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ROYAL SOCIETY OF CHEMISTRY

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To ensure the sustainable development of human society, economy, and living environment, pollution control of water resources has become a focus of people's attention. Fluoride ions are a common harmful ion that poses a serious threat to ecosystems and human health. LDH has a large specific surface area, good ion exchange performance, and high adsorption capacity, therefore it has promising application prospects in fluoride ion adsorption. The advancement of this work will help reduce the impact of fluorinated wastewater on the environment and ecosystem, protect people's health and ecological balance. At the same time, it will also promote the realization of sustainable consumption and production, and contribute to the sustainable development of human society (SDGs of 3, 6, and 12).

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REVIEW ARTICLE

Exploring layered double hydroxide efficiency in removal of fluoride ions from water: material insights, synthesis and modification strategies and adsorption mechanisms

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Fluoride ion pollution is currently one of the important factors causing chemical risks in drinking water. Adsorption method is an important way to solve this problem due to its simple operation and low cost. The key to the adsorption method is to develop efficient fluoride ion adsorption materials. Among many adsorbents, layered double hydroxide (LDH) material has the characteristics of simple preparation, adjustable layer composition, adjustable interlayer anion type, and high adsorption capacity. Thus, it is considered to be a highly potential fluoride ion adsorbent. This work provides a comprehensive summary of LDHs used for fluoride ion adsorption, from the perspectives of composition, synthesis, modification, environmental factors affecting adsorption performance, adsorption mechanism. Especially important, this work distinguishes between LDH and its derivatives such as mixed metal oxides because they have different fluoride adsorption mechanisms. That is, the general discussion is focused on the LDH phase, while MMO and complexes are discussed in the modification section. Additionally, problems and future directions in the development of LDH-based fluoride ion adsorbents are prospected.

1 Introduction

Fluorine is one of the essential trace elements for the human body. However, excessive intake can be harmful to health. For example, long-term intake of low concentration fluoride in human body will cause dental fluorosis and bone fluorosis, and if the concentration of fluoride is high, it will immediately cause strong stimulation and corrosion to human skin, further leading to dehydration and dissolution of skin tissue protein.[1] As a result the World Health Organization (WHO) proposed that the content of fluoride in drinking water should be strictly controlled below 1.5 mg/L.[2]

Fluoride ion is a major source of fluoride in water. Two main reasons account for the excessive fluoride ion content in drinking water. One is the existence of natural fluoride minerals in the environment, and the other is the discharge of fluoride-containing wastewater in modern industries such as steel metallurgy, aluminum electrolysis, rare earth elements separation, photovoltaic cells and semiconductor etching. Due to the huge demand for modern industrial products, the latter type is undoubtedly the main fluoride pollution source in water.

At present, among the methods used to remove fluoride ions in

water, ion exchange and reverse osmosis are too expensive to be suitable for large-scale fluoride removal in water. Electrocoagulation and precipitation methods give rise to still high residual fluoride ion concentration in wastewater so that further processing steps are required resulting in increased fluoride removal costs. In comparison, the adsorption method is easy to operate and requires simple equipment, so it has a higher practical value. Consequently, the development of efficient fluoride ion adsorbents becomes the key to solve the fluoride ion pollution in water.

Layered double hydroxides (LDHs), have the chemical formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]x^+(A^{n-})_{x/n} \cdot mH_2O$, also known as hydrotalcite-like materials, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, located in the brucite layer. A^{n-} is the anion located between brucite layers, such as carbonate, nitrate, phosphate, etc. x is the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$; m is the number of water molecules between the sheets. In LDH structure, the divalent cations form octahedrally coordinated units with six surrounding oxygen. When some divalent cations are partially replaced by trivalent cations, the brucite layer is electrically positive. Therefore, negative anions are introduced between layers to maintain electrical balance.[3] Interlayer spacing can be adjusted through anion exchange.[4, 5] In addition, LDH structure has a 'memory effect', that is, after LDH is converted into mixed metal oxide (MMO) along with the removal of interlayer water molecules, anions and hydroxyl groups by thermal activation at 300 ℃~500 ℃, the LDH structure can be spontaneously restored by exposing MMO to anionic aqueous solution.[6]

LDH can be either natural or artificially synthetic. Natural LDH has low reserves and often contains many impurity minerals, so industrial LDH is usually obtained by artificial methods.[7] Compared with other fluoride ion adsorbents such as activated alumina,[8] zeolite,

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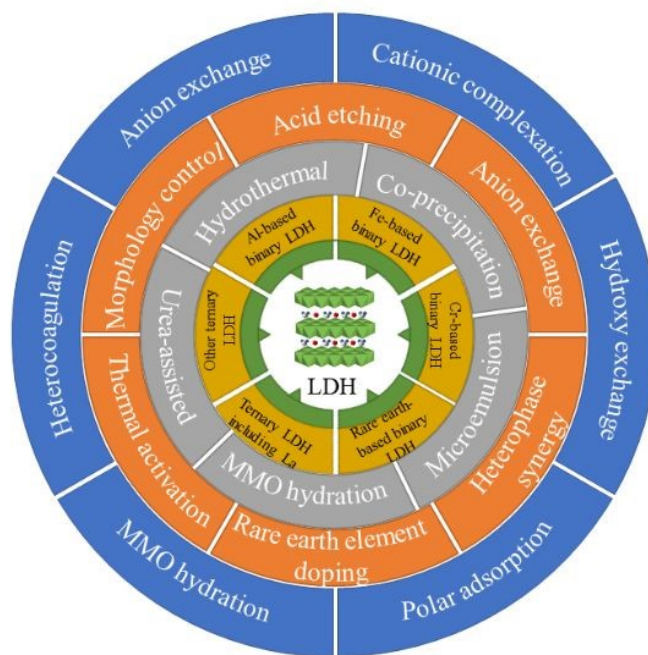
Scheme 1 Categories of LDH fluoride ion adsorbents based on the logical relationship from materials, synthesis, modification to adsorption mechanism, indicated in the pie chart from the inside to the outside.

[9] ion exchange resin,[10] and activated carbon,[11] the preparation process of LDH is simple and inexpensive, and its morphology and size can be conveniently adjusted by controlling the type and proportion of introduced metals which form the layer, to achieve the optimization of fluoride adsorption performance. In addition, the fluoride ion removal capacity of LDH can be further improved by rare element doping, heterocoagulation, anion exchange and thermal activation. All in all, LDH's excellent fluoride adsorption capacity, simple synthesis and flexible performance regulation are becoming more and more valuable in the context of the current tightening environmental pressure and increasing demand for clean drinking water. Therefore, LDH has gained a lot of attention in recent decades. However, there is only one review on LDH for fluoride ion adsorption published by Tajuddin et al. in 2023.[12] In their work, the synthesis, characterization, advantages, and composite adsorbents of LDH were reviewed. In addition, conventional defluorination methods, as well as new technologies and new concerns for defluorination in the context of Industrial Revolution 4.0 (IR4.0) were also discussed. However, the modification methods for LDH and the impact of environmental parameters on fluoride adsorption were not included, and there was a lack of statistics and analysis on the adsorption performance of LDH. Therefore, a more comprehensive review is needed to provide an overview of the current state of research progress in LDH fluoride adsorption materials.

