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INFLUENCE OF THE SYNTHESIS METHOD OF LAYERED DOUBLE HYDROXIDES ON THE TEXTURAL PROPERTIES AND NITRATE REMOVAL

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Abstract

Layered double hydroxides were prepared by co-precipitating Mg^{2+} and Al^{3+} ions at constant pH. Three different methods of solution additions and two temperatures for synthesis and aging were tested in each method. Through X-ray diffraction, it was confirmed that all the synthesized solids have a hydrotalcite-type structure, obtaining more crystalline compounds when one solution of Mg/Al is added to another with CO_3^{2-}/OH^- and compounds with greater interlaminar spacing when three different solutions are added (Mg/Al, CO_3^{2-} and OH^-). In addition, the solids obtained by this last method have a higher specific surface area and total pore volume, as confirmed by the N_2 adsorption-desorption. A similar trend occurs with synthesis and aging temperatures where better textural properties are obtained at a higher temperature, reaching surface area values of $242\text{ m}^2/\text{g}$ and pore volume of $0,93\text{ cm}^3/\text{g}$. All the synthesized solids were active for removing nitrates in water, obtaining the best results with the samples prepared by dripping three different solutions at $60\text{ }^\circ\text{C}$ ($26\text{ mgNO}_3^-/\text{g}$.) This fact demonstrates the correlation between the synthesis method and the textural properties of the material with its potential application in removing contaminants.

Keywords: Layered Double Hydroxides · Synthesis · Textural properties · Adsorption · Water · Nitrate removal

1 Introduction

Water pollution with nitrates is a problem far from being solved and cheaply. The technologies available today, such as reverse osmosis, ion exchange, electro-dialysis, and biological denitrification, are unavailable to most affected populations [1]. A series of different techniques to remove nitrates from water are currently under study, including dissimilatory nitrate reduction to ammonium (DNRA) [2], electrochemical reduction [3], catalytic reduction [4], and adsorption [5]. All these methods have their deficiencies; for example, in DNRA and catalytic reduction methods, dangerous products like ammonia and nitrite are formed [6,7]. Adsorption is a convenient method compared to others due to the simplicity and ease of operation design, not generating harmful by-products, and low operational cost [5]. Among the adsorbent materials for nitrate removal, activated carbons [8], zeolites [9], natural clays [10], and layered double hydroxides (LDH) [11] stand out.

LDH or hydrotalcite-like compounds belong to the class of anionic clays whose structure is based on layers similar to brucite ($\text{Mg}(\text{OH})_2$), in which some divalent cations have been replaced by trivalent ions that give place to positively charged layers. This charge is balanced by the intercalation of anions in the hydrated intermediate layer, called anionic clays. Weak hydrogen bonds connect the metal hydroxide sheets from interlayer water molecules that can be easily broken through thermal treatment, generating a mixture of oxides that recovers the original structure of the LDH when it is submerged in an aqueous solution with some anion of interest [12]. This property is known as the memory effect, which can be used to synthesize the LDH with a specific shape for trapping a specific anion after calcination [13,14].

LDH's can be represented by the general formula $[\text{M}^{+2}_{1-x} \text{M}^{+3}_x (\text{OH})_2]^{+x} (\text{A}^{-n})_{x/n} \cdot y\text{H}_2\text{O}$. The identities of the divalent and trivalent cations (M^{+2} and M^{+3} , respectively) and the intercalating anion (A^{-n}), together with the value of the stoichiometric coefficient (x), can vary across a wide range, resulting in a large class of isostructural materials [15]. In nature, layered double hydroxides are available as minerals [16]. However, they can be synthetically prepared in the lab or large scale [17]. Layered double hydroxides were discovered in Sweden around 1842 as natural hydroxycarbonate, and the first synthesis was reported by Feitknecht in 1942 [18]. In recent years several reviews have described different synthesis methods and the influence of the methods on the formation and structure of layered double hydroxides [13,19–25].

The easy control of the composition of the anionic clays and the possibility of increasing the surface area and the interlaminar volume with the appropriate choice of intercalated cations allow an optimal adjustment of their properties, allowing to synthesize a material according to the desired properties and the final application [26–28]. Thus, LDHs are of great importance for applications such as fertilizer vehicles for their sustained release, catalysts, flame retardant,

biomedical applications, synthesis of polymer nanocomposites, and lubricant additives, among others. [11,29]. Many authors are interested in using these materials in environmental applications to eliminate heavy metals[28,30–33] and dangerous inorganic anions[27]; among them, numerous studies of nitrate removal using hydrotalcites [11,34–36].

Among a great variety of synthesis methods for obtaining LDH, we can mention co-precipitation [37], anion exchange [21], the sol-gel method [38], mechanochemical synthesis [24], and hydrothermal synthesis [39]. The co-precipitation process is the most conventional and studied among these methods. The synthesis parameters most evaluated for this method are the pH, the base solution's nature and concentration, the aging time and temperature, and the M^{2+}/M^{3+} molar ratios [40]. All studies agree that the increase in aging time and temperature promotes the formation of LDH with higher crystallinity and larger crystallites. However, it is difficult to determine which temperature should be applied since it is necessary to have different particle sizes for different applications of LDH [22]. For this reason, it is still interesting to study the effect of the synthesis temperature of the material on its ability to adsorb a specific anion.

Cao et al. found that the change in reactant concentration influenced the morphology and size of particles of the LDH. In contrast, the pH difference caused by different metal ion concentrations may remarkably affect the intercalated anions [41]. It is well known that synthetic minerals like LDH are produced in reaction rates faster than the formation of the same natural mineral. Some synthetic minerals had not enough time to equilibrate into a minimal energy state affecting some properties of the synthetic material [25]. Consequently, it is expected that the order of addition of the reagents in the synthesis of LDH strongly influences the material obtained. However, other authors have not yet studied this. The co-precipitated method of LDH can be expected to contain larger crystallites whose nucleation sites formed early in the co-precipitation and smaller crystallites formed closer to the end of reagent addition and therefore experienced a shorter aging time [37].

