

Review

Layered Double Hydroxides as Next-Generation Adsorbents for the Removal of Selenium from Water

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Abstract: This research paper provides a comprehensive overview of the use of layered double hydroxides (LDH) in the removal of selenium species from contaminated water sources. Key studies on sorption mechanisms and the impact of competing ions on selenium removal are presented, and the effectiveness of LDH is compared across different structures and compositions. Scholarly sources extensively document the application of conventional LDH for effective selenium removal, with notable advancements achieved through innovative synthesis approaches. Comparative studies between LDH synthesized through various methods reveal the potential of tailored LDH for enhanced selenium adsorption. The paper further explores the influence of competing anions on LDH efficacy, emphasizing the impact of sulfate on selenium removal. Additionally, investigations into calcined LDH and commercially available variants underscore the potential for industrial applications. Beyond conventional LDH, the paper delves into iron-based LDH, LDH with intercalated thiomolybdate anions, and layered rare earth hydroxides, exploring their effectiveness in separating different selenium species. The role of pH in the removal of selenium species and the impact of three-metal cation LDH are also discussed. The study extends to nanocomposites, combining LDH with zero-valent iron, carbon-based materials, and organic compounds, illustrating their potential for selenium species immobilization. The presented findings offer valuable insights for researchers and practitioners in environmental science, addressing the growing demand for efficient selenium remediation strategies.



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1. Introduction

Selenium (Se) is an essential micronutrient that serves as a vital component in numerous compounds, playing a crucial role in many physiological processes for all living organisms, including humans. Selenium compounds actively contribute to antioxidant defense mechanisms, bolster thyroid function, boost the immune system, promote reproductive health, and assist DNA synthesis and repair [1,2]. Selenium has a dual nature, manifesting both beneficial and detrimental effects, contingent on its concentration and chemical form [3]. While selenium is indispensable in trace amounts, excessive levels or prolonged exposure to elevated concentrations can be toxic. The toxicity of selenium varies depending on its chemical form, with inorganic forms typically being more harmful than organic ones [4]. This explains why the majority of environmental studies aimed at removing selenium from contaminated samples primarily address the inorganic selenium species. To predict the behaviors of the studied species accurately, it is important to have comprehensive information about them.

Selenium exists in four oxidation states: selenide (Se(−II)), elemental selenium (Se(0)), selenite (Se(IV)), and selenate (Se(VI)), each with distinct chemical and toxicological properties. Various environmental conditions can result in the presence of different selenium

species. Selenate, representing the fully oxidized form of selenium, can exist in solution as hydrogen selenate (HSeO_4^-) or selenate (SeO_4^{2-}), with an estimated pK_a value of 1.80 ± 0.10 [5]. Under oxidizing conditions, selenate predominates, displaying high solubility and minimal retardation due to its low adsorption and/or precipitation capacities. On the other hand, selenite is commonly found in environments with moderate redox potential and neutral pH. In an aqueous solution, Se(IV) exists as a weak acid in the forms of selenious acid (H_2SeO_3), hydrogen selenite (HSeO_3^-), or selenite (SeO_3^{2-}), with corresponding pK_a values of 2.70 ± 0.06 ($\text{H}_2\text{SeO}_3/\text{HSeO}_3^-$) and 8.54 ± 0.04 ($\text{HSeO}_3^-/\text{SeO}_3^{2-}$) [5]. In reducing environments, water-insoluble elemental selenium can persist across a wide pH range. Under strongly reducing conditions, selenide remains thermodynamically stable and can exist as insoluble metal selenides or as $\text{H}_2\text{Se(g)}$ produced through microbial processes [5,6].

A diagram illustrating the various stable forms of inorganic selenium under different pH and redox potential conditions is available in the paper published by Santos et al. [6].

The fate and transport of selenium species in the environment are governed by a complex interplay of biogeochemical processes, including redox reactions, sorption, solubility, volatilization, and biotransformation. These processes can alter the speciation, mobility, bioavailability, and toxicity of Se across various environmental compartments. Therefore, it is important to monitor and control the Se levels and forms in various matrices, such as water, soil, sediment, air, and biota. Addressing the complexities of selenium remediation, this study evaluates the efficacy of layered double hydroxides (LDH) as sorbents. We explore a range of LDH variants, including traditional forms, iron-enriched versions, those combined with rare earth elements, multiple metal cations, thiomolybdate anions, as well as nanocomposites incorporating zero-valent iron, carbon substances, or organic compounds. The study investigates the unique adsorption properties, selectivity, and mechanisms (e.g., chemisorption, ion exchange, and adsorption) that LDH utilize to remove selenite and selenate from contaminated waters. It systematically assesses the effectiveness of LDH, focusing on performance enhancement through material modifications, the impact of different synthesis methods, and how variations in LDH structure and interlayer anions influence the efficiency of selenium removal under diverse conditions. Figure 1 outlines the key focus areas of the study.

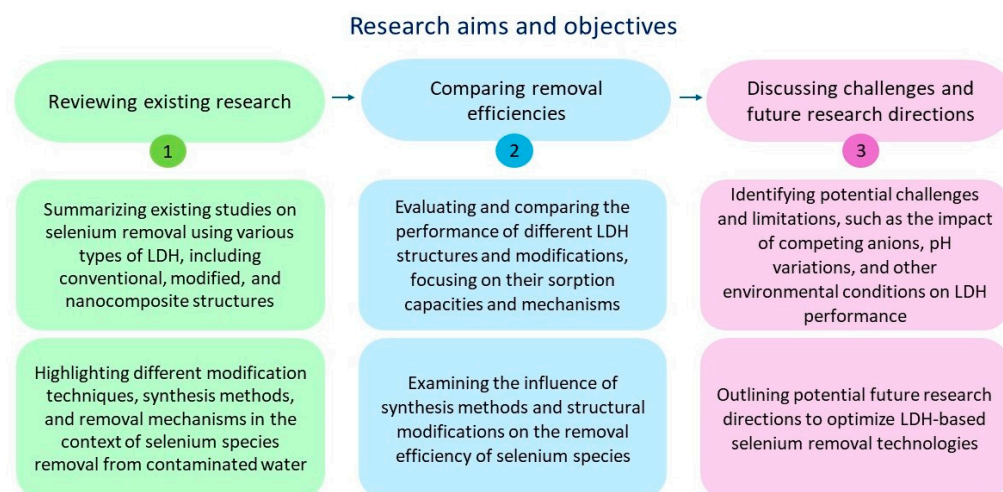


Figure 1. Study aims and objectives.

2. Separation of Selenium from Aqueous Media

While some populations exhibit alarmingly low selenium status, there are areas where selenium levels in the environment have far exceeded the norm. These circumstances give rise to two distinct research avenues: (1) the accurate measurement of (ultra)trace selenium concentrations in water, soil, and food samples within regions characterized by low selenium content, and (2) the efficient removal of selenium from contaminated environmental compartments in regions where elevated levels of this element are prevalent. In this

literature review, our focus will be on the latter objective. Given that the majority of studies are centered around aqueous environments, our paper will primarily address this medium and the procedures employed in decontaminating water samples containing selenium.

Various methods have been explored for selenium removal from water. There have been comprehensive reviews published on this topic. For instance, Lichtfouse et al. [7] reviewed wastewater treatment technologies, covering options based on zero-valent iron, iron oxyhydroxides, supported materials, nanofiltration, reverse osmosis, chitosan-enhanced ultrafiltration, electrodialysis, and activated granular sludge. Similarly, Li et al. [4] offered a critical review of the applications, characteristics, and latest developments in current selenium removal methods, systematically analyzing and comparing their overall efficiencies, applicability, advantages, and drawbacks.

The extraction procedures using suitable solid sorbents achieved remarkable results. The selection of a sorbent mainly depends on factors such as the specific form of selenium to be removed and the concentration of selenium in the water. There are various sorbents that can be utilized for the effective separation of this element, including activated carbon [8], zero-valent iron [7], iron oxyhydroxides [7,9,10], mono-metal oxides and hydroxides such as alumina (Al_2O_3), titania (TiO_2), zirconium hydroxide ($\text{Zr}(\text{OH})_4$) [8], bimetallic composites such as iron-manganese oxides [11,12], iron-zirconium oxides [13], and more. Among them, LDH stand out as highly efficient and versatile sorbents.

Depending on the desired outcome and specific requirements, LDH can be applied in different modes of operation. The two main modes are (1) column arrangement and (2) dispersive arrangement. Each mode has its benefits and drawbacks. The column arrangement may encounter some problems, such as sorbent leaching, cartridge channeling, and cartridge clogging, which can make the procedure longer than desired [14]. The dispersive arrangement involves adding an appropriate amount of the sorbent to the liquid sample and stirring it for a few minutes. Then, the phases are separated, usually by centrifugation [14]. However, this mode poses a challenge of separating the sorbent quantitatively after extraction, especially when the sorbent is in its nanoform. Some of the sorbent may still remain in the solution even after centrifugation. Therefore, an additional separation step, such as filtration, is required.

3. Layered Double Hydroxides

Layered double hydroxides (LDH), also known as hydrotalcite-like compounds or anionic clays, are an intriguing class of inorganic materials with unique structural properties. They consist of positively charged layers of metal hydroxides with charge-balancing anions and water molecules located between the layers. Their chemical composition is often represented by the following formula: $[(\text{M}^{2+})_{1-x}(\text{M}^{3+})_x(\text{OH})_2]^{x+}[(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}]^{x-}$ where M^{2+} and M^{3+} represent a divalent and a trivalent cation, respectively, which are octahedrally coordinated in hydroxide layers; A^{n-} represents an interlayer n -valent anion; and x represents the molar ratio of $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$, determining the layer charge density [15]. The pure hydrotalcite phase can be obtained when x is in the range of 0.20–0.33, resulting in the $\text{M}^{2+}/\text{M}^{3+}$ ratios of 2–4 [16]. For $x > 0.33$, an increased number of neighboring M^{3+} containing octahedra leads to the formation of $\text{M}(\text{OH})_3$, and for $x < 0.20$, a high density of M^{2+} containing octahedra in the hydroxide layer results in the precipitation of $\text{M}(\text{OH})_2$ [17]. This information emphasizes the importance of strictly adhering to the specified value of x [18].

Positively charged hydroxide layers contain cations with similar effective ionic radii. Some examples of M^{2+} cations include Mg (86 pm), Zn (88 pm), Fe (92 pm), Co (88 pm), Ni (83 pm), Cu (87 pm), and Mn (97 pm); some examples of M^{3+} cations include Al (67 pm), Fe (78 pm), Cr (75 pm), V (93 pm), Ga (76 pm), In (84 pm), and Rh (80 pm) [19]. Charge-balancing anions (A^{n-}) can vary and may include common inorganic ones, such as NO_3^- , Cl^- , CO_3^{2-} , SO_4^{2-} , and ClO_4^- , as well as various organic anions and some complex ions [20]. In the interlayer region, anions and a variable amount (m) of water molecules are

present. These, along with the charge, size, shape, and orientation of the hydrated anions, affect the interlayer space. Figure 2 provides a schematic structural representation of LDH.

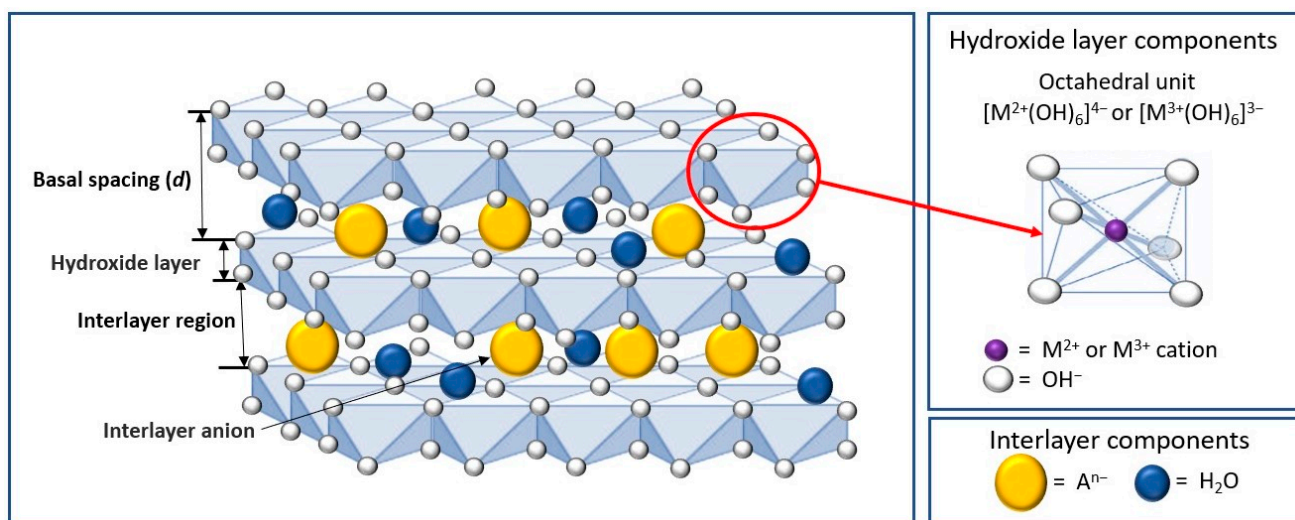


Figure 2. Schematic illustration of layered double hydroxide (LDH) structure with intercalated anions. This figure depicts brucite-like LDH sheets, with intercalated anions occupying the interlayer region. The light blue octahedra represent the positively charged hydroxide layers, featuring octahedrally coordinated M^{2+} and M^{3+} cations (marked in purple). The exchangeable anions are indicated in yellow, and the associated water molecules are shown in dark blue. The diagram highlights the orderly arrangement of hydroxide layers and anions within the structure.