Based on this, the research progress since Duan's first report[13] of LDH-based fluoride adsorbent in 2006 is reviewed in detail here. Firstly, the types and synthesis methods of LDHs used for fluoride ion adsorption are systematically sorted out, and then the modification procedures of LDHs are classified, including morphology regulation, rare earth element doping, anion exchange, heterocoagulation, and thermal activation. Next, the influencing factors and defluorination mechanism of LDH are discussed. Finally, current problems in LDH research are proposed as well as perspectives on future research.

The framework of this review is shown in Scheme. 1.

It is worth noting that for a large number of LDH thermal activation studies, the fluoride is actually adsorbed by MMO instead of LDH, but most of the publications still use LDH as the title, which brings some ambiguity to the summary of LDH adsorbents. Specifically, for example, when counting LDH synthesis methods, the LDH produced by some synthesis methods is directly used as a fluoride removal agent, while the product obtained by some synthesis is only used as a raw material for MMO, so it is not appropriate to put these two types of LDH synthesis methods together. In order to reduce this confusion, in this work, the main line is based on the phase of LDH, that is, in Section 2 and Section 3, the types and synthesis methods of LDH directly used as fluoride ion adsorbents are counted and classified, corresponding to the performance of the basic structure of LDH. The LDH modification research is reviewed in Section 4, and MMO is introduced as the product of the thermal activated modification of LDH. In Section 4, the morphology control (Section 4.1) is to regulate and modify LDH directly through controlling the synthesis conditions, and it is the original phase of LDH that plays the role of fluoride adsorption; the phase of adsorbent modified by acid etching (Section 4.2), rare earth element doping (Section 4.3) and anion exchange (Section 4.4) is still LDH, so all of these methods can be classified as intrinsic structural modifications. While the modification using LDH and other substances to perform adsorption at the same time, belongs to heterocoagulation (Section 4.5). The adsorption mechanism of thermal activation is substantially different from that of LDH, so it is classified as the last modification method (Section 4.6). In the current classification, the discussion objects of each part of Sections 2-4 (such as different types of LDHs in Section 2, synthetic products in Section 3, and modified products in Section 4) are fluoride ion adsorption materials, instead of precursors or intermediate transition substances. This classification strategy also conforms to

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the progressive logic from basic structure, synthesis to performance improvement after modification.

Finally, the three LDH-related terms frequently used in this review are specially explained: ***LDH original adsorbent***, ***LDH intrinsic adsorbent*** and ***LDH-based adsorbent***. LDH original adsorbent refers to an adsorbent with a basic LDH structure obtained through simple synthesis regulation (corresponding to most LDHs in Section 3 and 4.1); LDH intrinsic adsorbent means that no matter which synthesis and modification method is adopted, the LDH structure is finally retained and used for fluoride ion adsorption, so in addition to LDH original adsorbent, there are also modified products maintaining the phase of LDH (corresponding to most LDHs described in Section 3 and 4.1-4.4); while LDH-based adsorbents generally refer to adsorbents containing LDH or LDH derivative MMO, thus covering LDH original adsorbent, intrinsic adsorbent and all other modified adsorbents.

2 Types of LDHs used for fluoride ion adsorption

Using different metal ions to synthesize LDH will affect the adsorption of fluoride ions from LDH's intrinsic characteristics. According to the number of metal types found in the structure, LDH used for fluoride ion adsorption can be divided into binary LDH and ternary LDH. Depending on the trivalent metals, binary LDH can be further divided into Al-based, Fe-based, Cr-based and rare earth-based, ternary LDH can be further divided into La-based ternary LDH and other-based ternary LDH (Table 1) based on the known studies.

2.1 Binary LDH

2.1.1 Al-based binary LDH

LDH composed of trivalent Al as a metal element and one other monovalent or divalent metal elements is currently the most common type of LDH. Among this type of LDHs, MgAl-LDH is the first to be reported for the removal of fluoride ions and is the most widely studied.[13] Compared with other types, it has the advantages of cheap raw materials, large adsorption capacity, and good fluoride removal effect. In addition to using Mg(II) element with great affinity to F, Ca(II) can also be used to form CaAl-LDH, which can release Ca^{2+} to complex with fluoride ions, thereby increasing the fluoride ion removal capacity. The theoretical maximum fluoride ion removal capacity of CaAl-LDH can reach 146.6 mg/g.[14]

CoAl-LDH with interlayer carbonate anions was synthesized by micro-emulsion method and had a rod-like and hexagonal plate-like mesoporous structures. Although CoAl-LDH has a larger specific surface area, its theoretical maximum fluoride ion removal capacity (14.80 mg/g) is not very large, possibly due to the low affinity of divalent Co to fluoride ions.[15] A similar behavior has been observed for ZnAl-LDH.[16]

Taking advantage of the fact that the ionic radius of Li^+ (0.060 nm) is similar to that of Mg^{2+} (0.065 nm), LiAl-LDH is prepared by using Li^+ to replace Mg^{2+} in MgAl-LDH. On the one hand, Li maintains the structural stability of LDH. On the other hand, using monovalent Li ions to replace divalent ions can increase the charge polarity of the LDH layer. Therefore, the electrostatic attraction of the LDH layer to fluoride ions increases, with the theoretical maximum fluoride removal capacity of more than 46.53 mg/g.[17]

2.1. 2 Fe-based binary LDH

Although Al-based LDH has been proven to have good fluoride ion removal ability, the released Al ions will pose certain risks to human health, due to the dissolution of LDH during use at relatively low pH. Therefore, the development of trivalent Al-free LDH becomes a research focus. Fe is widely available and harmless to the human body, so it is naturally used to synthesize Fe-based LDH.

The most studied LDH of this type is MgFe-LDH, which is often synthesized using co-precipitation or hydrothermal methods [18] and modified through interlayer ion exchange, thermal activation, etc. to obtain greater fluoride ion removal capacity. However it is noted that the actually theoretical maximum fluoride ion removal capacity of MgFe-LDH is only 50.91 mg/g ,[19] which is far less than that of Al-based LDH, even after modification.

NiFe-LDH with high crystallinity and carbonate anions was synthesized by high-temperature solvent method, whose ion exchange capacity in fluoride ion adsorption process can be improved by introducing high-concentration Cl^- ions to modify the interlayer of LDH. The theoretical maximum adsorption capacity of NiFe-LDH synthesized by this method can reach 174.68 mg/g, which is significantly higher than NiFe-LDH synthesized by traditional methods.[20]

2.1. 3 Cr-based binary LDH

The introduction of trivalent chromium into the brucite-like structure is also one of the directions of LDH research in recent years.[21] Research on Cr-based binary LDH mainly focuses on the LDH with intercalated NO^{3-} and Cl^- anions. For example, the NO^{3-} type ZnCr-LDH synthesized by coprecipitation method has a better fluoride ion removal effect at a molar ratio of 3:1 between Zn and Cr than at other ratios; at the same time, it can continuously maintain stable fluoride ion removal capacity in a wide pH range from 3 to 9 with a theoretical maximum removal capacity of 33.00 mg/g.[22] The fluoride ion removal rates of Cl^- type MgCr-LDH at pH 7 are 88.5% and 77.4% respectively, when the initial fluoride ion concentrations are 10 mg/L and 100 mg/L. The adsorption process is more consistent with pseudo-first-order kinetics and the theoretical maximum removal capacity is 13.16 mg/g.[23]

