Study of the effect of the LDH cations precursors in the removal of arsenic in aqueous solution

María Martha Barroso Quiroga, Mònica Iglesias Juncà and Nora Andrea Merino

ABSTRACT

Layered double hydroxides (LDH) are anionic clays, mainly used as adsorbents, ion exchange material, and catalysts. Generally, they present high specific surface areas, alkaline character, high metallic dispersion, and high thermal stability. If they contain a transitional element in their structure, the solid may present redox properties. LDH were synthesized with the following combinations: MgAl, MgFe, and ZnMgFe, aiming to determine the effect of cationic nature in the structure and the functionality of the synthesized clay as adsorbents in polluted aqueous effluents. The textural properties were determined by nitrogen adsorption isotherms. Crystalline structure was studied by XRD and the presence of the anions of the interlayer was determined by FTIR spectroscopy.

The studies of removal of As(III) and As(V) from aqueous solutions, using the LDH, show that after 24 h the solids reach a high removal efficiency. ZnMgFe solid removed both species of arsenic with values of 95 and 98% for As(II) and As(V), respectively. The MgFe solid showed some selectivity to the uptake of As(V), while the MgAl only removed As(V). This selective behaviour can be beneficial in studies of arsenic speciation.

Key words | As(III), As(V), LDH, MgAl, MgFe

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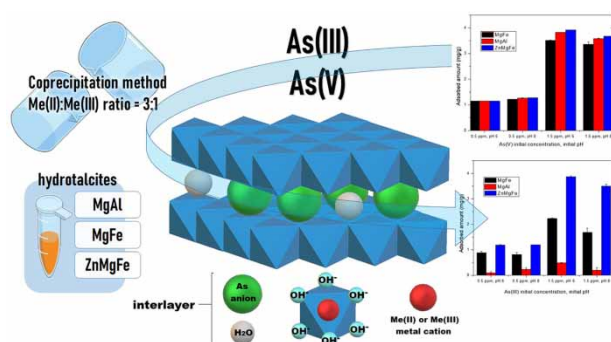   – CP: 17003 Girona,
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HIGHLIGHTS

- Al and Fe present different electrostatic interactions which modify the LDH activity.
- The different chemical behaviour of the constituent metals has influenced the morphology.
- The solids present more than 88% of removal of As(V) in less than 24 h.
- MgAl mostly removed As(V).
- ZnMgFe had an excellent performance for both arsenic species.

GRAPHICAL ABSTRACT

INTRODUCTION

Arsenic (As) is a highly toxic, mutagenic, and carcinogenic element. The continuous ingestion of polluted waters could cause skin, lung, bladder, and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis) neurological disorders, muscular weakness, loss of appetite, and nausea. Children are more susceptible than adults to develop adverse effects of arsenic, and dermatological diseases appear faster in them. Recent studies show that children exposed during the prenatal and postnatal period may have lower neurological performance than unexposed children (Mohan & Pittman 2007; WHO 2017).

When it comes to the regulations, the World Health Organization has lowered the guideline level for arsenic in drinking water from 0.05 to 0.01 mg L^{-1} (WHO 2017). In Argentina, the maximum acceptable level for As in drinking water is still under discussion. In 2012, an addendum was included in articles of the Argentine Food Code, which indicates a new extension to reach the level of 0.01 mg L^{-1}, until the completion of an epidemiological study to be carried out by government authorities (Litter *et al.* 2019).

About 14 million people of the almost 500 million that inhabit Latin America are at risk of suffering from diseases due to prolonged ingestion of arsenic in drinking water (Singh *et al.* 2015). In Argentina, the population exposed to this problem is approximately 2 million inhabitants (Litter *et al.* 2019).

Nowadays, a significant percentage of the population of the Province of San Luis (Argentina) lacks access to a drinking water network and water is supplied by underground wells. The low quality of water leads not only to a decrease in the settlement of the population in the region, but also generates low meat production per hectare and makes it difficult to install new activities, in addition to costs of public health derived from the treatment of diseases associated with arsenic. Therefore, the study, development and optimization of techniques and materials for the removal of arsenic on a small scale, which can be effective, low-cost and applicable in a short period, is imperative.