In this work, the MgAl-LDH was synthesized, and the influence of temperature and reagent addition on its morphology, composition, structure, and nitrate adsorption behavior was investigated comprehensively. The novelty of the research focuses on the relationship of preparation, structure, and properties by investigating the influence of reagent addition and temperatures of synthesis and aging on the structure and nitrate adsorption properties.

2 Materials and methods

The LDHs were synthesized via co-precipitation of solutions of $Mg(NO_3)_2$ and $Al(NO_3)_3$ (Mg/Al molar ratio = 3) at constant pH (near to 10) in the presence of NaOH and Na_2CO_3 .

Variations were made in the addition of these solutions: in **method A**, two solutions were added simultaneously, a solution of Mg-Al salts and another with NaOH and Na₂CO₃, whereas, in **method B**, the Mg-Al solution was added to the NaOH/Na₂CO₃ solution, and in **method C**, three solutions were mixed, the Mg-Al solution, NaOH and Na₂CO₃. The solutions were added drop by drop in all the cases under constant stirring. Once the drip was finished, it was kept in that condition for 3 hours at room temperature. Thus, we obtained the LDH_A, LDH_B, and LDH_C samples. Then the three syntheses were repeated at 60 °C in all stages, and we obtained LDH_{A60}, LDH_{B60}, and LDH_{C60}. Finally, each one was filtered and washed with milli-Q water until a pH of 7.0 was reached. The synthesized samples present carbonate ions filling the interlaminal spaces; the solids will be calcined to eliminate the interlayer anions before the nitrate removal analysis. The calcination was done by heating the samples to 450 °C and keeping them at this temperature for 6 hours under nitrogen flow. A summary scheme of these syntheses is shown in Figure 1.

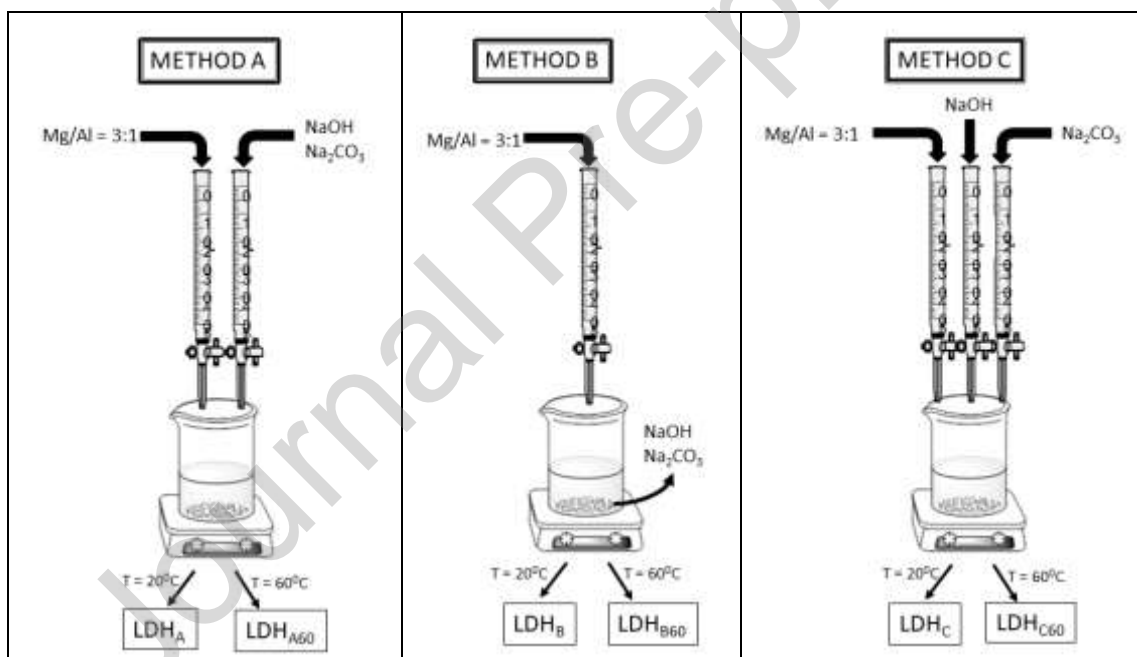


Fig. 1 Scheme of the three synthesis methods to obtain LDHs

The X-ray diffractograms (XRD) were obtained in a BRUKER-D2 Phaser diffractometer using Cu radiation, a step of 0.02°, a velocity of 2° /min, and a sweep interval of 5 to 70° in units of 2θ. The basal spacing was determined from the Bragg equation: $n \cdot \lambda = 2d_{hkl} \cdot \sin \theta$ where n is the order of peak reflection, λ is the X-ray wavelength used, d is the basal spacing corresponding to the Miller indexes' crystallographic positions (hkl), and θ is the Bragg angle determined through the peak of the sample.

Nitrogen (N_2) adsorption-desorption isotherms at 77 K were carried out on an automatic sorptometer (Micromeritics – ASAP 2050). The samples were previously outgassing at 100 °C for 12 h. Specific surface area (S_{BET}) was calculated by Brunauer, Emmett, and Teller methods for 12 h. Specific surface area (S_{BET}) was calculated by Brunauer, Emmett, and Teller methods using the IUPAC recommendations [42,43]. The mesopore size distributions (MPSD) were determined by Villarroel-Barrera-Sapag (VBS) method [44] using cylindrical pore geometry and nitrogen desorption data, and total pore volume (V_{TP}) was obtained by the Gurvich's rule [45].

Infrared vibrational spectroscopic data were collected using a Perkin-Elmer Spectrum 65 FT-IR spectrometer coupled to a Perkin-Elmer Universal ATR sampling accessory. The analysis range was 400–4000 cm^{-1} .

Morphological characterization of samples was carried out using Scanning Electronic Microscopy (SEM) obtained in a LEO 1450 VP equipment with an energy dispersive X-ray probe (EDX) EDAX Genesis 2000.