2.1. 4 Rare earth (RE)-based binary LDH

Rare earth elements have a greater affinity for fluoride ions, therefore when used as a component of binary LDH, a greater fluoride ion removal capacity can be reached. This type of LDH includes MgLa-LDH [24] and ZnCe-LDH.[25] Using cheap periclase (MgO) and lanthanum salt as raw materials, nano-needle-shaped MgLa-LDH (with carbonate anion) can be prepared through urea assistance and hydrothermal environment. La enters the hydroxide lattice to replace the divalent Mg cation, making the brucite layer more positively charged. At the same time, more active oxygen is generated in the structure, which tends to be converted into active hydroxyl groups with a higher anion exchange rate in the aqueous solution. Consequently, MgLa-LDH have a high adsorption capacity, and its theoretical maximum adsorption capacity can reach 75.97 mg/g.[24] In addition, ZnCe-LDH can also be successfully obtained through traditional co-precipitation method and its maximum adsorption capacity can reach 167.62 mg/g.[25]
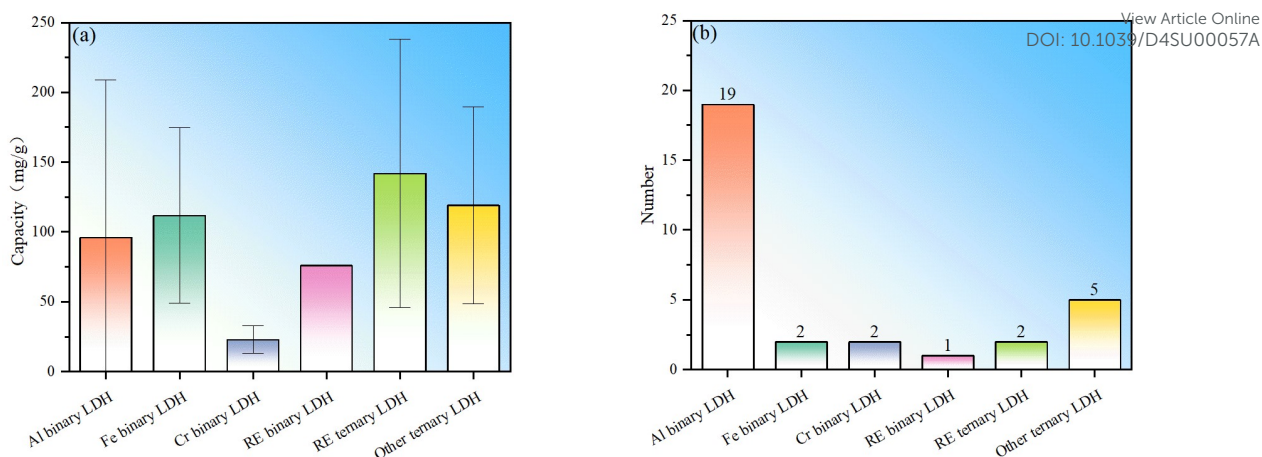
Fig. 1 Statistical histogram of intrinsic LDH fluoride ion removal agents. (a) removal performance expressed as adsorption capacity, (b) the number of studies (Note: heterocoagulated composite or LDH derivative MMO are not considered here, only intrinsic LDH adsorption is compared. There are no error bars for rare element-based binary LDH because of only one study.)

2.2 Ternary LDH

2.2.1 RE based Ternary LDH

Although rare earth elements have a high affinity for fluoride, they are very expensive which limits their use for LDH synthesis. One method to overcome this is to add a small amount of rare earth elements to binary LDH, with optimizing the ratio of rare earth elements and other metals to obtain the improved cost-effectiveness. The main element added in current research is La. This type of LDH includes MgAlLa-LDH [26, 27] MgFeLa-LDH [28, 29] and LiAlLa-LDH.[30, 31] Among these LDHs, only a small amount of La is needed to achieve high fluoride removal capacity. For example, MgFeLa-LDH with a molar ratio of Mg : Fe : La equal to 3 : 0.9 : 0.1 achieved a high fluoride ion removal capacity.[28, 29] Note that not all of these ternary LDHs were used directly as adsorbents, but most of them were further modified.

2.2.2 Other ternary LDH

Among many ternary LDH, in addition to La^{3+}, other common trivalent or divalent metal ions can also be introduced. LDHs containing two trivalent metal elements mainly include MgAlFe-LDH ;[32-35] LDHs containing two elements of divalent metals include CdNiFe-LDH ,[36] MgMnAl-LDH ,[37] MgCaAl-LDH ,[38, 39] MgCaFe-LDH [40] etc.

Partial replacement of Al ions with Fe ions at the trivalent metal position is beneficial for the stability of LDH in fluoride ion adsorption and reduces the formation of soluble aluminum fluoride complexes. MgAlFe-LDH synthesized by co-precipitation at a molar ratio of Mg : Al : Fe equal to 3 : 0.5 : 0.5 has an equilibrium fluoride removal capacity of 4.08 mg/g (12.73 mg/g after thermal activation) as compared to 2.78 mg/g observed for MgAl-LDH with Mg:Al ratio of 3:1.[33] LDH containing Ca can achieve efficient fluoride ion removal by releasing Ca^{2+} ions into the solution and then forming CaF precipitate. The theoretical maximum fluoride ion removal capacity of NO_3^- type MgCaAl-LDH with a molar ratio of Mg : Ca : Al of 1.25 : 3.75 : 1 can reach 248.44 mg/g.[40]

2.3 Summary

To sum up, LDHs currently used for fluoride ion removal can be divided into two categories: binary and ternary LDHs (Table 1), which can be further subdivided according to the type of trivalent cations. Among binary LDHs, Al-based LDH has the largest number of studies. This is mainly based on the high availability of Al element and corresponding salts. The fluoride ion removal performance of Al binary LDH is good, but it is noted that their fluoride removal performance has large fluctuations (Fig. 1). LDH in which M^{3+} is Fe^{3+} shows better fluoride ion removal performance, but the number of studies is still small (Fig.1b). Binary LDHs using other transition elements such as Cr or rare earth elements occupying the M^{3+} position does not show obviously better performance than that of Al or Fe binary LDH. The following reasons may contribute to the high fluoride adsorption performance by Fe binary LDH: I. The introduction of iron ions can introduce lattice distortion and change morphology of LDH, leading to an increase in adsorption sites and a larger specific surface area. II. The filled 3d orbitals give the iron ions a strong electron transfer capability, which may enhance the electronic interaction between fluoride ions and iron ions, making it easier for fluoride ions to be adsorbed on the surface of LDH. III. There may be a synergistic effect between iron ions and other metal ions in iron-containing LDHs, thereby enhancing the overall adsorption capacity of the material.

Trivalent metal-based LDHs have also been synthesized. The composite site where two elements coexist can be a divalent metal site or a trivalent metal site. The composite element can be a common metal or a rare earth metal. La or Ce is found to occupy trivalent metal sites. This type of ternary LDH showed the best average adsorption performance, indicating that the addition of rare earth elements and the synergistic effect of multi-metal components are conducive to performance improvement. Similarly, even ternary LDH without the addition of rare earth elements also showed good fluoride removal performance, further indicating that the synergy of multi-metal components promotes the absorption of fluoride ions.

