



Revista Brasileira de Ciência do Solo

ISSN: 0100-0683

revista@sbcs.org.br

Sociedade Brasileira de Ciência do Solo
Brasil

Figueredo Benício, Luiz Paulo; Alvarenga Silva, Rejane; Lopes, Júnia Aparecida; Eulálio, Denise; Morais Menezes dos Santos, Rodrigo; de Aquino, Leonardo Angelo; Vergütz, Leonardus; Ferreira Novais, Roberto; Marciano da Costa, Liovando; Garcia Pinto, Frederico; Tronto, Jairo
LAYERED DOUBLE HYDROXIDES: NANOMATERIALS FOR APPLICATIONS IN AGRICULTURE
Revista Brasileira de Ciência do Solo, vol. 39, núm. 1, enero-febrero, 2015, pp. 1-13
Sociedade Brasileira de Ciência do Solo
Viçosa, Brasil

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REVISÃO DE LITERATURA

LAYERED DOUBLE HYDROXIDES: NANOMATERIALS FOR APPLICATIONS IN AGRICULTURE

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ABSTRACT

The current research aims to introduce Layered Double Hydroxides (LDH) as nanomaterials to be used in agriculture, with particular reference to its use as storage and slow release matrix of nutrients and agrochemicals for plant growing. Structural characteristics, main properties, synthesis methods and characterization of LDH were covered in this study. Moreover, some literature data have been reported to demonstrate their potential for storage and slow release of nitrate, phosphate, agrochemicals, besides as being used as adsorbent for the wastewater treatment. This research aims to expand, in near future, the investigation field on these materials, with application in agriculture, increasing the interface between chemistry and agronomy.

Keywords: layered compounds, nutrient slow release, eutrophication, nutrient reuse.

RESUMO: HIDRÓXIDOS DUPLOS LAMELARES: NANOMATERIAIS PARA APLICAÇÕES NA AGRICULTURA

Este trabalho de revisão tem como objetivo apresentar os Hidróxidos Duplos Lamelares (HDL) como nanomateriais para serem aplicados na agricultura, com destaque para a utilização desses como matrizes para

Received for publication on December 20, 2014 and approved in January 20, 2015.

DOI: 10.1590/01000683rbc20150817

o armazenamento e a liberação lenta de nutrientes e agroquímicos para o cultivo de plantas. São abordadas as características estruturais, as principais propriedades e os principais métodos de síntese e de caracterização dos HDL. São também reportados trabalhos da literatura, demonstrando a potencial aplicação desses materiais no armazenamento e na liberação lenta de nitrato, fosfato, agroquímicos, além da utilização como adsorventes. Pretende-se com esta pesquisa expandir, em um futuro próximo, o campo de investigação desses materiais com aplicação na agricultura, aumentando a interface entre a química e a agronomia.

Palavras-chave: compostos lamelares, liberação lenta de nutrientes, eutrofização, reuso de nutrientes.

INTRODUCTION

Population growth in the coming years will have a direct impact on world agriculture. Increase food production together with environment preservation will be crucial factors for constant agricultural innovation. Raising the amount of arable land, not yet explored, can be one way to solve this problem. A further possibility is to develop new products with innovative techniques for increasing crop yields, by using environmentally clean chemistry, also known by several authors as “green chemistry” (Praveen et al., 2012; Krishnaswamy et al., 2014).

Some studies have demonstrated the use of nanomaterials and host matrices for storage and slow-release of biologically active products, which are referred as guests (Cunha et al., 2010; Zhao et al., 2010). The synergistic effect between host-matrix and guest, which may be a drug, a hormone, an agrochemical, among others, results in a material with unique chemical and physical properties that are not found in both host matrix and guest.

In this paper, it is presented a review on Layered Double Hydroxides (LDH) as nanomaterials with potential for agriculture, with emphasis on soil and plant nutrition. Structural aspects, main properties, besides the main methods of synthesis and characterization of LDH are presented. Furthermore, potential applications of these materials in plant growth and development are reported as slow release systems for nutrients and agrochemicals. Moreover, it is also approached their use in adsorption processes for environmental decontamination of soil and water.

NANOPARTICLES

A nanometer is a metric unit of length and denotes one billionth of a meter or 10^{-9} m. The term “nano” is used to describe objects, systems or phenomena occurring in nanometric scale. In turn, nanomaterials are arranged structurally in nanoscale, in general, between 1 to 100 nm. These materials can be classified according to structure

type: zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D) and three-dimensional (3-D). The first ones have all dimensions smaller than 100 nm (length = width) and are the simplest building blocks that may be used to form other materials (Richards, 2009). Nanoparticles, nanoclusters and nanocrystals are examples of 0-D nanomaterials. The second building block class are 1-D nanomaterials, in which one dimension is out of nanoscale (length > width), with the diameter ranging between 1 and 100 nm and length in micrometric range or larger. Nanowires, nanofibers and nanotubes are examples of that. On the other way, 2-D nanomaterials have two dimensions out of nanoscale; showing a plate form with width inferior to 100 nm; nanoclays and graphene are examples of them. Two and three dimension nanomaterials might be composed by spatial arrangements of 0-D and 1-D building blocks. Moreover, 3-D ones can also be formed by aggregation of amphiphilic molecules such as surfactants, lipids and some copolymers, thus forming micelles, liposomes etc.

The LDH, also known as hydrotalcite-like compounds or anionic clays, are 2-D nanomaterials that can be used as storage matrix (hosting), and control the release of different anionic species (Cavani et al., 1991; Forano et al., 2006). In this case, anion species (guests) are intercalated between the lamellae of the LDH, which is called interlayer space.

LAYERED DOUBLE HYDROXIDES (LDH)

LDH have two-dimensional structures such as clay minerals (Cavani et al., 1991; Forano et al., 2006). Such materials may be represented by the following formula:



where M represents metallic ions and A^{n-} an interlamellar anion.