Nitrate removal tests were performed in batches under continuous agitation on a SOLAB Orbital Stirring Table, SL-180 / D, placing 100 mg of LDH in 50 mL of 100 mg/L solutions of KNO_3 . Nitrate content was measured in spectrophotometer UV-Vis brand BioTraza, reading at 220 nm in a quartz cell, discounting matter organic read at 275 nm. Nitrate adsorbed was calculated by equation 1:

$$q_t = (C_0 - C_t) V / m \text{ Equation (1)}$$

where q_t is the adsorptive capacity of adsorbent at time t (mg/g), V is the volume of solution (L), C_0 and C_t (mg/L) are the initial concentration of nitrate, and at time t , respectively, and m is the mass of adsorbent (g).

3 Results and discussion

Fig. 2 shows the XRD diagrams of the synthesized Hydrotalcites. In all cases, the typical laminar structure of the hydrotalcite was obtained [46](Pattern ref. 22-0700, JCPDS) with intense and thin peaks corresponding to the planes (003), (006), (009), (110) and (113) and a broader peak attributable to the plane (015).

The less intense and broader peaks of LDH_A compared to LDH_B and LDH_C would indicate a lower crystallinity and structural ordering in the solid obtained with this synthesis method. On the other hand, LDH_B exhibits these solids' higher crystallinity and structural ordering. According to Cavani et al. [47], under conditions of low supersaturation, more crystalline precipitates are formed due to the higher crystal growth rate versus nucleation rate. Therefore, this process is favored if, in the synthesis of LDH, the solution of metal cations is added to the

basic solution (method B) and not both solutions at the same time (method A and C) since the nucleation sites are formed earlier when the metal cations fall into a basic environment.

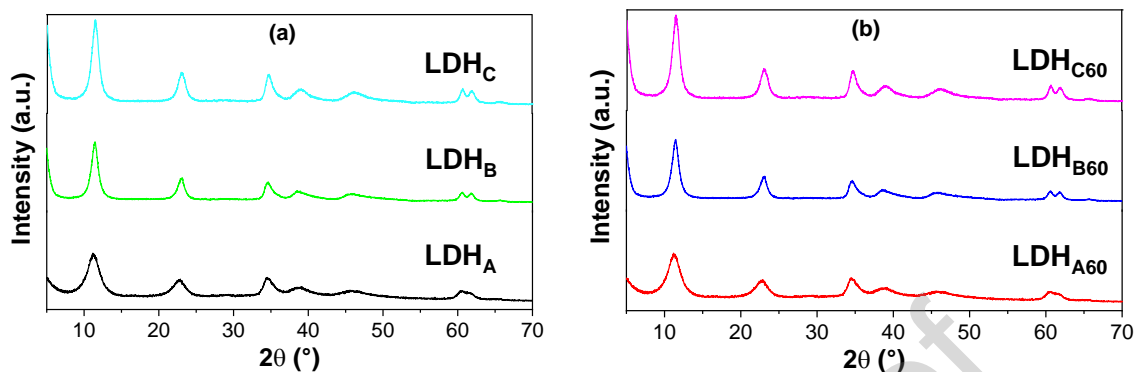


Fig. 2 XRD of LDH's synthesized at room temperature (a) and at 60 °C (b)

In the syntheses made at 60 °C, a slight increase in the definition and intensity of the peaks can be seen for the syntheses developed at room temperature, which would indicate that more crystallinity and order are achieved by performing the synthesis at high temperature, probably, because higher temperatures in the co-precipitation and aging stages favor the rate of crystal growth over the nucleation rate, which is in agreement with other authors [39,41].

Table 1 Crystallographic parameters from XRD analysis

Parameters	LDH _A	LDH _B	LDH _C	LDH _{A60}	LDH _{B60}	LDH _{C60}
d_{110} (Å)	1.529	1.527	1.529	1.530	1.526	1.530
a (Å)	3.059	3.053	3.059	3.060	3.053	3.060
d_{003} (Å)	7.773	7.706	7.814	7.814	7.666	7.814
c (Å)	23.319	23.117	23.443	23.442	22.997	23.442
Interlayer spacing (Å)	2.973	2.906	3.014	3.014	2.866	3.014

From the XRD plots, the crystallographic parameters were determined using the $d_{(003)}$ and $d_{(110)}$ peaks. Parameter a is the distance between the metallic cations ($a=2 \cdot d_{110}$), c is the distance between three brucite-type sheets plus their interlaminal space ($c=3 \cdot d_{003}$), and the spacing of the interlaminal region was calculated according to Wan et al. [36]. The results are listed in Table 1. Compared with the results of other authors, all of these lattice parameters correspond to the layered structure of hydrotalcite-like compounds [11,29,42] and agree with the values obtained from theoretical calculations [26]. Furthermore, since the anions were adsorbed into the interlayer and formed a negative layer, large interlayer spacing was favorable for nitrate adsorption; because of this, we expect the solid LDH_{C60} to have higher adsorption capacities because it has the largest interlayer spacing [36,48].

For all solids, the obtained N_2 adsorption-desorption isotherms (Fig. 3) were of Type IV, according to the IUPAC classification, which is characteristic of mesoporous materials. Regarding hysteresis loops, the materials synthesized with method C (LDH_C and LDH_{C60} samples) present a Type H3 hysteresis loop, typical of the LDH, associated with rigid aggregates of particles in the form of plates originating Slit-shaped pores [49]. Instead, the materials obtained by methods A and B exhibit Type H1 hysteresis loops, corresponding to agglomerated or compact pores of uniform arrangements and sizes. These results show that depending on the synthesis method, modifications of the mesoporous structure of the LDH are obtained. Respect to the effect of the temperature of synthesis (RT and 60 °C) on the shape of the hysteresis loop, it can be seen that with methods A and C, no changes were observed. However, with method B, the LDH obtained at 60 °C presented a nitrogen isotherm with a Type H1 hysteresis loop more defined than the LDH synthesized at RT, indicating that (employing method B) at a higher temperature of synthesis, more uniform mesopores were obtained. The specific surface area values (S_{BET}) and the total pore volume (V_{TP}), calculated from the nitrogen adsorption data included in Table 2, show typical values for this type of solids similar reported by other authors [46,49–51] and in all materials, there is no the presence of micropores. LDH_{C60} displayed greater pore volume and specific surface area, desirable results for the application in the nitrate removal from water.