It should be pointed out that the statistics in Fig. 1 mainly include materials with LDH structures that show fluoride adsorption, and do not include samples prepared through heterocoagulation approach and thermal activation modification. This is mainly to

directly compare the differences in adsorption capabilities of different intrinsic LDH. In heterocoagulated materials, the contribution of LDH to the overall fluoride ion adsorption performance is difficult to judge. And for MMO sample, the fluoride adsorption effect is exclusively caused by the oxide phase, not the LDH phase.

Table 1 LDH classification, synthesis, modification and fluoride removal performance statistics

Classification	LDH name	M^{2+}/M^{3+}, $M_A^{2+}/M_B^{2+}/M^{3+}$, $M^{2+}/M_A^{3+}/M_B^{3+}$	Synthesis method	Modification method	Thermodynamic model	Kinetic model	pH at maximum adsorption capacity	Maximum adsorption capacity（mg/g）	Ref
Al-based binary LDH	MgAl-LDH	3:1	Co-precipitation	-	Freundlich	-	5	38.9	41
		2:1	Co-precipitation	-	-	-	6	84	42
		2:1	Co-precipitation	-	Lamgmuir - Freundlich	-	6	319.80	43
		2:1	Urea-assisted	-	Freundlich	-	7	28.60	44
		2:1	Co-precipitation	-	Langmuir	2nd	7	41.3	45
		2:1	Co-precipitation	-	-	2nd	-	-	46
		2:1	Co-precipitation	-	-	-	-	-	47
		2:1	Co-precipitation	-	Langmuir	2nd	-	62.69	48
		3:1	Co-precipitation	Morphology control	Langmuir	2nd	-	21.72	49
		2:1	Urea-assisted	Morphology control	Freundlich	2nd	6	27.03	50
		2:1	Co-precipitation	Morphology control +Thermal activation	Langmuir	-	6	47.70	51
		3:1	Co-precipitation	Morphology control +Thermal activation	-	-	-	82.45	52
		4:1	Co-precipitation	Morphology control (various aging treatments)	Redlich-Peterson	2nd	-	44.4	53
		2:1	Co-precipitation	Acid etching	Freundlich	-	3.5	416.67	54
		2:1	Co-precipitation	Heterocoagulation	Temkin - Phyzev	2nd	5.3~7.1	14.10	55
		3:1	Co-precipitation	Heterocoagulation	Langmuir	2nd	6	2.63	56
		-	Hydrothermal	Heterocoagulation	Langmuir	2nd	5-7	58.70	57
		-	Hydrothermal	Heterocoagulation	Langmuir	2nd	5.71	15.21	58
		2:1	Urea-assisted	Heterocoagulation	-	-	-	-	59
		2:1	Hydro/solvothermal	Heterocoagulation	Freundlich	2nd	5	40.17	60
		5:1	Co-precipitation	Heterocoagulation+ Thermal activation	Langmuir	-	5	5.03	61
		2:1	Co-precipitation	Heterocoagulation+ Thermal activation	Langmuir	-	7.5	28.52	62
		3:1	Co-precipitation	Thermal activation	-	-	7	-	63
		2:1	Co-precipitation	Thermal activation	-	-	6	222	42
		2:1	Urea-assisted	Thermal activation	Freundlich	2nd	7	55.22	64
		4:1	Co-precipitation	Thermal activation	Langmuir	2nd	7.2	119.04	65
		2:1	Co-precipitation	Thermal activation	Langmuir	2nd	6	36.86	66
		3:1	Co-precipitation	Thermal activation	-	-	-	-	67
		3:1	Co-precipitation	Thermal activation	Freundlich	-	5	107.60	41
		2:1	Co-precipitation	Thermal activation	Freundlich	2nd	-	91.40	68
		2:1	Urea-assisted	Thermal activation	Freundlich	-	6	213.22	13
		3:1	Co-precipitation	Thermal activation	Langmuir	2nd	-	20.94	69
	CaAl-LDH	2:1	Co-precipitation	-	Freundlich	-	-	146.60	14
		2:1	Co-precipitation	-	-	-	7	247.1	70
		1:1	Co-precipitation	-	Langmuir	2nd	6	29.57	71
		3:1	Urea-assisted	Heterocoagulation	Langmuir	2nd	5.87	63.11	72
		2:1	Co-precipitation	Heterocoagulation	-	-	7	90.00	70
		2:1	Co-precipitation	Thermal activation	-	-	-	59.60	73
		3:1	Co-precipitation	Thermal activation	Freundlich	-	-	108.69	74
		2:1	-	Thermal activation	Freundlich	2nd	8	8.4	75
	CoAl-LDH	1:9	microemulsion	-	Langmuir	2nd	7	7.13	15
		1:9	microemulsion	Thermal activation	Langmuir	2nd	7	14.80	15
		2:1	Co-precipitation	-	Langmuir-Freundlich	2nd	10	122.54	76
	NiAl-	2:1	Co-precipitation	Thermal activation	Langmuir—	2nd	-	1.20	77

	LDH				Freundlich				
	ZnAl-LDH	1:3	Co-precipitation	-	Temkin	-	6.4	-	78
		1:1	Co-precipitation	-	Temkin	2nd	6	4.16	79
		1:1	Co-precipitation	-	-	-	-	25.18	80
		5:2	Urea-assisted	Heterocoagulation	-	-	-	-	81
		2:1	Co-precipitation	Heterocoagulation	-	2nd	6.5	-	16
		2:1	Co-precipitation	Heterocoagulation	Freundlich	2nd	6.4-6.5	8.85	82
		1:1	Co-precipitation	Heterocoagulation	-	-	-	5.29	81
	LiAl-LDH	1:2	Hydrothermal	Heterocoagulation	Sips	2nd	7.1	62.50	83
		1:2	Co-precipitation	Heterocoagulation	Temkin	-	6.6	-	30
		2:1	Co-precipitation	Thermal activation	Freundlich	2nd	6~7	46.53	17
		3:1	Urea-assisted	Thermal activation	Freundlich	2nd	7	158.70	84
		1:2	Urea-assisted	-	Langmuir	-	7	156.09	85
Fe-based binary LDH	MgFe-LDH	3:1	Co-precipitation	-	Langmuir	2nd	6~7	49.00	86
		3:1	Co-precipitation	Heterocoagulation	Langmuir	2nd	6~7	52.4	86
		3:1	Co-precipitation	Heterocoagulation+Thermal activation	Langmuir	1st	7	27.56	87
		2:1	Hydrothermal	Thermal activation	Langmuir	2nd	7	28.65	18
		5:1	Co-precipitation	Thermal activation	Langmuir	2nd	7	50.91	19
	CoFe-LDH	3:1	Co-precipitation	Heterocoagulation	Jovanovich	2nd	7	110.1	88
	CaFe-LDH	10:1	Co-precipitation	Thermal activation	-	2nd	-	463.16	89
	NiFe-LDH	3:1	MMO hydration	Anion exchange	Langmuir	2nd	-	174.68	20
Rare element (RE) binary LDH	MgLa-LDH	-	Urea-assisted	-	Sips	2nd	6	75.97	24
	ZnCe-LDH	1:1	Co-precipitation	Heterocoagulation	Freundlich	2nd	-	167.62	25
Cr-based binary LDH	ZnCr-LDH	3:1	Co-precipitation	-	Langmuir	2nd	-	32.80	22
	MgCr-LDH	3:1	Co-precipitation	-	Langmuir	1st	7	13.16	23
RE ternary LDH	MgFeLa-LDH	3:0.9:0.1	Urea-assisted	Rare earth element doping+Thermal activation	Langmuir	2nd	6.8	73.80	28
		3:0.9:0.1	Hydrothermal	Rare earth element doping+Thermal activation	Langmuir	2nd	6.8	59.98	29
	MgAlLa-LDH	3:0.9:0.1	Urea-assisted	Rare earth element doping+Thermal activation	Sips	2nd	6	51.03	26
		3.3:1:0.1	Co-precipitation	Rare earth element doping+Thermal activation	Langmuir	2nd	6	62.33	27
	LiAlLa-LDH	3:1:0.3	Co-precipitation	Rare earth element doping	Freundlich	2nd	7	46.00	31
		-	Hydrothermal	Rare earth element doping+Heterocoagulation	Sips	2nd	7	75.70	90
	NiAlCe-LDH	3:0.95:0.5	Co-precipitation	Rare earth element doping	Freundlich	2nd	3	238.27	91
Other ternary LDH	MgAlFe-LDH	1:0.5:0.1	Co-precipitation	Morphology control+Heterocoagulation	Langmuir	-	-	-	32
		1:0.8:0.2	Co-precipitation	Thermal activation	Langmuir	1st	6	14.92	34
		3:0.5:0.5	Co-precipitation	Thermal activation	Langmuir	2nd	-	42.74	33
		3:1:0.5	Co-precipitation	Thermal activation	Langmuir	-	4	71.94	35
	CoMgAl-LDH	1:2:1	Co-precipitation	-	Langmuir	2nd	6	38.01	92
	MgCaAl-LDH	2.5:0.5:1	Co-precipitation	-	Langmuir	2nd	5	82.35	38
		2.72:1:0.29	Co-precipitation	Thermal activation	Langmuir	2nd	6	77.9	39
	MgCaFe	1.25:3.75:1	Co-precipitation	-	Freundlich	2nd	-	248.44	40