In order to understand LDH structure, it should start by observing brucite mineral. This mineral has the formula $Mg(OH)_2$, and Mg cations

occupy the center of the octahedron, which have hydroxyls in the edges. These octahedra share their edges forming flat and neutral layers, which are connected by H-bonds. In this type of structure, when divalent cations are isomorphically replaced by trivalent cations, the lamellae show a positive residual charge. For the electro neutrality of the system, the presence of anions between the lamellae is required; together with water molecules these anions promote stacking of layers of LDH with an interlayer field poorly ordered. In this case, the lamellae are not only linked by hydrogen bonds, as in the case of the brucite, but also by electrostatics between the positively charged plates and interlayer anions. The LDH structure scheme is displayed in figure 1.

LDH layers can be stacked in two symmetries, resulting in rhombohedral or hexagonal unit cells. Most of the synthetic LDH display hexagonal

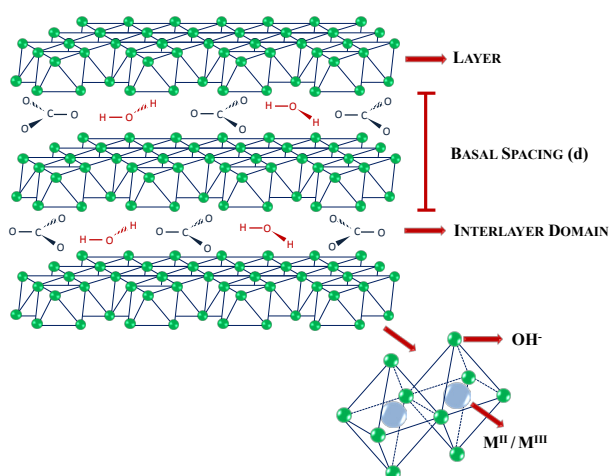


Figure 1. Layered Double Hydroxides (LDH) structure scheme.

unit cell; solely LDH with M^{2+}/M^{3+} ratio equals to 1 exhibit orthorhombic unit cell (Evans and Slade, 2006).

Metallic cations that make up the lamella must necessarily present octahedral shape and ionic radius within the range of 0.50 to 0.74 Å to form LDH. By varying metallic cations, their ratio and the interlayer anions, it can be formed a great number of LDH types. Several cations may be part of the structure, including Mg^{2+} , Al^{3+} , most cations of the first transition period, Cd^{2+} , Ga^{3+} , and La^{3+} , among others. Furthermore, the synthesis of LDH containing more than one divalent cation and/or trivalent is possible, increasing the number of possible LDH. This ratio may vary due to the initial concentration of reagents and the method used for synthesis. This variation promotes different charge density in the lamellae, since the charge is generated from isomorphous substitution of M^{2+} by M^{3+} in lamellar structure. For most of synthetic LDH, the x value (presented in the general formula of LDH) may vary from $0.10 \leq x \leq 0.33$. According to De Roy et al. (1992), M^{2+}/M^{3+} ratio can vary from 1 to 6; however, Cavani et al. (1991) reported this variation from 2 to 4. Nevertheless, some researchers have reported the production of LDH with different ratios from those above-mentioned (Lopez et al., 1996; Wang et al., 1999). Table 1 shows common M^{2+} and M^{3+} cation combinations used to obtain LDH.

Virtually, there is no limitation to the nature of anions able to balance positive residual charge of LDH lamellae. On the other hand, it is not easy to obtain pure and crystalline materials. In general, simple inorganic anions with a higher charge/radius ratio are more likely to get in. This is because these anions have increased electrostatic interaction with the inorganic layers. For organic anion intercalation, especially anionic polymers, it should be taken into account factors such as anion geometry, interaction to each other, their size and the relationship between their size and charge.

Table 1. Possible combinations of metallic cations M^{2+} and M^{3+} in LDH

Divalent cation	Trivalent cation														
	Al	Fe	Cr	Co	Mn	Ni	Sc	Ga	Ti ⁽¹⁾	La	V	Sb	Y	In	Zr ⁽¹⁾
Mg	•	•	•	•	•		•	•		•	•	•	•	•	•
Ni	•	•	•	•	•	•		•		•					
Zn	•	•	•					•							
Cu	•		•												
Co	•	•	•	•					•	•					
Mn	•		•		•			•							
Fe	•	•													
Ca	•														
Li ⁽²⁾	•														
Cd	•														

⁽¹⁾ tetravalent, and ⁽²⁾ monovalent.

Properties

LDH present a great number of properties due to their varied compositions and methods of synthesis. In this section, it will be discussed some of the properties that enable LDH application in agriculture.

a) Anion Exchange Capacity

For LDH, the Anion Exchange Capacity (AEC) depends on the metallic cation ratio, the ability of the involved anion in stabilizing lamellar structure and molecular mass of the cations and anions involved. As reported by Leroux and Besse (2004), AEC values might change between 200 and 450 cmol_c kg⁻¹. Values below 200 cmol_c kg⁻¹ are not possible, once the M²⁺ and M³⁺ ratio is very low to support LDH structure.

b) Colloidal properties

The small particle size and low charge density of some LDH are important for systems with colloidal characteristics and/or delamination (stacking structure loss). The large size of the host anion often cause interlayer diffusion problems. Thus, in order to overcome these problems, colloidal and/or delaminated systems, which are formed from LDH, allow a better arrangement of the lamellae between host and anion. Several studies have reported the formation of systems with colloidal features by combining LDH and organic molecules (Zhao et al., 2002; Leroux and Besse, 2004). From colloidal suspensions of LDH, Gardner et al. (2001) have produced continuous and transparent films. LDH of hydrophobic nature and colloidal characteristics were prepared from the combination of hydrotalcite and anionic surfactants, such as heptane, benzene, toluene and propanol. Leroux et al. (2001) performed the delamination of Zn₂Al-LDH intercalated with dodecyl sulfonate. Organically modified LDH suspended in butanol resulted in the formation of highly stable translucent colloidal solutions. Hibino and Jones (2001) performed LDH delamination intercalated with amino acids, and observed excellent results when LDH were intercalated with glycine in formamide solutions. As stated by these authors, the process of delamination does not result from the driving force generated by solvent inclusion; however, it is considerably influenced by solvent boiling point. Solvents with high dielectric constant are known to facilitate this process. The enlargement of alcohol alkyl chain provides an increase in the boiling point with consequent decrease of the dielectric constant.

c) Morphological properties

Physical properties such as morphology, surface area, porosity and particle size are extremely important to describe LDH and, of course, can define its applications. Conventional preparation methods of LDH provide limited control over these properties.