According to XRD, methods B, and C presented structures with better textural properties than those obtained with method A. The same behavior appears when the synthesis temperature increases. In non-highly porous compounds such as these, it is expected that as the crystallinity increases, the specific surface area of the solid decreases [52]. From the XRD results, it was found that the LDH_B sample has better crystallinity than the LDH_C , and that is due to the textural properties of the latter reaching higher values than the first. However, it is expected that sample LDH_A would have higher values of specific surface area, but this trend is not observed. This fact could be explained if we consider that the so-called Ostwald ripening occurs during the synthesis of LDH [53]. According to this mechanism, in the aging stage of the synthesis, the small particles in suspension dissolve and reprecipitate, increasing the size of the crystals; in this way, small particles that block the pores at the beginning of aging can grow and leave the pores free of access for N_2 (closed porosity). We believe that in the case of LDH_A this recrystallization does not occur to a great extent, and therefore, a large part of the pores is still blocked, thus generating a lower S_{BET} .

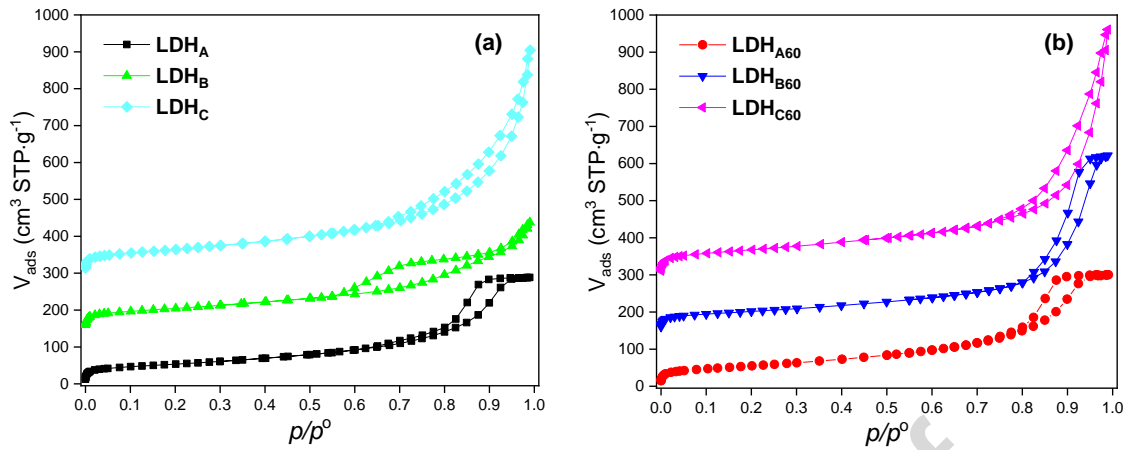


Fig. 3 Nitrogen adsorption-desorption isotherms of LDH's synthesized at room temperature (a) and 60 °C (b)

As mentioned above, in figure 3, the difference among the hysteresis shapes of samples synthesized with the three methods and at different temperatures is evident. This difference indicates that the mesopores, given by the aggregate particles, are changing their size and the way they are packed. In this sense, the mesopore size distributions (MPSD) were obtained using the VBS method, as shown in Figure 4. It can be seen that employing the: i) method A at 60 °C and RT, similar MPSD is obtained for both, with the same modal mesopore size of 14 nm; ii) method B, narrow MPSD at RT was obtained, while at 60 °C a wider MPSD was found, where the modal mesopore size shift from 5.6 nm to 21.6 nm, respectively; and iii) method C, widest MPSD were obtained (for both temperatures) with mesopores sizes higher than 6 nm.

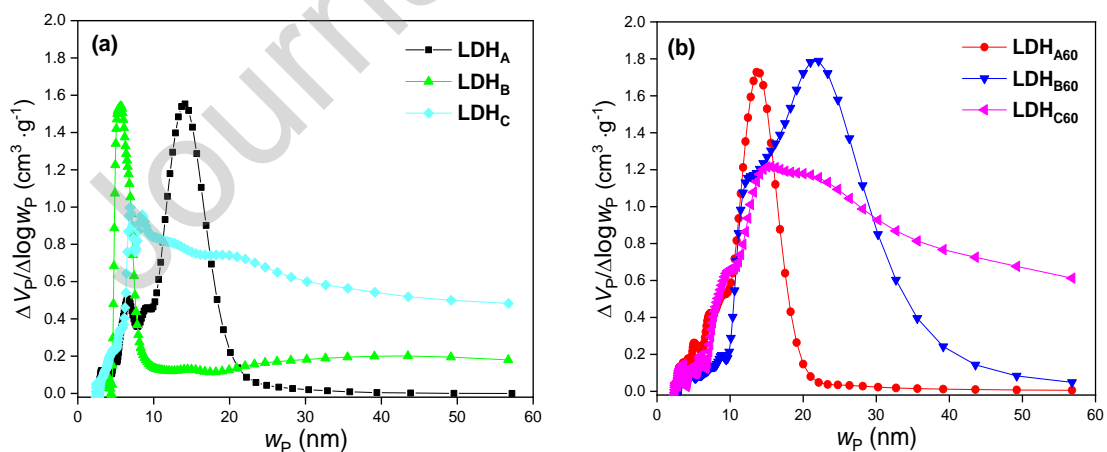


Fig. 4 Mesopore size distribution of LDH synthesized at room temperature (a) and 60 °C (b)

