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Current Advances on Layered Double Hydroxides: Synthetic Routes, Structure Modification, Characterization, Topical Applications, and Future Prospects

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Abstract

Layered double hydroxides (LDHs) are clay frameworks whose structure is formed of brucite ($Mg(OH_2)$) layers allied with anion between the formed layers. The structure of the layered double hydroxide is represented in the following formula: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$, where M^{3+} and M^{2+} represented trivalent and divalent cations in the building units (sheets), x represents the ratio of M^{3+} to $(M^{2+}+M^{3+})$ cations in the structure and A^{n-} is the interlayer anion. LDHs can be prepared using simple techniques which can control the structure of layers, chemical composition, and the shape of the produced crystals by adjusting the preparation conditions. The first technique of preparing LDH is the intercalation process which includes the insertion of inorganic or organic precursors in their structure using an anion exchange process to fabricate inorganic/inorganic and/or inorganic/organic composite which can be used in various applications. The second technique is the simple physical mixing process between the prepared LDHs and smart materials such as activated carbon, graphene, and carbon nanotube to be used as base material to be applied in the storage of energy, super-capacitors, photo- and electrocatalysts, water splitting, and removal of toxic gases from the atmosphere. The last technique is polymer-LDH composite formation through introducing smart polymers during the preparation of the different LDHs to obtain nanocomposites used in energy, flame retardant, gas barrier, corrosion inhibitor films, and wastewater remediation. To determine the chemical, composition, morphology, porosity, crystalline structures, thermal stability, and catalytic activity of the layered double hydroxides, several analytical tools are used. These tools are X-ray diffraction, Fourier transforms infrared, Raman spectroscopy, thermogravimetric differential analyzer, scanning electron microscopy, transmission electron microscopes, surface area, programmed temperature reduction, and X-ray electron spectroscopy. LDHs are considered specific fine chemicals type which can be tailored with the required chemical composition and activity to be used in several applications including oxidation, reduction, bromination, water splitting, ethoxylation, aldol condensation, NO_x and SO_x reduction, and biofuel synthesis. LDH compounds do not harm the environment, which makes the various applications using these catalysts unique from a green chemistry point of view because they are reusable and environmentally friendly catalysts. This review discussed the different techniques used for the preparation of LDHs and the modification of the prepared composites by calcination at elevated temperatures, intercalation of their structures by small-, medium- and high-nuclear anions, and supported by carbon materials. The characterization techniques of the LDHs were reported about the different methods regarding the thermal stability, surface, texture, crystalline, and activity. Then the most effective potential applications were reported extensively including biofuel production, catalysis, water splitting, charge transfer, and wastewater treatment. The prospective sight of LDHs is pointed out based on the most recent research and the expected future development in this field.

Keywords: Layered Double Hydroxide; Calcination; Biofuel; Fire Retardancy; Water Treatment.

Introduction

Layered double hydroxides (LDHs) eventually comprise two metal cations; divalent cations, and/or trivalent cations in the double lamellar or double-layer form. The interlayer spaces between the layers can be packed basically by equivalent anions and water molecules [1-4]. The general formula of LDHs is denoted as [M2+(1−x) M3+x(OH)2]x+. [Ax/n] n−. mH2O; where M2+: divalent metal cations, M3+: trivalent metal cations, An-: associated anion, x: signify the ratio M3+/ (M2+ + M3+) where (0.1 < x < 0.5). The unalloyed phases of LDHs forms arise at (x) values of 0.20-0.34. Separate metal salts or metal hydroxides are mostly produced in case of (x) ratio is not comparable to these values. Additionally, it is essential for the construction of LDHs that the ratio of M2+/M3+ must be located in the 1-6 range [5-7].

Organizationally, LDHs are derived from brucite (mineral clay), which is formed mainly from $Mg(OH)_2$. During the formation of LDH based on brucite, a part of the divalent metal cations (M^{2+}) is substituted by an identical number of trivalent metal cations (M^{3+}). That creates positive residual charges on the surface of the layers, which are compensated by equivalent anions and water molecules the water and anions that fill the inter-lamellar region. The compensation of the formed positive charges by anions endorsing the assembling of the lamellae and forming the characteristic LDH structures [8]. The cations M^{2+} and M^{3+} are consistently disseminated in the lamellar structures, where the hydroxide layers are housed in the centers of an octahedral structure (Figure 1) [7,9].

The electrostatic attraction between the positively charged layers of LDHs and the negatively charged anions presented between these layers is the main factor responsible for the stability of the LDHs structures. The ratio between the divalent cations and trivalent cations in the framework of the LDHs layers determined the density of the residual positive charges on these layers, and consequently the number of negatively charged anions associated with the structure. The relation between these two types of different ions and the valence of the cations has a substantial influence on the properties of the layered double hydroxide materials, mainly the crystallinity, porosity, and ion exchange tendency [10].

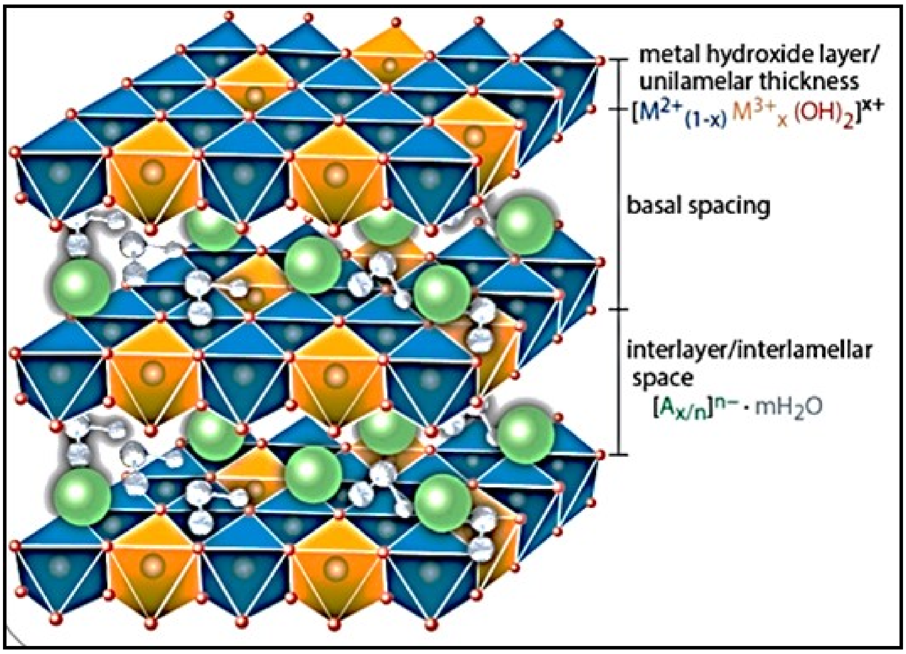


Figure 1: The characteristic distances and spaces of the layered double hydroxides

Synthetic Methods of Layered Double Hydroxides

Layered double hydroxides are prepared by different methods. Each method can produce a characteristic product with specific properties, mainly the surface area, morphology, crystallinity, and physical and chemical properties. The most applied methods used for the preparation of layered double hydroxides are the Co-precipitation method, hydrothermal method, and sol-gel method.

Co-precipitation method

The co-precipitation method is the common method for the preparation of layered double hydroxides. The procedure of this is to mix diluted solutions of metal cation salts under vigorous stirring at definite temperatures ranging between 50 and 90 °C [11-13]. Then, the formed metal oxides are precipitated by changing the pH of the medium into alkaline using sodium hydroxide or ammonium hydroxide in the presence of a quite suitable concentration of carbonate salt in the form of sodium carbonate (Na_2CO_3). The formation of the layered double hydroxides is affected by the reaction time, the rate of turning the medium into alkaline, and the final pH of the medium. The improvement of crystallinity, morphology, and surface area of the produced layered double hydroxides can be achieved at a pH of 9-12, stirring for 24 h, and a very low rate of titration [14-16].