Scanning Electron Microscopy (SEM) can be used to assess the morphology of these materials.

Besides being related to constituent cations and anions, the specific surface area of LDH also depends on methods and conditions of synthesis. For these materials, the specific surface area of LDH can vary widely between 50 and 200 m² g⁻¹. When calcined under specific conditions of temperature and atmosphere, LDH may form oxides and/or mixed oxy-hydroxides with specific surface areas larger than the precursor LDH. Normally, LDH porosity can vary greatly within the microporous to mesoporous range. Geraud et al. (2006) demonstrated the feasibility of macroporous material synthesis from the combination of MgAl-LDH and colloidal polystyrene crystals (PS). The three-dimensional macroporous materials are created using PS beads as template and open two-dimensional structure of LDH as "wall" (filling the gaps between the PS beads). After calcination, X-ray diffraction (XRD) and SEM imaging confirm the presence of three-dimensional macroporous structure.

LDH particle size can vary widely due to composition and crystallinity differences. Additionally, the various techniques used for particle size measuring may have different values for the same materials. The Scherrer equation determines crystallite sizes from peak widths at half-height (sometimes referred as FWHM - Full Width at Half Maximum), which are obtained from diffractograms (Patterson, 1939). Laser scattering, SEM and Transmission Electron Microscopy (TEM) techniques can also be used for particle size measurement.

Specific surface area, porosity and particle size are crucial factors to determine LDH application in agriculture.

d) Thermal stability

Thermal stability is another important property of LDH. Thermal characterization of these materials is performed by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) techniques.

Thermal decomposition temperatures are dependent on several factors such as, LDH crystallinity, nature, cations molar ratio (M²⁺/M³⁺), and the interlayer anion type (organic or inorganic).

When organic anions are within LDH layers, resulting in intercalated nanomaterials, it usually shows higher thermal stability relatively to the free organic anion. Some researchers have speculated that the nature of organic and inorganic component interface is the reason for thermal stability improvement. Another hypothesis is that LDH may act as a protective layer, delaying the byproduct crystallization and inducing unusual solid formation after heat treatment under inert atmosphere.

SYNTHESIS OF LAYERED DOUBLE HYDROXIDES

LDH occur naturally but can also be synthesized at low cost and by environmentally clean chemistry (green chemistry). This section describes the main methods for synthesizing LDH nanoparticles. For the synthesis of LDH, several factors must be considered, e.g., the degree of cation substitution of M^{2+} by M^{3+} , cation and interlayer anion nature, synthesis pH, and, in some cases, atmosphere control. Moreover, for more crystalline materials, the following factors must be controlled: solutions concentration, the rate of addition of one solution over the other, stirring degree, final pH of the resulting suspension (for variable-pH methods), pH during the addition (for constant-pH method), and temperature of the final solution, that is usually carried out at room temperature.

There are several methods for LDH synthesis that could be divided into two categories:

Direct Synthesis Methods: salt-base or coprecipitation, salt-oxide, hydrothermal synthesis, induced hydrolysis, sol-gel, and electrochemical preparation (Taylor et al., 1984; Reichle et al., 1986; Cavani et al., 1991; Indra et al., 1994; Lopez et al., 1996; Wang et al., 1999; Forano et al., 2006).

Indirect Synthesis Methods: simple anion exchange, reconstitution of calcined material, and anion exchange using double phase with salt formation within surfactants (Cavani et al., 1991; Kooli et al., 1997; Crepaldi et al., 1999; Forano et al., 2006).

Hereafter, some of the main methods of synthesis are detailed.

Direct Synthesis Method

a) Coprecipitation

The coprecipitation method can be divided into three types according to pH: coprecipitation at i) increasing pH, ii) decreasing pH, and iii) constant pH (Reichle et al., 1986; Cavani et al., 1991; De Roy et al., 1992).

The first one, also called as titration method, consists on simultaneous precipitation (coprecipitation), when an alkaline solution containing the anion to be intercalated is added on a solution with cations. Since trivalent cations tend to precipitate at lower pH than bivalent ones, crystalline LDH would hardly ever be obtained by this method (Cavani et al., 1991).

The experimental procedure of coprecipitation at decreasing pH comprises in adding a solution with the cation onto a solution with the alkaline solution and the anion to be intercalated. This quite simple method has shown good results (Reichle et al., 1986).

LDH preparation by coprecipitation at constant pH is the most widely used method of synthesis to obtain various types of synthetic LDH. This method usually has highly satisfactory results, obtaining LDH with good structural organization and phase purity. In this method, a solution containing metallic cations is added into another with the anion to be intercalated. During synthesis, a NaOH or KOH solution is continuously added to keep pH constant at a high value for coprecipitation. Figure 2 shows the optimum pH ranges for obtaining different LDH (De Roy et al., 1992).

Most often, coprecipitation is carried out at room temperature; however, in some cases, synthesis can be carried out at higher temperature (65 °C). Solution concentration may vary from 0.1-0.5 mol L⁻¹. With regard to addition rate, a lower saturation is achieved when metallic cation addition into the solution is slow, e.g., up to 1 mL min⁻¹. Low saturation condition is applied to obtain more crystalline materials since it brings a higher nucleation rate and, consequently, a greater number of reduced size particles.

b) Salt-oxide Method

In this method, a bivalent metal oxide suspension is reacted with a trivalent metallic cation solution and the anion to be intercalated. The pH should be kept slightly acidic to occur slow hydrolysis of the divalent cation oxide. This method has some requirements, such as, the need for the divalent cation oxide undergo slow hydrolysis and the anion to be intercalated must be able to form a soluble salt with the trivalent cation and be stable in acidic medium (Boehm et al., 1977).