Table 2 Textural properties of LDH's synthesized

Sample/Temperature	RT		60 °C	
	S_{BET} (m^2/g)	V_{TP} (cm^3/g)	S_{BET} (m^2/g)	V_{TP} (cm^3/g)
LDH_A	104	0.46	127	0.46
LDH_B	196	0.42	184	0.73
LDH_C	233	0.84	242	0.93

The synthesized solids were studied through the scanning electron micrographs (SEM) technique to study the morphological changes, crystal sizes, and the network of pores they form. Fig. 5 shows the micrographs of all LDH materials studied. The samples show agglomerates of small particles with heterogeneous sizes. In all cases, it can be seen as an aggregate of plate-like particles with slit-shaped pores, according to the results obtained from the N₂ adsorption isotherms technique and the results of other investigations [51,54]. It can also be observed that when going from solid LDH_A to LDH_B and LDH_C, the structure appears more porous, showing a mixing of a coral-like morphology with large lamellar-shaped materials. Some authors propose that the coral-like surface is just plate-like particles arranged in a "hollow-block" fashion, generating higher porosity evidenced in the N₂ adsorption isotherms technique [55]. On the other hand, the SEM technique does not show changes in the morphology of the solids obtained by changing the synthesis temperature.

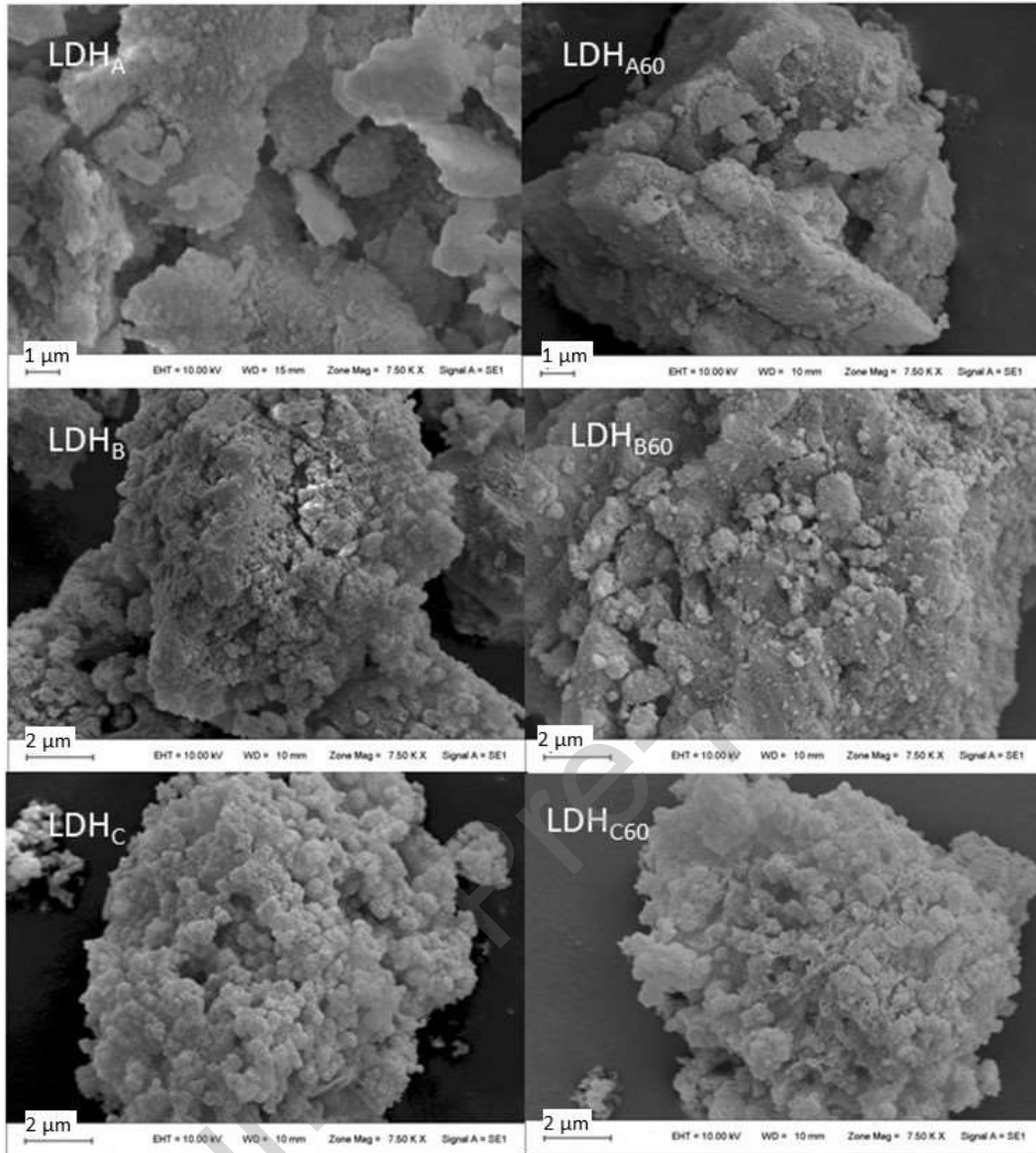


Fig. 5 Scanning electron micrographs of materials

Fig. 6 EDX analysis reveals the presence of the typical elements for these compounds, with the appearance of Fluoride and Sodium impurities. The Mg/Al ratios in the analysis were 2.27 for LDH_A, 1.83 for LDH_{A60}, 2.14 and 2.04 for LDH_B series, and 2.11 and 2.58 for LDH_C series. The precipitation process was not completely efficient because we expected molar values observed for calcined solids closer to the nominal ratios used for preparing the starting solutions (Mg/Al = 3). Only in the case of LDH_{C60} do we obtain an Mg/Al ratio close to the desired value, which agrees with the other characterizations and shows again that this synthesis has the best nitrate removal properties. As the Mg/Al ratio increases, the electric charge density between the layers becomes weaker, so the interlayer spacing increases, as demonstrated in Table 1, where LDH_{C60} exhibits the largest spacing [36].