The selection of the treatment technology for the reduction/elimination of arsenic concentrations from water is related to several aspects: the economic factor, the size of the population, the incidence of chronic diseases, the lack of drinking water, the conditions of poverty, as well as other socioeconomic variables. Among the available technologies for As removal, adsorption presents many advantages, such as (i) high efficiency, (ii) low cost, (iii) large adsorbent volume and additional chemicals are not needed, (iv) easy to operate (v) without harmful by-products (Singh *et al.* 2015).

Within the layered double hydroxides (LDH) clay family, hydrotalcites (HTs) belong to the main class and they are anionic clays that have been widely used as sorbents for the removal of inorganic species from aqueous media (Jabłonska *et al.* 2013). HTs are lamellar solids with a structure like brucite, $M(OH)_2$, where M is a divalent cation, octahedrally coordinated with six hydroxyl groups. When M^{2+} ions are replaced by M^{3+} cations, a positive charge arises, pH$_{pzc}$ around 8–12.5 depending on the composition (Goh *et al.* 2008), that is neutralized by interleaved anions in the interlaminar regions. It is possible to produce hydrotalcite type materials with different divalent cations (Mg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) and trivalent ones (Al^{3+}, Ni^{3+}, Co^{3+}, Fe^{3+}, Cr^{3+}), as well as different anions (CO_3^{2-}, NO_3^-, SO_4^{2-}, WO_4^{2-}, CrO_4^{2-}) (Jabłonska *et al.* 2013; Li *et al.* 2019). The calcination of the hydrotalcites results in different phases of

simple, bimetallic, or trimetallic oxides, depending on the calcination temperature and the metal components of the structure (Cavani *et al.* 1991). The most interesting properties of these oxides are high surface area, synergistic effects between the elements, and memory effect (Cavani *et al.* 1991). These properties added to their low cost, they are easy to upscale, and versatile; they allow the use of oxides derived from hydrotalcites in multiple applications (Jabłonska *et al.* 2013).

This work aims to evaluate the behaviour of three layered double hydroxides (LDH) with different trivalent cations, Fe and Al, as adsorbents of arsenical species present in aqueous solutions and to study the effect of the modification of the cation in its application. The effect of factors such as initial pH and initial As concentrations were also tested.

METHODS

Hydrotalcite-like compound synthesis

Layered double hydroxides of Mg, Fe, and Al, with a molar ratio of $Me^{2+}/Me^{3+} = 3/1$, were synthesized by the coprecipitation method (Cavani *et al.* 1991). Two solutions were mixed, the first was a mixture of the salts of the metal precursors, that was dropwise mixed with the second one, an alkaline mixture of KOH and K_2CO_3 in distilled water, with vigorous mechanical agitation, using a constant pH of 9.5–10 and at 70 °C. The salt solution mixed consisted of $Mg(NO_3)_2 \times 6H_2O$ (Biopack), $Zn(NO_3)_2 \times 6H_2O$ (Riedel-de Haen), $Al(NO_3)_3 \times 9H_2O$ (Merck), and $Fe(NO_3)_2 \times 9H_2O$ (Anedra). The suspension was aged at room temperature for 24 hours. The precipitate was washed until a pH of 7 was reached and then dried, in a SE33 T model San Jor oven, at 110 °C for 24 hours. An aliquot of dried solid was calcined, in a 134 model Indef electric furnace, at 500 °C, keeping it at this temperature for 1 hour. From now on, the solids obtained will be called MgAl110, MgFe110 and ZnMgFe110 (dried) and MgAl500, MgFe500 and ZnMgFe500 (calcined).

