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Review

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Functionalized layered double hydroxide applied to heavy metal ions absorption: A review

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Abstract: The use of functional material can help mitigate the pollution by heavy metals, which presents an array of risks to human production and life. This work provides a comprehensive review of the current knowledge on functionalized layered double hydroxide (LDH) as a heavy metal absorption material, by synthesizing the information from a total of 141 relevant publications published since 2005. LDH provides a potentially highly efficient method to adsorb heavy metal ions, which is simple to prepare and of low cost. The lack of functional groups and structural components of pristine LDH, however, limits the absorption capacity and widespread applications of LDH. Through intercalation, surface modification, or loading on substrates, functional groups or structural components are introduced into the pristine LDH to prepare functionalized LDH. In this process, the hydroxyl group and the valence state of [Mg $(OH)_6$] octahedrons play a crucial role. Functionalized LDH can be endowed with selective absorption capacity and enhanced stability and recyclability. After adsorbing heavy metal ions, functionalized LDH can be readily separated from the liquid phase. These aspects are discussed, along with the structure and composition, shape and size, and synthesis methods and research tools of LDH. This work concludes with the discussion of preparation and utilization and a look to the future in terms of identified research needs regarding the preparation, use, and recycling (or upcycling) of economical and environmental-friendly LDH.

Keywords: LDH, intercalation, surface modification, loading on substrates, selective absorption, wastewater

1 Introduction

The pollution of natural environment by heavy metal ions is a ubiquitous issue with dire consequences. Heavy metals with a density greater than 4.5 g/cm^3, such as Hg, Cr, Ni, Fe, Cu, Zn, and Mn, are closely related to human production and life. Heavy metals are widely used in electronic components, antibacterial materials, batteries, photosensitive materials, etc. If the heavy metals are not properly disposed, they may cause many environmental or health risks [1]. For example, in soil contaminated by heavy metal ions, the growth of crops is slow and the yield is reduced, while heavy metal ions are enriched in the plants [2]. Similarly, heavy metals not only affect the growth of organisms and plants in water but also become enriched in aquatic organisms and plants [3]. Even at low concentrations, heavy metal ions accumulate in the human body through the food chain and drinking water, thereby threatening human health [4].

Heavy metal ion pollution can be mitigated through precipitation, electrolysis, membrane separation, ion exchange, and absorption, among which absorption is the method widely used because of its simple operation, low cost, and high efficiency [5,6]. The precipitation method is mainly achieved by adding hydroxide, sulfide, ferrite, etc., in water, causing the heavy metal ions to react with them to generate precipitate. However, its effluent concentration does not meet the requirements and needs further treatment. The electrolysis method uses direct current to remove heavy metal ions in water through the process of redox reaction, but its electric energy consumption is high, and the method is only suitable for wastewater with high heavy metal ion concentration. The ion exchange method uses the

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exchange groups of the ion exchanger to exchange heavy metal ions in water. However, the operating and raw material costs are high. The membrane separation method involves choosing a suitable membrane that will hinder the passage of heavy metal ions but the strength of the membrane is poor and easily blocked. Absorption is a common phenomenon that exists at the solid–liquid interface. Loose porous and large specific surface area absorbents have been leveraged to adsorb heavy metal ions in water.

Absorbents fall into three main categories: inorganic absorbents, organic absorbents, and biological absorbents. Inorganic absorbents (layered double hydroxide [LDH], graphene, activated carbon, zeolite, mesoporous silica, etc.) have large specific surface areas and controllable pore structure [7]. Organic absorbents are mainly coordinated by unpaired electrons and heavy metal ions in nitrogen, oxygen, sulfur, and other atoms of the contained functional groups. The advantages of bioabsorbents are their renewable nature and highly selective absorption ability. Table 1 provides some absorption properties of various materials for heavy metal ions.

Among the common absorbents, LDH has been widely studied because of their low cost, high efficiency, and easy preparation [23–25]. However, due to the lack of functional groups and structural components of pristine LDH, the absorption capacity and further applications of LDH is limited [26]. Compared with that of pristine LDH, functionalized LDH has better absorption capacity.

Cumulative studies have been conducted over the last 15 years or so and have resulted in a wealth of information related to preparation and utilization of functionalized LDH as well as the structure and composition, shape, and size of LDH. Currently, there is an urgent need to synthesize the renewed knowledge and individual case studies on these subjects and help identify common trends and knowledge gaps. In this context, the main purpose of this study is to provide a comprehensive review of the current knowledge on functionalized LDH as heavy metal ion absorption material. To this end, this study followed the following four steps: (1) selecting review topics relevant to the specific application of LDH for heavy metal removal, as follows: LDH, heavy metal, intercalation, modification, LDH composite, selective absorbability, particle size, and nanostructure; (2) a total of 141 publications published since 2005 were included in this study by using the following criteria: relevance to the topics, representation and credibility, absorption property, and modification method; (3) through reading and analysis, these articles are classified and summarized based on the modification methods, absorption properties, composition, and structure; and (4) identifying future research needs to reduce environmental impact and economic costs to facilitate LDH synthesis and use. The findings and rationale of this study will promote the preparation and utilization of functionalized LDH as heavy metal ion absorption material.

This review article is organized in four main sections. Following this introduction is a brief discussion of the structure and composition, shape and size, and synthesis methods and research tools. In Section 3 the preparation methods of functionalized LDH are classified, including intercalation, surface modification, loaded on substrates. In Section 4 the practical properties of functionalized LDH are discussed, with a focus on selective absorbability, liquid–solid separation, stability, and recyclability. Section 5 provides conclusions regarding the preparation methods and practical properties and a look to the future in terms of identified research needs regarding the preparation, use, and recycling (or upcycling) of economical and environmental-friendly LDH.

Table 1: Absorption capacity (mg/g) of different absorption materials for heavy metal ions

	Hg^{2+}	Ag^{+}	Pb^{2+}	Cd^{2+}	Ref.
Kaolin	30.10		34.5		[8,9]
Cellulose	48		52	68	[10]
Mesoporous silica			102.7		[11]
Potato starch phosphate	51.38		106.25	91.84	[12]
Coal gangue	179.2		332.8	110.4	[13]
Graphene	400	114.9	270.3	70.10	[14–16]
Zeolite	117	446.7	303	34.85	[17–20]
LDH	582	565	359.7	368.1	[21,22]

2 LDH

The structure, composition, shape, and size of LDH are closely related to the absorption properties, which is also the basis of the preparation of functionalized LDH. For different functional groups or structural components, different preparation methods have been explored to introduce them into LDH. To shed light on the structure, properties, and absorption mechanism of functionalized LDH, scientific research tools are necessary. These subjects are discussed in the following subsections.

2.1 Structure and composition

The structural formula of LDH is $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, and A^{n-} is an interlayer anion. The crystal structure of MgAl–CO_3–LDH is shown in Figure 1.

The crystal structure shown in Figure 1 belongs to the $R\bar{3}m$ (166) space group, with unit cell parameters a = 3.054 Å, c = 22.81 Å, and c/a = 7.4689. $[Mg(OH)_6]$ octahedrons with common edges making up the unit layer. Part of the Mg^{2+} is replaced by Al^{3+} resulting in a positively charged layer. The presence of $CO_3{}^{2-}$ between layers makes the overall structure electrically neutral. The bonding force between the cationic layer and the anion is poor, and the anion is easily replaced by other anions or molecules. When adsorbing heavy metal ions, the type and quantity of interlayer anions can be adjusted according to the demand [27,28]. Because different kinds of ions have different valence states and ionic radii, their kinds and quantities are closely related to the crystal structure and layer charge density. Therefore, the absorption performance of LDH with different ion types and ratios was studied [29–31]. The anions between pristine layers are usually $CO_3{}^{2-}$, $SO_4{}^{2-}$, Cl^-, or $NO_3{}^-$ [32]. The combination of divalent and trivalent cations in LDH used to adsorb heavy metal ions is shown in Table 2.

Among them, MgAl–LDH absorption of heavy metal ions is the topic of most existing studies. In addition to LDH consisting of divalent and trivalent metal cations, the absorption capacity of other LDH consisting of cations of other valences has been studied [33,34]. For example, LiAl–LDH intercalated with triethylenetetramine was used to absorb Nd^{3+} and Sr^{2+}. Due to the poor stability of Li metal chelate, the Li–Al LDH has free triethylenetetramine ions in the interlayer, which can effectively improve its heavy-metal-ion-absorption capacity [35].

