2+} , Al^{3+} or Fe^{3+} have been intensely studied as heavy metal sorbents [9–12]. The dissolution reactions of LDH layers increase the pH of the contaminated media, which induce the precipitation of the corresponding heavy metal hydroxides, either as part of an LDH phase or separately [11]. Also, these solids can be intercalated with a functional ligand (edta, citrate, malate, etc.), that capture heavy metal ions and incorporate them to the LDHs interlayer [10,13,14]. The heavy metal containing LDHs obtained by either of these mechanisms present value for practical applications as catalysts [6,15] or sorbents [16,17].

In this work, the precipitation of heavy metals as LDHs is introduced as a remediation technique for pyrite ore mining wastewaters and its performance is compared to that of an Mg-Al-LDH used as sorbent. A simulated wastewater, based on the heavy metal, sulfate concentrations and pH of wastewaters from the mining pit of Aznacollar (informed by MAGTEL, which holds the rights for Aznacollar pyrite mine operation), was used as polluted media. Heavy metal scavenging by precipitation was performed by two complementary methods that allowed the competition between Mg^{2+} and heavy metal ions, and the formation of increasing LDH amounts to be studied. The removal percentage in the supernatants was determined and the structural characterization of the solid residues was performed. The results obtained were compared to those produced in the same wastewater by addition of carbonate-intercalated Mg-Al LDHs.

2. Materials and methods

All reagents were purchased from Panreac, S. A. and were used without previous purification. The solutions were prepared with distilled water.

A simulated wastewater was prepared with the following metal ion concentrations: 70 ppm Cu^{2+} , 800 ppm Zn^{2+} , 0.3 ppm Pb^{2+} , 500 ppm Al^3 , while the sulfate concentration was 41.1 mmol L^{-1} and the pH was 3.8.

A carbonate-intercalated Mg-Al LDH (LDH-CO_3) was obtained by the coprecipitation method at a constant pH, as previously described [18]. The carbonate intercalated LDH (LDH-CO_3) presented typical PXRD diagrams and FTIR spectra [19–21] and its chemical formula was calculated as $\text{Mg}_{0.76}\text{Al}_{0.24}(\text{OH})_2(\text{CO}_3)_{0.12}\cdot 0.64\text{H}_2\text{O}$ ($\text{Pm} = 78.6\text{ g/mol}$).

Series of removal experiments were performed on the simulated wastewater, either by LDH addition or by in situ formation

of LDHs. In situ formation of LDHs was produced by the consecutive addition of Mg^{2+} ions and OH^- either in this order or upturned.

2.1. LDH- CO_3 addition

Simulated wastewater (100 mL) was added to increasing amounts of LDH- CO_3 (up to 1.2 g). The dispersions thus obtained were placed in closed bottles and agitated with an orbital agitator for 24 h. The pH was then measured in the equilibrated dispersions, which were centrifuged to separate supernatants and solids. The heavy metal concentrations were determined in the supernatants while the solids were dried at 60 °C without previous washing in order to carry out a structural characterization.

The heavy metal ions (Cu^{2+} , Pb^{2+} and Zn^{2+}) concentration of the supernatants was determined by atomic absorption spectrometry (AAS) in a Perkin Elmer AAnalyst400 instrument in samples diluted to meet the calibration range. For both Zn^{2+} and Pb^{2+} , the standard addition method was used in order to reduce the interferences by other ions.

The removal percentage (% removal) was calculated as:

$$\% \text{ removal} = \frac{C_0 - C_e}{C_0} \cdot 100$$

where C_0 and C_e are the initial and equilibrium heavy metal concentration, respectively.

The structural characterization of the solids was performed by PXRD and FTIR. 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 Bruker Tensor 27 spectrophotometer.

2.2. In situ formation of LDHs

For the study of in situ formation of LDHs, two series of experiments were performed. In the first one, the solution pH was increased to 10 and then a variable mass of $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ was added. In another series, the pH increase was performed after the addition of $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$.

In the first case, simulated wastewater (95 mL) was mixed with a 1 M NaOH solution until a pH = 10 was reached, which was maintained constant for 5 min using a 691 pH-meter coupled to an automatic 725 Dosimat dispenser (Metrohm). After the pH increase, $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ (up to 1.37 g) was added and the resulting dispersions were brought to the final volume (100 mL) and agitated for 24 h. The pH was then measured in the equilibrated dispersions, which were centrifuged to separate supernatants and solids. The heavy metal concentration in the supernatants and the structural characterization of the solids were determined as previously described.