Analytical methods

The temperatures of phase changes and the choice of calcination temperature were observed by the thermogram analysis using a TGA-50 Shimadzu thermobalance. In the TGA-DTA essays, approximately 30 mg of sample were used, in a nitrogen atmosphere with a flow of 20 mL min^{-1}, with a heating rate of 5°/min, from room temperature up to 900 °C, keeping

at this temperature for 30 minutes. BET specific surface areas of samples were calculated by the BET method. A Gemini V from Micromeritics apparatus was used. Samples were degassed at 250 °C for 1 h and the nitrogen adsorption isotherms measured at −196 °C. The diffraction patterns were obtained by using a Rigaku Ultima IV Type II diffractometer operated at 30 kV and 20 mA by Cu Kα Nickel filtered radiation ($\lambda = 1.5406$ Å). The spectra were collected at 2θ ranges of 5°–70°, at a scanning speed of 3° min^{-1}; the crystalline phases were identified by reference to powder diffraction data. The presence of the anions was studied by infrared spectroscopy with Fourier transform (FTIR) using Perkin-Elmer Spectrum RX1 equipment. The solids were diluted with KBr. The redox behavior of metals and precursor anions in synthesized solids was analyzed by the temperature-programmed reduction (TPR) technique. It was performed in a quartz U-type tubular reactor using a thermal conductivity detector, and 100 and 200 mg samples were used. The reducing gas was a mixture of 10% v/v H_2/N_2 at a total flow of 30 mL min^{-1} and the temperature was increased at a rate of 10 °C/min from room temperature to 600 °C and maintained at this temperature for 1 hour. The samples were pretreated at 200 °C, in a nitrogen atmosphere.

Arsenic removal

The removal capacity of As(III) and As(V) ions was evaluated by adding 0.4 g_{LDH}/L to 25 mL of $NaAsO_2$ (Fluka) or $Na_2HAsO_4.7H_2O$ (Merck) solutions in Milli-Q water, with initial concentrations of 0.5 ppm and 1.5 ppm. The pH of the arsenic solutions was adjusted to 6 or 8 by the addition of HCl or NaOH diluted solutions and using a glass pH electrode. The suspensions were kept stirred for 24 h at room temperature on a Labinco model (Dinko Instruments) rotator shaker, at 40 rpm. The tests were performed in duplicate. Afterward, the suspensions were centrifuged and then filtered with a 0.1 μm cellulose acetate membrane filter. The filtrate was analyzed for residual As(V) or As(III) concentration by ICP-OES using an Agilent 5100 VDV and measuring in axial view configuration 4% of ethanol 96% v/v was added to improve sensitivity (Colón *et al.* 2011).

RESULTS AND DISCUSSION

Layered double hydroxides characterisation

The anionic clays were synthesized by the coprecipitation method, using an acid solution with the precursors, the

nitrates of the constituent metals of its structure, and a solution with KOH and K_2CO_3, used as a precipitating agent and to maintain the pH constant. The dried and calcined solids were physicochemically characterized to study the influence of the trivalent cation in the structure of the laminar clay and the oxides obtained from their calcination. The thermograms of the dried samples showed a loss of endothermic mass at temperatures up to 200 °C, which occurs at lower temperatures with the replacement of aluminum by iron. The two subsequent mass losses are exothermic processes, the first occurs between 180 and 300 °C, and the third stabilizes approximately between 550 and 600 °C. The first decomposition is attributed to interlaminar water removal and the remaining ones to the reactions of dehydroxylation and decomposition of the interlaminar anions (Carja et al. 2002). The calcination temperature was chosen because at 500 °C simple oxides are present, but in an unstable way, so the hydrotalcite structure can be obtained again, since its property of memory effect.

Table 1 shows the textural properties of synthesized, dried, and calcined solids, obtained from physisorption tests with nitrogen. It is possible to observe a different behavior of solids according to the trivalent cation present in the structure.