-LDH								
MgMnAl-LDH	-	Co-precipitation	Thermal activation	Freundlich	2nd	-	58.33	37
CdNiFe-LDH	0.5:3:1	Urea-assisted	Heterocoagulation	-	-	-	-	36
ZnCoCr-LDH	1:1:2	Hydrothermal	-	Langmuir	2nd	5	108.97	93
NiMnAl-LDH	2.85:0.15:1	Co-precipitation	-	Temkin	2nd	5	117.94	94

In order to further present to readers the current popularity of various types of LDH in fluoride removal research, further statistics on all LDH-based fluoride removal agents (including heterocoagulated composite and MMO samples) are shown in Fig. 2. It can be seen that Al-based LDH is still the most studied LDH, and it is also found that using conventional metals to prepare ternary LDH-based fluoride adsorbents is relatively hot. Generally, adjusting the type of metal ions, metal ion ratio, defect concentration, particle morphology, interlayer anion types, etc. can only improve the intrinsic performance to a limited extent, and excessive adjustments may lead to unstable LDH layer structure. To further improve the fluoride ion adsorption performance of LDH, other modifications may be further supplemented (Section 4).

3 Synthesis

During the formation of LDH, supersaturation is the driving force for LDH nucleation, which is affected by reaction temperature, pH value, composition and proportion of materials, etc. In addition, reaction time is also a key factor in determining the kinetics of LDH formation. Therefore, reasonable control of these parameters enables the adjustment of LDH grain size, structure and micromorphology. Currently, hydrothermal, co-precipitation, urea-assisted and MMO hydration methods are found to synthesize related fluoride-removing LDH.

3.1 Hydrothermal
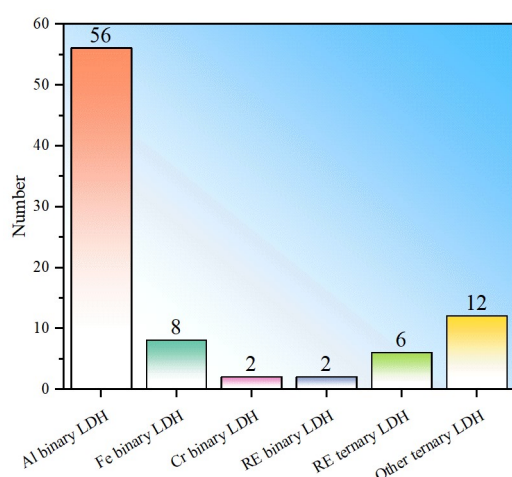
Fig. 2 Statistical histogram of the number of researches on LDH-based fluoride removers (including heterocoagulated composites and MMO derived from LDH).

Hydrothermal is a synthesis method that utilizes chemical reactions of substances in solution under certain temperature (≥100°C) and pressure (1~100MPa) conditions.[95] Sodium hydroxide, ammonia or soda is usually added as an alkali source in LDH synthesis. For example, orderly stacked MgAl-LDH can be synthesized using ammonia as the alkali source and soluble metal nitrate as the metal ion source.[96] When caustic soda was used as the alkali source, the crystallinity of MgAl-LDH gradually improved with the extension of hydrothermal time and the increase of temperature. The obtained particles were oblate and had a narrow particle size distribution, which gradually became larger with the increase of aging time and reaction temperature (Table 2). This can be attributed to the fact that the crystal growth rate is proportional to the reaction temperature.[97]

Insoluble oxides can also be used as metal ion sources to synthesize LDH. Using MgO and Al_2O_3 as raw materials, MgAl-LDH was synthesized through hydrolysis and precipitation of oxides under high temperature and high pressure conditions without adding other alkali sources ;[98] while adding NaCl, $NaHCO_3$ or Na_2CO_3 during the synthesis, MgAl-LDH with Cl^- or CO_3^{2-} as the interlayer anion can be obtained.[99] However, it is noted that there are relatively few studies on the synthesis of LDH adsorbent through high-temperature hydrothermal using insoluble oxides or hydroxides as raw materials, due to the low efficiency of the reaction.

3.2 Co-precipitation

Co-precipitation is the most common method for preparing LDH materials, by mixing divalent and trivalent metal salt solutions in a certain ratio, and adjusting the pH of the solution to reach supersaturated conditions to produce metal hydroxide precipitation.[100] The co-precipitation method is divided into low saturation and high saturation co-precipitation. In the low-saturation co-precipitation method, the metal salt mixed solution is slowly added to the separate aqueous solution, and at the same time, the alkaline solution is added dropwise to maintain the pH required for co-precipitation, while in high-saturation co-precipitation, the metal salt mixed solution is added directly to the alkaline solution. Since the latter approach results in relatively low crystallinity and the formation of other metal hydroxide impurities, further thermal treatment is often required.[101] In general, the co-precipitation is a reliable, simple and low-cost way to synthesize most types of LDH materials.