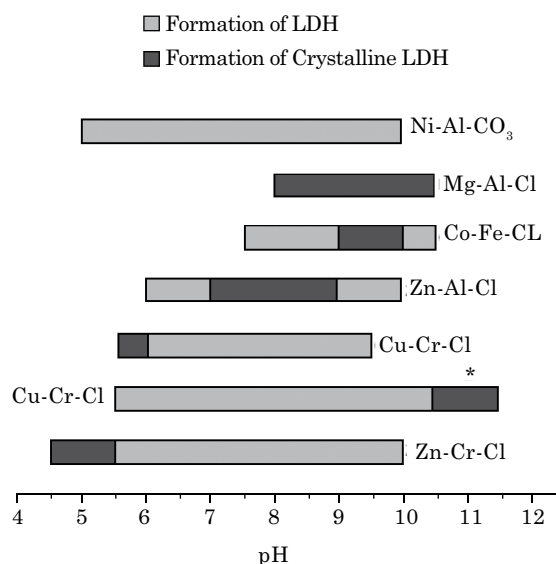


Figure 2. pH domains and optimal ranges for the formation of some LDH. * Hydrothermal treatment. Adapted from De Roy et al. (1992).

c) Hydrothermal Synthesis Method

The hydrothermal synthesis method uses suspension of oxides and/or hydroxides of M^{2+} and M^{3+} cations. Into this suspension, it is inserted a solution with acid or salt. The reaction occurs at high pressure and temperature. The great advantage of this method, when compared with other coprecipitation ones, is to avoid undesirable waste discard, which may be harmful to the environment, such as NO_3^- , Cl^- , OH^- , etc (Wang et al., 2013).

d) Induced Hydrolysis Method

It consists of the precipitation of M^{3+} cation hydroxide at pH slightly below that in which M^{2+} cation hydroxide precipitation occurs. The aqueous suspension of M^{3+} is added into the M^{2+} one, maintaining pH at a fixed value by simultaneous addition of a NaOH solution (Taylor et al., 1984).

e) Sol-Gel Method

In this method, the reaction occurs in an alcohol solution of magnesium ethoxide dissolved in HCl with a solution containing Al tri-sec-butoxide. The mixture is heated to reflux and stirred until gel formation. The material prepared by this method has controlled pore size and high specific surface area. The sol-gel method has been used in LDH synthesis as it has a great advantage of producing materials with higher purity (Wang et al., 1999).

Indirect Synthesis Methods

The LDH synthesized by direct methods are the precursor materials for indirect synthesis methods. The high mobility that some anions present when inserted within the interlayer enables new material production by substitution reactions. This replacement can be performed in several ways and involves the ability of the host anions to stabilize lamellar structure. Miyata (1983) described the stabilization ability order of some anions in LDH layers, as follows:

Monovalent anions: $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$

Bivalent anions: $CO_3^{2-} > C_{10}H_4N_2O_8S^{2-} > SO_4^{2-}$

a) Ion Exchange in Solution Method

This method consists of adding a LDH precursor usually containing interlayer anions Cl^- or NO_3^- , in a concentrated solution with the anion of interest. In this method, the exchange efficiency varies a lot, the exchanged anion should have the greatest ability to stabilize the lamella (more likely to be intercalated) and/or be in a higher proportion than the LDH precursor anion, which is normally Cl^- or NO_3^- (Lal and Rowe, 1981; De Roy et al., 1992; Newman and Jones, 1998).

b) Ion Exchange in Acidic Medium Method

In this method, the LDH precursor must have an interlayer anion capable of undergoing acid

attack. Thus, over a LDH precursor suspension a weak acid solution whose conjugate base is desired to be intercalated is added. The reaction is based on balance displacement because the precursor anion is protonated and “leaves” the interlayer space, which is now occupied by the conjugate base of the acid; thus, maintaining the system electro neutrality (Crepaldi and Valim, 1998).

c) Regeneration

This method is based on “*memory effect*” of some LDH. The LDH with carbonate anion is often used as precursor, due to its behavior during calcination. Calcination must be performed at proper temperature to breakdown partially the hydroxyls from lamellae and convert interlamellar anion into volatile, forming a double oxyhydroxide. After calcined, a solution containing the anion of interest is added, regenerating the LDH by hydrolysis and the new intercalated anion. In general, during regeneration process, pH is raised, so it must be corrected to avoid hydroxyl from occupying the interlayer space (Miyata, 1980; Newman and Jones, 1998).

CHARACTERIZATION METHODS

In this section, it will be discussed some of the main methods for LDH characterization.

X-ray Powder Diffraction (XPD)

Material crystallinity, as well as LDH baseline distances, can be measured by X-ray powder diffraction (XPD). LDH X-ray diffraction pattern shows 00 l baseline peaks related to the lamellae stacking sequence (Cavani et al., 1991; De Roy et al., 1992; Forano et al., 2006). Non-baseline peaks, considered non-harmonic, are related to the lamellae structure. For LDH, diffraction peak indexing shall be provided by comparison with hydrotalcite diffractogram from the diffraction equipment database (JCPDS-ICDD, PDF Database) or with a series of LDH described in the literature. Figure 3 shows a diffractogram of a ZnAl- NO_3 -LDH.

Interlayer distances are calculated from 2 θ values by using Bragg's equation:

$$n \lambda = 2d_{hkl} \sin \theta \quad (1)$$

where n is the diffraction order, λ is the wavelength of the X-ray, d_{hkl} is the interlayer distance for hkl peak, and θ the Bragg's angle, which is determined by diffraction peak. Repeating d value at $n = 1, 2, 3, \dots$, indicates the formation of lamellar material.