Table 2: Combination of divalent and trivalent cations in LDH

	Ca^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}	Fe^{2+}	Co^{2+}	Mn^{2+}
Al^{3+}	√	√	√	√	√	√	√	√
Fe^{3+}	√	√		√	√		√	
Cr^{3+}				√	√			

2.2 Shape and size

In addition to the type and quantity of ions, the size and shape of LDH are closely related to its absorption performance. The size of the particles is affected by the type and amount of the agent, preparation method, temperature, time, and other factors [36]. For instance, Yuki Arai and Makoto Ogawa prepared CoAl–LDH with particles the diameter of 1–38 μm by adjusting the glycerol/water ratio, heating temperature, and time [37]. The milling technology can also reduce the particle size of MgAl–LDH without significantly altering its shape and crystallinity [38]. Particle size is closely related to absorption performance. Yang et al. studied the effect of MgAl–LDH particle size on the absorption performance of As^{5+}, and the results show the absorption rate of MgAl–LDH increases while the particle size decreases, but the absorption capacity does not change significantly [39]. Ricardo Rojas believes that the removal capacity of MgAl–LDH increases with the decreasing particle size. Although the affinity of MgAl–LDH for Cu^{2+} is independent of particle size, the volume of the layer available for Cu^{2+} incorporation increased [40]. The existing conclusions are not uniform and limited. The effect of LDH particle size on the absorption capacity of heavy metal ions merits further investigation.

A variety of preparation methods can be employed to synthesize LDH of different dimensional nanostructures. The quaternary microemulsion (CTAB, water, n-hexane, n-hexanol) was selected to prepare NiAl–LDH nanotube

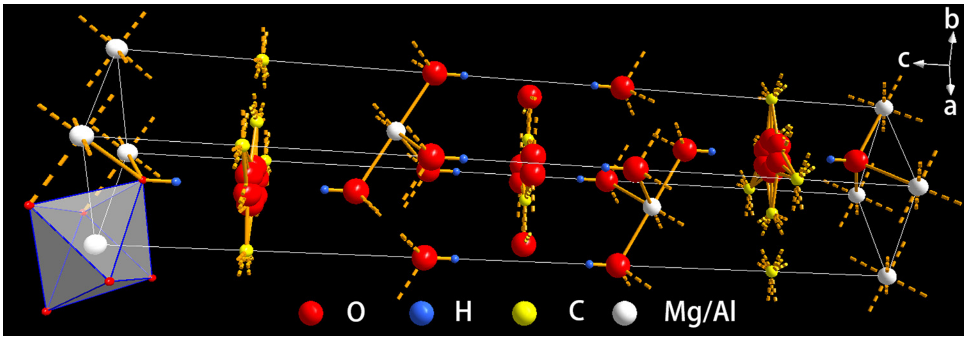

Figure 1: Crystal structure diagram of MgAl–CO_3–LDH.

(1D) [41]. To prepare MgAl–LDH monolayer nanosheets (2D), nitrate-intercalated MgAl–LDH was delaminated by sonication [42]. Polystyrene beads were chosen as a template to prepare MgAl–LDH hollow nanoshells (3D) [43]. The structure reconstruction method was also selected to synthesize ZnAl–LDH hierarchical sphere [44]. The nanostructure mentioned earlier is shown in Figure 2.

Among them, hierarchical sphere LDH has attracted much attention due to its porous structure and structural stability, which are beneficial to the absorption of heavy metal ions [45]. LDH hierarchical sphere composed of cross-linked nanosheets is synthesized by the hydrothermal method, which is a low-cost and simple technology method [46,47]. The structure of calcined layered double hydroxide (CLDH) prepared by calcining hierarchical sphere LDH was not changed, showing 99% removal of As^{6+} and Cr^{6+} in 5 min. The wastewater after 20 min of absorption meets the WTO standards for drinking water. The maximum absorption capacities of hierarchical sphere CLDH for As^{6+} and Cr^{6+} ions are 178.6 and 148.7 mg/g, respectively [48]. Due to its unique hierarchical sphere structure, hierarchical sphere LDH is a promising heavy metal ion absorbent featuring better absorption capacity and absorption efficiency than powdery LDH.

2.3 Synthesis methods

The synthesis methods of LDH mainly include the coprecipitation method, sol–gel method, hydrothermal synthesis method, ion exchange method, structure reconstruction method, mechanochemical method, etc. The metal salt solution and alkali solution are mixed to cause coprecipitation, and LDH crystals are generated by crystallizing the precipitated product under certain conditions (coprecipitation method). LDH is synthesized using organometallic salts through the sol–gel transformation process (sol–gel method). The metal salt solution and the alkali solution are quickly mixed, and the mixed solution is immediately transferred to an autoclave. After crystallization at a certain temperature, it is filtered, washed, and dried to obtain LDH (hydrothermal synthesis method). The original anion is replaced by other anions to prepare the required LDH (ion exchange method). The CLDH is added to a liquid medium containing an anion, and its structure can be partially restored to an ordered layered structure (structure reconstruction method). Under the action of high-energy mechanical force, the physical and chemical properties and structure of the reactants are induced to change (mechanochemical method). Table 3 provides a summary to compare the advantages and disadvantages of the aforementioned methods.

In addition to the aforementioned preparation methods, *in situ* synthesis method in waste liquid or from solid waste has been explored to prepare LDH, which brings additional environmental and economic benefits [49–51]. For instance, Francisco et al. added magnesium ions and hydroxide to waste liquid (including SO_4^{2-}, H^+, Pb^{2+}, Al^{3+}, Cu^{2+}, Zn^{2+}) to prepare MgAl–CO_3 LDH. In the absence of Mg^{2+}, (Zn–Cu–Mg) Al LDH was formed [52]. Waste serpentine tailings (including 34 wt% MgO and 4.27 wt% Fe_2O_3) were used to prepare MgFe–LDH, and Mg^{2+} and Fe^{3+} were dissolved by adding nitric acid. To increase the conversion rate and yield, the preparation process needs further exploration [53].

2.4 Research tools

As an absorption material, the main evaluation parameter of LDH resides with its absorption properties.

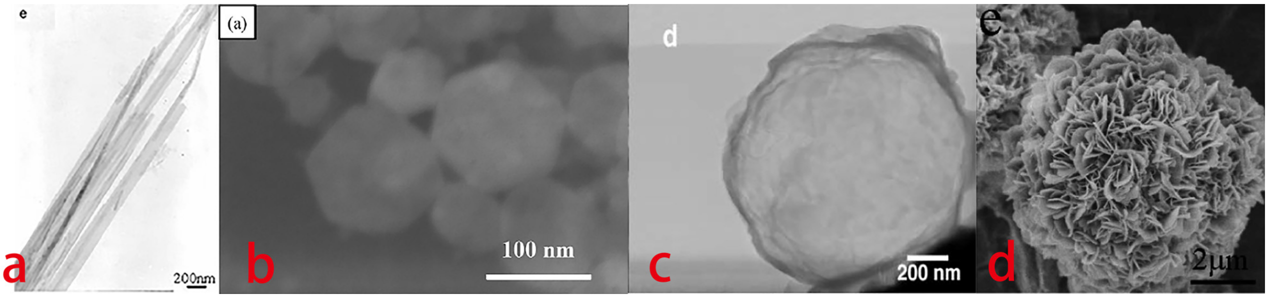

Figure 2: The SEM micrograph of different LDH micro-structure: (a) nanotube [41]; (b) nanosheets [42]; (c) nanoshells [43]; and (d) hierarchical sphere [44].

Table 3: Comparison of different preparation methods

Method	Advantage	Disadvantage
Coprecipitation	Simple process	Uneven particles and time-consuming
Sol–gel	Good uniformity	Low output and high cost
Hydrothermal synthesis	Good crystallinity and controllable size	Low output
Ion exchange	Insert large anionic groups	Complex composition
Structure reconstruction	Higher purity anion	Impure crystal phase and bad crystal form
Mechanochemical	Low pollution and high reactivity	Impure crystal phase

According to the absorption properties, the types and proportions of raw materials and preparation methods can be optimized. To achieve a fundamental understanding of the absorption mechanism, the experimental data are fitted to the most appropriate absorption model and advanced tools (XRD, zeta, BET, TEM, SEM, FT-IR, XPS, XRF, etc.) are used to characterize LDH before and after absorption. Figure 3 presents a schematic overview on the absorption properties, model, and characterization of LDH.