Hydrothermal method

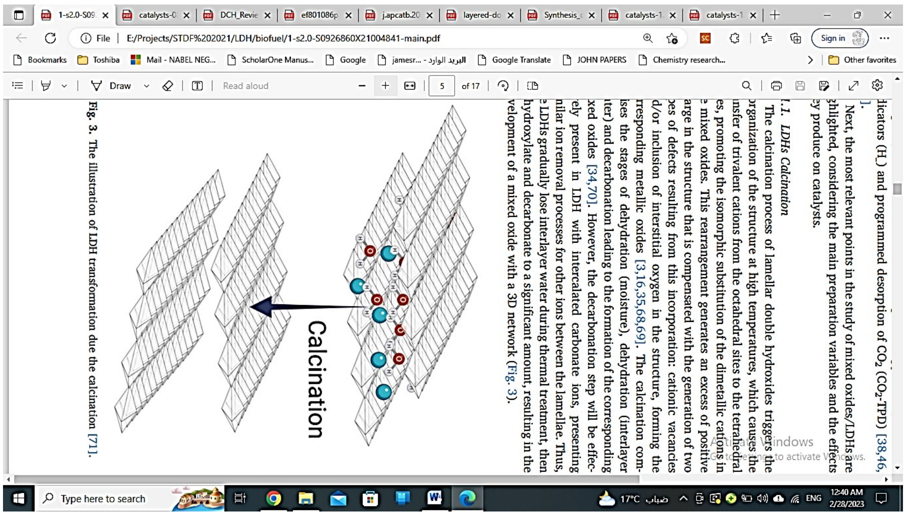
The hydrothermal method involves the preparation of the layered double hydroxides under pressure and at elevated temperatures reached to 180 °C. This method can be performed for the starting reactants or after the mixing of the metal cations and mixing [17-18]. The obtained layered double hydroxides prepared by the hydrothermal methods at elevated temperatures are characterized by their sharp crystals and very high surface area.

Sol-Gel method

The sol-gel method is performed in which the salts of the metals are precipitated in alkoxide forms. The most usable alkoxides are aluminum tri-isoperoxide and titanium tetra-isoperoxide. The precipitation then can be accomplished by the hydrolysis of the alkoxides under the thermal condition of 70 °C [19-20].

Calcination of layered double hydroxides

The calcination method of layered double hydroxides is restructuring their lamellar structures at high temperatures. This process causes a change in the crystalline structure of LDH from octahedral to tetrahedral and leads to the formation of mixed metal oxides. This process is responsible for increasing the number of positively charged cations. These charges are compensated by the defects formation in the generated crystalline structures. These defects are the cationic vacancy and participation of oxygen in the structure [21-25]. Three types of reaction occurred during the calcination of layered double hydroxides: dehydration of adsorbed water, dehydration of interlayer water molecules, and de-carbonation of metal precursors to obtain the corresponding 3-D network mixed metal oxides (Figure 2) [26-27].



dicators (H_) and programmed desorption of CO_2 (CO_2-TPD) [38,46,
].

Next, the most relevant points in the study of mixed oxides/LDHs are ghlighted, considering the main preparation variables and the effects ey produce on catalysts.

.1. LDHs Calcination

The calcination process of lamellar double hydroxides triggers the organization of the structure at high temperatures, which causes the nsfer of trivalent cations from the octahedral sites to the tetrahedral es, promoting the isomorphic substitution of the dimetallic cations in e mixed oxides. This rearrangement generates an excess of positive arge in the structure that is compensated with the generation of two pes of defects resulting from this incorporation: cationic vacancies d/or inclusion of interstitial oxygen in the structure, forming the rresponding metallic oxides [3,16,35,68,69]. The calcination comises the stages of dehydration (moisture), dehydration (interlayer ter) and decarbonation leading to the formation of the corresponding xed oxides [34,70]. However, the decarbonation step will be effecely present in LDH with intercalated carbonate ions, presenting nilar ion removal processes for other ions between the lamellae. Thus, e LDHs gradually lose interlayer water during thermal treatment, then hydroxylate and decarbonate to a significant amount, resulting in the velopment of a mixed oxide with a 3D network (Fig. 3).

Fig. 3. The illustration of LDH transformation due the calcination [71].

Figure 2: 3-D LDH network mixed metal oxides

Characterization of Layered Double Hydroxides

Layered double hydroxides are commonly characterized using numerous techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA).

X-Ray Diffraction Spectroscopy (XRD)

The XRD diffraction profile of layered double hydroxides is the most important spectroscopic method used for determining the degree of crystallinity of the prepared LDHs and the extent of arrangement of the formed layers and the spaces between these layers. Each LDH has its fingerprint indicating its geometrical and crystalline arrangement, which can be considered as an indication of the purity and satisfactory factor of the structure. The unique crystalline structure unit of LDHs is the hydrotalcite structure [28], based on JCPDS file no. 22-700, which determines the characteristic sharp, narrow, and symmetric reflections relevant to low values of 2-theta (θ) of characteristic basal planes (003), (006), and (009). It also revealed the appearance of asymmetric and broad reflections at the higher 2--theta for non-basal (012), (015), and (018) planes. The characteristic 2-theta values of the different LDHs are fixed for each type of LDH, whatever the method used for the preparation, but the difference occurred only in the d-spacing between the LDH layers which depend on the size and type of intercalated ions between the layers.

Scanning Electron Microscopy (SEM)

The SEM is one of the effective reflections for the structural unit of the LDH framework (hydrotalcite). The SEM images of layered double hydroxides commonly expose highly porous plate-like crystalline arrangements in a hexagonal-ordered crystal form [29].

FTIR analysis

The FTIR spectra of the layered double hydroxides represented the characteristic bands of the hydrotalcite compounds. The broad and strong band at 3400 cm^{-1} was ascribed for the stretching of hydroxyl groups and inserted H_2O molecules between the layers of LDHs. The shoulder at 3050 cm^{-1} is due to H_2O-CO_3^{2-} interlayer bridging. The weak band at 1630 cm^{-1} is for the H_2O bending deformation. The intense and sharp bands around 1370-1380 cm^{-1} are designated for the asymmetric stretching of CO_3^{2-} groups. The bands at 460, 550, and 790 cm^{-1} can be endorsed respectively for Al-O groups, Zn/Al-OH translation, and Al-OH deformation [30].

X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a significant tool for identifying the chemical configuration and assessing the oxidation states and the electronic structure of layered double hydroxide surfaces [31].

DTA-TGA analysis

DTA-TGA analyses study the behavior of weight change of the compounds as a function of temperature. TGA determines the variation of the compounds' masses after heating or cooling under different atmospheres or gases. TGA analysis of Zn-Al, as a famous type of LDH, determines the loss of adsorbed or interlayer water molecules, in addition to the intercalated groups of CO_3^-, NO_3^-, and SO_4^{2-} as a function of rising the temperature. Wang and co-authors studied the thermogravimetric analysis of Zn-Al LDH (**Figure 3**) and found that bout 10-14% of the weight was decreased due to the loss of the interlayer water molecules in the range of 50-250 °C [Wang et al., 2019]. In the case of Zn-Al-CO_3, the thermogram showed two stages with a total loss of 21% at 150 °C and 250 °C. The first (at 150 °C) was due to the dehydration of adsorbed and interlayer water molecules, while the second was due to the loss of carbonate groups located within the LDH interlayers. In the case of Zn-Al-NO_3 LDH, four thermogram stages have appeared at 150, 250, 350, and, 450 °C. The first two stages were due to the loss of surface water and interlayer water molecules. The second two stages at 350 °C and 460 °C with a total loss of 21.5% were due to the dehydroxylation of Zn-Al LDH and the decomposition of the interlayer NO_3^- anions.