LiAl-LDH synthesized by the co-precipitation method has smaller particles than LDH synthesized by the urea method, and has a highly crystalline and ordered layered structure. The maximum adsorption capacity of fluoride ions can reach 46.53 mg/g.[17] Note that in current research, LDH synthesized by the co-precipitation method is mostly used as the basis before further modification, such
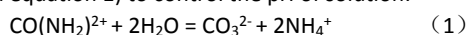
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Table 2 Effects of aging time, reaction temperature, and total metal ion concentration on LDH particle size.[97]

Synthesis method	Aging time（h）	Temperature（℃）	Total metal concentration （M）	Particle size（nm）	Standard deviation（nm）
Hydrothermal	12	100	0.133	85	14
	24	100	0.133	100	15
	48	100	0.133	115	13
	72	100	0.133	120	23
	48	100	0.133	115	13
	48	125	0.133	210	28
	48	150	0.133	290	56
	48	180	0.133	340	29
urea-assisted	6	90	0.6	860	490
	30	90	0.6	1930	330
	45	90	0.6	2140	240
	69	90	0.6	2200	300
	672	65	0.87	1170	220
	672	65	0.65	2140	330
	672	65	0.44	2740	790
	672	65	0.065	4470	420

as MgAl-LDH synthesized by the co-precipitation method was used to produce MMO with 82.3% fluoride removal capacity at pH= 7 and an initial fluoride ion concentration of 5 mg/L.[63]

3.3 Urea-assisted method

Essentially, the urea-assisted method is a type of co-precipitation method, but due to its stable pH control and frequent use, it is classified separately here. Compared with hydrothermal method, which uses caustic soda, ammonia or soda to provide an alkali source, the method mainly decomposes urea to produce ammonia (Reaction equation 1) to control the pH of solution:

$$CO(NH_2)^{2+} + 2H_2O = CO_3^{2-} + 2NH_4^+ \quad \quad （1）$$

Since the decomposition rate of urea can be controlled by the reaction temperature, the particle size distribution of LDH can therefore be controlled.[102] However, because the urea method is usually performed slightly above room temperature, the LDH nucleation rate is low and eventually larger particles are formed than other methods (Table 1).[97] This method can be used for the purposeful synthesis of large-sized, well-shaped LDH.[84, 103]

Most of the research on using urea-assisted method to synthesize LDH for fluoride adsorption uses a reaction temperature above 100°C to increase the decomposition rate of urea and thus the nucleation rate of LDH.[104] In addition, since urea can produce carbonate ions during the decomposition process, the method mainly synthesizes carbonate intercalated LDH. The presence of carbonate is not conducive to the adsorption of fluoride ions, so further modification is usually required.

3.4 Microemulsion

Microemulsion is a thermodynamically stable dispersion system formed by two incompatible liquids with the assistance of surfactants. It is divided into water-in-oil microemulsion (w/o) and oil-in-water microemulsion (o/w). The particle size of microemulsion droplets is 5 to 70 nm, and the internal space can be used as a microreactor. Particle growth ends when the reactants are consumed. Therefore, microemulsion can control the size of

nanoparticles without the use of expensive equipment. Microemulsion is an important approach to prepare monodisperse nanoparticles, which has been greatly developed and improved in recent years. For example, a mixed nitrate solution of Co and Al was used as the water phase and aviation kerosene was used as the oil phase to form a microemulsion. Then ammonium bicarbonate solution was added to provide an alkaline environment, and the reaction was carried out under high temperature and high pressure conditions. Finally, CoAl-LDH with rod-shaped and hexagonal plate-shaped was synthesized.[15]

3.5 MMO hydration

The "memory effect" of LDH can be used to rehydrate (reconstruct) the layered structure. The calcination of (thermal activation) will gradually remove the interlayer structural water, anions and hydroxyl groups, thereby leading to MMO; when MMO is dispersed in an aqueous solution with anions, MMO can be rehydrated and the LDH layered structure is restored; at the same time, the interlayer space is filled with hydrated anions from the solution. It was noted that MMO is hydrated while adsorbing fluoride ions. The adsorption process essentially reflects the fluoride ion adsorption capacity of MMO, rather than that of LDH obtained after MMO hydration. At present, the only relevant study on the preparation of defluorination agent from LDH after MMO hydration is to soak the oxide precursor ($NaNi_{0.75}Fe_{0.25}O_2$) prepared by high-temperature flux method in ultrapure water for topological orientation transformation.[20] The cationic valence state of the oxide layer changes from Ni^{3+} to Ni^{2+}, and carbonate (CO_3^{2-}) and water molecules are embedded between the layers at the same time. However, the LDH product was not directly used as an adsorbent in the study, but was further modified by anion exchange (Section 4.4).

3.5 Summary

To sum up, there are currently five main types of synthesis methods for LDH fluoride ion scavenger, hydrothermal, co-precipitation, urea-assisted, microemulsion and MMO hydration
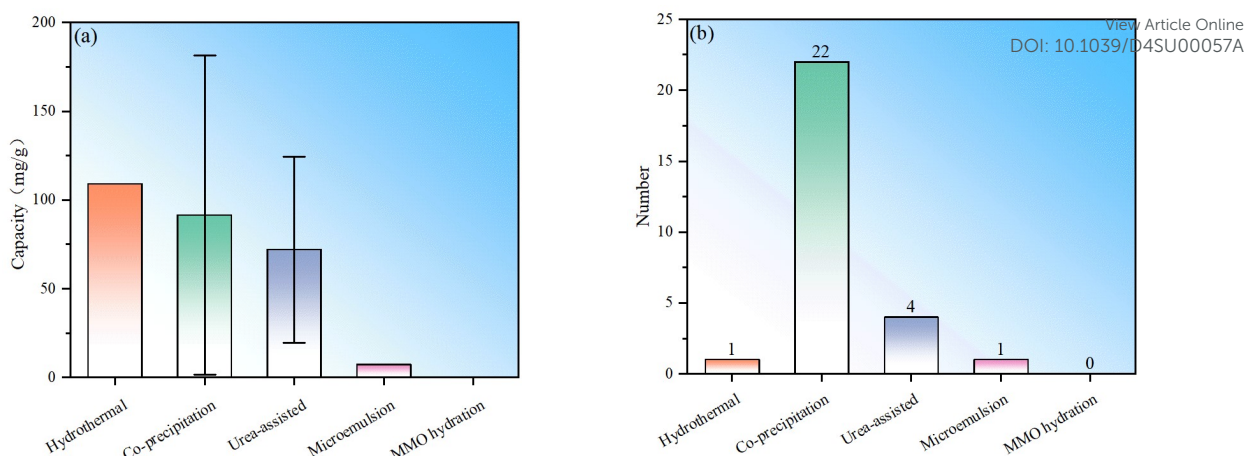
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Fig. 3 Statistical histogram of the synthesis of LDH original fluoride adsorbent. (a) Fluoride ion removal performance corresponding to different synthesis methods, (b) the number of studies corresponding to different synthesis methods (Only the basic LDH phase obtained by adjusting synthesis conditions in Sections 3 and 4.1 is counted. There is only one study on hydrothermal and microemulsion respectively, thus there is no error bar for them).