The absorption properties of LDH include absorption capacity, selective absorbability, recyclability, and stability. The absorption capacity usually refers to the maximum absorption capacity of heavy metal ions in one cycle, and little attention has been paid to the total absorption capacity of the entire life cycle. Considering the environment and cost implications, however, the recyclability of LDH is one critical property. The temperature, type and quantity of ions, and pH value of wastewater value are all variable, so selective absorbability and stability are also important. The difference between the absorption properties of functionalized and pristine LDH will be discussed later.

In evaluating LDH, its absorption results can be used to fit a model. When the absorption reaches equilibrium at a constant temperature, the concentration of adsorbate on the surface of the absorbent and in the solution is distributed according to a certain rule. There is a certain functional relationship, known as the absorption isotherm, with the common used models being Langmuir and Freundlich absorption isotherms. Dubinin–Radushkevich, Temkin, and Flory–Huggins absorption isotherms are also used sometimes. Furthermore, kinetic simulation of the absorption process is used to characterize the change of absorption with time under certain temperature conditions. Commonly used absorption kinetic models are pseudo-first-order kinetics, pseudo-second-order kinetics, Elovich and intraparticle diffusion. Absorption thermodynamic parameters include ΔG (Gibbs free energy), ΔH (enthalpy), ΔS (entropy), and E_a (activation energy). These parameters can be calculated according to certain formulas and experimental data. The combination of experimental and theoretical analysis can better carry out research on materials [54].

The mechanisms of LDH removing heavy metal ions mainly include isomorphic substitution, complexation, and electrostatic interaction [55,56]. The process of electrons interacting with donors and electron acceptors to form complexes is complexation, which is the most important absorption mechanism for functionalized LDH. When the radius or valence of the heavy metal ions is similar to those in the crystal structure, isomorphic substitution may also occur. Isomorphic substitution refers to the replacement of cations on the LDH lattice sites by

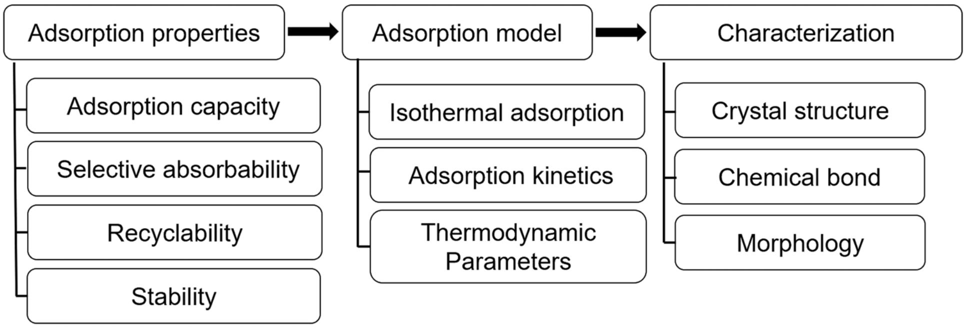

Figure 3: Schematic overview of LDH research tools.

heavy metal ions. Heavy metal ions can also be adsorbed on the surface of LDH by electrostatic interaction. To further explore the absorption mechanism, it is necessary to characterize the LDH before and after absorption. The easiest way to characterize crystal structure is XRD. Due to the change of anion and cation type, quantity and valence state, the crystal structure also changes, which will be directly reflect to the intensity and position of the XRD characteristic peak. Hence, the XRD patterns before and after absorption can be used to analyze the change of crystal structure and the formation of new phases. In addition to XRD, TEM can be used to characterize the crystal structure. The type of chemical bonding can be judged based on the electron binding energy obtained by XPS or absorption frequency obtained by FT-IR. The focus of XPS and FT-IR are the analysis of the valence state of metal elements and the functional groups composed of C, O, and H. Morphology is mainly characterized by SEM and TEM. For example, as shown in Figure 4 (previous research study of our team) [55], when CaAl–LDH adsorbs Co^{2+}, Co^{2+} replaces Ca^{2+} in the crystal lattice. Due to the difference in ionic radius Co^{2+} and Ca^{2+}, the crystal structure (Figure 4a, f, and g), chemical bond (Figure 4b and c), and morphology (Figure 4e, d, and h) have changed. Furthermore, the specific surface area and pore size tester characterize the pore structure parameters (specific surface area, pore volume, pore size) of LDH. The zeta potentiometer tests the electromotive force, which is an important indicator for characterizing the stability of the colloidal dispersion system. LDH can absorb charged ions with opposite surface charges and repel ions with the same charge. The element analyzer and XRF can determine elemental composition of LDH. Such tools enable a more mechanistic understanding and help unravel the absorption mechanism of LDH.

3 Synthesis methods of functionalized LDH

Due to the lack of functional groups and structural components of pristine LDH, the absorption capacity and further applications of LDH are limited. To solve this issue, functionalized LDH has been prepared by introducing functional groups or structural components. In this process, due to the presence of hydroxyl groups on the surface and the positively charged $[Mg(OH)_6]$ octahedrons, LDH can interact electrostatically and chemically with functional groups or structural components. The preparation methods of functionalized LDH are divided into three categories: Intercalation method is used for small organic or inorganic molecules, whereas surface modification method is used for larger organic molecules. In addition, for the substrates that can provide attachment sites, LDH is loaded on the substrates. These are detailed in the following subsections.

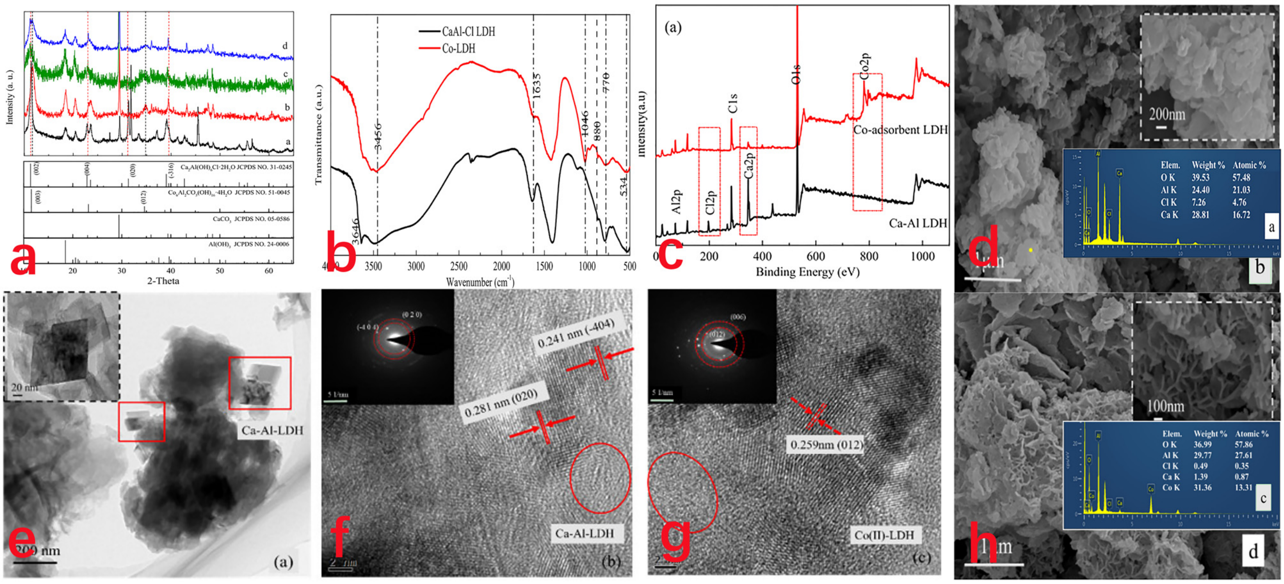

Figure 4: The characterization of LDH before and after absorption Co^{2+} [55]: (a) XRD; (b) FT-IR; (c) XPS; (d) CaAl–LDH SEM; (e) and (f) CaAl–LDH TEM; (g) Co^{2+}–LDH TEM; and (h) Co^{2+}–LDH SEM.

3.1 Intercalation

To increase absorption capacity for heavy metal ions, LDH is intercalated with molecules, which can cause complexation with the heavy metal ions. LDH that is intercalated with sulfide has good absorption capacity for heavy metal ions, and its selective absorption has attracted wide attention, which will be described later [57,58]. In addition, LDH is mainly intercalated with organic molecules, which can significantly improve absorption capacity for heavy metal ions [59–62]. For example, compared with the maximum absorption capacity of LDH, the maximum absorption capacity of LDH intercalated with SDBS and citrate for Cu^{2+} increased by 72.7 mg/g [63]. These organic-containing functional groups such as –SH, –COOH, and $–NH_2$ contain many coordination atoms which can provide electron pairs. Therefore, organic compounds and heavy metal ions can undergo complex reactions to form complexes.