From the above, it is evident that the composition of LDH can vary significantly. This variation is attributed not only to the combination of different octahedrally coordinated M^{2+} and M^{3+} cations and the presence of diverse A^{n-} anions but also to the intercalation of various molecules in the interlayer space. Some intercalates can form when water molecules are replaced with other polar molecules, such as polyols or amines, between the layers of a crystalline material.

There are many ways to synthesize LDH, some of which have been extensively covered in recent reviews [14,21]. Hence, we will not go into details here. In summary, commonly utilized techniques include co-precipitation, anion exchange, the memory effect method, and their modifications, each with its own set of advantages and disadvantages. Guan et al. [21] summarized the pros and cons of the most common synthesis methods in a well-organized table. It is worth highlighting that the choice of synthesis method can significantly impact the ultimate properties of the prepared LDH, thus influencing their suitability for the intended application [22].

Following the synthesis, it is essential to characterize the prepared LDH in order to assess their structure, composition, and physical and chemical properties. A recent paper by Hagarová and Nemček [14] provides an overview of LDH characterization methods, allowing for a brief summary here.

Crystalline solid structure analysis primarily relies on X-ray diffraction (XRD). Fourier transform infrared spectroscopy (FTIR) identifies molecular structures. Combining Raman spectroscopy with FTIR provides comprehensive molecular information. Energy-dispersive X-ray spectroscopy (EDX) reveals the LDH chemical structure, while elemental mapping determines its distribution. X-ray photoelectron spectroscopy (XPS) investigates chemical structure, valence states, and binding energies. X-ray fluorescence spectroscopy (XFS) detects cation ratios and trace elements. Microscopy techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution TEM (HR-TEM) reveal LDH shape, size, and orientation. The Brunauer–Emmett–Teller (BET) method determines specific surface area, pore volume, and diameters. Barrett–Joyner–

Halenda (BJH) analysis provides information on pore size and distribution. Additionally, differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) are valuable tools for understanding material transformations in response to temperature changes.

In practice, achieving a comprehensive LDH characterization often involves a combination of these techniques, as relying solely on one method may not yield all the necessary information. Research papers commonly utilize various combinations of these methods to thoroughly describe laboratory-synthesized LDH structures, compositions, and properties.

4. The Application of Layered Double Hydroxides for the Effective Removal of Selenium Species from Contaminated Environmental Waters

Selenium can be introduced into aquatic environments through both natural and anthropogenic processes. Worldwide, incidents of selenium contamination in water bodies are not uncommon, and such occurrences have been reported in several places, including China, the United States of America, Australia, New Zealand, and Finland [23].

Selenium primarily enters the aquatic environment in the form of inorganic species, specifically selenite (Se(IV)) and selenate (Se(VI)). Among these, selenite is recognized as more toxic and more easily absorbed by organisms as supported by available data [24,25]. Conversely, selenate is considered the more stable species [26]. Furthermore, selenate and selenite have varying adsorption mechanisms on inorganic anion exchangers, which results in selenate being more challenging to remove than selenite [27–29]. Despite these distinctions, both species have roughly the same number of published studies on their removal.

In the context of achieving drinking water quality standards through cleaning procedures, the following information may be of interest. Since the 1970s, selenium's presence in drinking water has been a subject of debate [30] due to its potential to make the water toxic and harmful to both humans and the environment. As a result of these controversial discussions, various selenium limits have been adopted. The upper limit for selenium concentration in drinking water varies across different countries and regions. Many countries like Canada, Australia, Japan, Thailand, and New Zealand, along with the European Union, follow the same limit of 10 µg/L. On the other hand, the U.S. Environmental Protection Agency (USEPA) has a considerably higher limit of 50 µg/L, while the California Environmental Protection Agency has a limit of 30 µg/L. The World Health Organization (WHO) recommends a guideline value of 40 µg/L for selenium in drinking water. These differences reflect the uncertainty and controversy over the health effects of selenium exposure. However, epidemiological studies investigating the effects of selenate, an inorganic selenium species commonly found in drinking water, have revealed evidence of toxicity at much lower concentrations than previously assumed. This indicates that health risks may occur at exposures even below the limit of 10 µg/L. As a result, a proposal to lower this limit to 1 µg/L has been put forward [30]. Nevertheless, most drinking waters have very low selenium content, only a few nanograms per liter. Therefore, changing the selenium standard to this level would not affect the use of most existing sources of drinking water.

Meeting the drinking water limit for selenium can be challenging when the water is highly contaminated. At this point, it is worth noting that these limits apply to the total amount of selenium in the water. Moreover, since selenium can exist in different forms, it is important to consider not only the total selenium concentration but also its speciation when developing an effective cleaning procedure.

In recent environmental science literature, numerous studies have delved into the removal of inorganic selenium species from contaminated water samples. As mentioned earlier, these species typically exist in their oxyanion forms in aqueous environments, with their presence influenced by pH and redox potential conditions. Figure 3 provides a schematic representation of the most frequently employed removal mechanisms that can be applied to any of these species using LDH structures. These mechanisms encompass surface adsorption through electrostatic attraction and outer-sphere complexation, which is mainly suitable for selenate ions, a unique type of chemisorption via inner-sphere complexation,

particularly effective for selenite ions, and anion exchange mechanisms that are applicable to both selenium species. These effective approaches for selenium species removal are depicted in Figure 3A. Additionally, the reconstruction of calcined LDH structures has been extensively explored and proven to be effective for this purpose, as illustrated in Figure 3B.

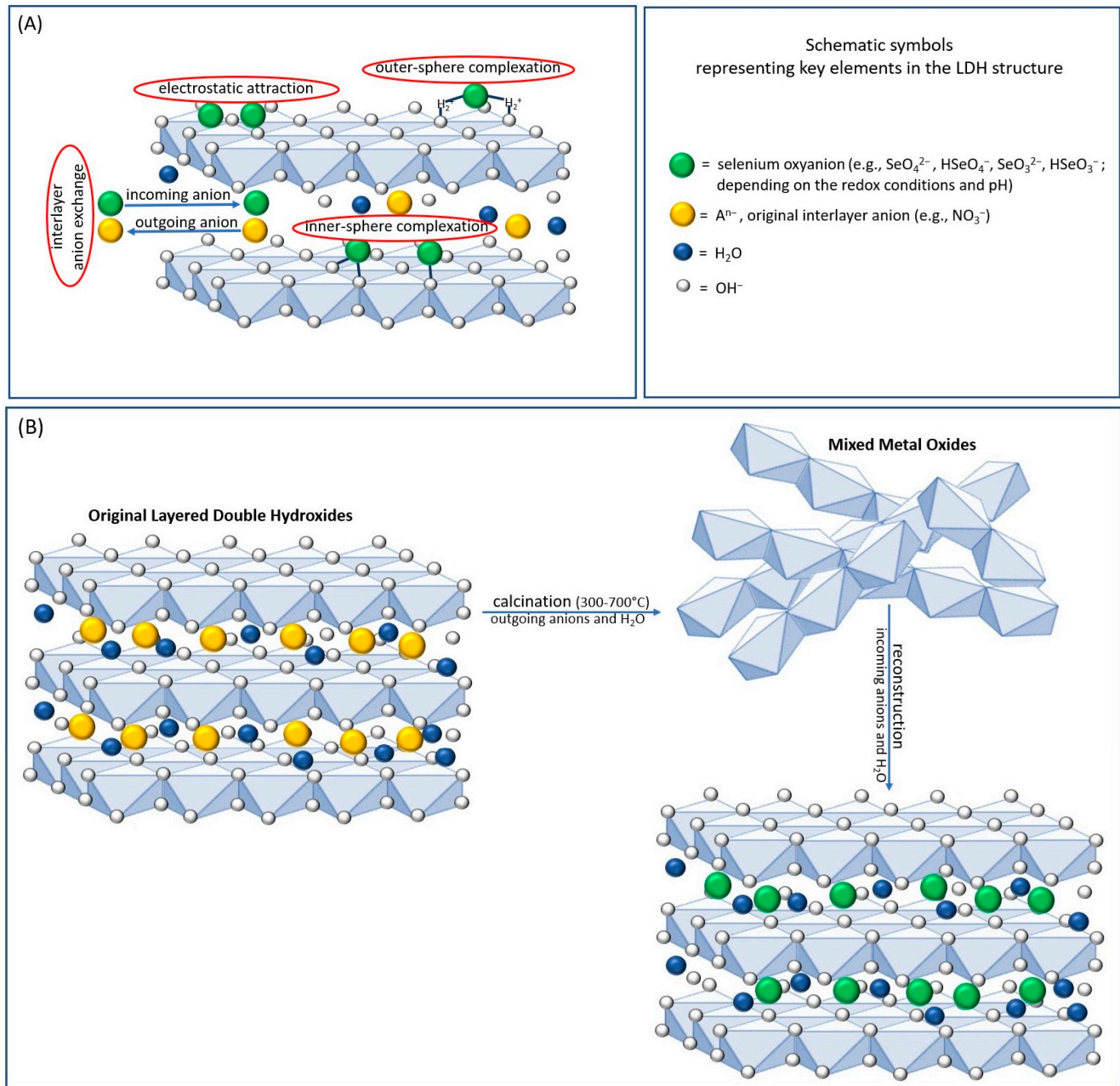


Figure 3. The application of layered double hydroxides (LDH) for water purification: a schematic illustration of its structure and selenium oxyanion adsorption. (A) Surface adsorption and anion exchange mechanisms. (B) Reconstruction of calcined LDH (so-called memory effect method).

The initial comprehensive investigations into selenium species sorption using two specific types of LDH, $\text{MgAl}(\text{Cl}^-)\text{-LDH}$ and $\text{ZnAl}(\text{Cl}^-)\text{-LDH}$, were carried out by You et al. in 2001 [31]. Since then, numerous researchers have probed deeper into the sorption mechanisms of selenium species. They have also examined how selenium species behave in the presence of other co-existing anion forms employing various LDH materials. In the following sections, we will explore conventional LDH structures, modified variants of these layered materials (including those containing iron, rare earth elements, three different

metal cations, and unique interlayer anions like MoS_4^{2-}), as well as nanocomposites that combine LDH with other materials (such as zero-valent iron, carbon nanodots, graphene oxide, reduced graphene oxide, carbon aerogels, chitosan, and amino acids).

4.1. Conventional Layered Double Hydroxides

The application of conventional LDH, such as $\text{MgAl}(\text{CO}_3^{2-})$ -LDH, for the removal of selenium species from contaminated water samples has been extensively documented in the existing literature [27,32–39]. Both laboratory-synthesized [27,32,33,36,38,40,41] and commercially accessible [34,35,37,39] variants of $\text{MgAl}(\text{CO}_3^{2-})$ -LDH have consistently demonstrated their effectiveness in these studies.