Solids with aluminum show an increase in specific surface area with calcination, as reported in the literature (Carriazo et al. 2011), since calcination leads to a destruction of the laminar structure, which causes the formation of low crystallinity phases (oxides of the constituent metals). On the other hand, solids with iron, after calcination, suffer an appreciable loss of their BET area, which could be attributed to their sintering. All synthesized, dried, and calcined solids have a pore size distribution in the mesoporous region (pore size between 20 and 500 Å), according to the IUPAC classification (He et al. 2005). The tendency in the growth of the diameter and volume of the pores is inverse. With aluminum, the pore volume increases, and the pore diameter decreases after calcination, while when the aluminum is partially or completely replaced by iron, the pore volume

decreases, and the pore diameter increases after calcination. Hydrotalcite has a mesoporous structure due to the size and shape of the particles and their interconnection pattern. It can be inferred from the results obtained that the morphology of these solids is modified by the initial synthesis conditions (different nature of the ions present in the synthesis medium, different concentrations of the precursor solutions, etc.) (Carja et al. 2002).

The diffraction lines of all the solids studied are presented in Figure 1. The diffractogram of the MgAl dried at 110 °C has the laminar structure of the corresponding hydrotalcite, although it could have impurities of simple and mixed spinel-type oxides. The calcination stage leads to the formation of the simple oxides of the metals present or the mixed phases of the oxides, depending on the nature of the metals. Besides, hydrotalcite calcination at high temperatures removes water and anions from the interlayer region, as well as hydroxyls, destroying the crystalline structure of the minerals (He et al. 2005; Dias & Ferreira-Fontes 2020).

The diffraction lines of MgAl110 show a shift towards lower diffraction angles when compared with those corresponding to a hydrotalcite structure at $2\theta = 11.66°$; 23.44°; 34.91° (PDF 089-0460). In addition, it is possible to observe peaks attributable to spinel phases, $2\theta = 38.82°$; 65.76° (PDF 002-1086) and $2\theta = 54.31°$ (PDF 087-0343). This calcined solid only has the MgO phase (PDF 089-7746). The alumina phase (Al_2O_3), which may be present, cannot be identified as being amorphous. Al^{3+} cations are forming this phase or crystalline phases of low concentration, highly dispersed.

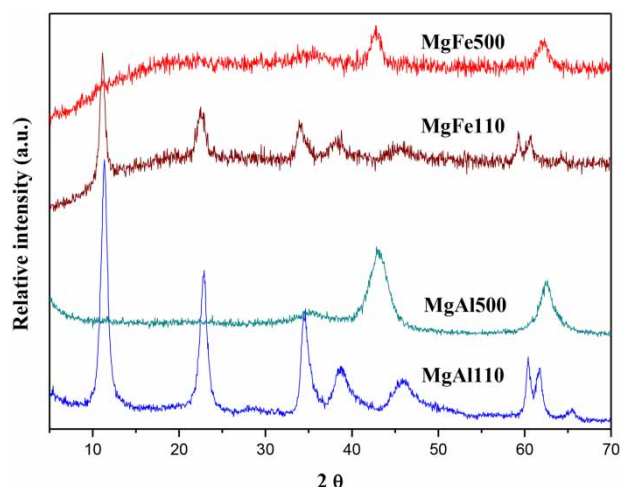The XRD patterns of ZnMgFe110 and its calcined sample ZnMgFe500 are shown in Figure 2. All the

Table 1 | Textural properties of the dried bimetallic solids

LDH	Specific surface area S_{BET} (m^2/g)	Pore volume Vp (cm^3/g)	Pore diameter Dp (Å)
MgAl110	103	0.632	176.2
MgAl500	128	0.796	192.3
MgFe110	63	0.376	181.9
MgFe500	39	0.262	173.1

Figure 1 | Diffractograms of the dried and calcined bimetallic solids.
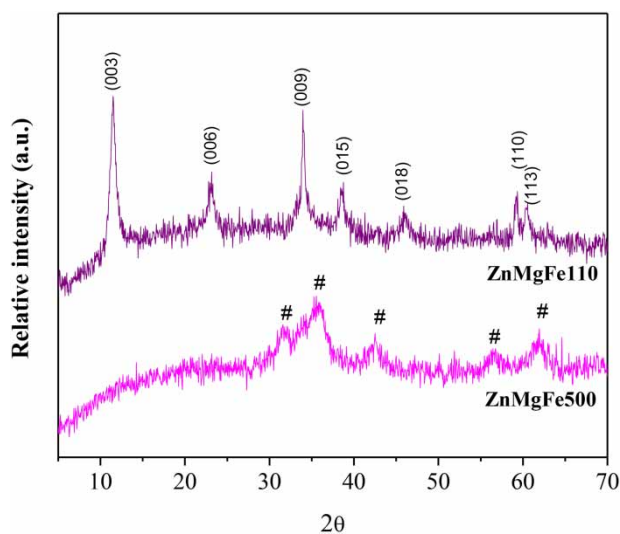
Figure 2 | Diffractograms of the dried and calcined trimetallic solid. # MgFe$_2$O$_4$ (PDF 88-1943) or ZnFe$_2$O$_4$ (PDF 82-1042).