(Fig.3). The samples prepared by the hydrothermal method appear to have the best performance, but the number used directly as defluoridation agents is relatively small and the statistics are weak. The average performance of samples synthesized by co-precipitation method is second best, but the number of studies is the largest (Fig. 3). The sample performance obtained by urea-assisted method is not as good as that of co-precipitation method. The reason may be that the LDH particles synthesized by the co-precipitation are smaller, while the size of LDH synthesized by the urea method is larger. In addition, the urea method will decompose to produce carbonate ions during the synthesis process, which further hinders the exchange and adsorption capacity of fluoride ions. Nevertheless, we must point out that the urea-assisted method has certain advantages in synthesizing LDH with regular shapes. The adsorption capacity of LDH synthesized by microemulsion is relatively low, which may be determined by the properties of the material itself in the example. This method can be used to synthesize other LDH materials for further testing. Regarding the hydrothermal and MMO hydration methods, no direct synthesis of LDH for fluoride ion adsorption has been found so far. The reason may be that hydrothermal has higher requirements for production equipment and processes. Although LDH obtained by rehydrating MMO is theoretically feasible, its practical value is not big.

To further demonstrate the research popularity of various synthesis methods in LDH-based fluoride ion adsorbents, the synthesis methods corresponding to all LDH-based fluoride adsorbents (including heterocoagulated and MMO samples) are also statistically analysed (Fig. 4). It can be seen that in the preparation of LDH-derived fluoride ion adsorbents, co-precipitation is still the most commonly used, proving the convenience of such synthesis. The urea-assisted and hydrothermal methods, which are similar to the co-precipitation method, are also relatively widely used. MMO hydration method has been rarely studied to synthesize MMO fluoride removal material precursor, indicating that this method may not have advantages in synthesizing fluoride ion adsorbent. In addition, microemulsion has also been investigated to synthesize MMO precursors, but the number of studies is currently sparse.

4. Modification

In order to increase LDH's fluoride ion removal efficiency, the LDH material is usually further modified through morphology control, acid etching, rare earth element doping, anion exchange, heterocoagulation and thermal activation. The first four modifications do not destroy the basic brucite-like layer of LDH; heterocoagulation involves mixing of LDH with other phases to achieve co-adsorption or additional properties; while thermal activation transforms the brucite-like layer into a mixed oxide structure.

4.1 Morphology control

By adjusting process parameters, LDH materials can have various morphologies and produce high-density adsorption sites, which help to improve the fluoride ion removal performance.. For example, a shorter hydrothermal aging time can be used to obtain MgAl-LDH with a larger specific surface area, while longer hydrothermal aging time will lead to the emergence of Al(OH)$_3$ phase and reduce the
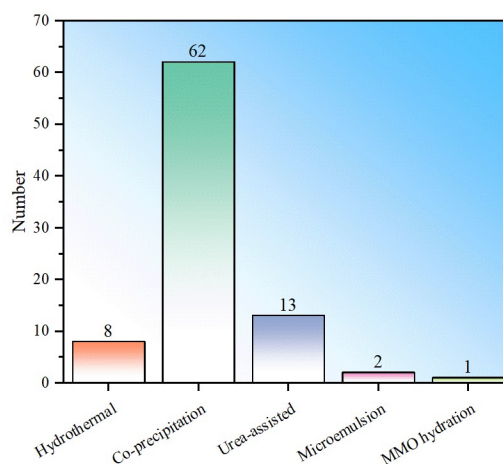

Fig. 4 Statistical histogram of LDH synthesis methods in LDH-related fluoride adsorbent (Note: including heterocoagulated or hydrotalcite derivative MMO samples)

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specific surface area.[50] The use of starch in the synthesis of MgAl-LDH can stabilize the micromorphology and form particles with smaller particle size and narrower distribution, thus significantly improving the fluoride ion removal performance.[49] It can be found that the LDH obtained by liquid nitrogen drying had a lower crystallinity, and was composed of fine agglomerated nanoparticles, so its adsorption performance was significantly improved compared to that of the sample dried in oven at 100°C.[52]

Some studies pointed out that the morphology of LDH basically remains unchanged after thermal activation.[84] Therefore, the morphology of MMO can be controlled by controlling the synthesis conditions of LDH. In other words, the morphology changes of MMO reflect the effect of the control conditions on the morphology of LDH. By changing the molar ratio of metal ions (Li^+/Al^{3+}=2, 3, 4, 5), the morphology of Li/Al-MMO can achieve the gradual evolution from hexagonal nanosheets to petal-like combinations to interconnected petal-like structures.[84] The crystallinity of the MgAl-LDH material can be adjusted by controlling the amount of doped La, and finally rice-like nano-Mg/Al/La-MMO nanoparticles are formed.[26] The particle size of MgAl-LDH prepared by co-precipitation assisted ultrasound is smaller (80 mm) than that prepared by traditional co-precipitation method (120 nm).[51]

4.2 Acid etching

Acid etching treatment of LDH will partially dissolve and release metal elements and protonate the LDH surface, thus the LDH surface can be activated. If the appropriate acid type is selected, the interlayer anions will be exchanged into acid ions that facilitate the next exchange with fluoride ions. For example, since the affinity of LDH to carbonate is much greater than that of fluoride ions, the presence of interlayer carbonate is not conducive to the adsorption of fluoride ions. Consequently, the reduction of interlayer carbonate and the replacement of carbonate by other acid ions can improve the subsequent fluoride ion exchange. In addition, the hydrogen ions in the acidification process may react with the intercalated carbonate ions to form CO_2 which is later released, by following the Equation (2) :[105]

$$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3 \rightarrow H_2O + CO_2 \qquad (2)$$
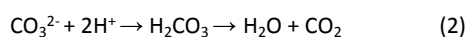
During acidification with hydrochloric acid or formic acid, carbonate ions between the layers were partially or completely removed, and Cl or formate ions were introduced between the layers, which are easily replaced by F^- ions. So, the fluoride ion adsorption performance of MgAl-LDH was significantly improved after acid etching (Table 3).

Note that the moderate acid etching can replace interlayer anions while bringing a large number of interlayer active sites, which is beneficial for further improvement of fluoride ion adsorption capacity. However, if the etching is excessive, it may destroy the LDH structure and damage the fluoride ion adsorption performance, and may also release a large amount of easily soluble elements, such as Al, Mg, etc., which may cause secondary pollution (Table 3).[54] However, there is no relevant research on the correlation between interlayer anion replacement and metal cation dissolution in the acid etching process.

4.3 Rare earth element doping

Adsorbent	Qe（mg/g）	Al（mg/L）	Mg(mg/L)
MgAl-LDH	39.48	-	-
MgAl-LDH etched by 0.1mol/L HCl	174.50	846.8	717.3
MgAl-LDH etched by 0.1mol/L HCOOH	176.00	438.0	1375.3
MgAl-LDH etched by 0.01mol/L HCOOH	83.08	48.5	250.5

Rare earth elements are considered to have the effect of improving the structure of the adsorbent, because they can provide more active sites for complexation or ligand exchange with fluoride. At present, most research is done on La element doping. For example, after LiAl-LDH was doped with La, it had high fluoride ion adsorption performance in a wide pH range of 5-9. The fluoride removal kinetic curve conformed to the pseudo second-order equation and the equilibrium Freundlich model. The maximum adsorption capacity is twice that of LiAl-LDH, and 7 times that of activated alumina, which can be attributed to the addition of La increasing the number of active sites that fluoride ions can bind to.[31]

Doping La during the preparation of MgAl-LDH can produce a three-dimensional rice-like micromorphology.[26] La not only adsorbs fluoride through interlayer adsorption and ligand exchange, but also serves as a structure inducer to adjust the crystallinity of the material.[26] In addition, some studies have shown that doped La can increase certain distortion of the LDH structure which influences the surface morphology and structure of LDH.[27, 29, 90]

4.4 Anion exchange

A distinctive feature of LDH is its high anion exchange capacity, which mainly depends on the type of anion used when the LDH sheet composition is fixed. The affinity order of LDH sheets for different common anions is the following:

$$NO_3^- < Br^- < Cl^- < F^- < OH^- < SO_4^{2-} < CO_3^{2-}$$
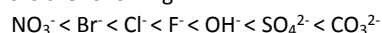
It can be seen that LDH has the greatest affinity for carbonate and sulfate anions, so when these anions dominate, it is difficult for fluoride ions to be adsorbed through ion exchange. The affinity of LDH to NO^{3-} [106, 107] and Cl^- are weaker than to fluoride ions, so these two types of anions can be used to modify LDH by interlayer exchange and then adsorb fluoride ions.