Significant efforts have been directed toward improving the synthesis of $\text{MgAl}(\text{CO}_3^{2-})$ -LDH, especially by Chubar in 2011 [42]. She introduced an innovative sol-gel synthesis approach, which differed from conventional methods. This technique, known as alkoxide-free sol-gel (AFSG) synthesis, eliminates the need for toxic and expensive metal alkoxides as precursor materials. In another study, Chubar et al. [38] compared three $\text{MgAl}(\text{CO}_3^{2-})$ -LDH samples prepared by different methods: AFSG synthesis, hydrothermal precipitation (HTP), and alkoxide sol-gel (ASG) synthesis. They used various methods to characterize the surface, structure, and adsorptive properties of the samples, with a particular focus on the speciation of interlayer carbonate, aluminum, magnesium, and moisture location. Valuable and complementary information was obtained from the surface area, pore size, pore volume data, and the shapes of the isotherms from N_2 physisorption and CO_2 chemisorption studies. This information allowed the research team to predict the adsorptive removal properties of the three $\text{MgAl}(\text{CO}_3^{2-})$ -LDH samples. They concluded that the alkoxide-free sol-gel synthesis route enabled the tailoring of highly reactive $\text{MgAl}(\text{CO}_3^{2-})$ -LDH with abundant surface hydroxyl groups and mobile interlayer ionic carbonate. Therefore, the authors suggested using this method to prepare LDH for the effective removal of selenium species from aqueous matrices. They supported this suggestion by showing that this LDH has the highest sorption capacities for selenite and selenate among the tested LDH (see Table 1).

The inorganic ion exchanger prepared through AFSG synthesis exhibited remarkable efficacy in simultaneously removing two selenium species [27]. This efficacy arose from different sorption mechanisms for these two species. Selenite adsorption by $\text{MgAl}(\text{CO}_3^{2-})$ -LDH was dominated by chemisorption (inner-sphere complex formation) rather than ion exchange. Conversely, selenate removal occurred exclusively through an ion exchange mechanism, entailing the exchange of surface OH^- ions and interlayer CO_3^{2-} ions.

Table 1. Comparison of sorption parameters for selenium oxyanions adsorbed by various layered double hydroxide (LDH) materials.

Oxyanion	LDH	Sorption Isotherm	Kinetic Model	Sorption Capacity	Reference
Selenate	MgAl(CO ₃ ²⁻)-LDH	LM	P-S-O	103 mg/g	[33]
Selenate	MgAl(CO ₃ ²⁻)-LDH	n.r.	n.r.	90 mg/g	[27]
Selenate	MgAl(CO ₃ ²⁻)-LDH	LM	P-S-O	66 mg/g	[37]
Selenate	MgAl(CO ₃ ²⁻)-LDH (AFSG)	n.r.	n.r.	46 mg/g	[38]
Selenate	MgAl(CO ₃ ²⁻)-LDH (HTP)	n.r.	n.r.	17 mg/g	[38]
Selenate	MgAl(CO ₃ ²⁻)-LDH (ASG)	n.r.	n.r.	5 mg/g	[38]
Selenate	MgAl(NO ₃ ⁻)-LDH	FM, LM	n.r.	77.4 mg/g	[43]
Selenate	MgAl(NO ₃ ⁻)-LDH	n.r.	n.r.	69.4 mg/g	[44]
Selenate	MgFe(SO ₄ ²⁻)-LDH	LM	n.r.	0.55 mmol/g	[45]
Selenate	MgFe(Cl ⁻)-LDH	LM	n.r.	0.83 mmol/g	[46]
Selenate	MgAl(MoS ₄ ²⁻)-LDH	LM	P-S-O	85 mg/g	[47]
Selenate	FeMgAl(MoS ₄ ²⁻)-LDH	LM	P-S-O	167.2 mg/g	[48]
Selenate	FeMgAl(MoS ₄ ²⁻)-LDH	LM	P-S-O	55.56 mg/g *	[49]
Selenate	FeMgAl(MoS ₄ ²⁻)-LDH	LM	P-S-O	53.48 mg/g **	[49]
Selenate	MgAl(NO ₃ ⁻)-LDH/C-dots	n.r.	n.r.	45.9 mg/g	[44]
Selenate	MgAl(NO ₃ ⁻)-LDH/GO	FM, LM	n.r.	65.9 mg/g	[43]
Selenate	MgAl(CO ₃ ²⁻)-LDH/chitosan	LM	P-S-O	12 mg/g	[50]
Selenate	LRH (Y ₂ (OH) ₅ Cl 1.5H ₂ O	LM	n.r.	124 mg/g	[51]
Selenite	MgAl(CO ₃ ²⁻)-LDH	LM	P-S-O	168 mg/g	[33]
Selenite	MgAl(CO ₃ ²⁻)-LDH	n.r.	n.r.	160 mg/g	[27]
Selenite	MgAl(CO ₃ ²⁻)-LDH	FM	P-S-O	66.89 mg/g	[40]
Selenite	MgAl ₂ O ₄ (CLDH)	FM	P-S-O	179.59 mg/g	[40]
Selenite	MgFe(CO ₃ ²⁻)-LDH	FM, LM	P-F-O	40 mg/g	[52]
Selenite	MgAl(CO ₃ ²⁻)-LDH (AFSG)	n.r.	n.r.	120 mg/g	[38]
Selenite	MgAl(CO ₃ ²⁻)-LDH (HTP)	n.r.	n.r.	21 mg/g	[38]
Selenite	MgAl(CO ₃ ²⁻)-LDH (ASG)	n.r.	n.r.	10 mg/g	[38]
Selenite	MgAl(Cl ⁻)-LDH	LM	P-S-O	119 mg/g	[53]
Selenite	MgFe(Cl ⁻)-LDH	LM	n.r.	0.63 mmol/g	[46]
Selenite	MgAl(MoS ₄ ²⁻)-LDH	LM	P-S-O	294 mg/g	[47]
Selenite	FeMgAl(MoS ₄ ²⁻)-LDH	LM	P-S-O	483.9 mg/g	[48]
Selenite	MgAl(NO ₃ ⁻)-LDH/CAs	LM	P-S-O	73.6 mg/g	[54]
Selenite	MgAl(CO ₃ ²⁻)-LDH/chitosan	FM	P-S-O	17 mg/g	[50]
Selenite	LRH (Y ₂ (OH) ₅ Cl 1.5H ₂ O	LM	n.r.	207 mg/g	[51]

n.r.: not reported; * in the presence of Cr³⁺ ions; ** in the presence of Cu²⁺ ions; LM: Langmuir model; FM: Freundlich model; P-S-O: pseudo-second-order; P-F-O: pseudo-first-order; AFSG: alkoxide-free sol-gel; HTP: hydrothermal precipitation; ASG: alkoxide sol-gel; C-dots: carbon nanodots; GO: graphene oxide; CAs: carbon aerogels; CLDH: calcined LDH; LRH: layered rare earth hydroxide.

To facilitate the transition of MgAl(CO₃²⁻)-LDH into industrial applications, its efficacy in removing selenite and selenate was assessed under both static and dynamic adsorption conditions. Special attention was given to the influence of competing anions such as phosphate, sulfate, carbonate, silicate, and chloride [33]. A few years later, further investigations into the impact of sulfate on the adsorption of selenate [36] and selenite [55] onto MgAl(CO₃²⁻)-LDH prepared via the ASFG synthesis were conducted. The authors utilized XPS surface analysis to delineate the influence of different phases of this LDH on the removal of selenium species in relation to two variables: the absence/presence of sulfate and varying pH levels.

In multiple studies, a simple co-precipitation method was employed to prepare MgAl(CO₃²⁻)-LDH [32,40,41]. Subsequent calcination steps at different temperatures, including 340 °C [32], 500 °C [40], or 550 °C [41], triggered various processes like dehydration, dehydroxylation, and carbonate loss. As a result of this thermal activation and the memory effect, selenite entered the interlayer of the calcined LDH (CLDH), forming

MgAl(SeO₃^{2−})-LDH hydrotalcite [32,40,41]. A comparison of the sorption capacity between LDH and CLDH revealed that CLDH was a more efficient sorbent for selenite removal, with sorption values more than double [40] and even over five times larger [41].

In a number of studies, commercially available MgAl(CO₃^{2−})-LDH were tested for their capacity to remove selenate [34,35,37]. In each of these studies, calcined LDH were utilized. In the research conducted by Li et al. [34,37], the characterization of commercially available granulated MgAl(CO₃^{2−})-LDH revealed that the manufacturer had removed interlayer water and carbonate anions. In another study by Bryan et al. [35], commercially available MgAl(CO₃^{2−})-LDH were calcined at 500 °C. After immersing the calcined LDH into a selenate aqueous solution, it demonstrated the ability to regenerate the layered structure. Post-reconstruction, the material exhibited proficiency in removing trace levels of selenate through surface adsorption, which is a rapid process. However, at higher concentrations, ion exchange played a more significant role due to the limited availability of surface sites [34,37].

Many research papers primarily focus on examining the influence of other co-existing anions on selenate removal. Given the chemical and physical similarities between selenate and sulfate, extensive research is conducted on water samples with elevated sulfate levels. When the sulfate concentration is much higher than the selenate concentration, it can reduce selenate removal by competing for ion exchange sites or forming precipitates. For instance, in a study where the sulfate concentration was more than 20,000 times higher than the selenate concentration [34], pre-treatment with BaCl₂ was necessary to improve selenate removal from 33% to 65% (which is approaching the rate of 74% obtained for selenate removal from deionized water). However, this also caused some selenate co-precipitate with BaSO₄.

Granulated LDH is a promising sorbent for removing selenate and other anions from power plant wastewater. It has high anion adsorption capacities and can function under dynamic sorption conditions. Laboratory column tests and field experiments have confirmed that granulated LDH can effectively remove selenate and other co-anions from wastewater [37]. Constantino et al. [39] studied the removal of both selenium species by a commercial MgAl(CO₃^{2−})-LDH and its calcined form. The calcination was carried out in the laboratory at 500 °C for 4 h. The material's sorption and desorption properties for selenite and selenate were thoroughly investigated in the presence of nitrate, sulfate, and phosphate ions. It was found that sulfate ions competed more with selenate, while phosphate ions competed more with selenite. A dual-mode Langmuir–Freundlich model was applied to explain how selenium species adsorbed to the material, overcoming some limitations of the Langmuir and Freundlich models, particularly in dealing with different types of sorption sites and affinities [56,57].

The sedimentation rate is an important parameter to consider when developing effective cleaning procedures in the dispersive mode. Keeping this in mind, Tsuchiya et al. [58] assessed the performance of two variants of LDH for selenate removal, MgAl-LDH and MgOAl-LDH. The co-precipitation method, which involves using Mg²⁺ and Al³⁺ salts, produces fine-particle LDH (<10 µm) with low solid–liquid separability. To enhance the settleability and separability of the sludge from the slurry, it is essential to produce larger particles. By using MgO instead of Mg²⁺ salts, MgOAl-LDH with particle sizes in the range of 10–250 µm can be obtained, resulting in a sedimentation rate that is 8.6–11 times higher. This improvement is highly beneficial for scaling up the process. However, it is worth noting that reusing and recycling this sorbent for further applications poses challenges.

4.2. Iron-Based Layered Double Hydroxides

The substitution of a potential risk element, such as aluminum, in LDH structures intended for drinking water treatment, has led to the development of iron-based LDH. The effectiveness of various MgFe-LDH structures with different interlayer anions (nitrate, chloride, sulfate, or carbonate) and different specific surface areas in separating selenite [46,52,59], selenate [45,46,59], and selenocyanate [59] was assessed.

Three MgFe-LDH variants with different interlayer anions (Cl^- , SO_4^{2-} , and CO_3^{2-}) underwent a kinetic evaluation to examine their ability to adsorb dissolved selenium species (selenate, SeO_4^{2-} , and selenite, $\text{HSeO}_3^-/\text{SeO}_3^{2-}$) [46]. The extent of selenium species uptake by MgFe-LDH depended on the identity of the interlayer anion, following the order $\text{Cl}^- > \text{SO}_4^{2-} > \text{CO}_3^{2-}$. This order reflects the varying strength of anion attachment within the interlayer, ranging from least strongly held to most strongly held. The interlayer anion exchange was confirmed as an important uptake mechanism for the studied selenium species using MgFe(Cl^-)-LDH and MgFe(SO_4^{2-})-LDH. The kinetics of selenium species uptake typically involved a rapid initial anion exchange phase, followed by a slower release back into the solution due to competition with displaced interlayer anions. This reverse exchange of selenium species was intensified by excess dissolved interlayer anions and high pH values.

Even though the crucial role of pH in selenite removal through adsorption on MgFe(CO_3^{2-})-LDH was also acknowledged by Das et al. [52], the authors confirmed that the adsorption is not solely achieved due to electrostatic forces of attraction between the negatively charged selenite species and the positively charged LDH surfaces. This is because a significant amount of selenite adsorption occurs even at pH above the pH_{pzc} (where the sorbent surface becomes negatively charged). This suggests that another type of sorption mechanism, most likely involving the formation of inner-sphere complexes, is responsible for selenite adsorption.