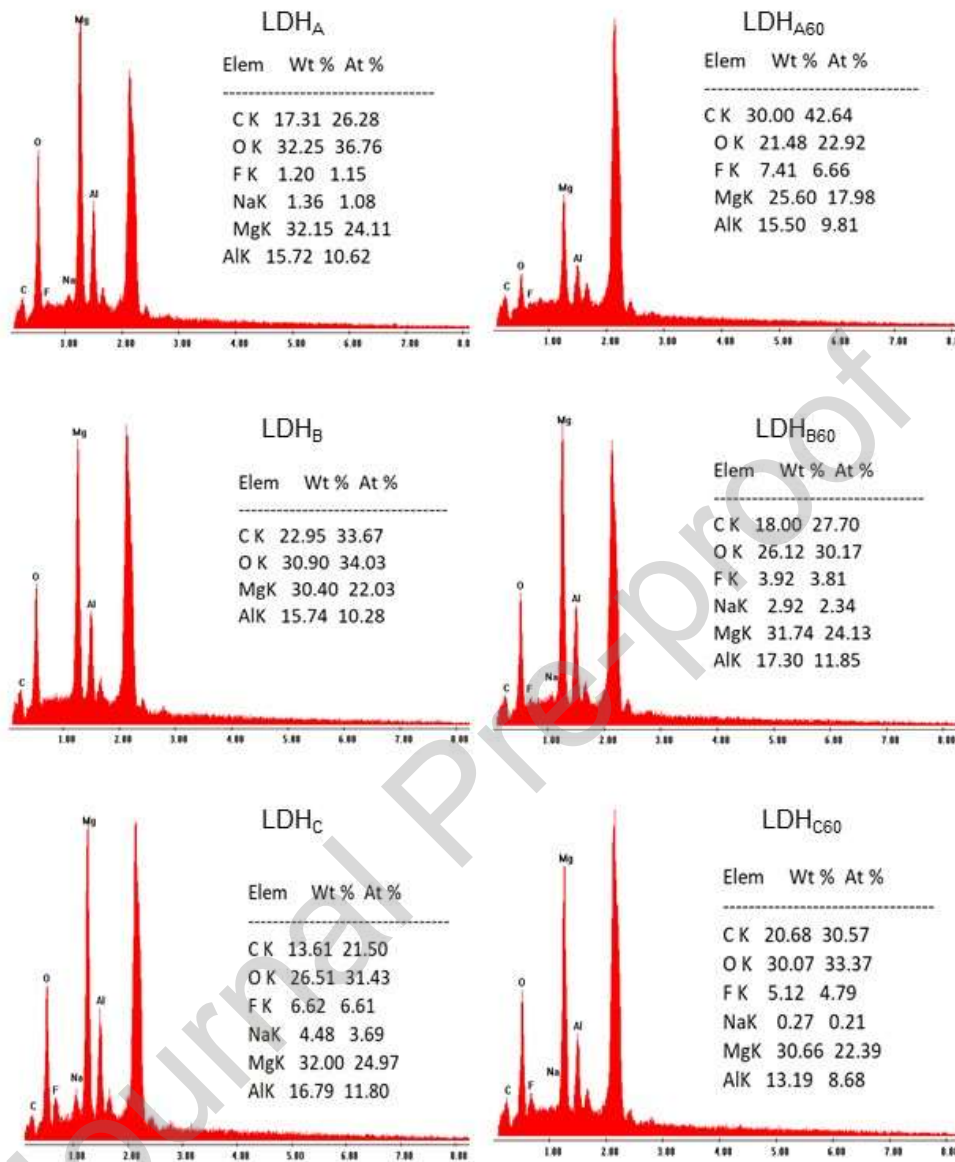


Fig. 6 EDX analysis of LDH materials

The nitrate removal capacities in water at different times were evaluated with each of the solids obtained (Fig. 7). All LDH's proved to be active for removal, reaching equilibrium before 2 hours of experiment in all cases, but with marked differences between them. On the one hand, the syntheses carried out at high temperatures obtained solids with greater adsorption capacity. On the other hand, the solid LDH_{c60} is the one that shows the best performance in adsorption. The syntheses carried out at higher temperatures, particularly the LDH_{c60} sample, exhibited an excellent degree of crystallinity in the XRD diagrams, higher interlayer spacing and specific surface area values, and total pore volume from the N₂ isotherms. We believe these

characteristics give a greater capacity of adsorption to these samples synthesized at a higher temperature, which would justify the better removal of nitrates from an aqueous solution. These results agree with those previously reported by other authors [11,36,56,57]. The maximum capacity reached by our adsorbents was 26 mgNO₃⁻/g or 0.42 meq/g, similar to those obtained by Halajnia et al. [35] and Wan et al. [36], who reached values of 0.3 and 0.4 meq/g, respectively, above the 18.17 mg/g obtained by Santos et al. [54], but below of 60 mg/g reached by Tong et al. [58] and 46.8 mg/g obtained by Zhou et al.[59] whit a MgAl-LDH doped with Fe in both. Regarding removal efficiency, our maximum value was 45.9%, similar to the 45% obtained by Hosni and Srasra [60] but below those obtained by Ivanova et al., Silva et al., and Socias-Viciano et al., reaching values above 70% [11,61,62]. It is worth mentioning that the nitrate removal capacity with LDH may involve an adsorption process as well as an anion exchange process. In this work, by calcining the samples prior to contact with nitrates, we seek to minimize the exchange process, although it cannot be completely ruled out.