To determine LDH anionic species orientation, interlayer and/or baseline spacing values from XPD data are compared with anion sizes. The latter may

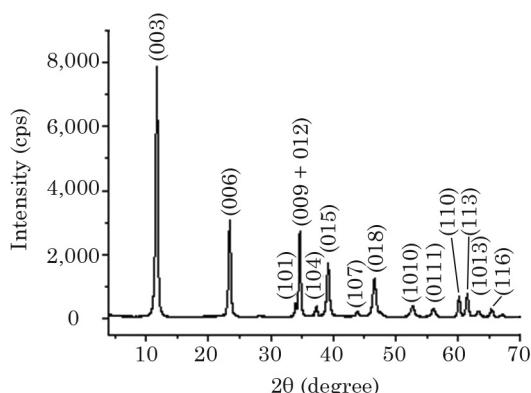


Figure 3. X-ray powder diffractogram of a ZnAl-NO₃-LDH. Source: Tronto (non-published data).

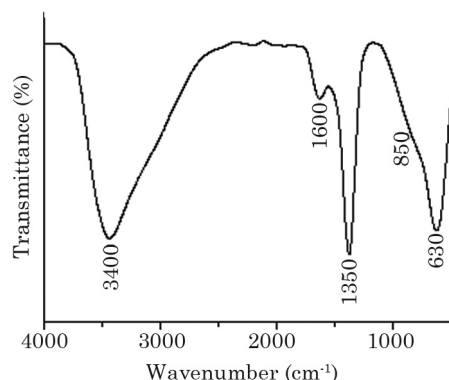


Figure 4. FTIR spectrum of a MgAl-CO₃-LDH. Source: Tronto (non-published data).

be obtained by means of specific computer programs, such as “VASP” (Vienna Ab-initio Simulation Package).

Fourier transform infrared spectroscopy (FTIR)

Functional groups and possible interactions between intercalated anion and inorganic lamellae can be determined by Fourier transform infrared spectroscopy - FTIR (Cavani et al., 1991; De Roy et al., 1992; Forano et al., 2006). FTIR analyzes are typically made on pellets produced from a solid mixture between LDH (98 wt. %) and KBr (2 wt. %) previously dried. Spectra are usually obtained within 4000-400 cm⁻¹ wavenumber range. A broadband ranging from 3800-2500 cm⁻¹ in all LDH spectra is characteristic of O-H stretching of water molecules and hydroxyl groups in the lamellae structure. The main bands related to intercalated and adsorbed anions are observed between 1800-1000 cm⁻¹. Bands related to anion vibrations, and in some cases, the metal-oxygen-metal vibrations can be found in the region of 1000-400 cm⁻¹. As an example FTIR analysis of LDH, figure 4 shows the absorption spectra for Mg and Al intercalated with carbonate (MgAl-CO₃-LDH). Broad and intense band between 3800-2600 cm⁻¹ is assigned to the stretching of O-H group. The band at 1650 cm⁻¹ is attributed to angular deformations of water molecules. In the specific case of CO₃²⁻, three bands are observed between 1380-1350 cm⁻¹ (ν₃), 880-850 cm⁻¹ (ν₂) and 690-670 cm⁻¹ (ν₄).

Thermogravimetric Analysis Coupled with Differential Scanning Calorimetry (TGA-DSC)

LDH thermal stability can be determined by thermogravimetric analysis. The results are obtained in the form of mass decay curves as a function of temperature. In the LDH, the thermal decomposition stages are generally overlapped and the exact temperature range

of each stage depends largely on LDH type, heating rate and atmosphere (N₂ or O₂). LDH thermal behavior is usually characterized by two main transition stages: (i) an endothermic process from room temperature to about 200 °C that corresponds to adsorbed and interlamellar water loss; this stage is reversible and occurs without lamellar structure collapse; and (ii) the second stage occurs with temperatures ranging from 200 to about 800 °C, and corresponds to lamellar hydroxyl group loss (dehydroxylation) as well as anions loss. Hydroxyl group loss is described as an endothermic process, whereas anion loss can be endothermic for inorganic anions and exothermic for organic ones. Phase transitions may occur in LDH above 800 °C. Figure 5 demonstrates an example of TGA-DSC thermogram for MgAl-CO₃-LDH.

Scanning Electron Microscopy (SEM)

LDH size and shape vary with the preparation method and chemical composition of the materials. Scanning Electron Microscopy (SEM) analyses are important to verify LDH morphologic properties. For SEM analysis, LDH samples are turned into powder and set in an Al sample holder. Because these materials do not have enough electrical conductivity to generate good images, an Au or C coating is applied on the samples before imaging. As example, figure 6 shows a SEM image of a ZnAl-Cl-LDH. It is possible to observe lamellar crystals formation with superposition of the layers.

Transmission Electron Microscopy (TEM)

For Transmission Electron Microscopy - TEM, LDH samples are dispersed in an epoxy resin; the dispersion is centrifuged and then dried at 65 °C for 24 h. After drying, thin sections cut by an ultramicrotome are mounted on Cu grids for TEM analysis. A second way to prepare samples is to form a suspension with acetone and LDH. Subsequently,

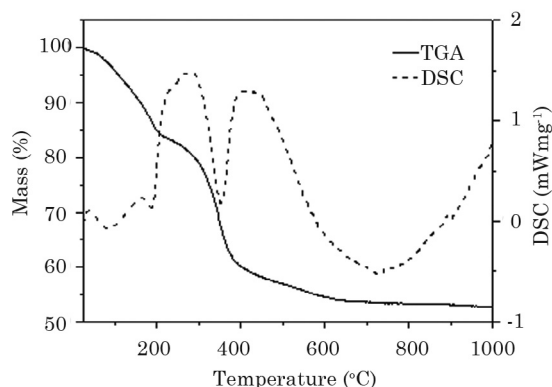


Figure 5. TGA-DSC thermogram of a MgAl-CO₃-LDH.
Source: Tronto (non-published data).

the Cu grid is dipped into the suspension and then dried at room temperature.

TEM has been used to examine LDH morphology. When LDH are crystalline, it is possible to determine interlayer distances through the images. This data can be compared with data obtained from XPD. Figure 7 shows a TEM image of a ZnAl-LDH intercalated with 4-pyrrol-1-ylbenzoate anions (PyH). This ZnAl-PyH-LDH material showed orderly inorganic lamellae, represented by the darker lines. Lamellae distance measured by TEM was coincident with XPD measurements.