A comparison of different LDH, specifically MgAl-LDH and MgFe-LDH with intercalated sulfate and carbonate ions, revealed that LDH containing interlayer SO_4^{2-} and CO_3^{2-} anions along with Fe^{3+} cation exhibit superior scavenging properties for selenate, molybdate, and arsenate [45] compared with LDH with CO_3^{2-} and Al^{3+} . In all cases, a higher adsorption rate was observed with an excess of sorbates, but the overall percentage of sorbate uptake decreased once the surface of LDH reached saturation. The sorbate uptake was also negatively affected by increasing pH levels and the presence of competing anions. For selenate and molybdate, outer-sphere complexation on surfaces and edges appears to be the primary sorption mechanism. In contrast, strong chemical bonds form between arsenate and MgFe-LDH, indicating a distinct mode of interaction.

Ibrahim and Vohra [59] recently examined the utility of MgFe(NO_3^-)-LDH for removing selenite, selenate, and selenocyanate. They explored a range of conditions, including LDH dosage (0.5–1.5 g/L), LDH calcination temperature (0–500 °C), and selenium species concentration (2.5–7.5 mg/L). The highest removal efficiency for selenite and selenate was achieved using MgFe-LDH calcined at 500 °C with a dosage of 1.5 g/L. In contrast, the highest removal efficiency for selenocyanate was observed for MgFe-LDH calcined at 250 °C. Interestingly, the kinetic and thermodynamic models for the studied selenium species did not show universal consistency.

4.3. Layered Rare Earth Hydroxides

Layered rare earth hydroxides (LRH), also known as RE-LDH, are a subclass of LDH that have rare earth elements in their cationic hydroxide layers. Although they have been synthesized relatively recently, they already have various applications in catalysis, adsorption, drug delivery, and environmental remediation. Preliminary environmental studies on LRH have confirmed their ability to exchange their interlayer anions (e.g., nitrate, chloride) with common inorganic anions (e.g., sulfate) as well as organic dicarboxylate anions [60,61].

In 2017, Zhu et al. [51] reported the synthesis of a novel compound, $\text{Y}_2(\text{OH})_5\text{Cl} \cdot 1.5\text{H}_2\text{O}$. The authors thoroughly characterized its chemical composition and demonstrated its potential for removing selenium species from aqueous samples. They conducted a series of experiments using a batch method to investigate the sorption kinetics, isotherms, selectivity, and desorption of selenite and selenate. The maximum sorption capacities for selenite and selenate were found to be 207 mg/g and 124 mg/g, respectively, ranking among the highest achieved for layered hydroxides (see Table 1). The sorption mechanisms were elucidated

through a combination of various techniques and methods. The results confirmed that selenate ions exchanged with chloride ions in the interlayer space, forming outer-sphere complexes. Selenite ions bound directly to the Y^{3+} centers in the positively charged layer of $[Y_2(OH)_5(H_2O)]^+$ through strong bidentate binuclear inner-sphere complexation, explaining the higher uptake of selenite compared with selenate. Furthermore, the authors drew an interesting conclusion from competitive experiments. In the low-concentration region, LRH almost completely removed selenium from aqueous matrices in the presence of all studied competitive anions, such as NO_3^- , Cl^- , CO_3^{2-} , SO_4^{2-} , and HPO_4^{2-} . However, the material exhibited some limitations, such as instability at relatively low pH levels and the inclusion of yttrium (Y), a critical rare earth element, restricting its broad practical use [62].

4.4. Layered Hydroxides Containing Three Different Metal Cations

If hydroxide layers contain three different metal cations, they are referred to as layered triple hydroxides (LTH), trimetallic layered double hydroxides (TLDH), ternary layered double hydroxides, or layered double hydroxides, with each metal specified (e.g., MgAlFe-LDH). These terms are interchangeable in the literature, but we follow the original author's nomenclature.

The variation in metal composition within the hydroxide layers of LDH leads to differences in specific surface areas and charge densities. By optimizing the composition, it is possible to enhance the efficiency of removal processes. Zhou et al. [63] discuss how the distribution of OH bonds among various metal oxides within ternary LDH affects the removal processes for selenate and chromate. They focus on MgCaFe(Cl^-)-LDH specifically. The study investigated four unique LDH structures with varying calcium and magnesium concentrations, denoted as $Mg_{3-x}Ca_xFe(Cl^-)$ -LDH, with x representing calcium content at values of 0, 0.3, 1.0, and 1.5. Special attention was given to the anion sorption process on LDH after the dissolution of Ca. The researchers found that the ternary LDH removed less selenate and chromate than $Mg_3Fe(Cl^-)$ -LDH. Selenate removal was three times lower. The observed reduction in selenate and chromate removal can be linked to the breakdown of the CaFe-LDH structure, which, in turn, diminished the MgFe-based LDH structure's capacity for anion adsorption. By 'Mg-Fe-based LDH', the authors likely refer to the fact that as calcium dissolved from the structure, the compound ceased to be a ternary LDH consisting of magnesium, iron, and calcium. Instead, it became a binary LDH containing only Mg and Fe.

In order to understand the effect of silicate on the phase transformations of different types of calcined LDH (CLDH) materials, five CLDH with different cation ratios were tested [64]. These CLDH samples were derived from calcining five LDH with carbonate in the interlayer and different proportions of Mg, Al, and Fe: Mg_2Al -LDH, $Mg_2Al_{0.75}Fe_{0.25}$ -LDH, $Mg_2Al_{0.5}Fe_{0.5}$ -LDH, $Mg_2Al_{0.25}Fe_{0.75}$ -LDH, and Mg_2Fe -LDH. The objective was to evaluate their effectiveness in immobilizing SeO_3^{2-} and SeO_4^{2-} at two different pH values, 10 and 13. The results of this study revealed that both pH and the presence of silicate had significant impacts on the immobilization of SeO_3^{2-} and SeO_4^{2-} by CLDH materials. At higher pH values, the sorption capacities for selenium oxyanions were notably reduced. Higher pH reduced the sorption capacities due to an increased OH^- concentration in the solution, which decreased the positive surface charge of the regenerated LDH and enhanced the competition between selenium oxyanions and OH^- in the interlayer space. Moreover, silicate ions impaired the memory effect of LDH by reacting with MgO and Al_2O_3 components in CLDH and forming magnesium silicate hydrate and geopolymer-like substances. These substances covered the CLDH surface, preventing the hydroxylation of metal oxides and hindering LDH regeneration.

Ismail et al. [65] reported the synthesis and characterization of $MgCuAl(CO_3^{2-})$ -LTH, a ternary LDH, and tested its ability to remove both inorganic selenium species simultaneously. The authors used a response surface methodology (RSM) to optimize the key process conditions, such as selenite concentration, selenate concentration, and adsorbent dosage. Their findings indicated that the adsorbent dosage was the most critical

parameter affecting the removal efficiency of both selenite and selenate in the mixed streams. By using a 2.5 g/L adsorbent dosage, with 1 mg/L initial concentrations of selenite and selenate each, they achieved almost complete removal of selenium species.

Trimetallic LDH, such as $\text{FeMgAl}(\text{MoS}_4^{2-})$ -LDH, that are employed for selenium species removal, are the topic of the following subsection. These LDH have thiomolybdate anions in their composition, and the S^{2-} from MoS_4^{2-} groups plays a crucial role in their selenium removal capabilities [48,49].

4.5. Layered Double Hydroxides with Intercalated Thiomolybdate Anions

Previous studies showed that replacing the conventional anions in the LDH interlayers with thiomolybdate anions (MoS_4^{2-}) not only functionalized the materials for capturing heavy metal cations through selective M-S bonding [66], but these materials also performed well in removing oxyanions such as HAsO_3^{2-} , HAsO_4^{2-} , and CrO_4^{2-} [67]. In this section, we will discuss both binary and ternary LDH with intercalated thiomolybdate anions and their applicability for the removal of selenium species from aqueous media [47–49].

The investigation of simultaneous removal of selenium oxyanions, specifically SeO_4^{2-} , HSeO_3^- , and SeO_3^{2-} , along with heavy metal cations, including Hg^{2+} , Cu^{2+} , and Cd^{2+} , using MoS_4^{2-} -intercalated MgAl -LDH, revealed that the presence of Hg^{2+} ions greatly enhances the capture of SeO_4^{2-} , while the three metal ions (Hg^{2+} , Cu^{2+} , Cd^{2+}) improve the removal of SeO_3^{2-} and HSeO_3^- [47]. There are several processes that contribute to the removal of the studied species. In the absence of other ions, SeO_4^{2-} can react with LDH- (MoS_4^{2-}) to form mixed phases of $\text{LDH}-(\text{MoS}_4^{2-}) \times (\text{SeO}_4^{2-})_y$. When a mixture of SeO_4^{2-} and M^{2+} is present, the enhanced removal capacity can be attributed to reactions between the introduced metal ions and the interlayer MoS_4^{2-} , allowing SeO_4^{2-} to access the interlayer space. The rapid uptake and high capacity for selenite can be attributed to the reduction of Se(IV) to Se^0 by the S^{2-} sites within the MoS_4^{2-} component of the $\text{MgAl}(\text{MoS}_4^{2-})$ -LDH.

A three-step procedure for the $\text{FeMgAl}(\text{MoS}_4^{2-})$ -LDH synthesis was outlined by Aregay et al. [49]. This ternary LDH was used for simultaneous removal of selenate anions and metal cations, particularly Cr^{3+} and Cu^{2+} . The presence of these cations has shown synergetic effect on selenate removal. Moreover, the simultaneous removal of selenate and metal cations has minimized the leaching of Mo from the LDH, likely due to co-precipitation reactions between leached MoS_4^{2-} , metal cations, and selenate anions. This process enhances selenate removal efficiency and minimizes secondary contamination caused by leached Mo.

A more thorough investigation into the potential roles of Fe ions in the ternary LDH, specifically in $\text{FeMgAl}(\text{MoS}_4^{2-})$ -LDH, was conducted by Liao et al. [48]. Their findings can be summarized as follows. The inclusion of Fe within the layers alters the layer charge density, allowing for the incorporation of more functional groups within the (inter)layers. Moreover, the presence of heterogeneous Fe acts as a catalyst for reductive reactions between selenium oxyanions and S^{2-} ions (from MoS_4^{2-} groups). This catalytic effect offers distinct benefits in terms of uptake capacities and efficiency for the sequestration of selenium species. The adsorption capacities were impressive, with values reaching 483.9 mg/g for Se(IV) and 167.2 mg/g for Se(VI) . For selenite, this represents the highest sorption capacity achieved using LDH (see Table 1).

4.6. Nanocomposites with Layered Double Hydroxides and Zero-Valent Iron

When it comes to remediation of contaminated environments, zero-valent iron (ZVI) stands out as a highly versatile material. It can degrade or immobilize a wide range of pollutants, encompassing both organic and inorganic substances. Recent studies, including those by Ling et al. [68], Liang et al. [69], Olegario et al. [70], and Sheng et al. [71], have highlighted the effectiveness of ZVI in immobilizing inorganic selenium species. However, there are still major challenges that need to be addressed. One of them is the aggregation of nanoscale ZVI (NZVI), which reduces its reactivity, durability, and efficiency, thereby

hindering its widespread use. This aggregation is caused by high surface energy and magnetic forces [72–74]. Binding NZVI to support materials has emerged as a promising solution. This approach effectively prevents agglomeration and provides a larger surface area for NZVI, enhancing its performance [75,76]. Hu et al. [77] and Xu et al. [78] investigated the potential of nanoscale zero-valent iron loaded on layered double hydroxides (NZVI/LDH) for selenate removal. They reported that MgAl-LDH with nano-ZVI helped prevent the agglomeration of the nanoparticles and that the FeAl(Cl[−])-LDH/ZVI larger-grained composite efficiently removed selenate in both batch and continuous experiments. The researchers explained that the immobilization mechanism of Se(VI) involved two steps: physical adsorption of Se(VI) on ZVI/LDH surface (through electrostatic attraction and anion exchange) followed by reduction of Se(VI) into Se⁰/Se^{2−} by ZVI. To clarify the exact mechanisms, more detailed and thorough investigations are required, but these studies demonstrate the potential of ZVI/LDH composites as strong reactive sorbents for transforming and immobilizing selenate in water treatment processes.

4.7. Nanocomposites with Layered Double Hydroxides and Carbon-Based Materials

Carbon-based materials (CBM) have been widely explored as adsorbents in the past two decades. They have remarkable characteristics and versatile applications in various domains, including chemistry, physics, and engineering [79]. Some of the most popular CBM are activated carbon (AC), graphene oxide (GO), carbon nanotubes (CNT), carbon nanofibers (CNF), carbon nanodots (C-dots), biochar (BC), and carbon aerogels (CAs). Many of these CBM have also been combined with LDH structures to form composite materials. These composites can remove selenium oxyanions from water samples, as discussed in this subsection.