characteristic peaks including (003), (006), (009), (015), (018), (110), and (113), corresponding to the trimetallic LDH, could be found. After calcination, the characteristic peaks of MgFe$_2$O$_4$ (PDF 88-1943) or ZnFe$_2$O$_4$ (PDF 82-1042) (Wang et al. 2017) were observed. The interplanar distance (d-spacing) decreased after calcination, indicating that partial interlayer molecules and ions were removed during thermal treatment, which could improve the adsorption capacity by ion intercalation during the layer reconstruction process (Kang et al. 2013; Liu et al. 2019).

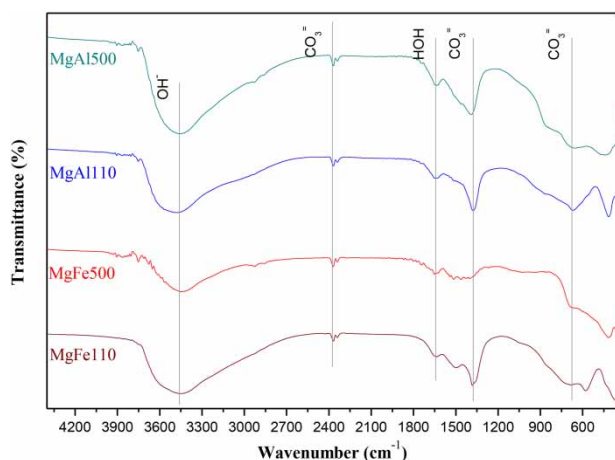The FTIR spectra of the bimetallic LDH are shown in Figure 3 and they are in concordance with those found in the literature for LDH-like materials. There is a broad band at approximately 3,560 cm^{-1}, which is related to the stretching vibrations of hydroxyls attached to Al and Mg sheets and water molecules in the basal interlayer (Guo et al. 2012). The band at 2,370 cm^{-1} is associated with CO$_2$ from air (Yoshida et al. 2015). The absorption band observed at 1,655–1,635 cm^{-1} is attributed to the bending vibration of the interlayer water; and the one around 1,340 cm^{-1} is due to carbonate group asymmetric stretching, which is present in the basal interlayer. Moreover, it is possible to assign the band at 1,380 cm^{-1} to the N–O antisymmetric stretching of nitrate ions (free nitrate ions). The bands observed at 1,500 cm^{-1} in the dried solids could be associated with the presence of bidentate nitrate species. In the calcined solid spectra, the intensity of these bands considerably decreased. Both anions, CO$_3^{2-}$ and NO$_3^-$, could be present in the hydrotalcites since they are the precursors of the synthesis of these materials. The bands observed in the region of low frequency, 400–1,000 cm^{-1}, are ascribed as the lattice vibration modes of metal-O and metal-OH vibrations (Guo et al. 2012).

