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Research about

Metal layer double hydroxide

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# نموذج تقييم مادة البحث والمقال

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## عنوان البحث: Metal layer double hydroxide

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### Abstract:

Layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite (HT)-like materials, are a family of materials that have attracted increasing attention In Recent years. LDHs have anionic exchange capacity, and the ability to capture organic And inorganic anions makes them almost unique as inorganic materials. This review presents the wide variety of methods that are available for the synthesis of LDHs and focus on the way In which the physicochemical properties of the materials vary with synthesis method **.** 

Also deals with the characterizations of LDHs and applications of LDHs In removal of heavy metals from water with different methods. This review aims to revise literature about the different types of LDHs and reach a conclusion of Its benefits and how to use it .

### **Introduction:**

Layered double hydroxides (LDHs), are a class of synthetic two-dimensional nanostructured anionic clays, characterized by there unique lamellar structure which consist of positively charged metal hydroxide layers intercalated with anions and water molecules, whose structure can be described as containing brucite-like layers, where a fraction of the divalent cations coordinated octahedrally by hydroxyl groups have been replaced isomorphously by trivalent cations, giving positively charged layers with charge-balancing anions between them. Their general formula is  $[M^{2+}_{1-x}M^{3+}_{x}(OH)_{2}]^{x+}[A^{n-}]_{x/n} \cdot mH_{2}O$ , where

M<sup>2+</sup> and M<sup>3+</sup> are divalent and trivalent metal cations, respectively, and A<sup>n-</sup> represents the interlayer anions. A large class of isostructural materials, which can be considered complementary to aluminosilicate clays, with widely varied physicochemical properties can be obtained by changing the nature of the metal cations, the molar ratios, as well as the type of interlayer anions.

LDHs, both as directly prepared or after thermal treatment, are promising materials for a large number of practical applications in catalysis, adsorption, pharmaceutics, photochemistry, electrochemistry and other areas. This is due to their high versatility, easily tailored properties and low cost, which make it possible to produce materials designed to fulfil specific requirements.



Fig. 1 Idealized structure of a layered double hydroxide with interlayer carbonate anions.

#### **Types of LDHs**:

#### A) Within the Hydroxide Layers:

There are a number of combinations of divalent and trivalent cations that can form LDHs. Besides Mg2+, the available divalent ions can be Ni2+, Co2+, Zn2+, Fe2+, Mn2+, Cu2+ (17,18,19,20), as well as  $Ti^2$ + (21), Cd2+ (22,23), Pd<sup>2</sup>+ (22,21,24) and Ca2+ (25,26,27). Similarly, the trivalent ions can be Al3+, Ga<sup>3</sup>+, Fe3+, Cr3+, Mn<sup>3</sup>+ (17,18,28), Co<sup>3</sup>+ (29,30), V3+ (31,32), In<sup>3</sup>+ (33), Y3+ (34), La<sup>3</sup>+ (21,24,35), Rh<sup>3</sup>+ (21,24,35-36), Ru<sup>3</sup>+ (35,36), Sc<sup>3</sup>+ (36), etc. For these ions, the only requirement is that their radii be not too different from those of Mg2+ and Al+.

#### **B) Between the Layers:**

As for the anions located in the interlayer gallery, the choice is much more versatile. There is almost no limitation to the nature of anions in the LDHs as long as the anions do not abstract the metal ions from the hydroxide layer and have a sufficient charge density in one cross section. Up to now, many kinds of anions have been reported to be included in the literature:

**1. Common inorganic anions:** halides (X-), CO3 2-, NO3 -, OH-, SO4 2-, Al(OH)4 - or H2AlO3 - (37,38), PO3 - PO4 3- HPO4 2-, H2PO4 -, P2O7 2- (23,39,40), AsO3 (41), borate and tetraborate (43,44), ClO4 - (45), TcO4 -, ReO4 - (46), MnO4 - (47,42), CrO4, Cr2O7 2- (41,48,49), MoO4 2- (50), HVO4 2-, VO4 3- (41,42), silicate anion (42,51), and C60 anion (52).

**2. Organic anions:** carboxylates (53,54,25), dicarboxylates (53,25,55,56), benzenecarboxylates (54,25,57,58), alkylsulfates (25,55,56), alkanesulfonates (53,25,55,56), chlorocinnamates (55), 1-butanoate anion (59), glycolate (60), glycerolate (CH<sub>2</sub>OH–CHOH–CH<sub>2</sub>O-) (61), and organic dyes (62).

# 3.Polymeric anions: poly(vinylsulfonate),

poly(styrenesulfonate), and poly(acrylate) (63,64), polyaniline (65), ionized poly(vinyl alcohol) (66), poly(ethylene glycol) (67), and even polystyrene oligomer anion (68).