The co-sorption of cationic species, represented by Sr²⁺, and anionic species, represented by SeO₄^{2−}, was studied using two types of nanocomposites: Mg/Al(NO₃[−])-LDH with carbon nanodots (C-dots) and Mg/Al(NO₃[−])-LDH with graphene oxide (GO) [43,44,80]. The removal mechanism of SeO₄^{2−} was the same for both nanocomposites, involving ion exchange with NO₃[−]. However, the adsorption mechanism of Sr²⁺ differed depending on the type of carbonaceous material. For the Mg/Al(NO₃[−])-LDH/C-dots nanocomposite, Sr²⁺ mainly coordinated with the carboxyl groups (−COO−) present on the surface of negatively charged C-dots [44]. For the Mg/Al(NO₃[−])-LDH/GO nanocomposite, Sr²⁺ could coordinate with both carboxyl and alkoxy groups (−COO−/−CO−) on GO [43]. The alkoxy groups were formed by the ring opening of epoxides on GO. In both nanocomposites, the interaction between LDH and Sr²⁺ was dominated by electrostatic and ionic forces [80]. A notable observation was that both Mg/Al(NO₃[−])-LDH/C-dots and Mg/Al(NO₃[−])-LDH/GO composites had lower sorption capacities for SeO₄^{2−} than Mg/Al(NO₃[−])-LDH without C-dots and GO (see Table 1). This could be attributed to the partial charge neutralization of LDH by the carbonaceous matter. Considering the higher sorption capacity of traditional LDH, one might argue that they represent a more favorable option for treating contaminated water, compared with nanocomposites. This advantage is further underscored by the fact that nanocomposites are more complicated and time-consuming to prepare, which also makes them more expensive.

A more complex composite material, which is referred to as Si-rGO/LDH-Fe, was synthesized by Suma et al. [81]. This sorbent was prepared from precursor materials such as reduced graphite oxide (rGO) and MgAl(NO₃[−])-LDH. The synthesis process involved emulsion polymerization and crosslinking to form Si-rGO/LDH, followed by modification with FeCl₃ to enhance its sorption capacity. These steps are important as they contribute to determining the composition and structure of the final sorbent, thereby influencing the sorption mechanisms for removing the contaminants of interest. As mentioned earlier, GO has many functional groups that contain oxygen and can attract positively charged species while repelling negatively charged ones. On the other hand, rGO is more effective in capturing anionic pollutants. The presence of Fe³⁺ also plays an important role in this composite. The pH of point of zero charge for Si-rGO/LDH-Fe was 5.6. This

means that below this pH, the hydroxyl groups attached to Fe become strongly protonated ($=\text{Fe}-\text{OH}^{2+}$), which helps to bind the oxyanions, such as HSeO_3^- and H_2VO_4^- , on the surface of Si-rGO/LDH-Fe [81].

In order to modify MgAl-LDH, Liu et al. [54] used carbon aerogels (CAs), which are made by treating sisal fibers with alkali, bleach, freeze-drying, and carbonization. The LDH-functionalized CAs have a three-dimensional network macropore structure and a high specific surface area, which help to adsorb more selenite, achieving a maximum sorption capacity of 73.6 mg/g (at 298 K and an initial selenium concentration of 200 mg/L). Among various desorption reagents tested, selenium species were effectively desorbed using a 0.1 M Na_2CO_3 solution over a 12 h period. After desorption, the sorbent was reused nine times. However, with each subsequent desorption cycle, there was a slight decrease in sorption capacity. To enhance the sorption capacity, the sorbent underwent regeneration with 1 M HNO_3 for 5 h. This regeneration restored the sorption capacity to an excellent level, surpassing 96% of the original value. The remarkable performance of CAs, demonstrated by their capacity for effective regeneration and reusability, stands out as a competitive advantage for reducing costs.

4.8. Nanocomposites with Layered Double Hydroxides and Organic Compounds

This subsection covers nanocomposites that have LDH and organic compounds, such as chitosan [50] and amino acids [82,83], as components.

Chitosan, a linear polyaminosaccharide, has the potential to remove various inorganic ionic species, whether used on its own [84] or when impregnated with metal oxide nanopowders [85,86]. Li et al. [50] presented two different synthesis routes to produce a composite of LDH and chitosan, which had varying sorption performances for selenium oxyanions. The effectiveness of LDH and chitosan at removing selenium species was compared in both nanopowder and granular forms. The results showed that the nanopowder form of both materials was less effective than the granular form. The LDH within the beads were well dispersed and chitosan acted as a hydrogel, which allowed selenium to access the LDH in the polymer network. On the other hand, the in-situ LDH nanoparticles tended to aggregate or agglomerate, which hindered selenium from reaching the chemisorption sites on the LDH surface. This reduced the effectiveness of selenium removal.

The sorption capacity of LDH for removing oxyanions from water samples can be enhanced by intercalating zwitterions (e.g., glycine (Gly)) into its interlayer. $\text{NiAl}(\text{NO}_3^-)$ -LDH and $\text{NiAl}(\text{Gly})$ -LDH, two variants of LDH with different interlayer anions, were compared by Asiabi et al. [83] for their sorption capacity for arsenate, chromate, and selenate. They reported that $\text{NiAl}(\text{Gly})$ -LDH had a significantly higher sorption capacity for all the oxyanions than $\text{NiAl}(\text{NO}_3^-)$ -LDH. For instance, for selenate, the sorption capacity was 208.6 mg/g for $\text{NiAl}(\text{Gly})$ -LDH and only 55.0 mg/g for $\text{NiAl}(\text{NO}_3^-)$ -LDH. This difference can be explained by the different sorption mechanisms of these two types of LDH. Previous research mainly suggests that (NO_3^-) -LDH remove oxyanions by exchanging them with the interlayer anions and adsorbing them on the surface. However, when NO_3^- ions are used as interlayer anions, anion exchange becomes challenging due to their strong electrostatic interaction with the layers, resulting in decreased sorption capacity for oxyanions. In the case of (Gly)-LDH, on the other hand, oxyanion adsorption occurs due to the strong electrostatic interaction between the positively charged protonated amine group of glycine and the negatively charged oxyanions. Moreover, (Gly)-LDH has a larger surface area than (NO_3^-) -LDH, which contributes to its higher sorption capacity.

In a related study, Wang et al. [82] explored a different aspect of LDH functionality. Instead of investigating the removal of selenate with LDH intercalated with amino acids, they focused on how amino acids affect the release of SeO_4^{2-} , which had been immobilized into hydrotalcite. The authors used Mg_2Al -LDH as the host material and compared the effects of amino acids with different molecular sizes and structures. Smaller amino acids, such as glycine (Gly), L-cysteine (Cys), and L-aspartic acid (Asp), facilitated the release of SeO_4^{2-} mainly through intercalation, Mg_2Al -LDH destabilization, and dissolution processes. The

intercalation of amino acids expanded the interlayer spacing of $\text{Mg}_2\text{Al}(\text{SeO}_4^{2-})\text{-LDH}$. Conversely, larger molecules like L-tryptophan (Trp) and L-phenylalanine (Phe) had a limited impact on SeO_4^{2-} release due to their bigger size and aromatic nature. In reactions involving Phe and Trp, the concentration of released SeO_4^{2-} was similar to or lower than that of the blank test. This indicates that there was little to no ion exchange between Phe and Trp and SeO_4^{2-} , and the primary factor affecting SeO_4^{2-} concentration was dissolution. These outcomes can be attributed to the interaction between the negatively charged carboxylic groups and thiol groups in amino acids and the positively charged $\text{Mg}_2\text{Al}(\text{SeO}_4^{2-})\text{-LDH}$.

5. Layered Double Hydroxides: Evolution and Future Research Directions

Almost two centuries have passed since the German-Austrian mineralogist Carl Christian Hochstetter first identified and described hydrotalcite [87], a naturally occurring mineral now recognized as an LDH. This early documentation of hydrotalcite is one of the foundational records recognizing a material that would later be classified as part of the versatile LDH family. Despite their early discovery, LDH did not receive significant scientific attention until the early 20th century. During that time, the focus was primarily on minerals with direct commercial applications, and LDH were not considered materials of practical importance. Some researchers even initially thought hydrotalcite was a mixture. It was not until Manasse's 1915 study [88], which included optical, thermal, and analytical characterization, that hydrotalcite was widely accepted as a distinct species. The scientist derived the currently accepted formula, which was later confirmed by Foshag [88–90].

In the mid-20th century (1940s–1960s), the structure of hydrotalcite and similar minerals began to be studied more systematically. The ability to prepare these materials in the lab opened up systematic investigations into their structures. This was a pivotal moment, marking the beginning of the controlled laboratory synthesis of LDH, a key step in understanding their structure and properties. The first synthesis of hydrotalcites was reported by Feitknecht and Gerber in 1942 [91], but their structure was not determined until 1968. The 1960s were marked by significant advancements in LDH synthesis and characterization. Allmann [92] and Taylor [93] were the first to analyze the structure using X-ray diffraction. Advancements in X-ray diffraction techniques during the 1970s enabled more detailed structural characterization, deepening the understanding of LDH and confirming their layered double hydroxide nature. LDH also began to attract attention for their potential in catalysis [94] as their anion exchange capacity and tunable chemistry made them useful as solid-state catalysts and precursors for mixed-metal oxides. This marked the first major industrial application of LDH (e.g., for water purification). Various synthetic routes, such as co-precipitation, hydrothermal synthesis, and ion exchange, were developed to create LDH with different metal combinations and interlayer anions during this period. Although still being referred to as “hydrotalcite-like compounds,” Miyata is credited with introducing the general formula of LDH in 1975 [95]. In his paper, he further formalized their structure and properties, making it one of the most frequently cited references for LDH structural formulas. This foundational work was further built upon by Reichle [96] in the 1980s, who advanced the understanding of synthetic LDH structures. The era of the 1980s marked substantial research into their use in catalysis, adsorption, and anion exchange applications. In the 1990s, research broadened to include environmental remediation and methods for targeting pharmaceutical compounds to their specific sites, resulting in a surge of studies exploring their practical uses.

In the 21st century, LDH began to be explored as components in nanomaterials, expanding their potential applications to areas such as energy storage in addition to their established roles in drug delivery and contaminant removal. Advancements in synthesis and functionalization techniques during the 2000s enhanced their adaptability across a wide range of fields. By the 2010s, research intensified on using LDH for water purification, waste treatment, heavy metal removal, and energy storage devices like batteries, supercapacitors, and fuel cells due to their excellent electrical conductivity and redox properties when converted to metal oxides. Studies from this period emphasized the multifunctional

capabilities of LDH. More recently, LDH have been explored in biomedical fields as drug carriers, owing to their ability to release drugs in a controlled manner. The 2020s continue to see innovations in LDH-based technologies, further enhancing their roles in energy storage and conversion, biomedicine, catalysis, gas adsorption, and environmental remediation.

Although the future is hard to predict, trends are likely to emphasize smart materials with adaptive properties, sustainable technologies, and advanced biomedical applications. We can expect innovations in integrating LDH with artificial intelligence for smart sensors, as well as a focus on recycling and reusing LDH to reduce environmental impact. High-performance energy solutions will also be a key area, with developments aimed at improving energy storage and conversion.

In terms of LDH as adsorbents for the removal of selenium from water, we can expect advancements in several key areas. Current research suggests that researchers are likely to develop LDH with enhanced selectivity for selenium ions, improving their efficiency in removing selenium even in the presence of other competing ions. There will be advancements in functionalizing LDH by incorporating specific functional groups or hybridizing them with other materials to boost their adsorption capacity and kinetics. Another trend is the emphasis on improving the regeneration and reusability of LDH, making them more cost-effective and sustainable for long-term water treatment use. The use of nano-formulations of LDH is anticipated to increase as these materials offer greater surface area and improved adsorption efficiency for selenium at lower concentrations. Additionally, integrating LDH with advanced technologies, such as redox treatment or membrane filtration, is likely to enhance the overall efficiency of selenium removal. Lastly, future research will also focus on assessing the environmental impact of LDH-based adsorbents, including their disposal and the lifecycle implications of their use in water treatment applications. The gradual evolution of LDH, from their discovery to their widespread application across various fields, along with future research trends, is illustrated in Figure 4.