BET-Specific Surface Area and Porosity

As the internal LDH surfaces are often not available, typical BET-specific surface area measurements of these materials range from 20-100 m² g⁻¹. The N₂ adsorption-desorption isotherms for simple anions intercalated between LDH are type II (according to format recommended by IUPAC) with a very narrow hysteresis loop that is typical for mesoporous materials. Figure 8 shows a N₂ adsorption-desorption isotherm (BET) of a ZnAl-CO₃-LDH. The adsorption-desorption curve presents a characteristic profile of mesoporous materials with a specific surface area of 98.31 m² g⁻¹.

Analytical methods for LDH chemical composition determination

The quantification of M²⁺ and M³⁺ metals is regularly done by analytical methods such as atomic absorption spectrophotometry (AAS) or inductively coupled plasma optical emission spectrometry (ICP-OES). The amount of several anions in LDH could be estimated by simultaneous CHNS analysis. The amount of water can be determined by TGA.

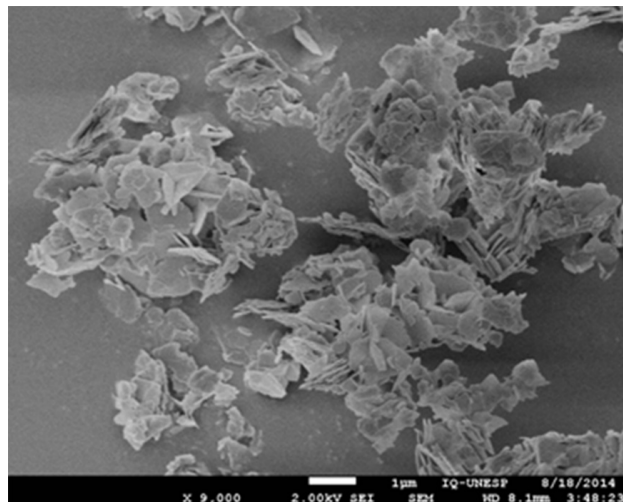


Figure 6. SEM image of a ZnAl-Cl-LDH. Source: Tronto (non-published data).

LAYERED DOUBLE HYDROXIDES APPLICATIONS IN AGRICULTURE

LDH may have various properties depending on reagents and synthesis methods. These different properties allow its application in different areas. From now on, it will be shown here the main possible applications of LDH in the agriculture and environmental care fields.

Source of Nutrient Storage and Controlled Release for Plants

The constant need for high agricultural yields has increased fertilizer use, especially N and P. Nitrogen and P maintenance in soil, mostly as nitrate and phosphate, is not an easy task. The N-NO₃⁻ could be denitrified and volatilized, as happens with the fertilizer based on urea (McInnes et al., 1986). There are also the N fertilizers consisting of ammonium nitrate and ammonium sulfate salts, among others, which are easily leached. Moreover, the efficiency of phosphate fertilizers is low due to P fixation by the soil (Rajan et al., 1994). Thus, it is necessary to search for new fertilizer technologies to provide, in a more efficient and sustainable way, elements such as N and P to plants. With this regard, intercalation of N and P within LDH comes as an interesting option to optimize N and P supply to plants. Studies have reported the use of LDH as slow release source of nutrients to plants.

Torres-Dorante et al. (2008) studied the potential use of MgAl-Cl-LDH, as a NO₃⁻ adsorber in soils, controlling its losses and availability. It was examined the adsorption capacity of NO₃⁻ by LDH in aqueous solution as well as anion adsorption selectivity. Exchange reversibility and NO₃⁻ adsorption and diffusion capacity with



Figure 7. TEM image of a ZnAl-PyH-LDH. Source: Tronto (2006).

respect to LDH in the soil were also evaluated. In aqueous solution, NO_3^- adsorption capacity was $1.54 \text{ mol}_c \text{ kg}^{-1}$ of LDH. Layered double hydroxides also showed high selectivity for NO_3^- when compared to other anions in solution (HCO_3^- , SO_4^{2-} , Cl^- , HPO_4^{2-}). In soil conditions, it was performed 15 complete anion exchange processes between LDH and NO_3^- , without significant loss of LDH exchange capacity. The NO_3^- depletion zone extension from LDH, in soil conditions, reached 8 cm in a week. Thus, MgAl-Cl-LDH has a high potential to be used as a nutrient exchanger, reducing NO_3^- leaching in this case.

Torres-Durante et al. (2009) investigated the use of LDH as a buffer for NO_3^- in the soil. The experiments were conducted with plants and soil in order to evaluate NO_3^- adsorption capacity by LDH during crop growth, its ability to adsorb mineralized NO_3^- during soil fallow period and its influence on this anion leaching. Additionally, it was assessed the NO_3^- exchange reversibility with other anions in LDH under cultivation conditions. Finally, it was determined the buffering capacity of NO_3^- concentration in the soil. The results showed that during the growth period of the plant, the presence of LDH did not alter the N accumulation in plants. Given the NO_3^- adsorption in LDH, the N-NO_3^- concentration in the soil solution at harvest was reduced by a factor of 10 compared to a soil without LDH. Therefore, LDH has efficiently adsorbed the mineralized NO_3^- in the soil during non-growing seasons, reducing leaching in approximately 80 % while keeping the NO_3^- available for the next crop. The buffering capacity of NO_3^- in soil after 15 months increased from 0.3 to 2.7 with the application of 10 g kg^{-1} of LDH. The researchers concluded that LDH has the potential to be used as a long-term exchanger to control NO_3^- movement within the soil, thus reducing NO_3^- leaching.