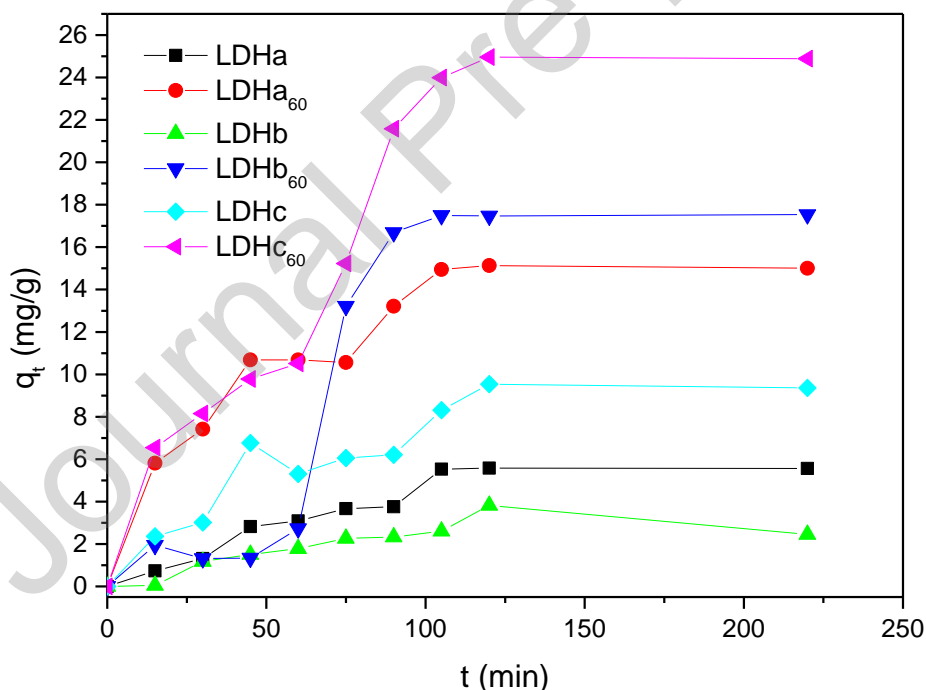


Fig. 7 Adsorption capacity of nitrate for the different LDH's

The effect of pH on nitrate removal with the sample LDH_{C60} was studied, and the results can be seen in Figure 8. The removal capacity did not significantly vary when varying the pH from 3 to 10. Then it decreased slightly, as other authors have mentioned[35,63]. Therefore, it is likely that when the pH is above 10, the high concentration of OH⁻ in the solution competes with the nitrate ion.

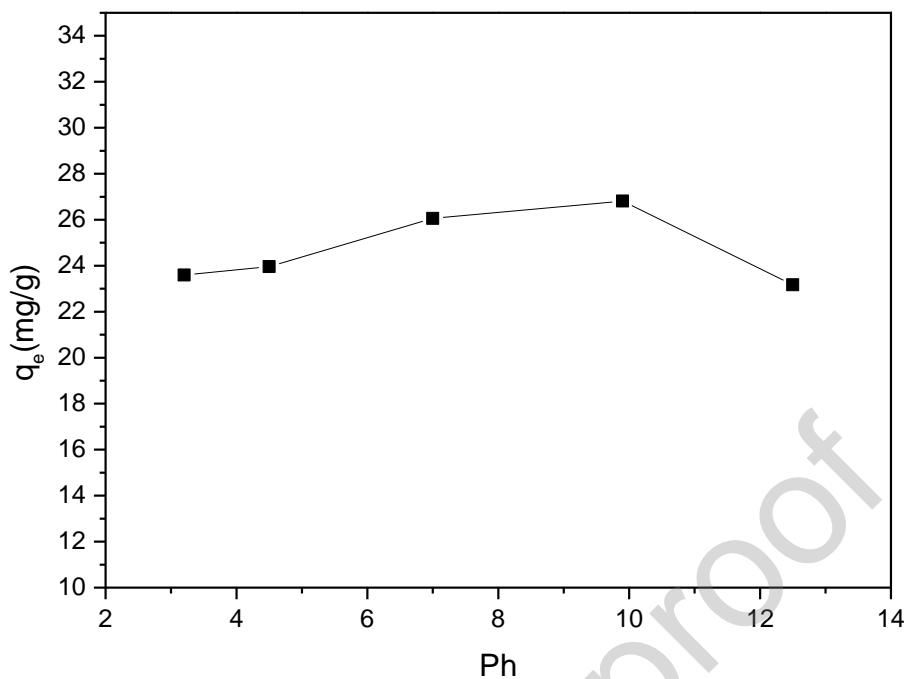


Fig. 8 Adsorption capacity of nitrate at different Ph

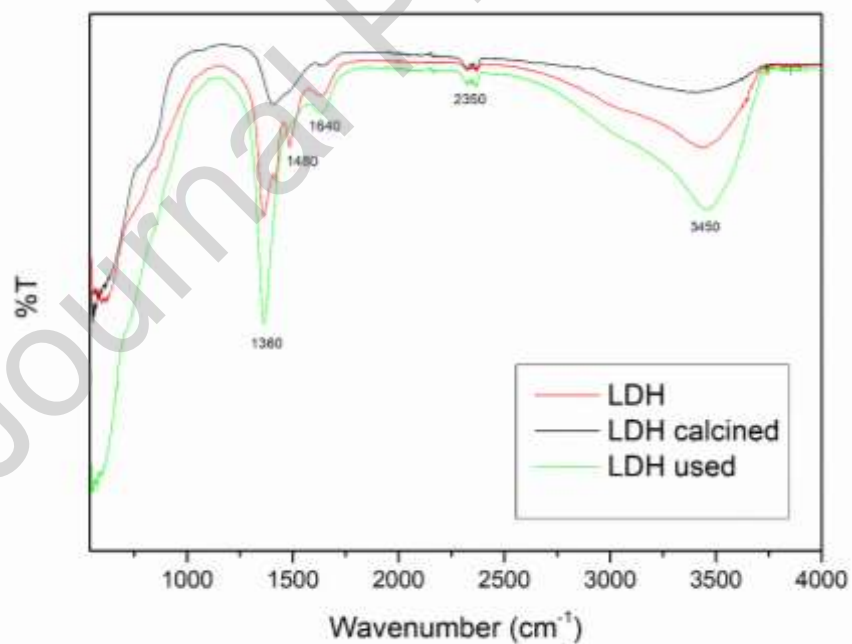


Fig. 9 FTIR spectra of LDH's

In order to demonstrate the effective capture of the nitrate ion in the LDH structure, we obtained the FTIR spectrum of the LDH_{C60} sample in three different states: as it was prepared and before being calcined (LDH), recently calcined (LDH calcined) and after being used in the removal of nitrates (LDH used). The spectra are shown in Fig. 9. The fresh LDH without calcination shows