Organic molecules are mainly combined with LDH through electrostatic interaction and chemical bonding. Usually when LDH was intercalated with molecules, the crystal parameters a and b of LDH were not changed, but the c was obviously changed. XRD is used to determine the powder crystal structure, which is the most intuitive and concise characterization method for intercalation. The arrangement of intercalated molecules between layers can also be analyzed by unit cell parameters (usually d_{003}). The basal spacing of LDH intercalated with molecules and arrangement of molecules between layers are shown in Table 4. Arrangement including horizontal, vertical, and inclination is shown in Figure 5.

As shown in Table 4, basal spacing is related to the type and arrangement of the molecules between the layers, which is closely related to absorption capacity for heavy metal ions. The arrangement is affected by many factors, such as concentration, temperature, intercalation method, etc. [77]. For example, the coprecipitation method is used to synthesis LDH intercalated with EDTA. When the pH value is 8.0, 9.0, and 10.0, the basal spacing between the layers is 15.2, 15.1, and 14.7 Å, respectively [78]. This basal spacing is also different from 7.9 to 13.9 Å, as shown in Table 4. The layer thickness is 4.8 Å, and interlayer spacing calculated are 10.4, 3.1, and 8.1 Å. Therefore, there are some differences in the arrangement of EDTA and the degree of binding between EDTA and LDH.

The interlayer composition and structure of LDH were adjusted by inserting molecules, which is also closely related to the intercalating process. The main synthesis methods of LDH intercalated organic molecules are coprecipitation, ion exchange, and structure reconstruction methods. The delamination/reassembling method (nanosheets prepared by ultrasound can reassemble in solution) is also feasible. Appropriate methods should be selected according to the physical and chemical properties of organic molecules.

3.2 Surface modification

Due to hydrodynamic radius, charge density, and other reasons, some molecules are difficult to enter the interlayer, so the surface modification method is selected to prepare LDH-based composites. Surface modification can improve the absorption performance of LDH-based composites for heavy metal ions and remove the limitations of other absorption materials in the process of adsorbing heavy metal ions. For example, biodegradable bioabsorption materials are environmental friendly, but their absorption performance is easily affected by the solution environment. Combining bioabsorbent materials and LDH with good stability can produce absorbent with excellent absorption capacity for heavy metal ions such as MgAl–LDH-based composites prepared using MgAl–LDH and proteins extracted from bael or bilva oil meal with an maximum absorption capacity of Pb^{2+} (625 mg/g) [79].

Direct cross-linking, indirect cross-linking, and *in situ* growth were mainly selected to modify the surface of LDH. The hydroxyl group on the surface of LDH plays an important role in surface modification. After surface modification, the structure diagrams of the LDH-based composites are shown in Figure 6.

Direct cross-linking refers to the direct bonding between molecules and LDHs. As shown in Figure 6a [80], the amino groups and hydroxyl groups contained in chitosan (CS) can directly dehydrate with the hydroxyl groups on the surface of MgAl–LDH, which leads to the direct cross-linking of CS with MgAl–LDH. When pH is above 3, CS–LDH exhibits excellent absorption capacity and stability. The absorption capacity of CS–LDH for Pb^{2+} and Cd^{2+} is better than that of CS and MgAl–LDH. The main absorption mechanism includes isomorphic substitution, chemical precipitation, and surface complexation. The hydrodynamic radii of the humic substance is 20–71 Å, making it difficult for the humus material to enter the interlayer [83,84]. Due to the hybridization of ZnAl–LDH surface and fulvic acid, ZnAl–LDH-based absorbents were prepared. Fulvic acid

Table 4: The basal spacing (Å) of LDH and arrangement of molecules

Origin anion	d_{003}	Intercalated molecules	d'_{003}	Arrangement		Ref.
NO_3^-	7.6	Glutamate	8.1			[64]
CO_3^{2-}	7.9	Malate	8.1			[65]
CO_3^{2-}	7.9	Tartrate	8.3			
NO_3^-	7.5	L-Cysteine	8.0	Horizontal	Monolayer	[66]
Cl^-	7.8	Humate hybrid	7.9			[60]
Cl^-	7.8	DTPA	14.2	Inclination	Monolayer	[67]
NO_3^-	8.8	DMSA	10.5			[68]
CO_3^{2-}	7.6	Tartrate	12.2			[69]
NO_3^-	8.58	Tripolyphosphate	10.35			[70]
CO_3^{2-}	6.5	L-Phenylalanine	11.84	Inclination	Monolayer	[71]
CO_3^{2-}	7.8	EDTA	7.9			[72]
NO_3^-	8.8	EDTA	13.9	Vertical	Monolayer	[73]
CO_3^{2-}	8.8	CMCD	19.0			[74]
CO_3^{2-}	7.65	D2EHPA	26.28	Inclination	Bilayer	[75]
NO_3^-	9	Rhamnolipid	33.9	Inclination	Bilayer	[76]

is rich in functional groups such as hydroxyl and carboxyl groups, which play an important role in the absorption of heavy metal ions [85].

When organic molecules cannot be directly cross-linked with LDH, other organic molecules are needed as a bridge to link organic molecules and LDH, which is called indirect cross-linking. For example, as shown in Figure 6b, since polyaniline cannot be directly cross-linked with CaFe–LDH surface, the 3-aminopropyl triethoxysilane was selected to modify the CaFe–LDH surface first. The presence of the Si–O–M vibration peak in the FT-IR spectrum proves the dehydration reaction of the silicon hydroxyl group of 3-aminopropyl triethoxysilane and the hydroxyl group of CaFe–LDH [81]. Polydopamine containing amino, hydroxy, and benzene rings connected MgAl–LDH and poly(methyl vinyl ether-*alt*-maleic anhydride) by mussel-inspired chemistry and a ring-opening reaction. The absorption capacity of this ternary absorbent is twice that of the pristine MgAl–LDH [86]. Polydopamine also can connect α-amino phosphonate chains and MgAl–LDH by a combinatorial procedure of mussel-inspired chemistry and Kabachnik–Fields [87]. The ternary absorbent containing MgAl–LDH, polyethylene polyamine, and tannic acid was prepared by combining catechol chemistry and Michael addition and/or Schiffbase reaction. Compared with pristine MgAl–LDH, the absorption capacity of ternary absorbent was also significantly improved. Electrostatic absorption and surface complexation are the main absorption mechanism [88].

Other absorbents can be covered on the surface of LDH by the *in situ* growth method. For example, as shown in

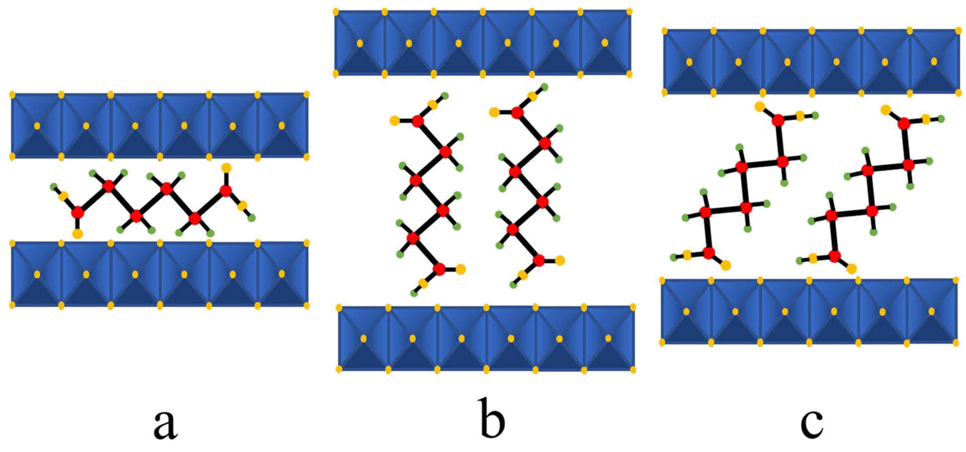

Figure 5: Arrangement of molecules: (a) horizontal; (b) vertical; and (c) inclination.