The experimental procedure in the second series of experiments was analogous but, in this case, $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ was added first and, then, the obtained solution was neutralized to pH = 10. The equilibration, separation and characterization steps were performed as previously described.

3. Results and discussion

3.1. LDH addition

The heavy metal sorption capacity by LDHs was studied in simulated wastewater as a function of the sorbent mass (m_{LDH} , Fig. 1). Increasing removal percentages of Cu^{2+} and Zn^{2+} were obtained as m_{LDH} increased, reaching a maximum value of 99% and 40%, respectively. On the other hand, the maximum Pb^{2+} removal per-

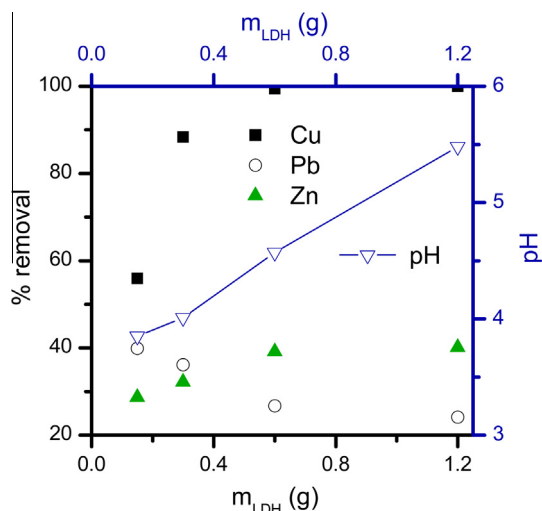


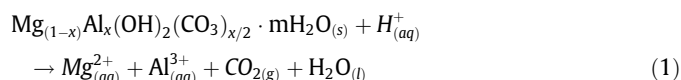
Fig. 1. % removal of heavy metal and pH vs. mass of sorbent (m_{LDH}) for simulated wastewater treated with LDH- CO_3 .

centage (40%) was obtained at the lowest m_{LDH} and then it diminished with increasing m_{LDH} to 25%. Finally, the pH of the dispersion continuously increased with increasing m_{LDH} up to 5.5 at $m_{LDH} = 1.2$ g.

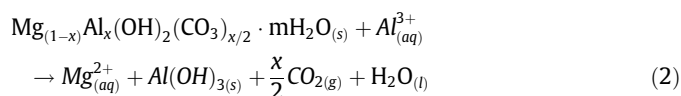
Fig. 2 shows the structural characterization of the solid residues obtained. At the lowest m_{LDH} , the PXRD pattern showed a wide band at 2θ with values between 10° and 40° that indicated the presence of an amorphous phase. Also, small peaks were obtained from a LDH phase matching that of copper aluminum sulfate hydroxide hydrate ($Cu_4Al_2SO_4(OH)_{12}\cdot xH_2O$, JCPDS 29-0001). This pattern also exhibited peaks matching the $ZnSO_4\cdot 6H_2O$ reference pattern (Bianchite, JCPDS 01-0352), an impurity due to the elimination of the solids washing step. On the other hand, the FT-IR spectra showed bands corresponding to the sulfate anion vibration modes at 630 cm^{-1} (ν_4), 986 cm^{-1} (ν_1), 1096 and 1146 cm^{-1} (ν_3). There was a splitting of the latter band, which was concordant with the presence of the zinc sulfate impurity [22]. As m_{LDH} increased, the relative intensity of the zinc sulfate phase diminished, while new peaks appeared matching that of Copper Zinc Aluminum Sulfate Hydroxide Hydrate ($(Zn,Cu)_{1-x}Al_x(OH)_2(SO_4)_{x/2}\cdot mH_2O$, JCPDS 53-0918), indicated the presence of a sulfate intercalated LDH phase. Simultaneously, the splitting of the ν_3 band diminished, indicating that the sulfate was mainly intercalated between LDH layers [23]. A second LDH phase with $d_{(003)} = 7.6\text{ \AA}$, assigned to a

carbonate intercalated LDH phase, appeared at the highest m_{LDH} . This was confirmed by the presence of a band at 1375 cm^{-1} corresponding to carbonate vibration mode in the FT-IR spectrum.