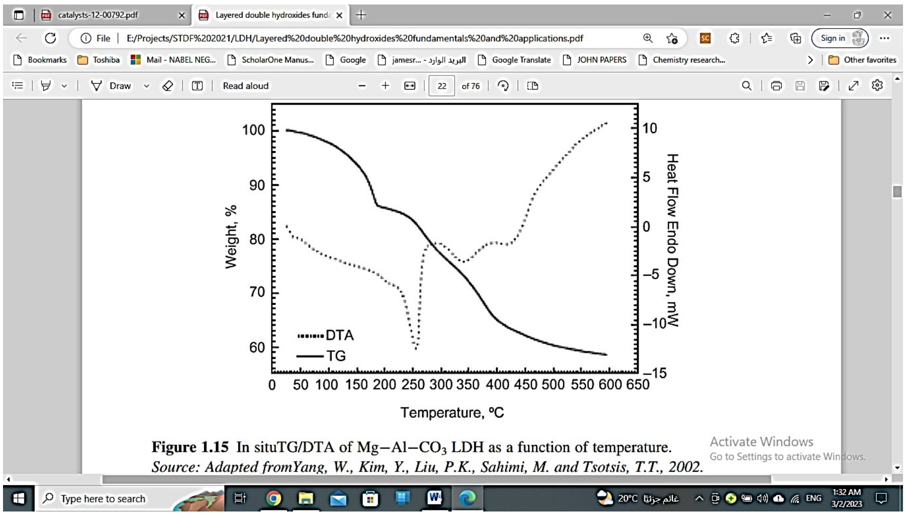


Figure 1.15 In situTG/DTA of Mg–Al–CO_3 LDH as a function of temperature.
Source: Adapted fromYang, W., Kim, Y., Liu, P.K., Sahimi, M. and Tsotsis, T.T., 2002.

Figure 3: Typical thermogram profile of Zn-Al LDH

Potential Applications of Layered Double Hydroxides

Layered double hydroxides are considered a promising nanomaterial due to their outstanding characteristics including the uniqueness in the nanostructure, occupation of several types of metal cations within their layers, active hydroxyl groups located on the surface, simplified synthetic routes, the non-toxicity, flexible tendency in the variation of both cations and anions, excellent anion exchangeability, memory retaining, highly chemical and thermal stability, high power to deliver the intercalated anion in a sustained manner, biocompatibility, electrochemical activity, high surface and pore size, high adsorption capacity, and efficiency, etc. As a result of these marvelous characteristics, layered double hydroxides and their intercalated form with different functional precursors and nanocomposites with superior nanomaterials mainly carbon nanomaterials are considered efficient precursors for vital applications. LDHs and their modified forms have several applications including transesterification for biofuel production, flame retardancy, catalysis, water splitting, and wastewater treatment.

Biofuel Production: Layered Double Hydroxides as Catalysis For Transesterification

The process of biofuel production from oils and fats includes two main processes: transesterification and pyrolysis. The transesterification process includes the reaction of triglycerides with short-chain alcohols to obtain the fatty acid mono ester. Pyrolysis is treating the triglycerides under the influence of heat in the absence of catalysts (thermal cracking), or in the presence of appropriate catalysts (catalytic cracking).

LDHs can be considered as Lewis base catalysts due to the electropositivity of the cations found in their composition, which acquire them active sites effectively in the transesterification process, in addition to the presence of the metal oxides [32]. The presence of the different metal cations in the layered double hydroxides increased their chemical activity. It is reasonable for the catalytic activities to be dependent on the valence and ionization states of the cations, and the temperature applied during the calcination process [33]. The role of the basic sites as well as of other physical-chemical properties of mixed oxides in the transesterification reaction has been widely studied and mentioned in several reports.

Layered double hydroxides with the chemical formula of $[Mg_{(1-x)}Al_x(OH)_2]^{x+}(CO_3)_{x/n}^{2-}$ (x=0.25-0.55) were synthesized by co-precipitation method [34]. The prepared compounds were applied during the transesterification of glyceryl tributyrate in the presence of methyl alcohol to produce the corresponding biodiesel. The conversion rate was increased with increasing the Mg content. The rate was correlated to electron density which increased by increasing the Mg concentration in the different LDHs due to the increased basicity [35]. showed from the comparison study between the thermally treated crab shell and laboratory-prepared CaO that there is no difference between the sources of CaO used in the transesterification process during the conversion of palm oil to biodiesel. Two triglycerides namely: glyceryl tributyrate and soybean oil were used to produce their corresponding biodiesels by methanol using three prepared calcined layered double hydroxides (Li-Al, Mg-Al, and Mg-Fe) [32]. The highest activity was obtained upon using Li-Al layered double hydroxide at 65 °C, while Mg-Fe and Mg-Al layered double hydroxides exhibited less activity in terms of fatty acid methyl ester yields. The higher activity of Li-Al layered double hydroxide was attributed to the presence of a high concentration of the medium and strong basic sites on its surface compared to the high concentration of weak basic sites on Mg-Al and Mg-Fe layered double hydroxides. These findings were provided from CO_2-TPD spectroscopy, which provides a good sight into the types of active sites and their strength on the catalyst surface. The calcination temperature of 450–500 °C gave the maximum activity for Li-Al due to the decomposition of the structure into the corresponding mixed oxide, and lack of crystalline lithium aluminate formation. In a similar conclusion by [36], calcined Ca-Al_2 LDH showed high activity during the conversion of edible, non-edible, and used cooking oils into their corresponding biodiesels. The activity of the used Ca-Al_2 LDH was attributed to the high basic characters of the catalyst which was determined from Hammett CO_2-TPD elucidation.

The transesterification reaction mechanism involves several reported steps, where the adsorption of the reactants takes place on specific points on the surfaces of the catalysts called the active sites [37-40]. Then the rate of the process can be organized by the mass transfer action.

The layered double hydroxides as heterogeneous catalysts are presented in the transesterification medium as solids, while the other components are the biodiesel and the glycerol. Then, the catalyst can be easily separated and recycled an important advantage of heterogeneous catalysts [41].

Structural Variables Influence the Activity of Ldhs During Biofuel Production

The conditions and procedures of the layered double hydroxide preparation have a great influence on the surface properties of the layered double hydroxides. The preparation conditions are including the calcination process of LDHs, acidity or basicity of the medium, reaction temperature, concentration of the reacted metal ions, and time of the reaction. The preparation procedures are including co--precipitation, hydrothermal, sol-gel, etc. [42].

Calcination Process of Ldhs

The thermal treatment (calcination process) of layered double hydroxides leads to substantial alterations in the organization of the components of LDHs [43]. This process endorses the catalytic activities of layered double hydroxides including the activity of the basic strength reactive sites, and greater reactive surface area.

Basicity and Basic Sites of Ldhs

The formation of the basic site mechanism can be described by the fact that deformation occurred in the crystalline structure of the catalyst crystals. Calcination cause the incorporation of metal oxides within the deformed crystals, which compensate for the generated positive charges. The presence of O^{2-} anion in the deformed system generates the basic active sites. The generated basic sites can be arranged as weak, medium, and strong sites when located in the function groups OH^-, Mg-O, and O^{2-} [4].

Doping of Metal Ions in Ldhs

It was reported that layered double hydroxide activity in terms of surface basicity is altered by modification of their chemical structures by different metals. The most reactivating metal ions are Fe^{3+}, Cu^{2+}, and Zr^{2+} [44]. The CO_2-TDP measurements showed that the layered double hydroxides doped by Cr^{3+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} were increased their catalytic activities during the transesterification process [45].