Silva et al. (2014a,b) reported LDH intercalated with NO_3^- as potential slow-release fertilizer. LDH were subjected to NO_3^- release tests in NaHCO_3

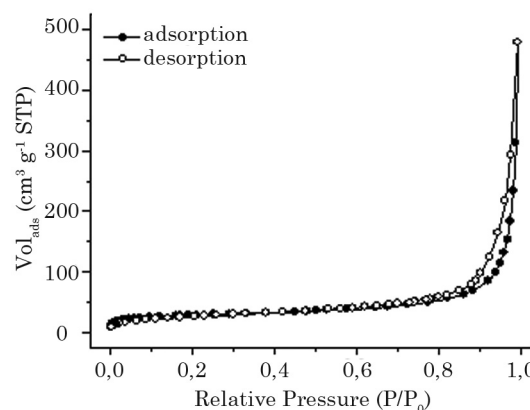


Figure 8. Nitrogen (N_2) adsorption-desorption isotherm of a ZnAl- CO_3 -LDH. Source: Tronto (non-published data).

buffered solution at pH 6.5 and distilled water. Release curves demonstrated two NO_3^- release events, a quick initial one followed by a slow and gradual event.

Berber et al. (2014) synthesized and characterized a $\text{MgAl-NO}_3\text{-LDH}$. This material was used as source of sustainable-release of NO_3^- in the soil. Nitrate release was monitored at different media with solutions that simulate soil composition, one simulating an acid soil solution and other a basic one. In addition, it was evaluated the influence of temperature (15, 25 and 35 °C) in the release of NO_3^- . The release of NO_3^- intercalated with LDH showed that in the acid soil the sustainable process lasted for 16 days at 15 °C, whereas in basic soil at the same temperature, this process lasted for 20 days. The results for the different pH and temperature conditions encourage the use of these materials as sources for slow release of NO_3^- in the soil.

In a current research by our group, we used $\text{MgAl-NO}_3\text{-LDH}$ as source of storage and slow-release of NO_3^- for plants. Bioassays were performed using the same soil and subsequent cultivation of different plant species: (i) *Raphanus sativus* (radish); (ii) *Lactuca sativa* (lettuce) and (iii) *Sorghum bicolor* L. Mornch (sorghum). The release of NO_3^- intercalated in LDH was compared with two N commercial fertilizers, urea and NH_4NO_3 . It was observed high feasibility of use of these materials as regulators of storage and slow-release of NO_3^- to the plants (Figure 9).

Orthophosphoric acid (H_3PO_4) is a polyprotic acid that in an aqueous medium produces conjugate bases H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} . These buffers hinder synthesis of LDH intercalated with phosphate by direct synthesis. Thus, for the synthesis of LDH intercalated with phosphate, it is commonly used indirect methods of synthesis, such as anion exchange from a LDH precursor intercalated with

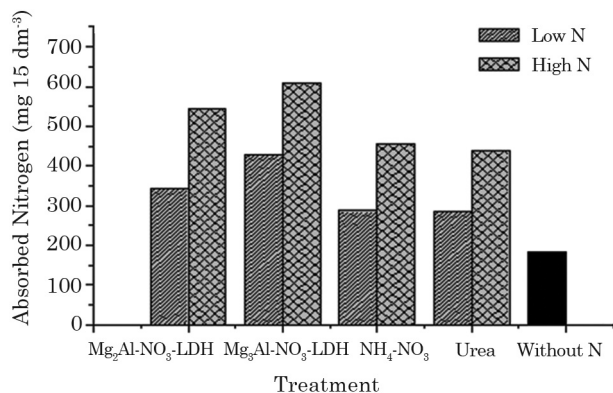


Figure 9. Absorbed nitrogen by successive crops of radish, lettuce and sorghum influenced by N sources and doses (low N: 40 mg dm⁻³ and high N: 100 mg dm⁻³).

NO₃⁻ or Cl⁻. Ookubo et al. (1993) studied phosphate intercalated in MgAl-LDH by indirect synthesis methods. First, a precursor LDH intercalated with Cl⁻ was prepared by coprecipitation at constant pH. Then, the synthesized material was subjected to an ion exchange reaction in a solution containing phosphate. Results showed that depending on exchange reaction conditions (solution pH); more than one phosphate type could be intercalated.

Khalidi et al. (1998), Badreddine et al. (1999) and Legrouiri et al. (1999) studied the influence of pH on phosphate exchange reaction by NO₃⁻ and Cl⁻ intercalated in LDH. Through infrared spectra, it was possible to verify different phosphate species intercalated within the LDH concerning the exchange reaction conditions.

Woo et al. (2011) studied the synthesis, crystallographic characterization and kinetics of the release of phosphate intercalated in a CaFe-LDH. These authors highlighted the importance of this material as phosphate slow-release fertilizer, although they have not carried out tests with plants to check the real effectiveness of the material.

Sources for Agrochemical Storage and Slow-Release

Agrochemicals are frequently applied at higher doses than needed to increase the pest control effectiveness. However, high doses of agrochemicals in soils generate a series of environmental problems such as soil and water contamination. The use of host inorganic sources for the encapsulation of agrochemicals in silicate clays and zeolites, bring LDH to be subject of several studies (Li et al., 2008; Bruna et al., 2009; Ramesh and Reddy, 2011). Synergistic effect benefits of the interaction between inorganic sources and agrochemicals may be used with environmental hazard reduction.

Cardoso et al. (2006) intercalated 2,4-D, MCPA [(4-chloro-2-methylphenoxy) acetic acid] and Picloram anionic herbicides in MgAl-LDH. The produced materials were characterized and tested by herbicide-release assays in water and soil leaching columns. In addition, herbicidal activity was also tested in bioassays using cress (*Lepidium sativum*) as test plant. According to the researchers, results have shown that LDH controlled the release of the herbicides.

Chaara et al. (2011) performed the preparation and characterization of materials from the intercalation of the anions dodecyl sulfonate and sebacate in Mg and Al LDH containing different cation molar ratios (Mg/Al = 2 and 3). The materials were used in adsorption experiments for removal of metolachlor and alachlor herbicides. Furthermore, LDH intercalated with the two herbicides were prepared based on the adsorption curves. The materials were used in experiments to measure herbicide-release kinetics. Results have demonstrated that the herbicides have slow-release profile and the produced materials are ideal to be used as nonionic pesticide carriers.