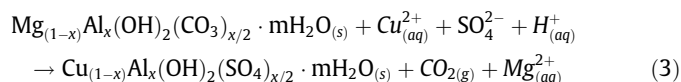
The obtained results indicated the complex behavior of the studied system due to the presence of different metal ions (Al^{3+} , Zn^{2+} , Cu^{2+}) and the addition of LDH- CO_3 . The simulated wastewater presents an acidic pH (≈ 3.8) and, consequently, LDH- CO_3 was partially dissolved according to the following reaction [24,25]:



As a consequence, the pH increased and the corresponding metal hydroxides are formed. Thus, on the basis of the respective solubility products of the corresponding metal ions (K_{SP} ($Al(OH)_3$) = $1.3\cdot 10^{-33}$, K_{SP} ($Cu(OH)_2$) = $2.2\cdot 10^{-20}$, K_{SP} ($Zn(OH)_2$) = $1.2\cdot 10^{-17}$, K_{SP} ($Pb(OH)_2$) = $1.2\cdot 10^{-17}$), we could propose the following removal mechanism. First, Al^{3+} in solution was precipitated as $Al(OH)_3$, according to the following reaction



This aluminum hydroxide precipitated as an amorphous phase [26], as detected on the PXRD pattern of the solid obtained at $m_{LDH} = 0.15$ g. As the m_{LDH} increased and the Al^{3+} ions in solution were exhausted, the next metal ion to be precipitated was Cu^{2+} . This metal ion precipitated as a LDH phase [10,11] but, as the CO_3^{2-} ions had been eliminated as $CO_{2(g)}$ at the pH of the media [27], they were replaced by sulfate anions. Thus, this reaction can be written as follows:



According to the literature [28–30], Cu^{2+} incorporation was produced by a mechanism called “diadochy”, an isomorphic substitution of Mg^{2+} ions by Cu^{2+} ions in the octahedral sites, instead of dissolution/precipitation processes. LDH- CO_3 was highly effective in removing Cu^{2+} ions, which were exhausted at $m_{LDH} = 0.6$ g. As $[Cu^{2+}]$ concentration decreased and pH increased, the Zn^{2+} ions were increasingly removed due to a mechanism similar to that described for Cu^{2+} ions. It is remarkable that the equilibrium pH was too low to produce either $Cu(OH)_2$ or $Zn(OH)_2$ precipitation [31], which indicated the larger stability of LDH phases [32]. When the pH was high enough (above 4.5), a portion of the LDH- CO_3

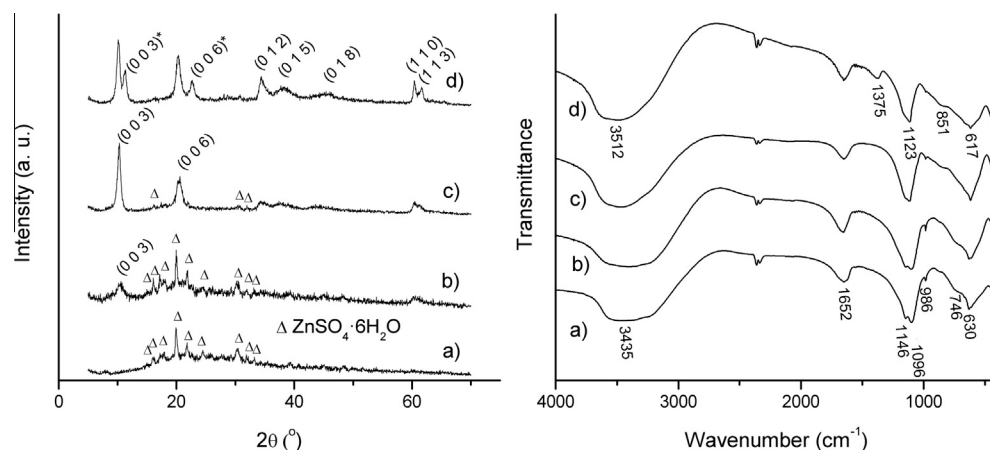


Fig. 2. PXRD patterns (left) and FT-IR spectra (right) of the solids obtained after treating simulated wastewater with $m_{LDH} = 0.15$ (a), 0.30 (b), 0.60 (c) and 1.20 g (d).

remains undissolved, which explained the presence of LDH phases containing either carbonate or sulfate anions. Finally, Pb^{2+} ions did not form LDH phases due to their size [11,29] and the solubility product of $Pb(OH)_2$ was too high to be precipitated at the pH range of the experiments. They were removed by adsorption on the amorphous alumina phase formed by the LDH dissolution and Al^{3+} precipitation (reaction (2)) [33,34]. Concordantly, the removal of Pb^{2+} ions, except for the first point, diminished with increasing LDH- CO_3 addition due increasing importance of reaction (3) which decreased $Al(OH)_3$ formation.