**4. Complex anions:**  $CoCl_4 \ ^{2-}$ ,  $NiCl_4 \ ^{2-}$  (69,70),  $IrCl_2 \ (71)$ ,  $Fe(CN)_6 \ ^{4-}$ ,  $Fe(CN)_6 \ ^{3-} \ (72)$ ,  $Mo(CN)_8 \ ^{4-}$  and  $Mo(CN)_8 \ ^{3-}$ ,  $Ru(CN)_6 \ ^{4-}$  and  $Ru(CN)_6 \ ^{3-} \ (234,235)$ ,  $Co(CN)_6 \ ^{3-} \ (73)$ , and  $MoO_2(O_2CC(S)Ph_2)_2^{2-} \ (74)$ .

**5. Biochemical anions:** (1) various amino acids (75); (2) DNA with 500-1000 base pairs (76).



### A. Induced Hydrolysis Method:

It consists of the precipitation of M3+ cation hydroxide at pH slightly below that in which M2+ cation hydroxide precipitation occurs. The aqueous suspension of M3+ is added into the M2+ one, maintaining pH at a fixed value by simultaneous addition of a NaOH solution (Taylor et al., 1984)(1).

#### **B. Hydrothermal Synthesis Method:**

The hydrothermal synthesis method uses suspension of oxides and/or hydroxides of M2+ and M3+ 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<sup>-3</sup>,  $Cl^{-}$ ,  $OH^{-}$ , etc (Wang et al., 2013)(2).

#### C. Coprecipitation in Nonaqueous Solutions:

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)(3,4,5). 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)(4). 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 guite simple method has shown good results (Reichle et al., 1986)(3). 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. (De Roy et al., 1992)(5) 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.

#### D. Ion Exchange in Solution Method:

This method consists of adding a LDH precursor usually containing interlayer anions Cl<sup>-</sup> or NO<sup>-</sup>3, ina concentrated solution with the anion of interest. Inthis method, the exchange efficiency varies a lot, theexchanged anion should have the greatest ability tostabilize the lamella (more likely to be intercalated)and/or be in a higher proportion than the LDH precursor anion, which is normally Cl<sup>-</sup> or NO<sup>-</sup>3 (Lal and Rowe, 1981; De Roy et al., 1992; Newman and Jones, 1998)(6,5,7).

#### E. 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)(8).

#### F. Preparation by Sol-Gel Techniques:

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)(2).

### **Characterization methods:**

#### A) 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 00l baseline peaks related to the lamellae stacking sequence (Cavani et al., 1991; De Roy et al., 1992; Forano et al., 2006)(4,5,9). 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-NO3-LDH.Interlayer distances are calculated from 2θ values by using Bragg's equation:

#### $n \lambda = 2dhkl sen \theta (1)$

where n is the diffraction order,  $\lambda$  is the wavelength of the Xray, dhkl is the interlayer distance for hkl peak, and  $\theta$  the Bragg's angle, which is determined by diffraction peak. Repeating d value at n = 1, 2, 3..., 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 be obtained by means of specific computer programs, such as "VASP" (Vienna Ab-initio Simulation Package).



Figure 3. X-ray powder diffractogram of a

ZnAl-NO3-LDH.

#### **B)** 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)(4,5,9). 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  $CO^{2-}$  3, three bands are observed between 1380-1350 cm-1 (v3), 880-850 cm-1 (v2) and 690-670 cm-1 (v4).



Fig. 4 FTIR spectra of MgAl-CO3-LDH (Zn/Mg = 0.125)

#### C) Thermogravimetric Analysis Coupled with

#### **Differential Scanning Calorimetry (TGA-DSC):**

LDH thermal stability be determined can 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 oC. Figure 5 demonstrates an example of TGA-DSC

Thermogram.





### D) Scanning Electron Microscopy (SEM):

LDH size and shape vary with the preparationmethod 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 isapplied 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.



Fig. 6 SEM image of a ZnAl-Cl-LDH

### E) 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, 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.

# F) Ultraviolet-visible:

(UV-vis) spectroscopy is applied to confirm the arrangement of cations as in-fluid arrangements in the layers. Sometimes when strongly colored anions exist in the interlayer, their retention groups cover them [10].

# **Properties of LDHs:**

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 of LDHs.

# 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 <u>Leroux and Besse (2004)</u>(11), AEC values might change between 200 and 450 cmol<sub>c</sub> kg<sup>-1</sup>. Values bellow 200 cmol<sub>c</sub> kg<sup>-1</sup> are not possible, once the M<sup>2+</sup> and M<sup>3+</sup> ratio is very low to support LDH structure.