Flame Retardancy Applications

Flame retardants by definition are quite different from the term flameproof. The former simply indicates that the product has been modified to reduce the flammability of the substrate, or, delay the combustion or reduce the rate of combustion. The flame retardant is likely to charge or melt in the presence of flame. All flame retardants act either in the vapor phase or in the condensed phase through a chemical and/or physical mechanism to interfere with one or more of several processes. Gas dilution: use of additives that decompose into non-flammable gases. This reduces both fuel and oxygen levels in the vicinity of the flame. This type of flame retardant includes organic halides and some nitrogen compounds. Thermal quenching: flame retardants that undergo endothermic decomposition reduce the rate of burning. This type of flame retardant includes metal hydroxides, metal salts, and some nitrogen compounds. Protective coating: additives that promote charring or the formation of a liquid barrier, thus shielding the flammable material from fire. This type of flame retardant includes phosphorus compounds and intumescent systems based on nitrogen or phosphorus compounds. Physical dilution: introduction of an inert non-flammable component (e.g. glass or minerals). Chemical interaction: a flame retardant that decomposes into radical species, which compete effectively with the burning process, and this type, include halogenated compounds.

Layered double hydroxides are swearing green flame retardant materials and can retard the development of flame in three ways. (1) It acts as a heat sink due to the endothermic deterioration, (2) It deteriorates to assemble mixed metal oxides which achieve an insulating film on the surface, (3) It discharges bounded water and carbon dioxide thereby diluting the flammable gases [46].

The flame retardancy of LDHs can be improved by intercalating appropriate anions such as borate, phosphate, etc. into the inter lamellar region of LDH so that a single substance such as LDH comprising zinc cations and borate anion can execute the synergistic influence of three commercial flame retardants magnesium hydroxide, aluminum hydroxide and zinc borate.

In the study of [47], pure ethyl vinyl acetate burned very fast after ignition with a sharp heat release rate (HRR) at 50-300 seconds accompanied by a total heat release of 1695 kW/m^2. The loading of the polymer on LDH to form an ELDH composite modified the value of HRR to 227 kW/m^2. Modification of the form of LDH by sodium dodecyl sulfate (SDS) and 3-aminopropyl) triethoxysilane (KH) to form the final polymer composites of ELDH-SDS, and ELDH-SDS-KH yielded a highly stable polymer with THR values of 221 kW/m^2, and 195 kW/m^2, respectively. The reason for the obtained stability was ascribed to the fact that [48], the generated carbonaceous layer (char), H_2O, and CO_2 diluted the oxygen and volatile products, and reduce the transfer of heat between the polymer matrix and the source of heat by captivating the prime heat and disturbing heat transfer at the polymer surface.

The flame retardancy synergistic effect of exfoliated layered double hydroxides (LDH) with halogen-free additives [49] such as hyperfine magnesium hydroxide (MH), microencapsulated red phosphorus (MRP), and expandable graphite (EG), in low-density polyethylene/ethylene vinyl acetate copolymer (LDPE/EVA) nanocomposites, was studied. The oxidative degradation temperatures of LDPE/EVA polymer composites modified by MH, MRP, and EG samples in the presence of LDH were increased up to 472, 476, and 479 °C, respectively, which are 7–12 °C higher than LDPE/EVA polymer composites with the same additives and in the absence of LDH. The reason was attributed to the high char residues formed in LDH-containing samples than in the samples without LDH, and it is reported that higher residual weight is accompanied by greater flame retardance ability. The higher thermal stability in the presence of LDH can be endorsed to the development of charred layers efficiently and hindered oxygen diffusion and flammable products.

Sulfamic acid-intercalated Mg-Al-LDH (SA-LDH) was prepared and introduced into polyamide 11 (PA11) by melt blending at 2.5% and 5% ratio, as well as the unmodified LDH [50]. The flame retardancy of the polymer and its modified forms with LDH and modified LDH were studied. The calorimeter results established that SA-LDH effectively decreases the heat release rate, which may be ascribed to the good distribution of SA-LDH compared to LHD in the PA11 matrix. Lamella-scattered LDH endorsed the establishment of protective charred layers. As a result, HRR was reduced and combustion was spread out over time. A higher modification ratio of SA-LDH decreased HHR to 592.9 kW/m^2 (13% more than PA11).

Polyethylene (PE) was modified by the addition of a layered double hydroxide of zinc aluminum oleate (Zn-Al) and commercial fire retardants [51]. Commercial additives included mainly phosphate derivatives such as ammonium polyphosphate, triphenyl phosphate, and resorcinol diphosphate. The thermal stability and the combustion behaviors of the new composite polymeric materials in the presence of Zn-Al LDH, in addition to antimony oxide, were improved. The addition of these additives leads to a high reduction in heat release rate (HRR) up to 72%, while the combinations of PE with other additives give reductions in the range of 20-40%.

Three LDHs composites were prepared including LDH, SDS-intercalated LDH (SLDH), and 2-carboxyethyl (phenyl) phosphinic acid-intercalated LDH (CLDH); followed by the compounding with ammonium polyphosphate (APP) and pentaerythritol (PER) as an intumescent flame retardant and tested their efficiency as flame retardant for polyethylene including their influences on the thermal degradation and combustion behaviors of the composites. According to the TG results, the interactions between LDHs and IFR encouraged the formation of intumescent char and enhanced the thermal stability of the char at a high temperature. LDH and CLDH improved the char formation of the composites while SLDH had negative influences on char formation ability.

Ammonium polyphosphate (APP) modified Mg-Al layered double hydroxide (LDH) flame retardants (FR) were prepared in APP concentrations of 5% (PLDH-5), 10% (PLDH-10), and 15% (PLDH-15) [52]. The PLDH-treated leathers showed an increase in the thermal stability of the endothermic dehydroxylation and decomposition observed in the DSC studies indicating the suitability of the PLDH as flame-retardant material. The application of 3% PLDH during leather making improved the flammability degree of leather by 18%. The prepared PLDH exhibited corresponding flame retardance performance compared to the reported flame retardant chemicals for leather protection. The spread of the fire was suggested to be prevented using the modified LDHs according to two steps (**Scheme 1**) [53,54]. Firstly, the endothermic dehydroxylation of Mg-Al layered double hydroxide generates metal oxides and water vapor (water decreases the temperature of the system). The firmness of the formed char is increased due to the presence of P-O-P linkage coming from the phosphate ions present inside the leather matrix. The compact char layer performs as a block barrier between the leather and fire. Moreover, in the presence of nitrogen (from APP/leather), phosphorous might exhibit swelling when heated as well.