3.2. In situ formation of LDHs

As previously described, two series of experiments were performed to study the in situ formation of LDHs as a method of heavy metal remediation. The change of the sequence of steps of Mg^{2+} addition and pH rising to 10, lead to different equilibrium states, as indicated by the final pH of the dispersions.

Fig. 3A shows the % removal vs. Mg/Al molar ratio ($r_{Mg/Al}$) curves for the experiments performed by setting the pH to 10 and then adding the Mg^{2+} ions. At $r_{Mg/Al} = 0$, an important percentage of Cu^{2+} and Pb^{2+} ions (99 and 95%, respectively) were removed, while it was quite smaller (44%) for Zn^{2+} ions. With the addition of Mg^{2+} ions, the removal percentage decrease was almost negligible for Cu^{2+} (from 99 to 98%) and Pb^{2+} (from 95 to 92%) but not for Zn^{2+} (from 44 to 31%). On the other hand, the pH of the dispersion decreased sharply from 11.5 to 6.8 approximately (Supporting information, Fig. S1A).

The structural characterization of the solids obtained upon precipitation showed that LDH phases were obtained in all cases (Fig. 4). At $r_{Mg/Al} = 0$, the PXRD pattern showed wide peaks of copper sulfate hydroxide hydrate ($Cu_5(SO_4)_2(OH)_6 \cdot 5H_2O$, PDF file 41-0007) and a carbonate intercalated LDH phase ($d_{(003)} = 7.6 \text{ \AA}$). Concordantly, bands of carbonate (1358 cm^{-1}) and sulfate (1124 cm^{-1})

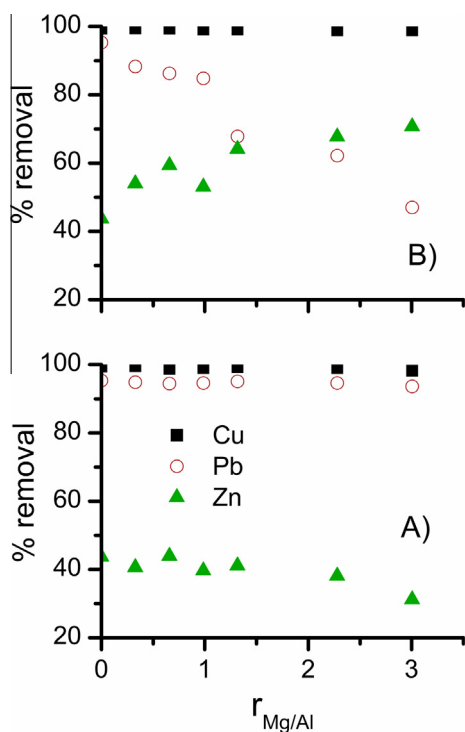
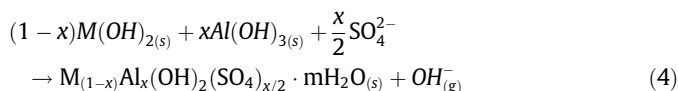


Fig. 3. % removal of heavy metal vs. Mg/Al molar ratio ($r_{Mg/Al}$) of dispersions obtained: A) by precipitation at pH = 10 and the posterior addition of Mg^{2+} ions; B) by precipitation at pH = 10 in solutions already containing the Mg^{2+} ions.

vibration modes were recorded in the FT-IR spectra. In contrast, a single LDH phase with $d_{(003)} = 8.9 \text{ \AA}$ was obtained at $r_{Mg/Al} = 0.66$ and the bands of carbonate vibration modes disappeared from FT-IR spectra, which indicated that sulfate is the only interlayer anion. The $d_{(003)}$ values of the LDH phases were quite similar for increasing $r_{Mg/Al}$, while some characteristic Na_2SO_4 peaks (due to the absence of sample washing) were registered.