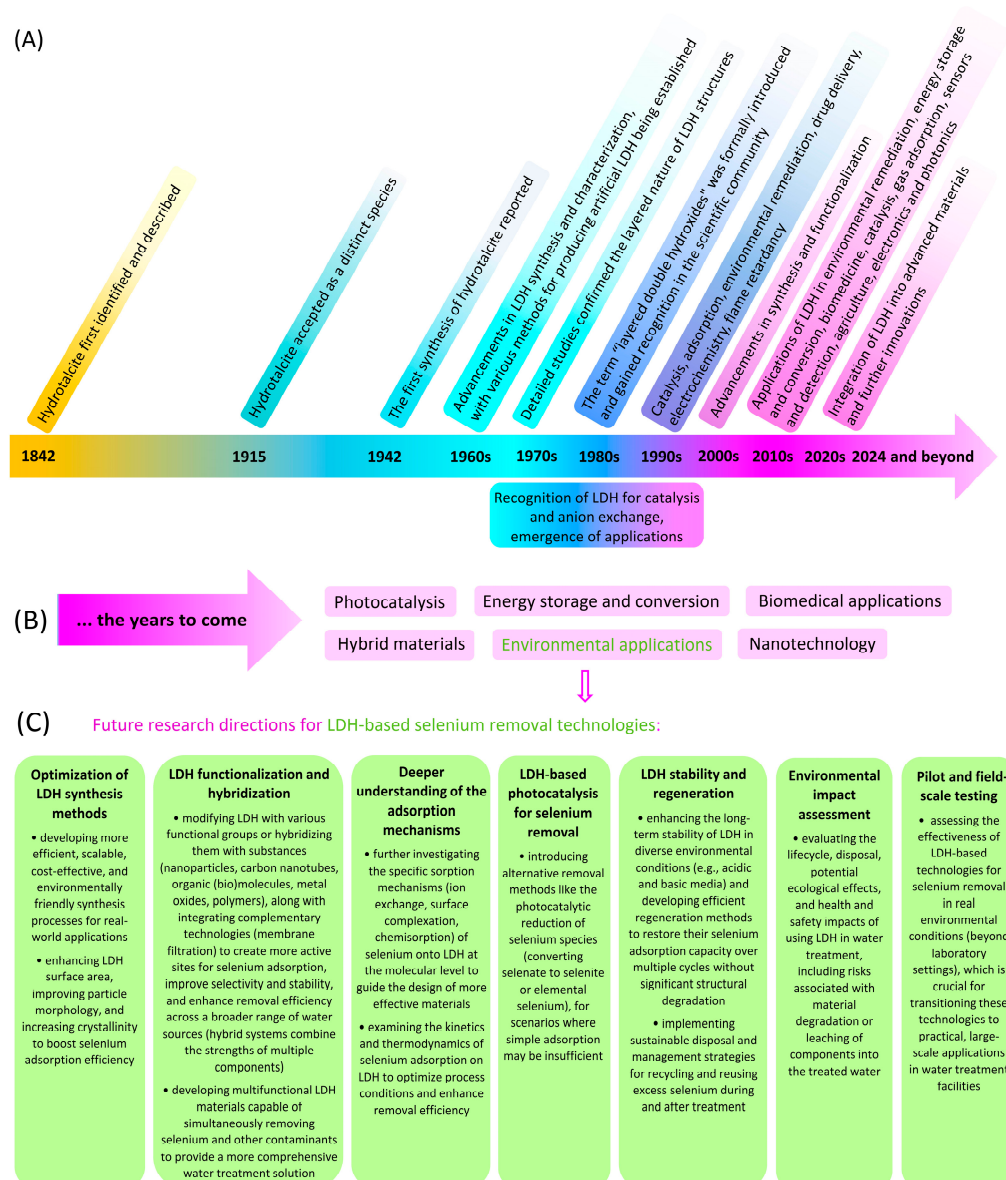


Figure 4. Layered double hydroxides (LDH): (A) historical timeline; (B) emerging research trends and applications; (C) future research directions for selenium removal.

6. Conclusions

LDH materials have garnered considerable interest from researchers due to their remarkable versatility and potential in various industrial applications. The composition of the layers and interlayer anions in LDH can be adjusted to tailor their properties for specific purposes. These materials have proven to be highly effective adsorbents and (photo)catalysts in a range of chemical processes. Their use extends to energy storage devices, where they serve as electrode materials to enhance performance, and as nanocomposites that improve the mechanical and functional properties of materials. LDH-based systems also show great potential in drug delivery, environmental remediation, and the development of highly sensitive sensors and biosensors, making them crucial components in catalysis, adsorption, and beyond. Given their versatility and effectiveness, it is particularly interesting to explore their application in specific areas. Composed of nontoxic, earth-abundant metals such as magnesium and aluminum, LDH are environmentally friendly compared with other materials. Their ability to be regenerated and reused multiple times further reduces waste and disposal concerns, contributing to a more sustainable process. Furthermore, LDH can be synthesized under relatively mild conditions, which reduces the energy consumption

and environmental footprint of their production. In this article, we focus on LDH's utility in removing selenium species from contaminated aqueous matrices.

Selenium primarily enters the aquatic environment in the form of inorganic species, namely, selenite and selenate. The adsorption mechanisms of these species on inorganic exchangers differ, making selenate more challenging to remove compared with selenite. Despite this fact, the published literature shows a balanced distribution of studies on the removal of both species.

In regard to LDH, both commercially available and laboratory-synthesized hydrotalcite-like materials have been used effectively to remove selenium oxyanions. To understand how selenate and selenite are sorbed on calcined and uncalcined LDH structures, the researchers conducted several studies on these variants. Calcined LDH (CLDH) proved to be more efficient than LDH, achieving higher sorption capacities. This is attributed to the thermal activation and memory effect, which allows selenium oxyanions to enter the interlayer of the CLDH, forming a MgAl(selenium oxyanion)-LDH hydrotalcite structure. In the case of LDH, simultaneous removal of selenite and selenate has been successful due to the different sorption mechanisms employed. Selenite adsorption by LDH involved chemisorption (formation of inner-sphere complexes) rather than ion exchange with interlayer anions. On the other hand, selenate removal occurred solely through ion exchange with surface OH^- ions and interlayer anions. The different sorption mechanisms on these structures accounted for the higher sorption capacities for selenite over selenate (often more than double). Binary LDH are not the only material that can remove selenium oxyanions effectively; ternary LDH and LDH-based nanocomposites have also yielded satisfactory results. The success of the nanocomposites arises from the synergistic effects of other materials, such as the reduction capabilities of zero-valent iron, the zwitterionic nature of incorporated organic substances, or the presence of numerous oxygen-containing functional groups present in carbon-based materials.

LDH containing yttrium cations in their hydroxide layers or thiomolybdate anions as counterions in the interlayer space have also been explored for their ability to remove selenium oxyanions from contaminated water samples. In the case of ternary LDH containing iron in the hydroxide layers and thiomolybdate as counterions, like $\text{FeMgAl}(\text{MoS}_4^{2-})$ -LDH, the presence of iron within the layers changed the layer's charge density, which let more functional groups enter the spaces between the layers. Furthermore, the heterogeneous iron catalyzed reductive reactions between selenium oxyanions and S^{2-} ions from MoS_4^{2-} groups. The iron-induced reduction along with a change in the layer's charge density led to the highest removal of selenium oxyanions by these structures.

Testing LDH sorbents in batch and column experiments indicated their potential for continuous flow systems. This could facilitate the transition from laboratory to field remediation. Furthermore, research on the simultaneous sorption of selenium oxyanions and heavy metal cations revealed that the presence of these cations improved the removal of selenium species, showing a synergistic effect.

The presence and effect of various anions in contaminated water samples, such as sulfate, phosphate, chloride, nitrate, carbonate, and silicate, were studied in many papers. Sulfate ions had a significant competitive effect on selenate sorption because of their similar geometry and ionic radius. For the same reason, phosphate ions competed with selenite ions.

To date, several treatment methods for selenium-contaminated waters have been evaluated, involving chemical, physical, and biological approaches. Many of these methods are limited by high cost, long treatment time, and operational complexity. Sorption procedures using LDH, however, have proven to be highly effective in removing selenium oxyanions from polluted media. Moreover, LDH offer both technical and economic advantages when it comes to treating waters and wastewaters containing these oxyanions, which makes them promising materials for remediation technologies.

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References

1. Au, A.; Mojadadi, A.; Shao, J.Y.; Ahmad, G.; Witting, P.K. Physiological benefits of novel selenium delivery via nanoparticles. *Int. J. Mol. Sci.* **2023**, *24*, 6068. [\[CrossRef\]](#) [\[PubMed\]](#)
2. Hogan, C.; Perkins, A.V. Selenoproteins in the human placenta: How essential is selenium to a healthy start to life? *Nutrients* **2022**, *14*, 628. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Hagarová, I.; Nemček, L. Reliable quantification of ultratrace selenium in food, beverages, and water samples by cloud point extraction and spectrometric analysis. *Nutrients* **2022**, *14*, 3530. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Li, T.X.; Xu, H.X.; Zhang, Y.X.; Zhang, H.S.; Hu, X.; Sun, Y.Y.; Gu, X.Y.; Luo, J.; Zhou, D.M.; Bin, G. Treatment technologies for selenium contaminated water: A critical review. *Environ. Pollut.* **2022**, *299*, 118858. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Séby, F.; Potin-Gautier, M.; Giffaut, E.; Borge, G.; Donard, O.F.X. A critical review of thermodynamic data for selenium species at 25 °C. *Chem. Geol.* **2001**, *171*, 173–194. [\[CrossRef\]](#)
6. Santos, S.; Ungureanu, G.; Boaventura, R.; Botelho, C. Selenium contaminated waters: An overview of analytical methods, treatment options and recent advances in sorption methods. *Sci. Total Environ.* **2015**, *521*, 246–260. [\[CrossRef\]](#)
7. Lichtfouse, E.; Morin-Crini, N.; Bradu, C.; Boussouga, Y.A.; Aliaskari, M.; Schäfer, A.I.; Das, S.; Wilson, L.D.; Ike, M.; Inoue, D.; et al. Methods for selenium removal from contaminated waters: A review. *Environ. Chem. Lett.* **2022**, *20*, 2019–2041. [\[CrossRef\]](#)
8. Ruj, B.; Bishayee, B.; Chatterjee, R.P.; Mukherjee, A.; Saha, A.; Nayak, J.; Chakraborty, S. An economical strategy towards the managing of selenium pollution from contaminated water: A current state-of-the-art review. *J. Environ. Manag.* **2022**, *304*, 114143. [\[CrossRef\]](#)
9. Matulová, M.; Urik, M.; Bujdoš, M.; Duborská, E.; Cesnek, M.; Miglierini, M.B. Selenite sorption onto goethite: Isotherm and ion-competitive studies, and effect of pH on sorption kinetics. *Chem. Pap.* **2019**, *73*, 2975–2985. [\[CrossRef\]](#)
10. Matulová, M.; Bujdoš, M.; Miglierini, M.B.; Mitróová, Z.; Kubovčíková, M.; Urik, M. The effects of selenate on goethite synthesis and selenate sorption kinetics onto a goethite surface—A three-step process with an unexpected desorption phase. *Chem. Geol.* **2020**, *556*, 119852. [\[CrossRef\]](#)
11. Szlachta, M.; Chubar, N. The application of Fe-Mn hydrous oxides based adsorbent for removing selenium species from water. *Chem. Eng. J.* **2013**, *217*, 159–168. [\[CrossRef\]](#)
12. Qureshi, S.S.; Memon, S.A.; Rafi-ul, Z.; Ram, N.; Saeed, S.; Mubarak, N.M.; Karri, R.R. Rapid adsorption of selenium removal using iron manganese-based micro adsorbent. *Sci. Rep.* **2022**, *12*, 17207. [\[CrossRef\]](#)
13. Thakkar, M.; Mitra, S. Bimetallic oxide nanohybrid synthesized from diatom frustules for the removal of selenium from water. *J. Nanomater.* **2017**, *2017*, 1734643. [\[CrossRef\]](#)
14. Hagarová, I.; Nemček, L. Analytical application of layered double hydroxides as high-capacity sorbents in dispersive solid phase extraction for the separation and preconcentration of (ultra)trace heavy metals. *Crit. Rev. Anal. Chem.* **2023**, 1–14. [\[CrossRef\]](#) [\[PubMed\]](#)
15. De Roy, A.; Forano, C.; Malki, K.E.; Besse, J.P. Anionic clays: Trends in pillaring chemistry. In *Expanded Clays and Other Microporous Solids*; Occelli, M.L., Robson, H.E., Eds.; Springer: Boston, MA, USA, 1992; pp. 108–169.
16. Bukhtiyarova, M.V. A review on effect of synthesis conditions on the formation of layered double hydroxides. *J. Solid State Chem.* **2019**, *269*, 494–506. [\[CrossRef\]](#)
17. Mishra, G.; Dash, B.; Pandey, S. Layered double hydroxides: A brief review from fundamentals to application as evolving biomaterials. *Appl. Clay Sci.* **2018**, *153*, 172–186. [\[CrossRef\]](#)
18. Jagtap, A.; Wagle, P.G.; Jagtiani, E.; More, A.P. Layered double hydroxides (LDHs) for coating applications. *J. Coat. Technol. Res.* **2022**, *19*, 1009–1032. [\[CrossRef\]](#)
19. Zikmund, M.; Hrnčiarová, K. Anionic clays. Structure, synthesis, applications. *Chem. Listy* **1997**, *91*, 169–178.
20. Li, Z.H.; Zhang, X.X.; Chen, J.Y.; Fang, X.; Yuan, W.Y.; Yu, J.X.; Qiu, X.H. Preparing of layered double hydroxide-alginate microspheres for Cr(VI)-contaminated soil remediation. *Colloids Surf. A-Physicochem. Eng. Asp.* **2023**, *658*, 130655. [\[CrossRef\]](#)
21. Guan, X.; Yuan, X.Z.; Zhao, Y.L.; Wang, H.; Wang, H.; Bai, J.; Li, Y. Application of functionalized layered double hydroxides for heavy metal removal: A review. *Sci. Total Environ.* **2022**, *838*, 155693. [\[CrossRef\]](#)
22. Johnston, A.L.; Lester, E.; Williams, O.; Gomes, R.L. Understanding layered double hydroxide properties as sorbent materials for removing organic pollutants from environmental waters. *J. Environ. Chem. Eng.* **2021**, *9*, 105197. [\[CrossRef\]](#)

