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Layered double hydroxides: Properties, synthesis and its application in heavy metal remediation of soil

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Abstract

Layered double hydroxides (LDH) are hydrotalcite-type clays, consisting of stacked positive layers of brucite-like hydroxides that are separated and neutralized by exchangeable anions in inter-lamellar galleries. They exhibit colloidal properties and are characterized by small size (200-300 nm) and high surface area (50-200 m² g⁻¹). The zero-point charge of these minerals is usually in the pH range of 10-12. Positively charged surface provides high anion exchange capacity to these minerals, which ranges between 200-450 cmol (-) kg⁻¹. Delamination and memory effect are imperative properties pertaining to the commercial application of LDHs. Various direct (co-precipitation, hydrothermal synthesis, salt oxide method and sol-gel synthesis) and indirect (ion exchange and structural reconstruction method) techniques are available for the synthesis of LDH. Layered double hydroxides are used to immobilize heavy metals through precipitation and the anionic contaminants through adsorption and intercalation reactions. Fe-Al LDH was used to remediate chromium contaminated (1039.92 and 2080 mg kg⁻¹) soils, and recorded complete immobilization of the pre-adsorbed Cr (VI). A high immobilization efficiency of 96.9 percent could be achieved for *in-situ* decontamination of cadmium in soil with application of Ca-Al LDH through formation of stable Cd-Al LDH mineral.

Keywords: Layered double hydroxides, properties, synthesis, immobilization, heavy metals

1. Introduction

Layered double hydroxides are naturally occurring positively charged minerals that exhibit ion exchange, sorption and precipitation behavior along with surface basicity making them materials of importance in soil remediation. It consist of stacked positive layers, which are separated and neutralized by exchangeable anions in the inter-lamellar galleries. LDHs are assembled by a non-covalent bond, where the positively charged main lamella includes divalent or trivalent cations and interlayer space consists of non-framework anions along with water molecules (Mishra *et al.*, 2018) ^[15]. Depending upon composition, these compounds are given many names, but the generally used term is hydrotalcite-type compounds and they are widely called as layered double hydroxides. The exploration in the field of LDHs started with the discovery of naturally forming hydrotalcite mineral by Hochstetter in 1842 (Evans and Slade, 2006) ^[5]. Chemical composition of layered double hydroxides are an exciting feature that defines their use in various applications and imparts phenomenal properties in these compounds (Hobbs *et al.* 2018) ^[10]. The empirical formula to describe the chemical composition is.



Where,

- M²⁺ = divalent metal cation
- M³⁺ = trivalent metal cation
- A = interlayer anion
- n- = charge on anion
- x and m are fraction constants
- n = 0 indicates that neutral layers are attracted by weak van der Waals forces and hydrogen bonding

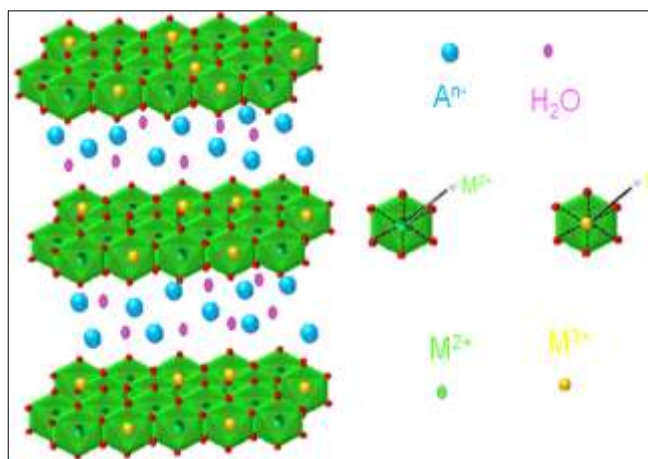


Fig 1: Structure of layered double hydroxide mineral

2. Structure of layered double hydroxides

The basic structure of LDH is derived by the substitution of a fraction of the divalent cations in a brucite-like lattice by trivalent cations such that the layers acquire a positive charge, which is balanced by the intercalation of anions between the layers (Siebecker *et al.* 2018) [18]. Metallic cations that make up the lamella must be present in octahedral shape and its ionic radius within the range of 0.50 to 0.74 Å. By varying the type of metallic cations, their cationic ratio and interlayer anions, a great number of LDH types can be formed. Several cations may be part of the structure, including Mg^{2+} , Al^{3+} , Cd^{2+} , Ga^{3+} , La^{3+} , *etc.* (Benício *et al.*, 2015) [3]. A number of anionic species can be intercalated between the layers during the synthesis of layered structure. Intercalated anions can belong to inorganic anions (F^- , Cl^- , CO_3^{3-} , NO_3^- , SO_4^{2-}), organic anions (carboxylate, phosphates, alkyl sulfates), and biomolecules (DNA, amino acids, vitamins, peptides, nucleosides) (He *et al.*, 2017) [8].