the typical bands for this type of compound [11,64,65]: The broad absorption band between 3300-3700 cm^{-1} is attributed to the stretching of the OH groups present in the brucite-type sheets, a broad peak at 1640 cm^{-1} for water bending vibrations of the interlayer water, a strong peak at 1360 cm^{-1} for NO_3^- intercalated in the interlayer space and between 400-700 cm^{-1} lattice stretching and bending vibrations characteristic of the hydroxyl groups attached to Al and Mg are observed. The band around 2350 cm^{-1} is due to the atmospheric background noise used in the measurement system [40]. In the spectrum corresponding to the calcined sample, these characteristic bands of the hydrotalcite-type structure are diminished or eliminated, which shows that the calcination process was effective. Finally, in the case of the LDH used, the characteristic bands of the hydrotalcite-type structure are again observed, with the band corresponding to adsorbed nitrate ions (1360 cm^{-1}) clearly increased. This indicates that the reconstruction of the hydrotalcite-like structure occurred with the incorporation of nitrates as interlayer anions [60]. In addition, it can be seen that the broad band at 3500 cm^{-1} is bigger with respect to the case of the LDH fresh and calcined samples, this is due to the fact that a large amount of interlaminar water was adsorbed during the removal test.

4 Conclusions

In this work, different Mg-Al hydrotalcites have been successfully synthesized using the co-precipitation method at constant pH with slight modifications in adding the reagents and in the synthesis and aging temperatures. Hydrotalcite properties were demonstrated to depend on the solution incorporation method in the synthesis. In our case, the most crystalline LDH was obtained when the Mg/Al solutions were added to the $\text{CO}_3^{2-}/\text{OH}^-$ solution since these conditions improve the crystal growth rate over the nucleation rate. In any case, the best properties for anion adsorption were obtained by dripping three solutions separately. This method obtains an LDH with greater interlaminar spacing, specific surface area, and pore volume. The same effect is achieved when higher temperatures are used in the synthesis and aging of the samples. Furthermore, all the synthesized solids showed to be active for removing nitrates in water, obtaining the best results with the method of three different solutions at 60 °C, demonstrating the crucial role of the temperature and the solution incorporation method in the synthesis in the interlaminar spacing and textural properties and therefore in the removal of nitrates using this type of compounds.

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6 Statements and Declarations

Ethical Approval: Not applicable.

Consent to Participate: Not applicable.

Consent to Publish: Not applicable.

Author Contributions: All authors contributed to the study's conception and design. Leonardo Cano, Deicy Barrera, Jhonny Villarroel-Rocha and Karim Sapag performed material preparation, data collection, and analysis. Leonardo Cano, wrote the first draft of the manuscript, and the other three authors contributed to improving it. All authors read and approved the final manuscript.

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Availability of data and materials: The datasets and materials generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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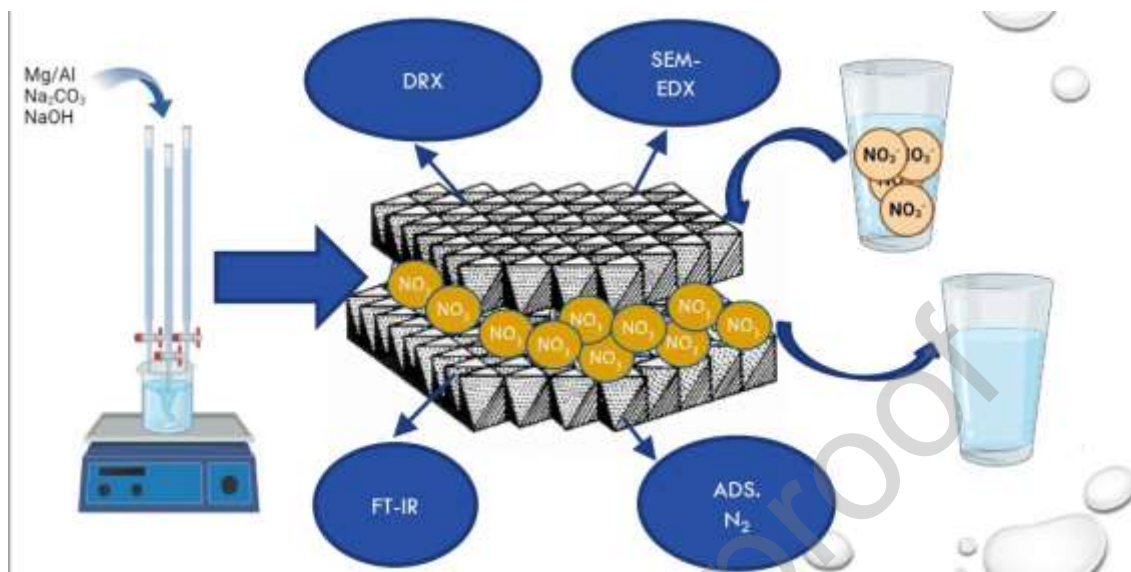
Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Graphical abstract



Highlights

- It was demonstrated that Layered Double Hydroxides properties depend on the solution incorporation method in the synthesis.
- The best properties for anion adsorption were obtained by dripping three solutions.
- The same effect is achieved when higher temperatures are used in the synthesis and aging of the samples.
- This method obtains a Layered Double Hydroxides with greater interlaminar spacing, specific surface area, and pore volume.
- We demonstrate the crucial role of interlaminar spacing and textural properties in the removal of nitrates using this type of compounds.