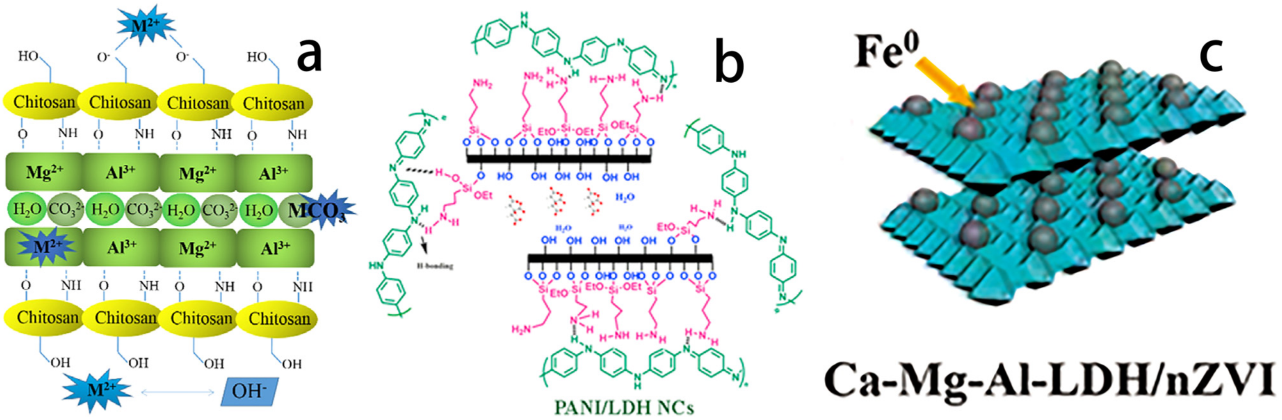

Figure 6: The structure diagrams of the LDH-based composite material: (a) direct cross-linking [80]; (b) indirect cross-linking [81]; and (c) *in situ* growth method [82].

Figure 6c, zero valent iron is fixed on the surface of CaMgAl–LDH by the *in situ* growth method. Because it contains abundant functional groups such as Fe–O, Al–O, and –OH, CaMgAl–LDH-based absorbent had high efficiency and excellent absorption capacities. The maximum absorption capacity of U^{6+} is 216.1 mg/g. The main absorption mechanism entails the reduction and absorption of zero valent iron and the absorption of CaMgAl–LDH [82]. Zeolitic imidazolate framework (MOF materials) with high porosity and good stability is a potential absorbent. Due to the small size of MOF; however, it is difficult to separate and recover after adsorbing heavy metal ions in the solution. CoAl–LDH-covered zeolitic imidazolate framework was successfully synthesized by the *in situ* growth method. The composites show excellent absorption capacity and recycle stability. The maximum absorption capacity of Cr^{6+} is 378 mg/g [89].

The surface modification method combines the advantages of LDH and other absorption materials. While increasing its cation-absorption capacity, the anion-absorption capacity of LDH remained. Therefore, surface modified LDH can simultaneously adsorb heavy metals in the form of different ions, which can be widely used in heavy metal ion absorption and even wastewater treatment. To the best of our knowledge, there are few related studies. Surface modification of LDH and its ability to simultaneously adsorb heavy metal cations and anions warrant further study.

3.3 Loading LDH on substrates

In addition to intercalation and surface modification, the LDH is loaded on the substrate by *in situ* growth, which can also effectively improve the absorption capacity of heavy metal ions. The substrate can provide stable attachment sites for LDH particles, and the aggregation of LDH particles is hindered to some extent. Absorption sites have also increased. Silica aerogel, N-doped carbon nanosheet, graphene, biochar, and other materials that can provide many absorption sites and stable attachment sites can be used as substrates [90–95]. Because carbon-based materials contain more functional groups and larger specific surface areas, they have been extensively studied [96–98]. For example, TiO_2/graphitic carbon nanocomposites were used for water treatment [99]. Carbon-based materials of different dimensions are studied as substrates and their microstructure is shown in Figure 7.

As shown in Figure 7a and d, due to its mechanical stability, good hydrophilicity, and high specific surface area, carbon nanofiber (1D) has been used as a substrate to grow NiAl–LDH *in situ*. Since the carbon nanofiber/NiAl–LDH composite material has porous and open nanostructures, the aggregation of carbon nanofiber and NiAl–LDH is hindered. The combination of the high exchange capacity of LDH and the higher number of active sites of carbon nanofibers, so the composites, can efficiently remove heavy metal ions mainly through surface complex and electrostatic interaction [100]. The surface negative charge of graphene (2D) containing many functional groups and positively charged LDH can self-assemble through electrostatic interaction. Both graphene and LDH have a unique layered structure, so the combination of graphene and LDH is the strongest. LDH/graphene composites contain a porous structure, which is conducive to heat and mass transfer and can expose more active sites at the same time [101]. Electron

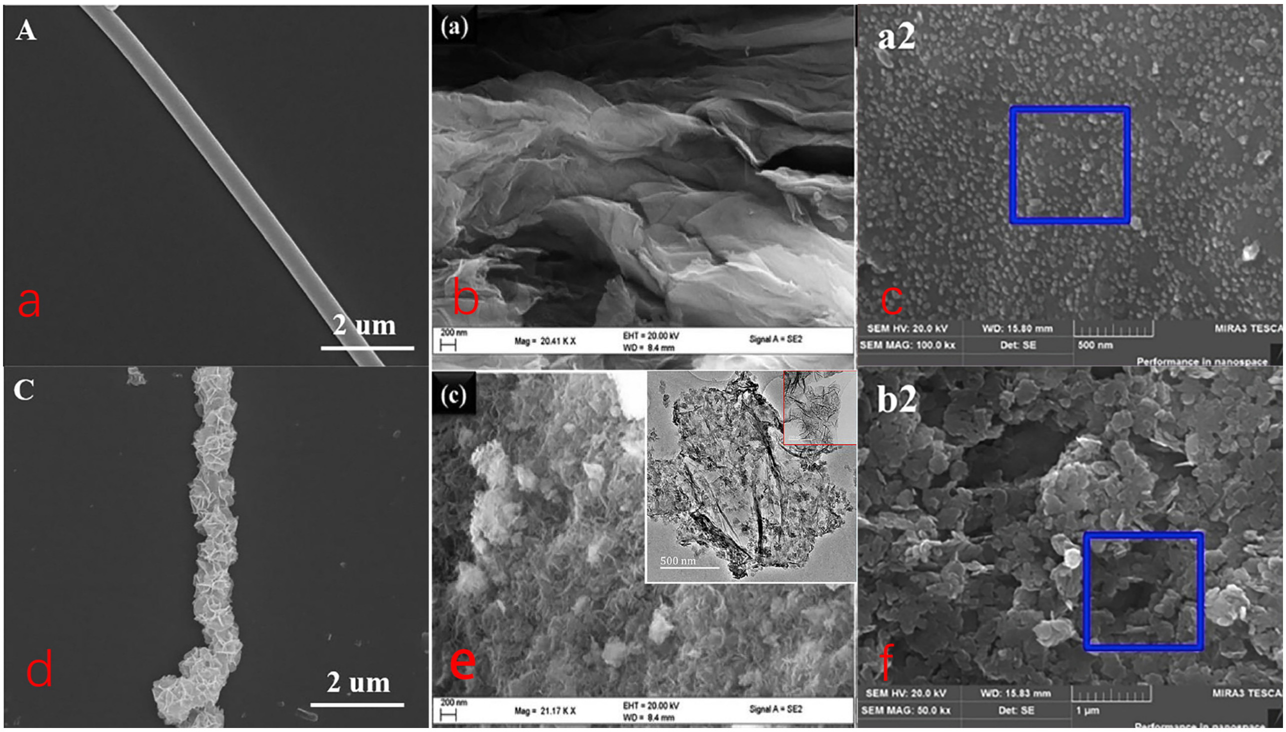

Figure 7: Microstructure of substrate and LDH loaded on substrate: (a) carbon nanofiber; (d) LDH loaded on carbon nanofiber [100]; (b) graphene; (e) LDH loaded on graphene [107]; (c) biochar; and (f) LDH loaded on biochar [108].

and stress transport networks are also easily formed between LDH and graphene [102,103]. Therefore, compared with other LDH/carbon-based composite materials, the LDH/graphene composite material is the more stable and effective [104–106]. The microstructures of graphene oxide and MgAl–LDH/graphene composites are shown in Figure 7b and e, respectively. The alkaline environment used for the *in situ* growth of LDH results in the reduction of part of the graphene oxide to reduced graphene oxide. Because the LDH nanoplates are vertically interwoven with reduced graphene oxide surface, the LDH/graphene composites have an open porous structure and a high surface area, which results in the composites being able to efficiently adsorb heavy metal ions [107]. Biochar (3D) prepared from solid wastes such as rice husk, straw, and fallen leaves have a high specific surface area, porous structure, and many functional groups. MgFe–LDH is loaded on the surface of biochar by the *in situ* growth method. Negative charged biochar can also be connected to LDH through electrostatic interaction. The microstructures of biochar and LDH/biochar composites are shown in Figure 7c and f, respectively. Biochar is a potential absorbent, but its functional groups are easily pyrolyzed. LDH has stable absorption performance but is easy to aggregate. Combining MgFe–LDH and biochar, the composite material has excellent absorption capacity and cyclic utilization. The maximum absorption capacity of Pb^{2+} is 476 mg/g [108].