3. Properties of Layered double hydroxides

LDH present a countless number of properties due to their varied compositions and structural features.

3.1 Confinement effect

Anionic clays provide a confined micro-environment to the intercalating molecules and hence they will get well orientation and ordered alignment (Yang *et al.*, 2022) [21].

3.2 Colloidal property

Anionic clays exhibit colloidal properties and are characterized by small size (200-300 nm) and high surface area ($50\text{-}200\text{ m}^2\text{ g}^{-1}$). Point of zero charge of a mineral is the pH at which surface charge on the mineral becomes zero. The ZPC of anionic clays are usually in the pH range of 10-12 (Johnston *et al.*, 2021) [12].

3.3 Anion exchange

Anion exchange capacity (AEC) of a molecule is the ability to retain and exchange anions with that of equilibrium solution. Permanent positive charge developed due to isomorphic substitution and pH dependent charge developed based on equilibrium solution pH are two important spots of anion exchange. It depends on the metallic cation ratio, the ability of

the involved anion to stabilize lamellar structure and the molecular mass of the cations and anions involved. The AEC values of anionic clays might change between 200 and 450 cmol kg^{-1} (Prasanna and Kamath, 2009) [16].

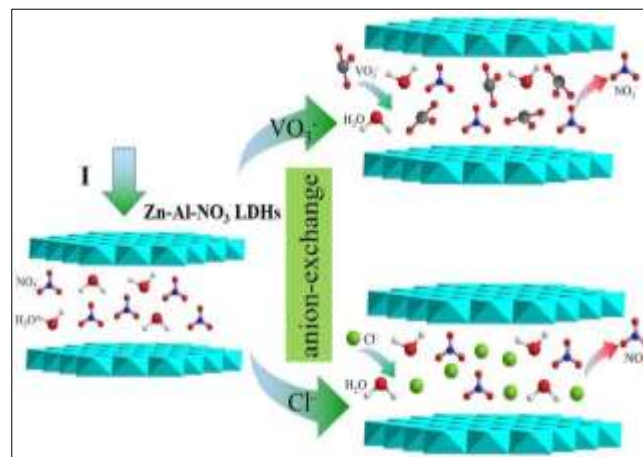


Fig 2a: Anion exchange phenomena in layered double hydroxides

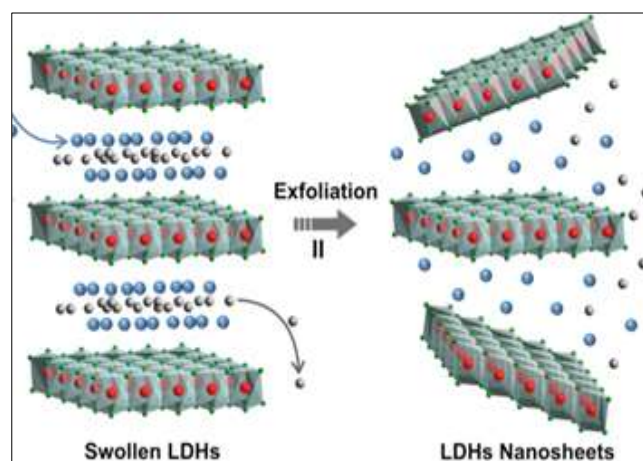


Fig 2b: Delamination in layered double hydroxides

3.4 Delamination

Delamination or exfoliation is a process in which layers of LDHs are peeled off into single or discrete sheets (Fig. 2). After delamination process nano-sheets of thickness 1~5 nm are obtained and the process is a difficult task because of strong electrostatic interactions among layers (Jamil *et al.*, 2019) [11].

3.5 Memory effect

Calcination of LDHs removes the interlayer water, interlayer anions and the hydroxyl groups, resulting in a mixture of metal oxide that cannot be achieved by mechanical means. The ability of the calcined LDH to regenerate the layered structure when they are exposed to water and anions are known as memory effect (Fig. 3). Water is absorbed to reform the hydroxyl layers, and anions and water are incorporated into the interlayer galleries. The anions incorporated may not be the anion that was in the original LDH (Arrabito, *et al.*, 2019) [1].