When the pH of the wastewater was increased to 10, the precipitation of the corresponding heavy metal hydroxides or hydroxide salts was initially produced. Cu^{2+} ions precipitate as hydroxide sulfate, as registered in the PXRD patterns (Fig. 4, left). On the other hand, the pH increase after setting the pH of the solution at 10 indicated that $Al(OH)_3$ and $Zn(OH)_2$ were formed in the first moments after the alkalization and afterwards converted to LDH phases according to the following reaction:



On the other hand, Pb^{2+} ions were not precipitated as LDH phases, but they sorpted on the surface of the formed LDHs [35] and/or metal hydroxides [33,34]. The addition of Mg^{2+} ions led to the formation of Mg-Al-LDHs, as demonstrated by the pH diminution. Nevertheless, the plateau at pH = 6.5 indicated that an equilibrium state was reached at low $r_{Mg/Al}$ and no additional Mg-Al LDH was formed with Mg^{2+} ions addition. Also, the peaks corresponding to copper sulfate hydroxide disappeared, indicating that Cu^{2+} ions were incorporated to the additional Mg-Al-LDHs formed upon the addition of Mg^{2+} ions. Although these ions did compete with Zn^{2+} and Cu^{2+} ions for the octahedral sites of LDH layers, Mg^{2+} ions present less affinity for these sites than these heavy metal ions, especially in the case of Cu^{2+} ions [10], whose removal percentage presented a negligible diminution. On the other hand, Zn-Al-LDHs present a more similar formation constant than Mg-Al-LDHs [32] and, consequently, the % removal of Zn^{2+} ions diminished with increasing $r_{Mg/Al}$. Finally, the addition of Mg^{2+} ions did not affect the % removal of Pb^{2+} ions, which present a maximum adsorption over Mg-Al-LDH at pH values above 6 [35]. Regarding the interlayer anions, a small amount of carbonate anions was incorporated as an impurity to the solids due to the alkaline pH in the experiments performed without $MgSO_4$ addition. On the other hand, the pH diminution when $MgSO_4$ was added produced their displacement of the interlayer by sulfate anions, as demonstrated by the FT-IR spectra in Fig. 4 (right).

Fig. 3B shows the % removal vs. $r_{Mg/Al}$ curves for the experiments performed by adding the Mg^{2+} ions and then setting the pH to 10, which increased the amount of LDHs formed. Obviously, the experiments and results at $r_{Mg/Al} = 0$ were the same than for the series with the inverted order of reactive addition. The addition of Mg^{2+} ions produced negligible effects in % removal of Cu^{2+} ions, while the effect was divergent for the removal of Pb^{2+} and Zn^{2+} ions. For the former, decreasing removal percentages (from 95% to 47%) were obtained with increasing $r_{Mg/Al}$, while an increase from 44% to 71% was obtained for Zn^{2+} ions. On the other hand, the pH of the dispersion increased from 11.4 to 11.6 approximately (Supporting information, Fig. S1B).

As expected, the structural characterization of the solids obtained upon precipitation showed that LDH phases were prevalent in all cases (Fig. 5) and $d_{(003)}$ values obtained increased from 7.7 \AA to 8.3 \AA when $r_{Mg/Al}$ increased from 0.66 to 3.00. Simultaneously, an intensity diminution of the characteristics carbonate bands in the FT-IR spectra was registered in the same order.

When Mg^{2+} ions were added before OH^- anions, the former were completely precipitated either as $Mg(OH)_2$ or Mg-Al-LDH, immediately after the solution was alkalized. Also, the LDH forma-

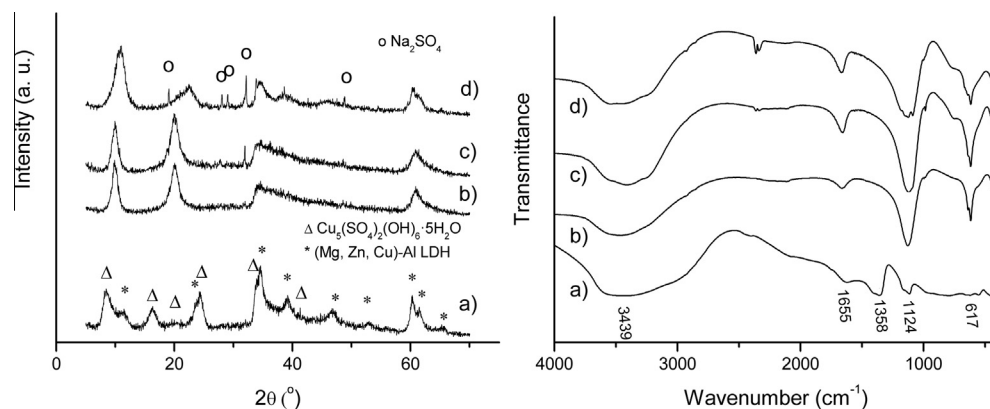


Fig. 4. PXRD patterns (left) and FT-IR spectra (right) of the solids obtained after treating simulated wastewater by precipitation at pH = 10 and the posterior addition of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. $r_{\text{Mg}/\text{Al}} = 0.33$ (a), 0.66 (b), 1.32 (c) and 3.00 (d).