Some materials such as zeolite, Fe_3O_4, and gravel provide little or no absorption sites, but can provide attachment sites that can also be used as a substrate [109,110]. The composites prepared by *in situ* growth of LDH on this type of substrate are usually a core–shell structure with the main purpose to facilitate solid–liquid separation. For example, Fe_3O_4/MgAl–LDH–RL (Rhamnolipid, RL) composite material with a core-shell structure is prepared as shown in Figure 8. MgAl–LDH grows *in situ* on the Fe_3O_4 surface by the coprecipitation method, then RL is inserted between the MgAl–LDH layers by the delamination/reassembling method. The magnetic absorbent is easily separated by an external magnetic field within 20 s [111].

4 Properties of functionalized LDH

Considering the varied temperature, type and quantity of ions, and pH value of wastewater as well as environment and economic cost, selective absorbability, liquid–solid separation, stability, and recyclability are important.

Due to the introduction of functional groups and structural components, selective absorbability, liquid–solid separation, stability, and recyclability of functionalized LDH are much better than that of pristine LDH. The following subsections discuss the difference between these absorption properties of functionalized and pristine LDH.

4.1 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 [112–114]. 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, MgAl–LDH removes Cu^{2+} and Ni^{2+} by forming hydroxides, and Pb^{2+} by forming carbonates [115]. On the other hand, the cations of LDH can be replaced by other cations with similar radii through isomorphic substitution, which can be applied to the preparation of LDH of different components and the selective absorption of heavy metal ions. Two aspects cause LDH to have a certain selective absorption. For example, because the stability of Cu^{2+} hydroxide is higher than that of Pb^{2+}, the presence of Cu^{2+} affects significantly the absorption capacity of FeMnMg–LDH for Pb^{2+}, whereas the presence of Mg^{2+} and Ca^{2+} does not significantly affect the absorption capacity of FeMnMg–LDH for Pb^{2+} [116].

Functionalized LDH prepared by intercalation, surface modification, and loaded on substrates also has selective absorption performance. For example, based on the analysis of element results, the different coordination number leads to different absorption capacity of MgAl–LDH intercalated with phytate. Based on molecular simulation, the bonding energy between MgAl–LDH-phytate and metal ion is different, which results in MgAl–LDH-phytate having selective absorption [117]. The surface of MgAl–LDH coated by Molybdenum disulfide can effectively remove Cr^{6+}, which is not affected by the presence of coexisting anions (K^+, Na^+, Ca^+, Mg^{2+}, Zn^{2+}, and Al^{3+}) or cations [118]. The K_{sp} (solubility product constant) follows the order of $K_{sp}(Cu(OH)_2) < K_{sp}(Zn(OH)_2) < K_{sp}(Pb(OH)_2) < K_{sp}(Ni(OH)_2) <$

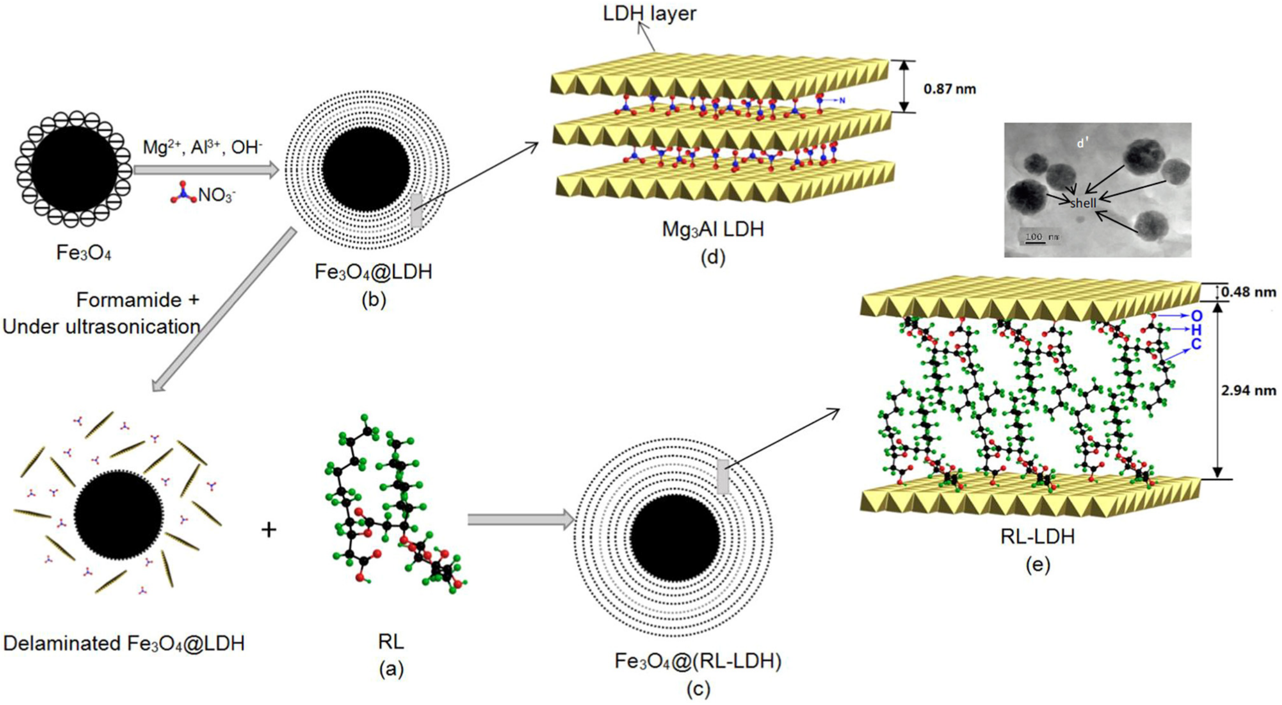

Figure 8: Schematic illustration of preparation Fe_3O_4/MgAl–LDH–RL [111].

$K_{sp}(Cd(OH)_2)$, and absorption of Cu^{2+} and Pb^{2+} by functional groups and isomorphic substitution between Cu^{2+} or Pb^{2+} and Mg^{2+} are easier. Hence, the selectivity absorption order of MgFe–LDH loaded with magnetic (Fe_3O_4) carbon spheres is as follows: $Cu^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+}$ [119].

As described earlier, many functionalized LDHs have selective absorption properties. Among them, the selective absorption performance of LDH composites with groups of sulfurated species has been widely studied [120,121]. The K_d (distribution coefficient) is an important index in evaluating the selective absorption performance. $K_d = V(C_0 - C_f)/m$, where V is solution volume, m is absorbent quality, and C_0 and C_f are the initial and final heavy metal ion concentrations, respectively. The K_d value of heavy metal ion absorption by LDH composite absorbent with groups of sulfurated species is shown in Table 5.

Table 5 reveals that the introduction of polysulfides, sulfides, and thiols can increase the K_d value, which reflects the absorption capacity of heavy metal ions. Therefore, the introduction of these functional groups increases the absorption capacity of LDH to heavy metal ions. Based on the hard–soft–acid–base theory, the sulfur-containing functional group is a soft base, the heavy metal ions are mostly soft acids, and the two form a strong bond. However, Ca^{2+}, Mg^{2+}, etc., are hard acids, and the combination of hard acids and soft bases is weak, so Ca^{2+}, Mg^{2+}, etc., do not occupy LDH absorption sites. For example, in the presence of high concentration levels of competitive ions (such as Na^+, K^+, Ca^{2+}, and Mg^{2+}), LDH intercalated with 2-mercaptoethanesulfonate has superior selectivity and higher absorption capacity for U^{6+}. The $K_d(Ca^{2+})$, $K_d(Mg^{2+})$, $K_d(K^+)$, $K_d(Na^+)$, and K_d (U^{6+}) are 96.5, 1.2×10^2, 3.0, 1.0, and 1.25×10^6, respectively [126]. To better reveal the materials' selective absorption performance, the separation factor ($SF_{A/B} = K_d^A/K_d^B$) is used to evaluate their ability to separate certain ions from mixture. Usually when the value of $SF_{A/B}$ is greater than 100, it indicates that this material can separate A from B [127]. It can be seen in Table 5 that the K_d ratio of the two heavy metal ions may also be greater than 100, indicating that LDH can be used not only to selectively adsorb heavy metal ions but also to separate heavy metal ions.