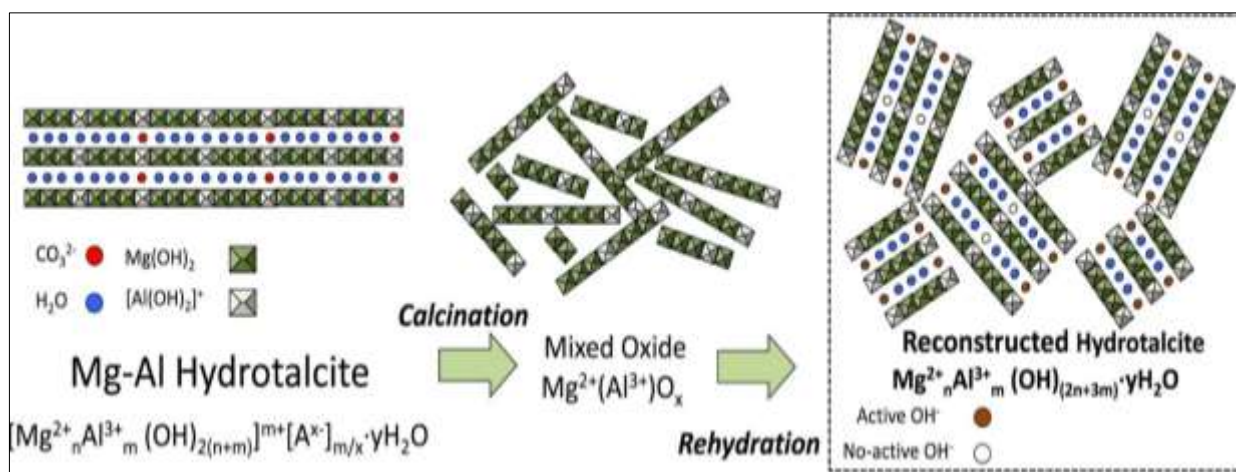


Fig 3: Memory effect of Layered double hydroxides

4. Synthesis layered double hydroxides

The commercial exploration of peculiar structural features and properties of anionic clays started with its artificial synthesis. Scientists developed different synthetic techniques, which are classified into direct and indirect methods. In direct methods, the reactants used are pure chemical compounds whereas indirect method uses a LDH precursor.

4.1. Direct methods

4.1.1 Co-precipitation

This is the most employed method to synthesize layered double hydroxides, because it can be performed in a single step with high yield and starting from cheap reagents. Bivalent and trivalent cations salt solutions are mixed together and with the solution of the anion to be intercalated, under continuous stirring. The pH of the mixture is maintained at the optimal basic value (pH range 6-11) by adding a solution of soda, to favor the simultaneous precipitation of cation hydroxides. To promote the intercalation of the desired anions, the preferred counter ions of cation salts are the nitrates or chlorides, which possess low affinity towards the brucite layers (He *et al.* 2006) [7].

4.1.2 Hydrothermal method

The hydrothermal synthesis starts from the suspension of oxides or hydroxides of M^{2+} and M^{3+} cations. Anion solution with the chosen acid or salt is inserted into this suspension, then the obtained dispersion is treated at high pressure and temperature in a hydrothermal reactor (Wijitwongwan *et al* 2019) [19].

4.1.3 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 to 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 (George and Saravanakumar, 2017) [6].

4.1.4 Sol-gel method

The sol-gel method involves the formation of a sol by hydrolysis and partial condensation of metallic precursor and

followed by the gel formation. As metallic precursor, metallic alkoxides, acetates, acetyl acetones and many inorganic salts are used. The properties of the LDH depends on the hydrolysis and condensation rates of the metallic precursors, which are modified by different parameters of the reaction like pH, nature and concentration of the precursor, solvent and temperature of the synthesis (Bini and Monteforte, 2018) [4].

4.2 Indirect method

4.2.1 Ion exchange method

In the anion-exchange method, the pre-formed LDH structure, usually containing Cl^- or NO_3^- as interlayer anions, is added to a concentrated solution of the anions of interest. The obtained solution is maintained under stirring for many hours at room temperature or at about 50-70°C. The exchange efficiency varies depending on the ability of the exchanged anions to stabilize the lamellae. Generally, the exchange ability of incoming anions increases with increasing charge and decreasing ionic radius. Order for simple inorganic anions decreases in the order $CO_3^{2-} > HPO_4^{2-} > SO_4^{2-}$ for divalent anions and $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$ for monovalent anions (Yan *et al* 2016) [20].