Bruna et al. (2009) studied different LDH ([Mg₃Al(OH)₈]Cl.4H₂O; [Mg₃Al_{0.5}Fe_{0.5}(OH)₈]Cl.4H₂O; [Mg₃Fe(OH)₈]Cl.4H₂O) and the product of ([Mg₃Al(OH)₈]Cl.4H₂O calcination with MCPA as adsorbent materials. The attributes evaluated during adsorption process were pH, contact time and pesticide concentration. To reduce environmental harmful effects of this herbicide, final materials were also used as sources for slow-release pesticide in water and soil leaching columns. Results showed a rapid adsorption of MCPA and LDH exhibit controlled release-properties, reducing herbicide leaching in the soil columns as compared to standard commercial MCPA formulation.

Adsorbents

LDH and their thermal by-products (mixed oxides and oxy-hydroxides) might be used as adsorbents for the removal of contaminant anionic species in water and soil. LDH multifunctionality allows, once adsorbed, that these anionic contaminant species can be released and reused. Thus, anionic species commonly used in agriculture e.g. nitrate, phosphates and agrochemicals in general can be removed from the environment by means of adsorption processes and then slowly released back to the plant growth or pest control, in a process of recycling or reuse.

Terry (2009), studying a clay mineral with a structure identical to LDH [Mg₂Al(OH)₆]CO₃.3H₂O, used the hydrotalcite as ion exchangers to remove nitrate and phosphate in solution. Ion residual concentration in solution was lower than the levels recommended by the Environmental Protection Agency (EPA) for drinking water.

Experiments were also conducted to determine the effect of one anion on the removal of the other. As a result, it was observed that NO_3^- in the solution, at low or high concentrations, did not affect phosphate removal. Similarly, the opposite happened. Anion removal results were compared with NO_3^- and phosphate pure solutions. Phosphate at concentrations recommended by the EPA was completely removed. On the other hand, NO_3^- was removed in a smaller amount than the limit recommended by the agency (30 mg L^{-1}).

Inacio et al. (2001) performed MCPA adsorption in Mg and Al LDH intercalated with carbonate, nitrate and chloride. The adsorption capacity was achieved by means of adsorption isotherms and kinetic study. The authors studied the influence of pH, $\text{Mg}^{2+}/\text{Al}^{3+}$ ratio, anion exchange capacity, intercalated anion nature and adsorbent morphology in the adsorption measurements. The Freundlich model best described adsorption isotherms with S-type tending to L-type at high equilibrium concentrations of MCPA. MCPA adsorption in LDH was made by anion exchange at two stages. The first stage consisted of MCPA adsorption on crystallite surface followed by anion exchange within interlamellar field. This behavior explains the change from S to L-type isotherms. The authors propose that the adsorption capacity depends on anion nature in solution, according to the following affinity order: $\text{NO}_3^- < \text{Cl}^- < \text{CO}_3^{2-}$.

Khenifi et al. (2010) studied the removal of glyphosate and glufosinate anion herbicides in aqueous solution, using $\text{Ni}_2\text{Al-NO}_3\text{-LDH}$ as adsorbent. Adsorption studies were conducted to evaluate the effect of various attributes such as contact time and the initial concentration. The experiments showed two distinct stages for herbicide adsorption into the $\text{Ni}_2\text{Al-NO}_3\text{-LDH}$, the first is the adsorption in outer crystallites followed by herbicide molecules intercalated within interlamellar field by anion exchange. These phenomena were confirmed by physical analyzes of $\text{Ni}_2\text{Al-NO}_3$ using XRD, FTIR and SEM techniques. The two-herbicide adsorption kinetics followed the pseudo-second order model. Adsorption isotherms are of H and L type for glyphosate and glufosinate adsorption, respectively, and they were well described by the Langmuir model. The results of this study indicated the important role of NiAl-LDH materials as potential adsorbents for organophosphate or organophosphonate pollutant removal in water.

Li et al. (2005) prepared MgAl-LDH intercalated with different NO_3^- , CO_3^{2-} and Cl^- . The materials were evaluated for glyphosate adsorption capacity. The adsorption experiments that examined glyphosate removal in aqueous solution by MgAl-LDH indicated two ways of adsorption: outer surface adsorption and interlamellar anion exchange. Glyphosate at low concentrations is

singly adsorbed on the LDH outer surface, while the interlamellar anion exchange occurs at high concentrations. Glyphosate adsorption capacity of MgAl-LDH increases with lamella charge density ($\text{Mg}^{2+}/\text{Al}^{3+}$ molar ratio) in LDH. The amount of agrochemical retained on MgAl-LDH decreases in the following order with respect to interlamellar anions: $\text{Cl}^- > \text{NO}_3^- > \text{CO}_3^{2-}$.

FINAL CONSIDERATIONS

In general, the studies found in the literature for the usage of LDH as matrices for slow release of nutrients or agrochemicals are mostly studied in terms of its physical-chemical properties (Seida and Nakamo, 2002; Hosni and Srasra, 2010; Woo et al., 2011; Berber et al., 2014), with no major studies of its agricultural applications.

The chemical characterization of LDH is highly evolved, with the use of a wide range of analytical techniques. However, the agronomic studies of these nanomaterials do not present the same level of sophistication to support its application in agriculture. Thus, it is essential to develop advanced agronomic techniques compatible with the basic studies of the chemistry of these materials. It is clear the existence of a chemistry/agronomy interface that is not properly developed.

Therefore, the Chemistry of Materials field has clearly a large space in current studies to develop new fertilizers based on the demands of plants and soils.

This review aimed to decrease this gap and improve synergism between chemists and soil scientists.

ACKNOWLEDGEMENTS

The authors want to thank the Fundação de Amparo à Pesquisa do Estado de Minas Gerais - FAPEMIG (APQ-01406-1), the Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq (502835/2009-5), and the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES for the financial support. FEG-SEM facilities were provided by LMA-IQ.

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