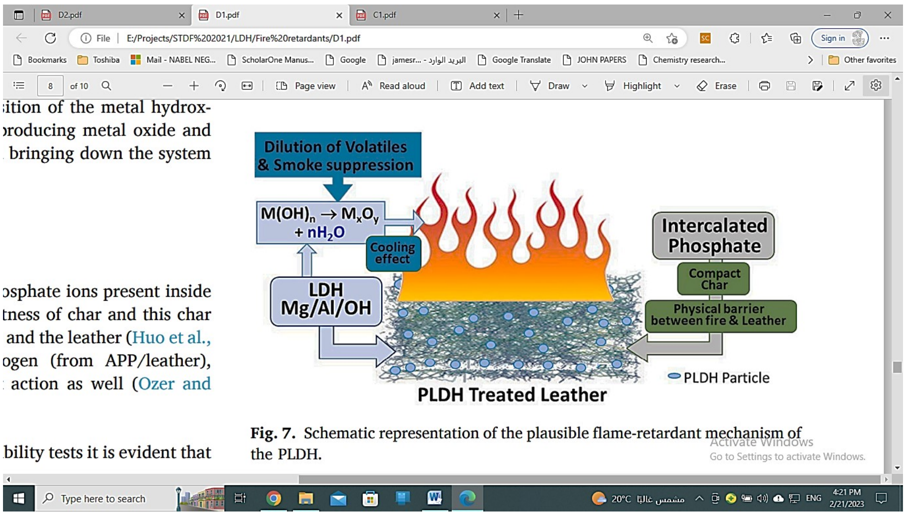


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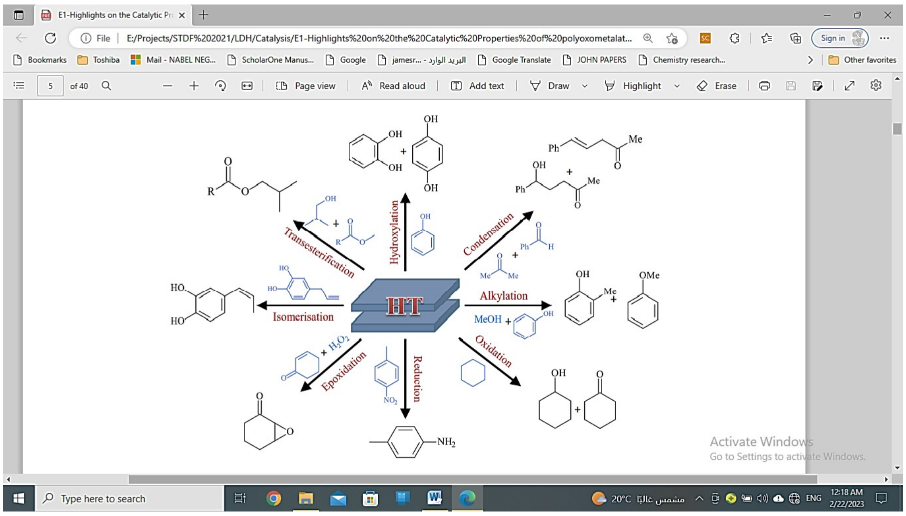
Fig. 7. Schematic representation of the plausible flame-retardant mechanism of the PLDH.

Scheme 1: Schematic presentation of the suggested flame retarding mechanism of the PLDH

The bamboo surface was successfully coated by uniform and dense in-situ one-step prepared Mg-Al-LDH. The ignition properties of the treated bamboo surface with Mg-Al-LDH were compared with the untreated bamboo. The Mg-Al-LDH-Bamboo-24 hour ignition time was stretched by 11 s, THR was decreased by 28%, and the total gas emission was also reduced by 89%. The results show that LDHs can effectively improve the flame-retardant and smoke characteristics of bamboo. The thermal stabilities of uncoated bamboo and that coated by Mg-Al-LDH were analyzed by thermogravimetric analysis and differential scanning calorimetric measurements under N_2-atmosphere and air. The inert gas released by Mg-Al-LDH and the charred coating molded by the decay of LDH can encourage the carbonization (char formation) of bamboo, which hinders its continuous decomposition. In the same manner [55], applied a coating of Mg-Al layered double hydroxide (LDH) on a wood surface for flame retardant applications by a two-step synthetic method and the formation of a coating on the surface of the wood was confirmed by SEM analysis. The limiting oxygen index enhanced from 19% to 39% and the heat release index and smoke emission decreased by 40% and 58%, respectively concerning untreated wood. The enhancement in flame retardancy can be attributed to the endothermic decomposition of LDH into mixed metal oxide which resulted in char formation.

Catalysis

The flexible composition and tunable fundamental properties of layered double hydroxides elucidate their catalytic usage and fit their field of applications [56]. As solid base catalysts, LDHs exhibit high potentials and selectivity towards various types of reactions, mainly organic transformations (Scheme 2), including alkylation, isomerization, hydroxylation, transesterification, hydroformylation, redox reactions, and condensation. Moreover, the mixed oxides that were obtained after thermally treatment (calcination) of the LDHs exhibit worthy catalytic activities, and several organic reactions [57].



Scheme 2: Schematic representation of different organic transformations

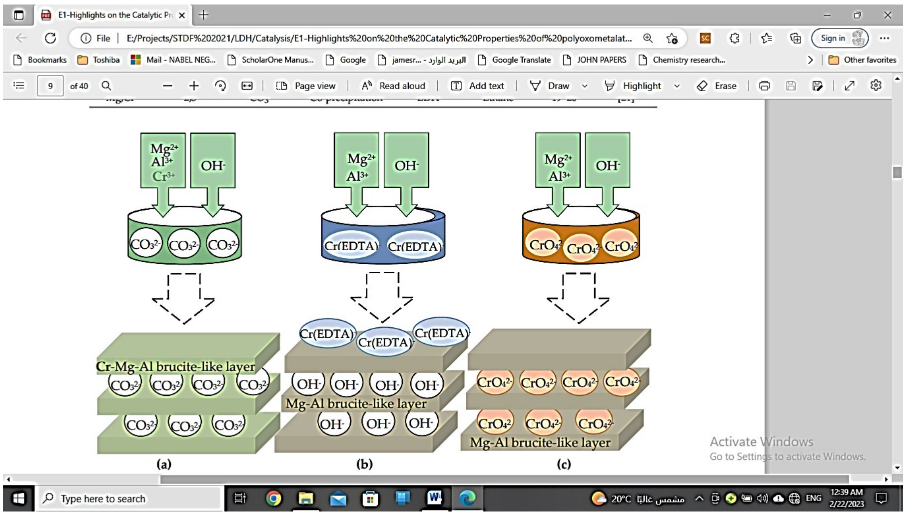
The thermally treated and untreated LDHs have been widely used as stable and recyclable heterogeneous catalysts or catalyst supports for a variety of reactions benefitting the flexible tuneability and uniform distribution of metal cations in the LDH layers and the facile exchangeability of intercalated anions. Layered double hydroxides are promising heterogeneous solid base catalysts for several organic transformations due to the abundance of hydroxyl groups. On heating between 450-500 °C, LDHs have been changed to mixed metal oxides having several Lewis base sites and enhanced surface area which results in high catalytic efficiency. The rehydration of mixed metal oxide in the absence of CO_2 can reproduce LDH with OH intercalated anion and this activated LDH possesses abundant Bronsted-type basic sites.

Intercalation of LDHs

The catalytic efficiency of binary LDH can be enhanced by incorporating a third cation to form a ternary LDH. The catalytic activities of layered double hydroxides are depending on the type of cations and the nature of the intercalated anion. The intercalated anions are different based on their size and chemical structure of these anions, i.e., nuclearity.

Small-Nuclear Polyoxometalate Anions Intercalated LDH

LDH systems host low-nuclear polyoxometalates, being mainly intercalated by chromate, dichromate, and chromium anions, such as Cr-(EDTA), $[Cr\text{-}(SO_3\text{-}salen)]^{2-}$. These types of LDHs had favorable catalytic activities, especially in the oxidation and alkoxylation of alcohols. CrO_4^{2-} and $Cr_2O_7^{2-}$ anions are deceptive anionic contaminants in wastewater, so the assimilation of chromates into layered double hydroxides justifies great attention because they can protect the aquatic environment, and also have valuable applications in the catalysis of several reactions with important products [58]. Co-precipitation, anion exchange, and reconstruction procedures were reported as efficient methods for the synthesis of LDH containing divalent/trivalent cations intercalated with chromate in the brucite-like layers, where the anions of CrO_4^{2-} and $Cr_2O_7^{2-}$ are located in the interlayer and mostly depending on the nature of the brucite-like cation [59-62]. The synthetic strategies that were applied for preparing LDH precursors of chromium catalysts can be seen in **Scheme 3**, and they consist of (i) conventional co-precipitation of metal cations with carbonate counter-ion under basic conditions; (ii) co-precipitation of Mg(II) and Al(III) with EDTA chelate of Cr(III) form a chelate of 1:1 stoichiometry with (EDTA), EDTA is thermodynamically stable than Mg(II) or Al(III) [63]; and (iii) co-precipitation of Mg(II) and Al(III) with CrO_4^{2-} anions presented at the slightly excess concentration required for stoichiometry in the medium. The LDH-intercalated sulphonato-salen-chromium(III) exhibited good catalytic activity during the preparation of dihydroxyacetone in the selective oxidation of glycerin in the presence of 3% H_2O_2. That was attributed to the balancing consequence that existed between the sulphonato-salen-chromium(III) and the weak base LDH [64,65] prepared a series of POM/LDH nanocomposites constructed by Cr^{2+} and Cu^{2+} cations in the construction of the layered double hydroxide and intercalated by CrO_4^{2-} or $Cr_2O_7^{2-}$ anions between the layers. The compounds have been tested in the catalytic synthesis of glycol ethers during the ethoxylation reaction of butyl alcohol by ethylene oxide.