The temperature-programmed reduction data is shown in Figure 4 and Table 2. The MgFe solids, dried and calcined, show a peak at low temperature (416 °C and 441 °C, respectively), associated with the reduction of iron species from Fe^{3+} to Fe^{2+} ions of the MgFe oxide; and another peak at high temperature (671 °C and 677 °C, respectively), which is attributed to reduction of Fe^{2+} to Fe^0 (Podila et al. 2020). This last peak could also be accredited to carbonates present in the samples, and which could be identified through FTIR. For the MgAl solids, dried and calcined, there is only a small slope at high temperature that could be ascribed to the carbonate ions mentioned before (Dussault et al. 2005).
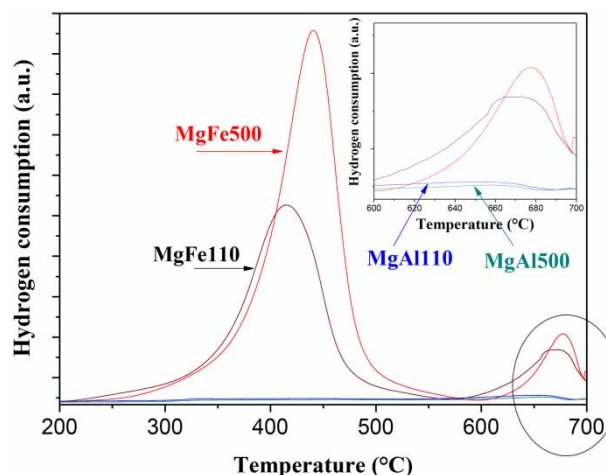

Figure 3 | FTIR spectra of the dried and calcined bimetallic solids.

Figure 4 | TPR data of the dried and calcined bimetallic solids.

Table 2 | Reduction temperatures of the bimetallic solids

Solids	T_{max1} (°C)	T_{max2} (°C)	T_{max3} (°C)
MgAl110			652
MgAl500			658
MgFe110	416		670
MgFe500		441	678

As absorption by LDH

As can be seen in Figure 5(a), when the initial concentration of As(V) is 0.5 ppm for both pH values, all the solids present similar adsorption capacity (range between 1.15 and 1.28 mg g^{-1}). When the initial concentration of As(V) is
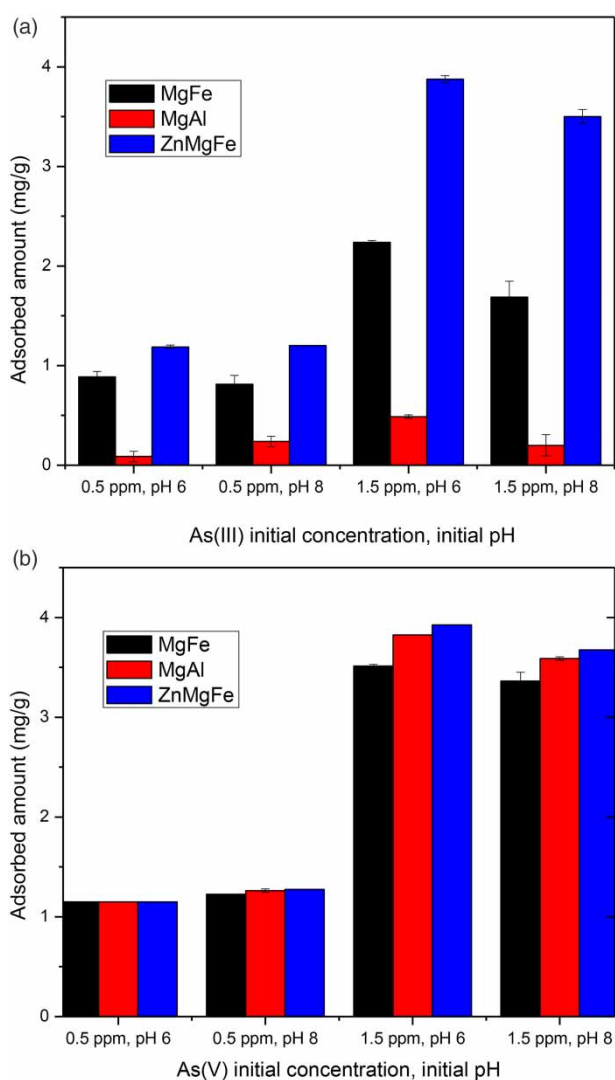

Figure 5 | (a) As(III) and (b) As(V) adsorbed amount by LDH. Effect of the pH and the initial concentration.