23. Winkel, L.H.E.; Vriens, B.; Jones, G.D.; Schneider, L.S.; Pilon-Smits, E.; Banuelos, G.S. Selenium cycling across soil-plant-atmosphere interfaces: A critical review. *Nutrients* **2015**, *7*, 4199–4239. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Etteieb, S.; Magdouli, S.; Zolfaghari, M.; Brar, S. Monitoring and analysis of selenium as an emerging contaminant in mining industry: A critical review. *Sci. Total Environ.* **2020**, *698*, 134339. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Dhillon, K.S.; Dhillon, S.K. Distribution and management of seleniferous soils. Sparks, D.L., Ed. *Adv. Agron.* **2003**, *79*, 119–184.
26. He, X.; Qiu, X.H.; Hu, C.Y.; Liu, Y.W. Treatment of heavy metal ions in wastewater using layered double hydroxides: A review. *J. Dispers. Sci. Technol.* **2018**, *39*, 792–801. [\[CrossRef\]](#)
27. Chubar, N. EXAFS and FTIR studies of selenite and selenate sorption by alkoxide-free sol-gel generated Mg-Al-CO₃ layered double hydroxide with very labile interlayer anions. *J. Mater. Chem. A* **2014**, *2*, 15995–16007. [\[CrossRef\]](#)
28. Elzinga, E.J.; Tang, Y.Z.; McDonald, J.; DeSisto, S.; Reeder, R.J. Macroscopic and spectroscopic characterization of selenate, selenite, and chromate adsorption at the solid-water interface of γ -Al₂O₃. *J. Colloid Interface Sci.* **2009**, *340*, 153–159. [\[CrossRef\]](#)
29. Han, D.S.; Batchelor, B.; Abdel-Wahab, A. Sorption of selenium(IV) and selenium(VI) onto synthetic pyrite (FeS₂): Spectroscopic and microscopic analyses. *J. Colloid Interface Sci.* **2012**, *368*, 496–504. [\[CrossRef\]](#)
30. Vinceti, M.; Crespi, C.M.; Bonvicini, F.; Malagoli, C.; Ferrante, M.; Marmioli, S.; Stranges, S. The need for a reassessment of the safe upper limit of selenium in drinking water. *Sci. Total Environ.* **2013**, *443*, 633–642. [\[CrossRef\]](#)
31. You, Y.W.; Vance, G.F.; Zhao, H.T. Selenium adsorption on Mg-Al and Zn-Al layered double hydroxides. *Appl. Clay Sci.* **2001**, *20*, 13–25. [\[CrossRef\]](#)
32. Liu, R.; Frost, R.L.; Martens, W.N. Absorption of the selenite anion from aqueous solutions by thermally activated layered double hydroxide. *Water Res.* **2009**, *43*, 1323–1329. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Chubar, N.; Szlachta, M. Static and dynamic adsorptive removal of selenite and selenate by alkoxide-free sol-gel-generated Mg-Al-CO₃ layered double hydroxide: Effect of competing ions. *Chem. Eng. J.* **2015**, *279*, 885–896. [\[CrossRef\]](#)
34. Li, M.; Farnen, L.M.; Chan, C.K. Selenium removal from sulfate-containing groundwater using granular layered double hydroxide materials. *Ind. Eng. Chem. Res.* **2017**, *56*, 2458–2465. [\[CrossRef\]](#)
35. Bryan, C.R.; Wang, Y.F.; Xu, H.F.; Braterman, P.S.; Gao, H.Z. As, Se, and Re sorption by Mg-Al layered double hydroxides. In Proceedings of the 26th Symposium on the Scientific Basis for Nuclear Waste Management held at the 2002 MRS Fall Meeting, Boston, MA, USA, 1–4 December 2002; pp. 671–676.
36. Chubar, N. The influence of sulfate on selenate sorption on Mg-Al-CO₃ layered double hydroxides prepared by fine inorganic sol-gel synthesis studied by X-ray photoelectron spectroscopy. *Appl. Surf. Sci.* **2018**, *459*, 281–291. [\[CrossRef\]](#)
37. Li, M.; Chowdhury, T.; Kraetz, A.N.; Jing, H.K.; Dopilka, A.; Farnen, L.M.; Sinha, S.; Chan, C.K. Layered double hydroxide sorbents for removal of selenium from power plant wastewaters. *Chem. Eng.* **2019**, *3*, 20. [\[CrossRef\]](#)
38. Chubar, N.; Gerda, V.; Megantari, O.; Micusik, M.; Omastova, M.; Heister, K.; Man, P.; Fraissard, J. Applications versus properties of Mg-Al layered double hydroxides provided by their syntheses methods: Alkoxide and alkoxide-free sol-gel syntheses and hydrothermal precipitation. *Chem. Eng. J.* **2013**, *234*, 284–299. [\[CrossRef\]](#)
39. Constantino, L.V.; Quirino, J.N.; Monteiro, A.M.; Abrao, T.; Parreira, P.S.; Urbano, A.; Santos, M.J. Sorption-desorption of selenite and selenate on Mg-Al layered double hydroxide in competition with nitrate, sulfate and phosphate. *Chemosphere* **2017**, *181*, 627–634. [\[CrossRef\]](#)
40. Tian, N.; Zhou, Z.X.; Tian, X.K.; Yang, C.; Li, Y. Superior capability of MgAl₂O₄ for selenite removal from contaminated groundwater during its reconstruction of layered double hydroxides. *Sep. Purif. Technol.* **2017**, *176*, 66–72. [\[CrossRef\]](#)
41. Jiménez-López, B.A.; Leyva-Ramos, R.; Salazar-Rábago, J.J.; Jacobo-Azuara, A.; Aragón-Piña, A. Adsorption of selenium(IV) oxoanions on calcined layered double hydroxides of Mg-Al-CO₃ from aqueous solution. Effect of calcination and reconstruction of lamellar structure. *Environ. Nanotechnol. Monit. Manag.* **2021**, *16*, 100580. [\[CrossRef\]](#)
42. Chubar, N. New inorganic (an)ion exchangers based on Mg-Al hydrous oxides: (Alkoxide-free) sol-gel synthesis and characterisation. *J. Colloid Interface Sci.* **2011**, *357*, 198–209. [\[CrossRef\]](#)
43. Koilraj, P.; Kamura, Y.; Sasaki, K. Cosorption characteristics of SeO₄^{2−} and Sr²⁺ radioactive surrogates using 2D/2D raphene oxide-layered double hydroxide nanocomposites. *ACS Sustain. Chem. Eng.* **2018**, *6*, 13854–13866. [\[CrossRef\]](#)
44. Koilraj, P.; Kamura, Y.; Sasaki, K. Carbon-dot-decorated layered double hydroxide nanocomposites as a multifunctional environmental material for co-immobilization of SeO₄^{2−} and Sr²⁺ from aqueous solutions. *ACS Sustain. Chem. Eng.* **2017**, *5*, 9053–9064. [\[CrossRef\]](#)
45. Paikaray, S.; Hendry, M.J.; Essilfie-Dughan, J. Controls on arsenate, molybdate, and selenate uptake by hydrotalcite-like layered double hydroxides. *Chem. Geol.* **2013**, *345*, 130–138. [\[CrossRef\]](#)
46. Schellenger, A.E.P.; Choi, S.; Onnis-Hayden, A.; Larese-Casanova, P. Selenium oxyanion exchange with Mg(II)-Fe(III) and Fe(II)-Fe(III) layered double hydroxides. *Appl. Clay Sci.* **2021**, *200*, 105959. [\[CrossRef\]](#)
47. Ma, L.J.; Islam, S.M.; Xiao, C.L.; Zhao, J.; Liu, H.Y.; Yuan, M.W.; Sun, G.B.; Li, H.F.; Ma, S.L.; Kanatzidis, M.G. Rapid simultaneous removal of toxic anions (HSeO₃)[−], (SeO₃)^{2−}, and (SeO₄)^{2−}, and metals Hg²⁺, Cu²⁺, and Cd²⁺ by MoS₄^{2−} intercalated layered double hydroxide. *J. Am. Chem. Soc.* **2017**, *139*, 12745–12757. [\[CrossRef\]](#)
48. Liao, Z.W.; He, T.X.; Shi, L.R.; Liu, Y.; Zhou, X.Q.; Wang, J.; Li, W.; Zhang, Y.; Wang, H.B.; Xu, R. Selenium oxoanions removal from wastewater by MoS₄^{2−} intercalated FeMgAl LDH: Catalytic roles of Fe and mechanism insights. *Catalysts* **2022**, *12*, 1592. [\[CrossRef\]](#)