4.2.2 Reconstruction method

The calcined LDH is able to regenerate the layered structure when it is exposed to water and anions. Water is absorbed to reform the hydroxyl layers, and anions and water are incorporated into the interlayer galleries. The anions incorporated do not necessarily need to be the anion that was in the original LDH material (George and Saravanakumar, 2017) [6].

5. Layered double hydroxides for removing heavy metal contaminants from soil

Heavy metal-contaminated soil poses heavy risk for human health and ecological sustainability. In situ immobilization and long-term stabilization of heavy metals in soil is the only strategy to prevent bio-magnification. Layered double hydroxides can remove the heavy metal pollutants *viz.* anion exchange, co-precipitation, and intercalation reactions.

5.1 Application of Fe-Al LDH for remediation of Cr contaminated soil

The study was conducted to evaluate feasibility of Fe-Al-

LDH for the remediation of Cr (VI) in soil. He *et al.* (2018) ameliorated different Cr (VI) contaminated soil with Fe-Al LDH at the rate of 1g/L. The treated soils were incubated for 80 minutes and they measured ratio of initial to final concentration of Cr (VI) in soil at every 20 minutes interval. Fe-Al LDH was synthesized using hydrothermal method. Complete immobilization of Cr (VI) from both soils (with Cr (VI) concentration 1039.92 and 2079.94 mg kg⁻¹ soil) was possible with the use of only 1g/L of Fe-Al LDH which shows high immobilization efficiency of the material. The proposed mechanisms of immobilization include (figure

- 4)
 - Ion exchange or surface adsorption of Cr (VI) on the surface of Fe-Al LDH
 - Oxidation of Fe²⁺ present in LDH structure and consequent reduction of Cr (VI) to Cr (III) by using the released electron
 - Dissolution of Fe-Al LDH and reduction of Cr (VI) by the oxidation Fe²⁺
 - Fe and Al co-precipitation with Cr (VI) or Cr (III) to form Fe (OH)₃, Fe₂O₃, Al (OH)₃ and Al₂O₃