Scheme 3: Synthetic approaches for the preparation of LDH precursors of chromium catalysts. Adapted from ref [63]

The safe influence on the environment, simple synthetic route for production, inexpensive precursors cost, and superior stability placed the intercalated layered double hydroxides with different chromium-based anions such as chromate, dichromate, Cr-(EDTA)$^-$ and [Cr-(SO_3-salen)]$^{2-}$ as talented catalysts for numerous catalytic reactions.

Medium-Nuclear Polyoxometalate Anions Intercalated LDH

Systems of LDH intercalated by medium-nuclear polyoxometalates accommodate either molybdenum or vanadium-based anions. Molybdate and vanadate layered double hydroxides (Mo-LDH, V-LDH) exhibit efficient catalytic activity during oxidation and epoxidation reactions.

Vanadates

The co-precipitation, anion exchange, reconstruction, and hydrothermal techniques are the most reported techniques for the preparation of the layered double hydroxides intercalated with vanadate anions hosting divalent/trivalent cations in the brucite-like layers. Vanadium anions can be interlayered in the layered double hydroxides based on the constructing cations and acidity or alkalinity of the medium and may be introduced as a cation V(III) in the layered double hydroxides of the brucite-type layers.

[66] reported the simple preparation of decavanadate-intercalated LDH containing Mg^{2+} and Al^{3+} cations using a direct ion exchange of nitrate precursor with mild acidic $NaVO_3$ solution after pre-swelling using terephthalate. The XRD patterns, Raman, and IR spectroscopic profiles demonstrated the existence of decavanadate ($[V_{10}O_{28}]^{6-}$) anions in the interlayer region. The prepared decavanadate-intercalated LDH is categorized as a selective epoxidation catalyst for allylic and homoallylic alcohols. In a similar protocol, [67] have synthesized LDHs intercalated with decavanadate and pervanadate anions instantaneously. The oxidative catalytic activity of the prepared LDHs was assessed during the catalytic oxidation reaction of the tetrahydrothiophene to sulfolane in the presence of hydrogen peroxide. Also [68], intercalated decavanadate anions in brucite-type layers of Mg-Al-LDH and proved the presence of two vanadate anionic types of $(VO_3)_n^{n-}$ and $[V_{10}O_{28}]^{6-}$ based on the Raman spectroscopy bands at 800-1000 cm^{-1} and 200-370 cm^{-1}.

Molybdates

The intercalation of molybdenum-based anions in the structure of layered double hydroxides depends on the pH of the medium and the concentration of Mo(VI) cations, where pre-dominant molybdate anions are $[MoO_4]^{2-}$, $[HMoO_4]^{-}$, $[Mo_6O_{19}]^{2-}$, $[Mo_7O_{24}]^{6-}$, $[HMo_7O_{24}]^{5-}$, $[H_2Mo_7O_{24}]^{4-}$, and $[Mo_8O_{26}]^{2-}$ [Davantes and Lefevre, 2013]. The intercalation of molybdates has been restricted in the interlayer space of layered double hydroxides due to the formed heptamolybdate $[Mo_7O_{24}]^{6-}$ ions which can be stabilized at low pH conditions and acted in expanding the spacing between the brucite-type sheets [69]. The anionic exchange method is widely applicable during molybdate assimilation in the framework of the MgAl-LDH composite. [70] described a new methodology based on the classical ionic exchange method, which comprises the preparation of an anion-pillared organic precursor that is consequently replaced by suitable polyoxometalate anion in acidic media.

Systems hosting high-nuclear polyoxometalates are mainly LDHs which are intercalated by tungsten-based anions. The reported catalyzing activity of LDHs intercalated with tungsten anions indicated their suitability during epoxidation of alcohols and oxidation of organosulfur compounds including sulfides, benzo- and dibenzothiophene. Polyoxotungstates have various configurations with fixed sizes and shapes and had diverse applications [71]. Preparation of the intercalated LDHs within tungstate-based anions is strongly dependent on the temperature, reaction time between LDH, polyoxometalates, and pH of the medium [72]. Polyoxotungstates structures intercalated the interlayers of the layered double hydroxides in different forms such as Keggin, Dawson, or Finke type.

Moderate chemoselectivity was obtained during the methoxybromination of aliphatic olefins, while regioselectivity and stereoselectivity were high in the case of methoxybromination of aromatic olefins and aliphatic olefins [73]. Mild oxidative bromination was exhibited using Mg-Al-Cl-LDH and Ni-Al-Cl-LDH exchanged with tungstate [74]. Cyclohexene epoxidation was catalyzed by modified Mg-Al-hydrotalcite-intercalated organotungstic complexes. The modified Mg-Al-LDH was performed by anionic exchange and complexation with incorporated phosphonic acid in the sheets [75]. Polyoxometalates $[H_2W_{12}O_{40}]^{6-}$ and $[W_4Nb_2O_{19}]^{4-}$ have synthesized and intercalated in brucite-like layers of Mg-Al- and Zn-Al-LDHs via anion exchange method using nitrate LDH precursors as a starting material. The modified LDHs were used to catalyze the epoxidation reaction of cyclooctene using hydrogen peroxide [76]. The photocatalytic degradation of malachite green (MG) was improved by LDH pristine Mg-Al-LDH and LDH composite of Mg-Al-$SiW_{12}O_{40}$ and Mg-Al-$PW_{12}O_{40}$ [77].

Layered Double Hydroxides Supported by Carbon-Based Materials

LDH/nanocarbon catalysts had substantial consideration for their importance in enormous reactions such as Michael addition [78], Knoevenagel reaction [79], Ullman reaction [80], Sonogashira reaction [81], Heck reaction [82], and chalcone synthesis [83]. Assembling hollow flower-like LDH [84] and N-, S-doped graphene acting as support for Pd-NPs gave hollow inner and mesoporous hierarchically flower composites. Sandwich-like structures were obtained by the intercalation of LDH and reduced graphene oxide (rGO) [85], and multi-wall carbon nanotube (MWCNT) [86]. The interfacial electron transfer is considered a chief specificity of LDH/carbon composites [87], which is promoted by significant electronic mobility in the carbon components. That leads to charge redistribution by the interaction with the less conductive LDHs. Carbon dots-based LDH/nanocarbon [88] offers opportunities for improving electron transfer. Ni-Al LDH/CNTs nanocomposite displays electro-catalytic activity during glucose electro-oxidation rather than Ni-Al LDH electrode or CNTs electrode [89]. This was attributed to the ability of carbon nanotubes (CNT) to transport additional electrons among Ni ions and electrodes, also CNT promotes the diffusion of the reactants throughout the provided porous complex framework [90].

It is significant to focus on the good strength and reusability of LDH/ CNT catalysts as crucial properties during the applications. It included high mechanical strength of CNT in pure form and assembled with LDHs. Further, the strong metal-CNT interaction performs good stability against leaching and efficient regeneration of the catalytic active sites.

Water Splitting

Hydrogen as a maintainable energy source is an alternative to traditional petroleum fuels to alleviate soil pollution and warming gases evolution [91].

Hydrogen production through the photochemical or electrochemical splitting of water is cheap, effective, and environmentally safe. Thereby, the problem of providing hydrogen as a fuel for energy production can be solved. Precious metal oxides of platinum and iridium/ruthenium oxides are the most used catalysts in the hydrogen evolution reaction and oxygen evolution reaction [92-94]. However, their high cost and poor stability limit large-scale utilization. Thus, it is crucial to fabricate highly efficient catalysts for electro-catalytic applications.