In the actual absorption process during implementation by industry, many ions in the solution may cause competitive absorption. Because many studies employed spectroscopy to test ion concentration, the presence of multiple ions can cause interference. Therefore, the selective absorption of LDH cannot be easily clarified and this is an important issue needing further investigation.

4.2 Liquid–solid separation

Due to the good hydrophilicity of LDH nanoparticles, solid–liquid separation needs to be performed by high-speed centrifugation or filtration (usually 0.45 μm membrane) after heavy metal ions are adsorbed in the research stage [128–130]. Yet, when absorbing heavy metal ions on a large scale, solid–liquid separation is costly and difficult to implement, which hinders the application of LDH. To facilitate solid–liquid separation, LDH is loaded on substrates [131,132].

Table 5: The K_d value of functionalized LDH

Functional molecules	**K_d (mL/g)**								**Ref.**
	Ag^+	**Pb^{2+}**	**Cu^+**	**Cd^{2+}**	**Zn^{2+}**	**Hg^{2+}**	**Co^{2+}**	**Ni^{2+}**	
Sulfonated calix [4] arene	9.43×10^2	1.36×10^4	1.03×10^6	—	—	—	—	—	[122]
Sodium citrate and L-cysteine	9.99×10^6	2.12×10^4	3.32×10^5	8.79×10^2	1.67×10^3	2.49×10^6	—	—	[123]
$(NH_4)_2MoS_4$	1.0×10^7	9.9×10^6	1.6×10^5	—	5.42×10^2	9.9×10^6	1.99×10^2	2.45×10^2	[124]
$(NH_4)_2MoS_4$	—	2.3×10^4	5.6×10^3	3.52×10^2	9.80×10^2	—	—	—	[45]
K_2S_4	8.8×10^6	3.0×10^3	2.4×10^3	3.96×10^2	3.05×10^2	8.4×10^6	80	47	[125]
K_2S_2	3.0×10^6	4.14×10^2	4.66×10^2	83	4.48×10^2	8.43×10^2	2.32×10^2	3.57×10^2	
K_2S_5	1.1×10^7	1.1×10^4	9.55×10^2	2.0×10^3	27	1.0×10^7	72	73	[22]
$(NH_4)_2MoS_4$	1.1×10^7	1.0×10^7	1.7×10^5	2.9×10^5	6.21×10^2	1.0×10^7	2.82×10^4	3.69×10^2	
CO_3^{2-}	8.5×10^3	4.7	80	77	3.41×10^2	96.59	80	1.48×10^2	
NO_3^-	4.3×10^3	1.09×10^2	1.33×10^2	1.0×10^2	3.67×10^2	95.34	11	2.4×10^2	

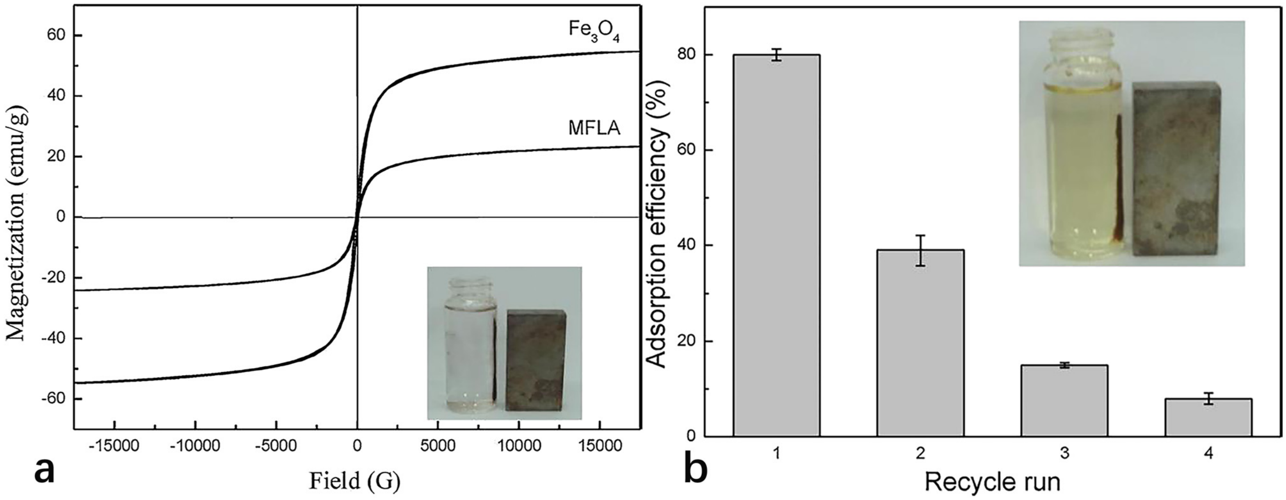

Figure 9: Magnetization characteristic curve (a) and the absorption efficiency in recycle runs (b) [136].

When the substrate is a magnetic substance, solid–liquid separation can be performed under the action of a magnetic field. Maghemite, $NiFe_2O_4$, Fe_3O_4, etc., can be used as a magnetic substrate [133–135]. Taking Fe_3O_4/ZnCr–LDH material as an example, its magnetization characteristic curve and the absorption efficiency in recycle runs are shown in Figure 9 [136].

As illustrated in Figure 9, Fe_3O_4/ZnCr–LDH was easily separated from the solution by a magnetic field. Even after four cycles, the absorption capacity of Fe_3O_4/ZnCr–LDH significantly decreased but was still easily separated. In addition, magnetic LDH composites can also be used in soil remediation. For example, humic acid-modified magnetic Fe_3O_4/MgAl–LDH is used to immobilize heavy metal ions in the soil through absorption. After adsorbing heavy metal ions, the magnetic LDH absorbent can be easily recovered, which is beneficial for recycling [137].

Loading LDH to zeolite, sand, etc., due to the large difference in particle size and density, solid–liquid separation can also be performed easily [138]. Such LDH composite materials can be applied in constructed rapid infiltration systems (CRIS). A schematic diagram of the preparation of Maifanite/Mg–LDHs and its application in CRIS is shown in Figure 10 [139]. Specifically, Maifanite/Mg–LDHs were placed into the device, the water was injected from above, and the filtered water flowed out from below. Since LDH was loaded on a maifanite stone, LDH was not dissolved into the water.

LDH can also be loaded on the surface of the biomaterial, which can also facilitate solid–liquid separation [140]. For example, MgAl–LDH is loaded on CS by *in situ* growth. MgAl–LDH/CS beads were prepared, and their size shown in Figure 11. Besides MgAl–LDH, CS also can adsorb heavy metal ions by

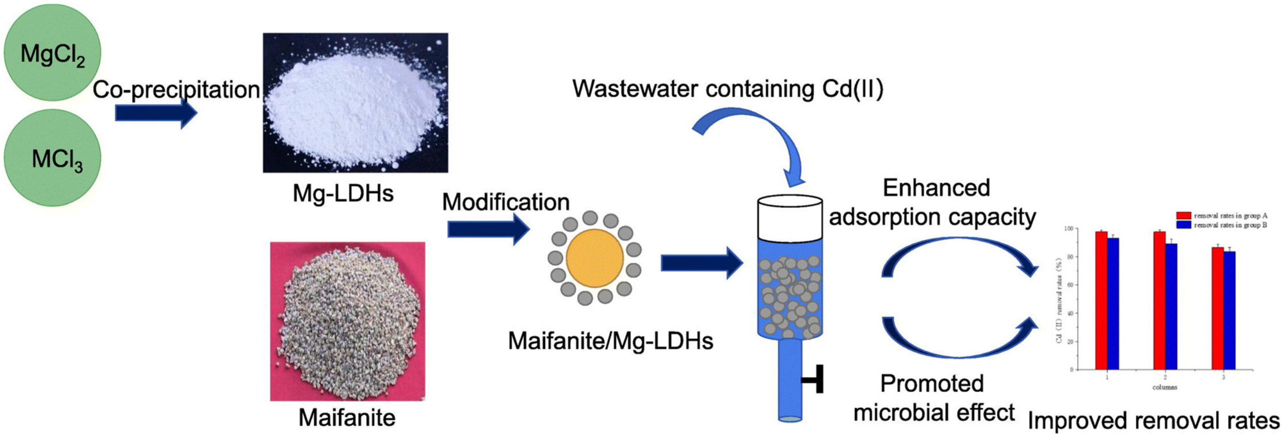

Figure 10: Schematic diagram of the preparation of Maifanite/Mg-LDHs and its application in CRIS [139].