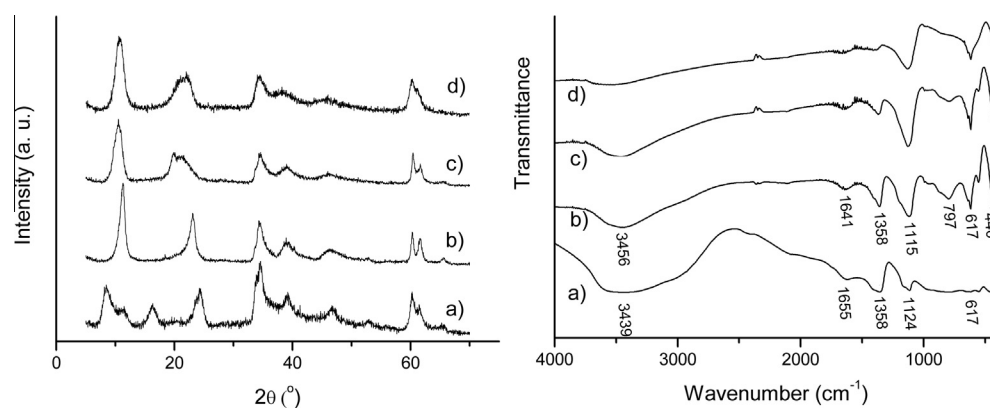


Fig. 5. PXRD patterns (left) and FT-IR spectra (right) of the solids obtained after treating simulated wastewater by precipitation at pH = 10 in solutions containing $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. $r_{\text{Mg}/\text{Al}} = 0.33$ (a), 0.66 (b), 1.32 (c) and 3.00 (d).

tion reaction from $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$, according to reaction (4) became increasingly important, as reflected by the slight but continuous increase of the pH of the dispersion at equilibrium. Unlike the previous precipitation experiments, the % removal of Cu^{2+} ions remained unaffected due to the low solubility product of Cu containing LDHs. On the other hand, solubilization of Pb^{2+} ions was produced due to the amphoteric character of these ions, that tend to be solubilized as $\text{Pb}(\text{OH})_3^-$ [31] as the media became increasingly alkaline. Similar results were obtained by Zhou et al. [35] for Pb^{2+} adsorption on Mg-Al LDHs. On the other hand, Zn^{2+} ions, although amphoteric, formed LDH phases with lower K_{ps} than the corresponding Zn hydroxide. Consequently, they competed with Mg^{2+} ions for the increasing amount of LDH, which increased their % removal. Regarding the interlayer anion, the carbonate presence in the solids diminished with increasing $r_{\text{Mg}/\text{Al}}$, which was assigned to the larger amount of LDHs formed in the series. As the carbonate impurity was approximately constant, the proportion of sulfate-intercalated LDHs increased.

4. Conclusions

In this work, heavy metal removal from a simulated mining wastewater was produced by sorption by a carbonate-intercalated Mg-Al LDH (LDH-CO_3) or in situ precipitation of LDH phases by addition of hydroxide and Mg^{2+} ions. Addition of LDH-CO_3 led to a pH increase and the precipitation of LDH phases containing Cu^{2+} and Zn^{2+} ions, while Pb^{2+} ions were removed due to sorption on $\text{Al}(\text{OH})_3$, formed in the mildly acid media of the

wastwaters. On the other hand, heavy metal removal by in situ formation of LDHs was dependent on the concentration of Mg^{2+} ions and on the order of the addition of Mg^{2+} and OH^- ions. In absence of Mg^{2+} ions, Cu hydroxide sulfate and (Zn-Cu-Mg)-Al LDH phases were formed upon the pH increase, while Pb^{2+} ions was removed due to adsorption processes on $\text{Al}(\text{OH})_3$ and/or LDH particles. When Mg^{2+} ions were added after OH^- ions, a small amount of LDHs was formed and Mg^{2+} competed with the heavy metal ions for the octahedral sites of LDH layers. On the other hand, when Mg^{2+} were added before OH^- ions, an increasing amount of LDHs was formed, which increased the number of sites for heavy metal removal but also increased the equilibration pH, diminishing the Pb^{2+} removal due to its amphoteric character. Then, although Cu^{2+} was eliminated with high efficiency in all cases, Pb^{2+} and Zn^{2+} removal needs a fine tuning of the removal process in order to achieve high efficiency.

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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.2016.08.054>.

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