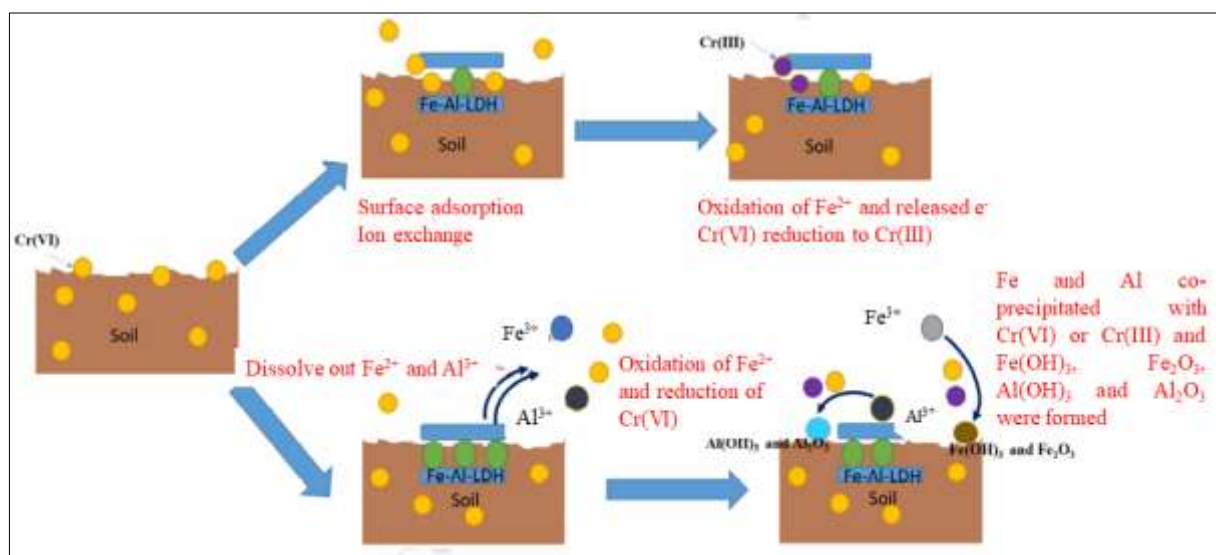


Fig 4: Remediation mechanism by Fe-Al LDH

5.2 Application of layered double hydroxides for permanent immobilization of cadmium

Cadmium-contaminated cropland has created severe risks to human health. A super-stable mineralization of Cd into Cd-Al LDH in Ca-Al LDH ameliorated soil was identified by Kong *et al.* (2020) [13]. The Ca-Al LDH used for the study was synthesized by co-precipitation method. Ca-Al LDH used as an amendment for soil contaminated with Cd at the rate of 3t/ha of Ca-Al LDH in 10 ha area of cadmium contaminated soil as a one-time application in 2016. It was observed that the average content of Cd in wheat grain was remarkably decreased to 0.08 mg/kg in the first year that is below the limit permitted (0.1 mg/kg), while the content was 0.22 mg/kg for the control field. Moreover, the average content of Cd in wheat grain continuously decreased in the following two

years also. The experiment showed that the transferability of Cd from soil to food was significantly reduced after the remediation by using CaAl-LDH.

The immobilization mechanism and formation of Cd-Al LDH was identified by TEM measurement at intermediate stages of reaction (Plate 1). Other findings that supported the formation of Cd-Al LDH are

- Continuous decrease in free energy of reaction at subsequent stages of formation
- A tenfold increase in residual fraction of cadmium and almost 10% decrease in acid-soluble fraction of cadmium in soil after remediation
- The solubility product of Cd-Al LDH was lower than Ca-Al LDH

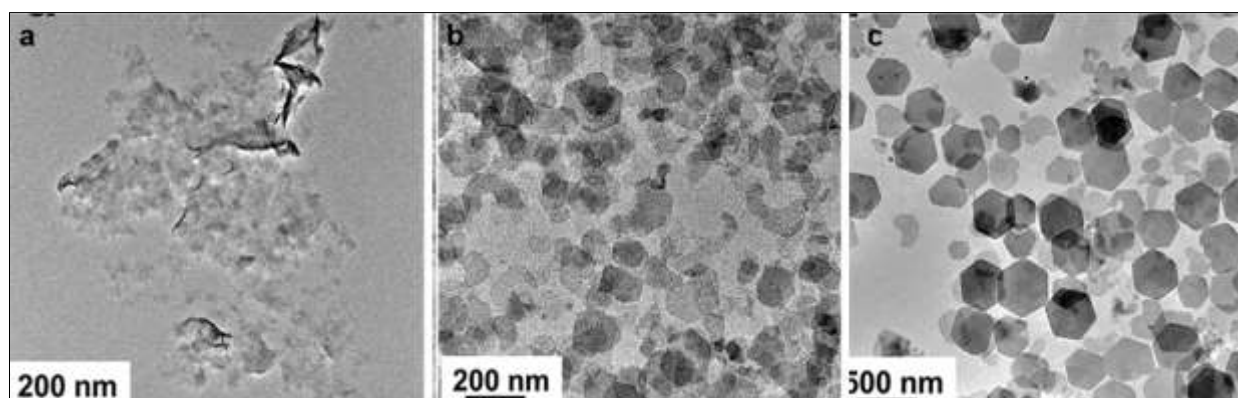


Plate 1: TEM images of samples during mineralization of Cd-Al LDH

a. Irregular nanosheets of CA-Al LDH b. TEM image at intermediate stage of immobilization c. Hexagonal nanosheets of Cd-Al LDH

(Plate 1a show irregular nanosheet structure of Ca-Al LDH transformed into aggregation of fragments just after dispersion in deionized water, which is attributed to the dissolution of CaAl-LDH. After the addition of Cd²⁺ ions (plate 1b), numerous irregular nanosheets with an average size of about 126 nm were observed. The irregular nanosheets are quickly evolved into well-defined hexagonal nanosheets as the reaction time increased (plate 1c) which are characteristic to Cd- Al LDH.)

13. Conclusion

Layered double hydroxides are positively charged clay minerals with great influence on soil properties and decontamination reactions. Layered double hydroxides can be synthesized with a huge number of cation-anion combinations. The versatility in chemical composition and unique intercalation properties of layered double hydroxides makes them matrices for immobilization of contaminants from soil. But extensive studies are required on field-level application strategies considering dose, method, time of application, and factors affecting activity in soil before commercial application.

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