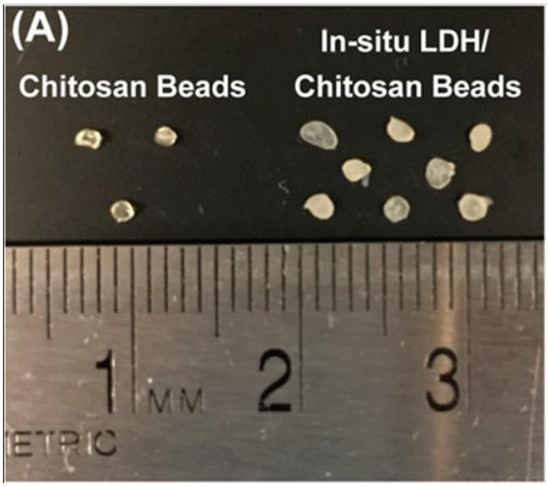

Figure 11: CS beads and MgAl–LDH/CS beads [141].

surface complex [141]. This provides new design ideas for the preparation of high-performance and sustainable LDH composites.

4.3 Stability and recyclability

Pristine LDH has poor stability and recyclability. The introduction of functional groups and structural components can increase its stability and cyclability to a certain extent. As shown in Figure 12a, LDH relies on the complexation of the surface hydroxyl groups and electrostatic action to adsorb heavy metal ions, so acidity (or alkalinity) of the solution has a greater impact on the absorption capacity of pristine LDH. However, functionalized LDH mainly depends on the complexation of functional groups, so functionalized LDH has good and stabilized absorption capacity for heavy metal ions whether in acid or alkaline solutions [76].

After adsorbing heavy metal ions, LDH has a poor ability to recycle and reuse, especially by isomorphous substitution to adsorb heavy metal ions. As shown in Figure 12b, after four cycles, the absorption efficiency of pristine LDH is less than 10%, while the absorption efficiency of functionalized LDH is more than 80% [86]. The current research focuses on the absorption capacity after each cycle and rarely discusses the reason for the decline in absorption capacity during the cycle.

5 Conclusions and outlook

This review has collected the published literature on LDH over the last 15 years, sorted out the main methods of preparing functionalized LDH, and discussed some practical properties of functionalized LDH. Intercalation, surface modification, and loaded on substrates can be used to prepare functionalized LDH. In this process, the hydroxyl group and the valence state of $[Mg(OH)_6]$ octahedrons play an important role. Functionalized LDH has better selective absorption capacity as well as stability and recyclability. Loading LDH to zeolite, sand, a magnetic substance, etc., may allow it to be more easily separated from the liquid. These properties

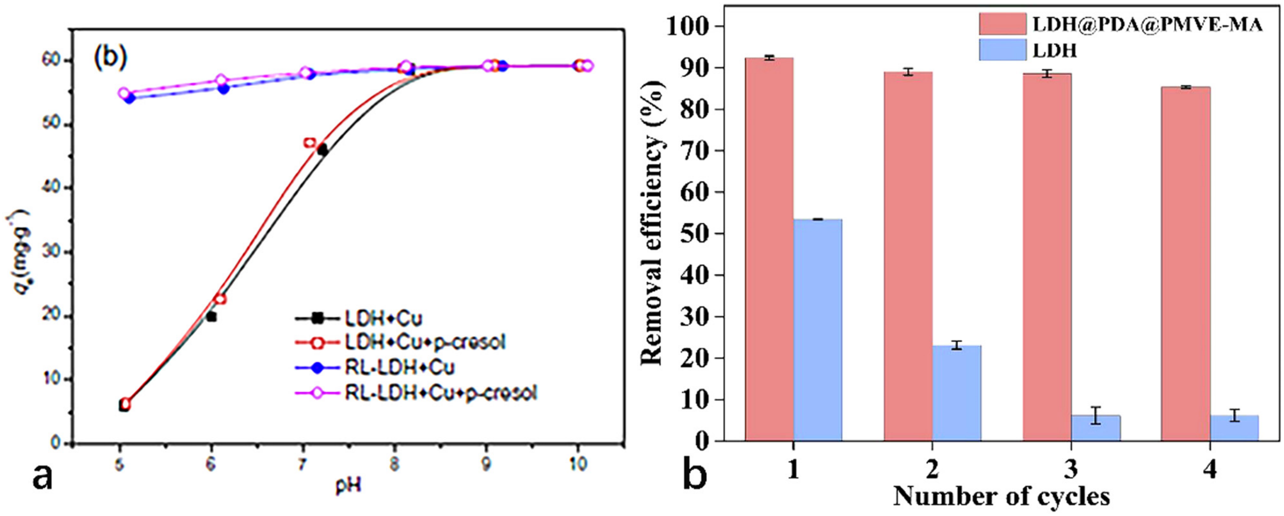

Figure 12: The stability (a) [76] and recyclability (b) [86] of functionalized LDH and pristine LDH.

are closely related to functional groups and structural components.

Relative to pristine LDH, functionalized LDH can more efficiently adsorb heavy metal ions in the solution to facilitate enrichment, recycling, and reuse, which solves the water pollution problem caused by heavy metal ions to a certain extent. However, its economic cost and environmental impact must be considered through life cycle, thus there are some aspects worthy of further study.

1. To reduce production costs and environmental footprint induced during the preparation of LDH, how to minimize the use of chemical reagents? The preparation of pristine LDH requires cations such as calcium, magnesium, and aluminum, which are abundant in waste liquids and solid wastes. This seems a logical direction to pursue. A large amount of waste liquid is generated in the LDH production process, how to reduce the waste liquid? One viable method is synthesis *in situ* in the waste liquid. Another viable method is to choose the mechanochemical method to synthesize LDH, but the resulting LDH is not as pure and additional research is needed to improve the LDH purity. So far, LDH used for adsorbing heavy metal ions has been synthesized mainly by coprecipitation and hydrothermal methods. For these two methods, innovations should focus on how to minimize the amount of water used during the LDH synthesis.
2. In the process of heavy metal ions adsorbed by LDH, some ions, functional groups, or structural components will leach into the solution, causing secondary environmental pollution. Existing studies have focused on improving the absorption properties of heavy metal ions, yet little attention or research has been devoted to how to minimize the amount of organic reagents used in the preparation of functionalized LDH. In addition, some LDHs remove heavy metal ions in water through isomorphic substitution, which will inevitably lead to partial ions leaching. The effect of these ions on the aqueous solution should also be evaluated, especially since LDH itself contains heavy metal cations. Therefore, the risk of secondary pollution should be regarded as an important indicator for evaluating LDH. Choosing environmental-friendly raw materials is the simplest solution. It is also desirable to develop a suitable preparation method for more stable LDH.
3. When treating wastewater on a large scale, a large amount of LDH will be used and this can help reduce the cost of LDH through economy of scale. How does one recycle and reuse the LDH that has reached the end of its service life? When LDH reaches its service life, if its structure has collapsed, one can add it as a filler to polymer materials or cement-based materials. If the structure has not changed significantly and only the introduced functional group or structural components fails, the LDH can be reused after being processed. The easiest way to handle this is calcination, since the calcined product can be transformed into LDH after structural reconstruction in solution.

In summary, the preparation, use, and recycling (or upcycling) of economical and environmental-friendly LDHs need further study. Based on the performance and structure of LDH, we propose the following hypothetical application scenario. In the first step, pristine LDH is used to absorb organic anions in waste liquid, such as dyes. In the second step, because organic anions contain many functional groups, they can complex with heavy metal ions, so LDH-organic anions are used to adsorb heavy metal ions. The third step is to choose a suitable method to remove the heavy metal ions adsorbed by LDH. Repeat the second and third steps until the functional group fails. Finally, the LDH is calcined, and the calcined product undergoes structural reconstruction while adsorbing organic anions in the waste liquid containing organic anions. When LDH-organic anions are then used to adsorb heavy metal ions, a cycle is formed. This is an intriguing hypothesis to be further tested, although some of the studies have been proven viable. More investigations should be conducted to clarify various dimensions of this cross-cutting issue and collect data to enable a reliable life cycle assessment of LDH for various decontamination applications.

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