increased until 1.5 ppm, the adsorption capacity of the adsorbents is also much higher and greater amounts of As(V) are adsorbed at pH 6 than at pH 8. This could be explained due to the pH$_{pzc}$ of the LDH. The pH$_{pzc}$ is an important parameter; it corresponds to the pH value of the liquid surrounding particles when the sum of surface positive charges balances the negative charges. The pH$_{pzc}$ values reported in the literature for this kind of material are around 10 (Guo *et al.* 2012). So, when the solution pH is higher than this pH$_{pzc}$, the surface of the LDH is negatively charged. Therefore, the arsenate anionic species have been repelled by the LDH surface. When the solution pH is lower than the pH$_{pzc}$ of the LDH, the surface of LDHs is positively charged, which is beneficial for the adsorption of the negatively charged anionic species (Guo *et al.* 2012; Caporale *et al.* 2013).

The effect of the pH of the initial solution on the adsorption of As(III) by LDH solids is similar to As(V) (Figure 5(b)). There is almost no effect when the initial concentration is 0.5 ppm, but at 1.5 ppm, when the pH is higher, the adsorption capacity lowers. The decrease in the sorption of As(III) with increasing pH could also be attributed to the increasing concentrations of hydroxyl ions, which have a high affinity for LDH surfaces (Caporale *et al.* 2013).

Bimetallic solids do not have a great affinity to As(III), and MgAl has a much lower adsorption capacity than MgFe. Several authors claim that the difference in the total amounts sorbed of As(III) and As(V) on the bimetallic adsorbents may be related to the different species found in the solution for these two forms of As with different oxidation states, such as $H_2AsO_4^-$ and $HAsO_4^{2-}$ versus H_3AsO_3 (Yang *et al.* 2005; Caporale *et al.* 2013).

On the other hand, ZnMgFe had almost the same adsorption performance for both As(III) and As(V). The presence of Zn on the trimetallic solid enhances the performance of the adsorption. The different behaviour of the MgAl solid and the ZnMgFe in relation to the adsorption of different species of As(III) and As(V) could be used to separate these species. Although the adsorption capacity of the LDH prepared in this work is lower than others reported in the literature for this kind of material (Zubair *et al.* 2017), the adsorption capacity is in concordance with the adsorbent dosage used in this study, as can be observed in the results of Bhowmick *et al.* (2014).

CONCLUSIONS

Layered double hydroxides with Al and Fe as trivalent metals were successfully synthesized by the coprecipitation

method from the nitrates of the metal precursors, as can be seen in the results presented above. Furthermore, the laminar structure evidenced by both XRD and TPR was obtained. Both cations have different electronic configurations and sizes of ionic radii, so their electrostatic interactions are different, which leads to a different crystallization degree of the solids at the same calcination temperature, and dissimilar reduction behaviour in the same temperature range. This information should be taken into consideration when it comes to the applicability of the solids for a specific reaction and/or process. Hydrotalcite has a mesoporous structure due to the size and shape of the particles and their interconnection pattern. The morphology differs according to the trivalent cation since the chemical behavior of metals is remarkably different. The IR spectra show the presence of carbonate and nitrate anions, as is expected, since the former is in the solution, which regulates the pH, and the latter in the precursor salts.

The studies of the removal of As(III) and As(V) from aqueous solutions showed that at 24 h, all the three solids had a good performance in adsorption for As(V) at pH between 6 and 8. The presence of Fe in the LDH composition enhances the adsorption capacity towards arsenic ions since it is well known that iron oxides have a high affinity to arsenic. Although MgAl only removed As(V), ZnMgAl had an excellent performance for both inorganic arsenic species: As(III) and As(V). This selective behavior of MgAl LDH could be beneficial in arsenic speciation studies.

AUTHOR CONTRIBUTIONS

Dr Barroso Quiroga: conceptualization, investigation, formal analysis, writing – original draft, writing – review, and editing, funding acquisition. Dr Iglesias Juncà: writing – review and editing, funding acquisition, supervision. Dr Merino: conceptualization, investigation, formal analysis, writing – original draft, writing – review, and editing; project administration.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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