49. Aregay, G.G.; Ali, J.; Chen, Z.Q. Enhanced simultaneous removal of toxic $(\text{SeO}_4)^{2-}$ and metals Cr^{3+} and Cu^{2+} using polysulfide intercalated Layered double hydroxide. *Sep. Purif. Technol.* **2021**, *279*, 119649. [\[CrossRef\]](#)
50. Li, M.; Dopilka, A.; Kraetz, A.N.; Jing, H.K.; Chan, C.K. Layered double hydroxide/chitosan nanocomposite beads as sorbents for selenium oxoanions. *Ind. Eng. Chem. Res.* **2018**, *57*, 4978–4987. [\[CrossRef\]](#)
51. Zhu, L.; Zhang, L.J.; Li, J.; Zhang, D.; Chen, L.H.; Sheng, D.P.; Yang, S.T.; Xiao, C.L.; Wang, J.Q.; Chai, Z.F.; et al. Selenium sequestration in a cationic layered rare earth hydroxide: A combined batch experiments and EXAFS investigation. *Environ. Sci. Technol.* **2017**, *51*, 8606–8615. [\[CrossRef\]](#)
52. Das, J.; Patra, B.S.; Baliarsingh, N.; Parida, K.M. Calcined Mg-Fe- CO_3 LDH as an adsorbent for the removal of selenite. *J. Colloid Interface Sci.* **2007**, *316*, 216–223. [\[CrossRef\]](#)
53. Mandal, S.; Mayadevi, S.; Kulkarni, B.D. Adsorption of aqueous selenite Se(IV) species on synthetic layered double hydroxide materials. *Ind. Eng. Chem. Res.* **2009**, *48*, 7893–7898. [\[CrossRef\]](#)
54. Liu, Y.; Jing, Z.F.; Zhang, T.; Chen, Q.Y.; Qiu, F.X.; Peng, Y.X.; Tang, S. Fabrication of functional biomass carbon aerogels derived from sisal fibers for application in selenium extraction. *Food Bioprod. Process.* **2018**, *111*, 93–103. [\[CrossRef\]](#)
55. Chubar, N. XPS determined mechanism of selenite (HSeO_3^-) sorption in absence/presence of sulfate (SO_4^{2-}) on Mg-Al- CO_3 layered double hydroxides (LDHs): Solid phase speciation focus. *J. Environ. Chem. Eng.* **2023**, *11*, 109669. [\[CrossRef\]](#)
56. Vargas, A.M.M.; Cazetta, A.L.; Kunita, M.H.; Silva, T.L.; Almeida, V.C. Adsorption of methylene blue on activated carbon produced from flamboyant pods (*Delonix regia*): Study of adsorption isotherms and kinetic models. *Chem. Eng. J.* **2011**, *168*, 722–730. [\[CrossRef\]](#)
57. Galunin, E.; Ferreti, J.; Zapelini, I.; Vieira, I.; Tarley, C.R.T.; Abrao, T.; Santos, M.J. Cadmium mobility in sediments and soils from a coal mining area on Tibagi River watershed: Environmental risk assessment. *J. Hazard. Mater.* **2014**, *265*, 280–287. [\[CrossRef\]](#)
58. Tsuchiya, K.; Fuchida, S.; Tokoro, C. Synthesis and selenate removal of magnesium-aluminum-layered double hydroxide particle using magnesium oxide. *Int. J. Environ. Sci. Technol.* **2023**, *20*, 9481–9494. [\[CrossRef\]](#)
59. Ibrahim, A.I.A.; Vohra, M.S. Mg-Fe-LDH for aquatic selenium treatment: Adsorption, RSM modeling, and machine learning neural network. *Water Air Soil Pollut.* **2023**, *234*, 433. [\[CrossRef\]](#)
60. Hindocha, S.A.; McIntyre, L.J.; Fogg, A.M. Precipitation synthesis of lanthanide hydroxynitrate anion exchange materials, $\text{Ln}_2(\text{OH})_5\text{NO}_3 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Y, Eu-Er}$). *J. Solid State Chem.* **2009**, *182*, 1070–1074. [\[CrossRef\]](#)
61. Geng, F.X.; Xin, H.; Matsushita, Y.; Ma, R.Z.; Tanaka, M.; Izumi, F.; Iyi, N.; Sasaki, T. New layered rare-earth hydroxides with anion-exchange properties. *Chem. Eur. J.* **2008**, *14*, 9255–9260. [\[CrossRef\]](#)
62. Cai, H.; Bao, H.L.; Zhang, X.W.; Lei, L.C.; Xiao, C.L. Highly efficient sorption of selenate and selenite onto a cationic layered single hydroxide via anion exchange and inner-sphere complexation. *Chem. Eng. J.* **2021**, *420*, 129726. [\[CrossRef\]](#)
63. Zhou, J.Z.; Su, Y.W.; Zhang, J.; Xu, X.X.; Zhao, J.; Qian, G.R.; Xu, Y.F. Distribution of OH bond to metal-oxide in $\text{Mg}_{3-x}\text{Ca}_x\text{Fe}$ -layered double hydroxide ($x = 0\text{--}1.5$): Its role in adsorption of selenate and chromate. *Chem. Eng. J.* **2015**, *262*, 383–389. [\[CrossRef\]](#)
64. Tian, Q.Z.; Guo, B.L.; Sasaki, K. Influence of silicate on the structural memory effect of layered double hydroxides for the immobilization of selenium. *J. Hazard. Mater.* **2020**, *395*, 122674. [\[CrossRef\]](#) [\[PubMed\]](#)
65. Ismail, U.M.; Onaizi, S.A.; Vohra, M.S. Novel MgCuAl-layered triple hydroxide for aqueous selenite and selenate treatment. *Emergent Mater.* **2023**, *7*, 521–532. [\[CrossRef\]](#)
66. Ma, L.J.; Wang, Q.; Islam, S.M.; Liu, Y.C.; Ma, S.L.; Kanatzidis, M.G. Highly selective and efficient removal of heavy metals by layered double hydroxide intercalated with the MoS_4^{2-} ion. *J. Am. Chem. Soc.* **2016**, *138*, 2858–2866. [\[CrossRef\]](#)
67. Ma, L.J.; Islam, S.M.; Liu, H.Y.; Zhao, J.; Sun, G.B.; Li, H.F.; Ma, S.L.; Kanatzidis, M.G. Selective and efficient removal of toxic oxoanions of As(III), As(V), and Cr(VI) by layered double hydroxide intercalated with MoS_4^{2-} . *Chem. Mater.* **2017**, *29*, 3274–3284. [\[CrossRef\]](#)
68. Ling, L.; Pan, B.C.; Zhang, W.X. Removal of selenium from water with nanoscale zero-valent iron: Mechanisms of intraparticle reduction of Se(IV) . *Water Res.* **2015**, *71*, 274–281. [\[CrossRef\]](#)
69. Liang, L.P.; Guan, X.H.; Huang, Y.Y.; Ma, J.Y.; Sun, X.P.; Qiao, J.L.; Zhou, G.M. Efficient selenate removal by zero-valent iron in the presence of weak magnetic field. *Sep. Purif. Technol.* **2015**, *156*, 1064–1072. [\[CrossRef\]](#)
70. Olegario, J.T.; Yee, N.; Miller, M.; Sczepaniak, J.; Manning, B. Reduction of Se(VI) to Se(-II) by zerovalent iron nanoparticle suspensions. *J. Nanoparticle Res.* **2010**, *12*, 2057–2068. [\[CrossRef\]](#)
71. Sheng, G.D.; Alsaedi, A.; Shammakh, W.; Monaque, S.; Sheng, J.; Wang, X.K.; Li, H.; Huang, Y.Y. Enhanced sequestration of selenite in water by nanoscale zero valent iron immobilization on carbon nanotubes by a combined batch, XPS and XAFS investigation. *Carbon* **2016**, *99*, 123–130. [\[CrossRef\]](#)
72. Shi, L.N.; Zhang, X.; Chen, Z.L. Removal of chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron. *Water Res.* **2011**, *45*, 886–892. [\[CrossRef\]](#)
73. Shi, L.N.; Lin, Y.M.; Zhang, X.; Chen, Z.L. Synthesis, characterization and kinetics of bentonite supported nZVI for the removal of Cr(VI) from aqueous solution. *Chem. Eng. J.* **2011**, *171*, 612–617. [\[CrossRef\]](#)
74. Liu, M.H.; Wang, Y.H.; Chen, L.T.; Zhang, Y.; Lin, Z. Mg(OH)_2 supported nanoscale zero valent iron enhancing the removal of Pb(II) from aqueous solution. *ACS Appl. Mater. Interfaces* **2015**, *7*, 7961–7969. [\[CrossRef\]](#) [\[PubMed\]](#)
75. Darab, J.G.; Amonette, A.B.; Burke, D.S.D.; Orr, R.D.; Ponder, S.M.; Schrick, B.; Mallouk, T.E.; Lukens, W.W.; Caulder, D.L.; Shuh, D.K. Removal of pertechnetate from simulated nuclear waste streams using supported zerovalent iron. *Chem. Mater.* **2007**, *19*, 5703–5713. [\[CrossRef\]](#)

76. Ponder, S.M.; Darab, J.G.; Bucher, J.; Caulder, D.; Craig, I.; Davis, L.; Edelstein, N.; Lukens, W.; Nitsche, H.; Rao, L.F.; et al. Surface chemistry and electrochemistry of supported zerovalent iron nanoparticles in the remediation of aqueous metal contaminants. *Chem. Mater.* **2001**, *13*, 479–486. [\[CrossRef\]](#)
77. Hu, B.W.; Ye, F.; Jin, C.A.; Ma, X.X.; Huang, C.C.; Sheng, G.D.; Ma, J.Y.; Wang, X.K.; Huang, Y.Y. The enhancement roles of layered double hydroxide on the reductive immobilization of selenate by nanoscale zero valent iron: Macroscopic and microscopic approaches. *Chemosphere* **2017**, *184*, 408–416. [\[CrossRef\]](#)
78. Xu, L.; Huang, Y.H. A novel layered double hydroxide coupled with zero valent iron system for selenate removal under anaerobic condition: Batch and continuous studies. *Chem. Eng. J.* **2019**, *359*, 1166–1174. [\[CrossRef\]](#)
79. Sabzehmeidani, M.M.; Mahnaee, S.; Ghaedi, M.; Heidari, H.; Roy, V.A.L. Carbon based materials: A review of adsorbents for inorganic and organic compounds. *Mater. Adv.* **2021**, *2*, 598–627. [\[CrossRef\]](#)
80. Koilraj, P.; Kamura, Y.; Sasaki, K. Synergetic co-immobilization of SeO_4^{2-} and Sr^{2+} from aqueous solution onto multifunctional graphene oxide and carbon-dot based layered double hydroxide nanocomposites and their mechanistic investigation. *J. Mater. Chem. A* **2018**, *6*, 10008–10018. [\[CrossRef\]](#)
81. Suma, S.; Seema, S.; Manoj, S.V.; Sumi, V.S.; Rijith, S. Synthesis and evaluation of Fe(III) embedded silane grafted layered double hydroxide with reduced graphene oxide support as an efficient adsorbent for V(V) and Se(IV) from aqueous systems. *Asian J. Chem.* **2021**, *33*, 1309–1318. [\[CrossRef\]](#)
82. Wang, M.M.; Akamatsu, H.; Dabo, I.; Sasaki, K. Environmental impact of amino acids on the release of selenate immobilized in hydrotalcite: Integrated interpretation of experimental and density-functional theory study. *Chemosphere* **2021**, *274*, 129927. [\[CrossRef\]](#)
83. Asiabi, H.; Yamini, Y.; Shamsayei, M. Highly selective and efficient removal of arsenic(V), chromium(VI) and selenium(VI) oxyanions by layered double hydroxide intercalated with zwitterionic glycine. *J. Hazard. Mater.* **2017**, *339*, 239–247. [\[CrossRef\]](#) [\[PubMed\]](#)
84. Wu, F.C.; Tseng, R.L.; Juang, R.S. A review and experimental verification of using chitosan and its derivatives as adsorbents for selected heavy metals. *J. Environ. Manag.* **2010**, *91*, 798–806. [\[CrossRef\]](#) [\[PubMed\]](#)
85. Yamani, J.S.; Miller, S.M.; Spaulding, M.L.; Zimmerman, J.B. Enhanced arsenic removal using mixed metal oxide impregnated chitosan beads. *Water Res.* **2012**, *46*, 4427–4434. [\[CrossRef\]](#)
86. Miller, S.M.; Spaulding, M.L.; Zimmerman, J.B. Optimization of capacity and kinetics for a novel bio-based arsenic sorbent, TiO_2 -impregnated chitosan bead. *Water Res.* **2011**, *45*, 5745–5754. [\[CrossRef\]](#) [\[PubMed\]](#)
87. Hochstetter, C. Untersuchung über die Zusammensetzung einiger Mineralien. *J. Prakt. Chem.* **1842**, *27*, 375–378. [\[CrossRef\]](#)
88. Manasse, E. Rocce eritree e di aden della collezione issel. *Atti Della Soc. Toscana Sci. Nat.* **1915**, *24*, 92.
89. Mills, S.J.; Christy, A.G.; Génin, J.M.R.; Kameda, T.; Colombo, F. Nomenclature of the hydrotalcite supergroup: Natural layered double hydroxides. *Mineral. Mag.* **2012**, *76*, 1289–1336. [\[CrossRef\]](#)
90. Foshag, W.F. The chemical composition of hydrotalcite and the hydrotalcite group of minerals. *Proc. United States Natl. Mus.* **1920**, *58*, 147–153. [\[CrossRef\]](#)
91. Feitknecht, W.; Gerber, M. Acknowledgement of the double hydroxide and base double salt III Magnesium-aluminium double hydroxide. *Helv. Chim. Acta* **1942**, *25*, 131–137. [\[CrossRef\]](#)
92. Allmann, R. Crystal structure of pyroaurite. *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* **1968**, *24*, 972–977. [\[CrossRef\]](#)
93. Taylor, H.F.W. Segregation and cation-ordering in sjögrenite and pyroaurite. *Mineral. Mag.* **1969**, *37*, 338–342. [\[CrossRef\]](#)
94. Bröcker, F.; Kainer, L. German Patent 2024282, 1970.
95. Miyata, S. Synthesis of hydrotalcite-like compounds and their structures and physicochemical properties-I: The systems Mg^{2+} - Al^{3+} - NO_3^- , Mg^{2+} - Al^{3+} - Cl^- , Mg^{2+} - Al^{3+} - ClO_4^- , Ni^{2+} - Al^{3+} - Cl^- and Zn^{2+} - Al^{3+} - Cl^- . *Clays Clay Miner.* **1975**, *23*, 369–375. [\[CrossRef\]](#)
96. Reichle, W.T. Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite). *Solid State Ion.* **1986**, *22*, 135–141. [\[CrossRef\]](#)

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