# **B)** Colloidal properties

The small particle size and low charge density of some important for systems with colloidal LDH are characteristics and/or delamination (stacking structure loss). The large size of the host anion often cause interlayer diffusion problems. Thus, in order to these problems, colloidal overcome 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 bv combining LDH and organic molecules (Zhao et al., 2002; Leroux and Besse, 2004)(12,11). From colloidal suspensions of LDH, Gardner et al. (2001)(13) 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)(14) performed the delamination of Zn<sub>2</sub>Al-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)(15) performed LDH delamination intercalated with amino acids, and observed excellent results when LDH were intercalated with glycine in formamide solutions.

# **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 m<sup>2</sup> g<sup>-1</sup>. 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. <u>Geraud et al.</u> (2006)(16) demonstrated the feasibility of macroporous material synthesis from the combination of MgAl-LDH and colloidal polystyrene crystals (PS).

# 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 ( $M^{2+}/M^{3+}$ ), and the interlayer anion type (organic or inorganic).

# **Applications of LDHs:**



# LDHs in removal of heavy metals from water:

As an environmentally friendly remediation agent, LDHs composites can be used in actual heavy metal pollution remediation such as electroplating wastewater and mining wastewater, and soil pollution in mines and heavy metal pollution (Yuan et al., 2018)(77). The existing examples of heavy metal restoration via LDHs based materials demonstrated an excellent restoration effect, thus presenting a promising application possibility.

Heavy metals are potent nonbiodegradable pollutants that are harmful at even low concentrations and contain zinc (Zn), lead (Pb), copper (Cu), cadmium (Cd), chromium (Cr), mercury (Hg), nickel (Ni), arsenic (As), and thallium (Tl). These contaminants are present in the effluent of oil refining, coal mining, metal plating, agricultural assets [78,79, 80,81].

## Removal methods:

### A) Selective absorbability

In the actual absorption process, heavy metal ions and other ions are present in the solution. These ions can occupy the absorption sites of LDH, so that its ability to adsorb heavy metal ions is reduced. Therefore, it is very important to prepare LDH with selective absorbability, which is beneficial for the detection and absorption of heavy metal ions [82,83,84]. In addition, LDH is expected to have different absorption capacities for different heavy metal ions, which is beneficial to the separation between heavy metal ions.

On the one hand, the binding capacity of different cations and anions and the solubility of the combined products in solutions are different, which influences the removal of heavy metal ions. For example, MgAI–LDH removes Cu<sup>2+</sup> and Ni<sup>2+</sup> by forming hydroxides, and Pb<sup>2+</sup> by forming carbonates [85]. On the other hand, the cations of LDH can be replaced by other cations with similar radii through isomorphic substitution.

### B) Ion exchange treatment

The ion exchange method is a reversible chemical reaction used to replace the undesirable metal ion with harmless and environmentally friendly ones(86). A heavy metal ion is removed from a wastewater solution by attaching it to an immobile solid particle as a replacement with the solid particle cation.

The material of solid ion-exchange particles could be either natural, e.g., inorganic zeolites, or synthetically produced,

e.g., organic resins. The ion-exchange method can remove target (some or all) heavy metal ions, such as  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $V^{4+}$ ,  $V^{5+}$ ,  $Cr^{3+}$ ,  $Cr^{4+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$  from wastewater(86). The ion exchange mechanism for metal removals can be explained in the following reaction as the ion exchange particle having ion exchanger of  $M^-EC^+$  ( $M^-$  is the fixed anion and  $EC^+$  is the exchange cation; Na<sup>+</sup> and H<sup>+</sup> are frequently used as exchange cations) to exchange its cation ( $EC^+$ ) with the wastewater cation ( $WC^+$ )(87).

 $M^{-}EC^{+} + WC^{+} \iff M^{-}WC^{+} + EC^{+}$ 



## **C) Precipitation**

Chemical precipitation (the so-called coagulation precipitation) is broadly used in industries and is considered one of the most effective and mature methods. It changes the form of dissolved metal ions into solid particles to facilitate their sedimentation. The reagent coagulation (coagulant) precipitates metal ions by changing pH, electro-oxidizing potential, or co-precipitation(88).



# **Conclusions:**

LDHs were reviewed with a brief introduction on synthetic methodologies, most-used characterization techniques, and some of its applications. The simple synthetic strategies make LDHs an alluring material for future applications, as they offer unique ion exchange properties. There is a possibility of inducing new structural features and adjusting physicochemical performance and tunable synthesis strategies. Thus, they can open new pathways in the fields of wastewater treatment, greenhouse gas mitigation, biomedical applications, and fire-retardant materials for safeguarding the environment and our biosphere in an eco-friendly manner.

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