Layered double hydroxide nanocomposites can act as excellent photo-catalysts and electro-catalyst for the water-splitting process. The important characteristics of the layered double hydroxide include cation-exchange capability, anion-exchange capability, high adsorption capacity offer augmentation during light absorption, anion-cation separation, electron transmission, electrode reaction kinetics, and roughness. Recently, the fabrication of LDH-based nanocomposites was highly progressed in the field of water splitting trend. To optimize the catalytic activity of LDHs, different modification strategies have been developed through the defect of formation and charge transfer.

Defect of Formation

The defect of crystalline structures is significantly accredited for promoting the slow reaction kinetics, which pointedly promotes the activity of the active sites, maximization of intrinsic kinetics, increasing the effective surface area, and enhancement the electric conductivity, which increases the water splitting efficiency [95]. Vacancies of oxygen are the famous anion vacancies in oxides of different transition metals due to the small energy of formation [96]. Metal oxides containing oxo-, and hydroxides with enormous oxygen vacancies offered higher activities compared to the untreated metal oxides [97]. Vacancy-merged CoOOH nanotube arrangements were designed for effective oxygen evolution reactions [98]. By introducing the oxygen vacancies, the Vacancy-merged CoOOH nanotube was compactly exposed by the generation of nano-sheets and nano--sized pores and showed a huge effective surface area compared to the untreated CoOOH. At alkaline pH media, vacancy-merged CoOOH exhibited 40 mV lowering at 10 mA.cm^{-2} current density after deficiency formation, which signified that vacancies of oxygen have a progressive role in directing oxygen evolution reactions. For instance, A-site cation–deficient $La_{1-x}FeO_{3-\delta}$ perovskites offered exceptional oxygen evolution reactions activities due to the development of oxygen vacancies (O_2^{2-}/O^- species) and low Fe^{4+} species [99]. Lattice disruptions and enlargement and distortion surface stepping, and boundaries are additional protocols that can be applied in the electro-catalysts frameworks for enhancing their efficiency.

Charge Transfer

Modified layered double hydroxides (LDHs) were studied as catalysts for optical and electrochemical processes due to their exceptional two-dimensional and compositionally tunable structures [100]. LDHs exhibit large adsorption capability and tunable band-gap, consequently, they are appropriate for the ionic exchange process (cation-anion exchange) and offer space and position separation of redox-reaction sites for effective generation of hydrogen and oxygen during the water splitting process [101]. Furthermore, the lamellar structures of LDH permitted different crystalline sizes, shapes, and morphology, in addition to the types of cations and anions. These properties strongly influence the effectiveness of charge transfer and separation, and consequently alerted the efficiency of the photo-catalytic energy process [102]. The recent modifications were focused on the modification of the chemical structure, morphology, size, and electrical properties of LDH. The modification of electrical properties and charge separation capability was achieved by picking innovative carbon supports, e.g., carbon quantum dot [103], graphene oxide [104], graphdiyne [105], and graphitic carbon nitrides [106]. These substrates have the talent to endorse the photo- and electro-catalytic capability of layered double hydroxides.

LDH materials containing transition metal cations, especially Ni and Co have been widely applied in electrocatalytic reactions. The intercalation of simple metal oxy-anions and POMs in LDH hosts can lead to photo-catalytic capability. Layered double hydroxides containing different transition metals (e.g., Co, Ni, Fe, etc.) are talented electro-catalysts due to their unique lamellar structure and rich active sites. [107] improved a technique for converting cheap Fe substrates into ultra-stable electrodes for the oxygen evolution process. This technique was attained by the corrosion process of Fe-substrates using aqueous solutions containing oxygen and Ni^{2+} at room temperature. The output of this technique was the nano-sheet growth of Fe-containing layered double hydroxides on iron instead of rust. [108] reported that the electrodeposit-support of graphene layers enclosed by NO_3^- ion was considerably improved. For the electro-catalytic oxygen evolution reaction, the resulting cerium dioxide in the nano-crystalline and amorphous forms of $Ni(OH)_2$ displayed a lower over-potential value of 177 mV at 10 $mA.cm^{-2}$ current, with high durability reached 300 hours at 1000 $mA.cm^{-2}$. Amorphous mesoporous Ni/Fe nano-sheets were established by direct electro-deposition on nickel foam and applied as oxygen electrodes used for oxygen evolution reaction in the water splitting process [109]. The electrode displayed high efficiency during the water splitting process in aqueous media with 200 mV potential to provide 500 $mA.cm^{-2}$ and 1000 $mA.cm^{-2}$ current densities at 240 mV and 270 mV potentials, respectively [109].

Layered double hydroxides modified by different transition metal ions such as Fe, Co, Ni, Zn, and Mn were widely investigated for oxygen and hydrogen evolution reactions. A catalysts series for oxygen evolution reaction in an alkaline aqueous medium were established such as metal oxides [110], metal hydroxides [111], metal selenides [112], metal sulfides [113], metal carbides [114], and metal phosphides [115,116]. Cobalt and nickel-modified layered double hydroxides were fabricated by Yang et al. [117], who intercalated their structures by $CoNiSe_2$ to catalyze H_2O--chemisorption and yield reactive hydrogen-containing intermediates to achieve an effective water-splitting process. In this consequence, the electro-deposition of amorphous NiFe hydroxides on the surface of NiFeP was performed to obtain a layered double hydroxide hybrid structure [118]. The obtained catalysts are characterized by electronic interactions with high capability towards enhancing the water-splitting reaction through depressing the adsorption energy of H_2O. Metal phosphides and NiFe layered double hydroxides can reimburse the presented weaknesses in each separate catalyst by combination and achieved bi-functional oxygen evolution reactions of hydrogen and oxygen simultaneously [119,120].

Wastewater Treatment

The discharge of huge amounts and types of contaminants into water bodies is occurred due to the accelerated progress of industrial and agricultural development [121,122]. Consequently, these developments cause contamination of rivers and underwater by diverse pollutants, including dyes, metals, Emerging organic compounds, and oxygenated anions. Several methods are used for the treatment of wastewater using LDHs (Figure 4).

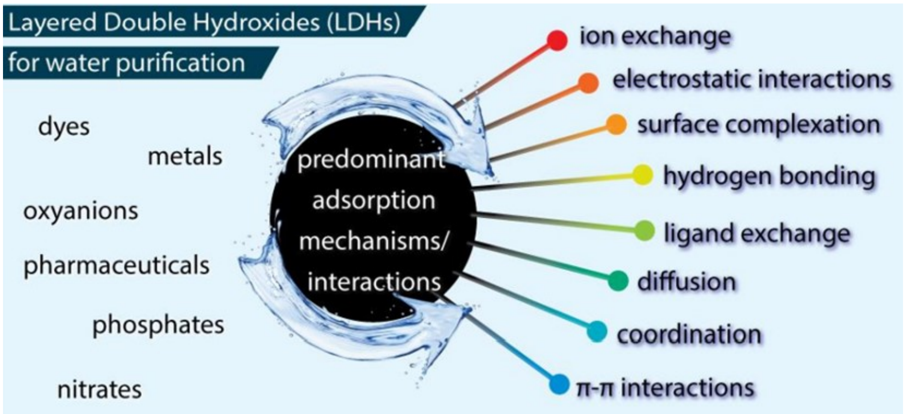


Figure 4: Methods performed during wastewater purification using LDHs

Dyes are used for textile dyeing, foodstuff, paper production, and pharmaceutical industries. Textile activities discharge about 10-15% of dyes in the water resources. The dyes comprise low concentrations a threat to the environment due to their reducing influence on photosynthesis and consequently the oxygen concentration for the aquatic organisms. Furthermore, the degradation pathways of different dyes produce toxic and carcinogenic intermediates

[123,124].

LDHs were reported as an effective eliminator for various industrial anionic and cationic dyes [125]. LDHs and activated carbon have the same attitude during the removal of anionic and cationic dyes, respectively [126]. It was reported extensively the high remediation efficiency and adsorption capacity for the removal of cationic dyes by various LDHs [125]. Two different layered double hydroxides (Mg-Al LDHs) were prepared by co-precipitation method using dodecyl sulfate (Mg-Al-DS) and carbonate (Mg-Al-CO_3) and were assessed for removal of methyl orange from the wastewater. Mg-Al-DS and Mg-Al-CO_3 exhibited optimum capacities of 185.1 mg/g and 97.5 mg/g, respectively. The pH of the medium does not influence the efficiency of Mg-Al-DS LDH, while acidic to neutral medium increases the efficiency of Mg-Al-CO_3 LDH. The mechanisms of the remediation process were suggested as anions exchange of Mg-Al-CO_3 for methyl orange anions dye; association of dye anions to positive charges of LDHs [127].

Carbonate anions LDH (Mg-Co-Al-CO_3 LDH) was synthesized through the co-precipitation technique and used for the removal of RB19 dye from the wastewater [128]. The suggested roles of the prepared LDH were electrostatic attraction, physical adsorption, and chemical bonding. Ahmed et al. [125] arranged Mg-Fe-LDHs nanoparticles using the precipitation technique and applied them for the adsorption of Congo red dye from an aqueous medium. The adsorption roles of the prepared LDH were physical and chemical interactions.

Metals are released into the environment from industrial activities, mainly: battery, electroplating, and mining industries, which release huge amounts of heavy metals such as cadmium, lead, mercury, copper, nickel, chromium, and arsenic. Transition metal ions are accumulative in nature (not-biodegradable) and have high toxicity [129,130]. LDHs were first reported as adsorbents for Pb^{2+}, Cu^{2+}, and Zn^{2+} by the Satoshi Fujji group [Fujji et al., 1992].

Several mechanisms or interactions were proposed for describing the adsorption of metal ions by LDHs, such as surface complexation, isomorphic substitution, surface precipitation, electrostatic interaction, and chelation [131,132]. Ca-Fe double hydroxides LDHs modified with 3-aminopropyl triethoxysilane were prepared and their nanocomposites with polyaniline in 5% and 10% mixing ratios were composed [133]. The prepared composites were applied during the adsorption of Pb^{2+} ions from their aqueous solution. LDH composite containing 10% polyaniline exhibited an adsorption capacity of 110 mg/g, while that containing 5% polyaniline had 56 mg/g capacity.

Zn-Ni-Cr double-layer hydroxides (Zn-Ni-Cr-LDHs) characterized by a surface area of 354 m^2/g were prepared using microwave hydrothermal technique and used for removal of Cr^{6+} ions from their solution. The proposed role of the prepared adsorbent was principally an electrostatic interaction of the Cr^{6+} ion and the adsorbent with an optimum capacity of 28.2 mg/g [132]. Sodium alginate intercalated with Mg-Al-LDH (SA-LDH) was prepared and applied during the removal of three metal ions from the aqueous solutions, mainly: Cd^{2+}, Pb^{2+}, and Cu^{2+} [134]. The prepared LDH exhibited optimum capacities at 60 mg/g, 243.7 mg/g, and 95.6 mg/g for Cu^{2+}, Pb^{2+}, and Cd^{2+} metal ions. The proposed roles of the prepared LDH were bonding or complexation with hydroxyl or oxygen groups at the surface, precipitation, substitution, and chelation mechanisms.

Organic compounds, especially benzene and poly-nuclear derivatives such as phenol, benzene, toluene, and xylenes have severe health harm to the lung, kidneys, and heart. Even though these contaminants are at low concentrations in water, their negative impact on the environment is very effective due to the accumulation tendency in all tissues [135].

Oxygenated anions contaminants are including the diverse type of anions found in the wastewater, including sulfates, nitrates, chromates, permanganates, arsenate, phosphates, selenates, and borates anions considered hazardous for living organism's humans at low concentrations [136,137].

Zirconium-modified Mg-Al-LDH layered double hydroxides were prepared according to the co-precipitation technique followed by calcination to obtain the oxide form Zr-LDO and used during adsorption of phosphate oxo-anions from their aqueous solution [Motandi et al. 2022]. Zr-LDH and Zr-LDO exhibited maximum adsorption capacities at 99.5 mg/g, and 80.3 mg/g, respectively. Mg-Al double hydroxides (Mg-Al LDHs) were prepared using a one-pot in-situ hydrothermal method [Jung et al., 2021] for the removal of phosphate and arsenate oxo-anions from their aqueous solution. The maximum removal capacities were obtained at 33.2 mg/g and 56.3 mg/g for phosphate and arsenate from Mg-Al LDH prepared using a 2:1 molar ratio of Mg and Al at 150 °C. In the case of a mixed system, these values were 20.3 mg/g and 16.2 mg/g for phosphate and arsenate. The ion exchange mechanism was suggested to occur during the removal of arsenate or phosphate anions through their exchange by the nitrate interlayer anions. While, in mixed anionic solutions, a coordination mechanism was suggested. The co-precipitation technique was applied in the preparation of Fe-Mg-Mn-LDH [Zhou et al., 2020]. The prepared Fe-Mg-Mn-LDH exhibited high removal capacity during the remediation of nitrate anions from their aqueous medium reached to 10.6 mg/g. The mechanisms of remediation of nitrate anions on the fabricated LDH adsorbent were electrostatic attraction and ion exchange mechanisms.

Mechanisms of Remediation by Layered Double Hydroxides

Several mechanisms were described for the remediation of pollutants from the environment using the layered double hydroxides, which are:

1- Physical adsorption: physical adsorption has occurred on the surface of the layered double hydroxides own to their comparatively higher surface area, and the presence of positively and negatively adsorptive active sites on their surface. That increased their adsorption capacities rather than the most known traditional adsorbents. Modification of the adsorption capability can be performed for the layered double hydroxides (LDH) throughout the calcination of their structures at elevated temperatures reaching 700 °C to obtain their oxide forms (LDO).

2- Ion exchange mechanism: this occurred as a result of exchanging the structural anions or cations presented in the interlayer's framework of LDHs by the cations and anions present in the medium as pollutants, and can be effectively applied for charged pollutants. This mechanism also can be associated with the chelation of the ionic species by the d-transition in the crystalline structure of LDHs.

Conclusion and Prospective

Studies have proven that replacing the layers-forming cation effectively regulates the role of anion exchange for LDH. Still, they focus only on the phenotypic and morphological description of their structures, and the results during LDHs are used without studying and analyzing the role of this mechanism. The coordination of metal cations in LDH systems either binary or multi-component and the variation of their crystalline structure is the role to control and regulate the crystal structures and the corresponding crystallinity. Only the coordination interaction between the metal cations in Ni-Fe system LDHs has, however, been thoroughly and methodically explored. The study in this field is too dispersed, and no regular theory has been compiled, although horizontal and longitudinal comparison trials are a useful strategy. Further research could close this gap.

As for the layered-double hydroxide compounds modified with active carbon, it was found that they have not yet been sufficiently analyzed during the photolysis of new pollutants that have now appeared and need to conduct more in-depth experimental studies in the coming topics.

1- The activated carbons that are combined with LDHs need to be diversified in terms of biomass sources used in preparation. Currently, there are many sources of carbon from biomass, but reports indicate that few can be used to produce LDH compounds industrially. In the future, more research should be done to study the preparation of LDH from biomass carbon.

2- Mechanistic analysis of the degradation of organic pollutants by LDH-Carbon composites is not precisely adequate. Although the performance of active radicals in photocatalytic decomposition reactions has now been confirmed, the improvement of carbon components in composites to pollutant decomposition is still unclear, as how the inclusion of carbon materials influences the transmission pathways or efficiency. It is unknown whether Photogenerated electrons are not described in detail. In the coming up, research on the mechanism by which organic hazardous waste is decomposed by LDH-C will be reinforced.

3- The application of research on LDH-Carbon-based composites in practical wastewater remediation isn't well developed. Research should be moved toward pilot plants and industrial production to study more parameters for the industrialization of wastewater remediation.

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