NiFe-LDH with carbonate ions is first prepared through NiFe-MMO hydration, and then Cl^- ions are used to replace CO_3^{2-} ions to obtain NiFe-LDH(Cl) adsorbent (Fig. 5). It has a high crystallinity, porosity and unique particle shape, with the highest F^- adsorption capacity of 176.15 mg/g^{-1}.[20]

NO^{3-} and Cl^- anions modified LDH have significant fluoride removal effect, and the pH of the solution after the fluoride removal will not increase obviously. However, it should be pointed out that because CO_3^{2-} ion contamination is prone to occur under conventional synthesis conditions, the regeneration conditions by this strategy need to be strictly controlled and are relatively
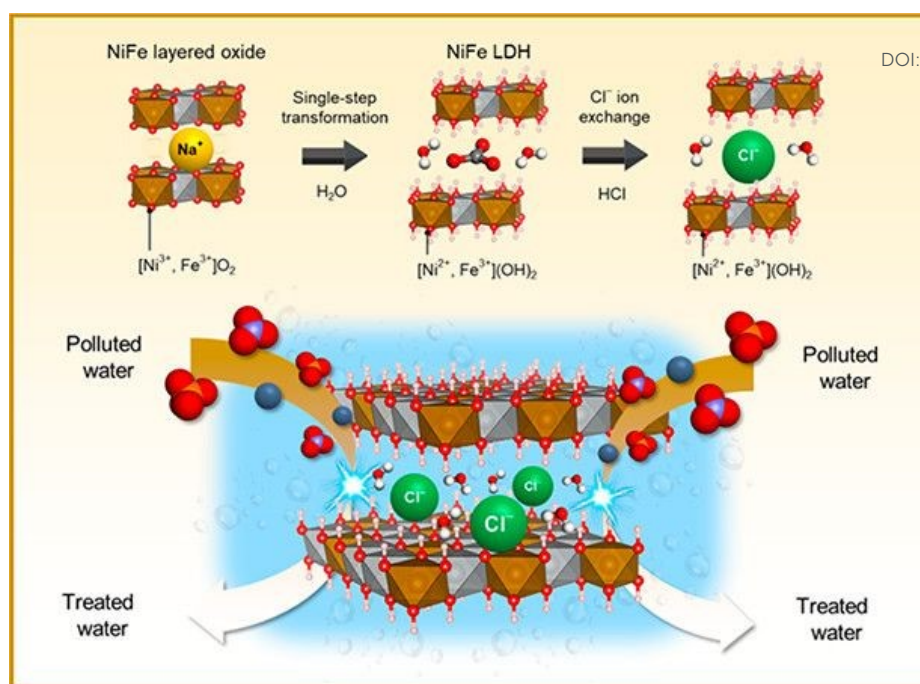
Fig. 5 Schematic diagram of the synthesis of NiFe-LDH with interlayer Cl ions.[20] Copyright 2021, American Chemical Society.

cumbersome.

4.5 Heterocoagulation

Although the aforementioned intrinsic modification methods such as morphology adjustment, acid etching, doping, substitution and other intrinsic modification methods can significantly improve the fluoride ion adsorption performance of LDHs, in many cases the nature of the material itself limits further improvement. Moreover, taking into account the growing multifunctional needs of industry, other possibilities must be explored. Such approach involves compounding LDH with other materials.. Materials compounding with LDH can mainly include organic materials, such as polystyrene,[83] thermoplastic polysulfone,[70] polyethersulfone,[30, 56] cellulose,[25, 72] and chitosan,[61, 87] etc.; carbon materials such as biochar,[39] graphene ;[81] metal-bearing materials such as aluminum foam; metal oxides such as magnetic iron oxide,[59, 62] Al_2O_3,[16, 57] CeO_2;[86] and other materials such as natural sand,[55] etc.

When LDH is compounded with heterophases, some LDH with small particle size is often loaded on some larger matrix materials, so that LDH nanoparticles are less likely to aggregate. Thus the active sites are then exposed to a greater extent, at the same time, its recycling is facilitated. For example, LiAl-LDH is loaded on commercial polystyrene anion exchanger. LDH particles are dispersed in the pores of polystyrene, improving their dispersion. At the same time, this compounding improves the chemical and mechanical stability of the composite, allowing it to be applied in a wide pH range from 3.5 to 12.[79] Organic materials with excellent fluoride ion adsorption properties can also be combined with LDH to form materials of high synergy for the removal of F⁻. For example, if a cellulose material rich in hydroxyl groups was used to composite with CaAl-LDH, the theoretical maximum adsorption capacity reached 63.1 mg/g, which is significantly higher compared with pure cellulose and raw LDH; the fluoride removal mechanism is mainly

chemical adsorption, which is consistent with the Langmuir model, indicating that significant hydroxyl displacement adsorption occurred.[72, 80]

4.6 Thermal activation

Converting LDH into MMO through thermal activation can improve the fluoride removal capacity of LDH materials. There are three reasons behind this phenomena: firstly, the thermal activation can remove intercalated carbonate ions; secondly, the dehydroxylation of LDH leads to the formation of mesopores and an increase in specific surface area, thereby increasing the number of adsorption sites ;[108] and thirdly, during the hydration reconstruction process, fluoride ions can be attracted into the LDH layer as a charge compensating ion, so the fluoride ion adsorption capacity is high by taking advantage of the "memory effect".[109]

The thermal activation temperature can have a significant impact on the LDH fluoride removal performance (Fig. 6). For example, as the thermal activation temperature of MgAl-LDH increased, the crystallinity of MgO in the product gradually increased; when the temperature was too high, the layer structure would not be destroyed and the $MgAl_2O_4$ spinel phase was generated. Although the specific surface area increased, the spinel phase could not be transformed into the LDH structure through the memory effect, so it hampered the fixation of fluoride ions.[67, 110] However, when the thermal activation temperature was too low, carbonate ions remained between the layers, and the brucite layer was insufficiently activated, which would also lead to poor fluoride ion adsorption performance. Therefore, it is crucial to optimize the LDH activation temperature to achieve satisfying fluoride ion removal performance.

It is generally believed that most LDHs have memory effects. However, when comparing the structural changes after calcination of MgAl-LDH, NiAl-LDH and CoAl-LDH, only MgAl-MMO could be
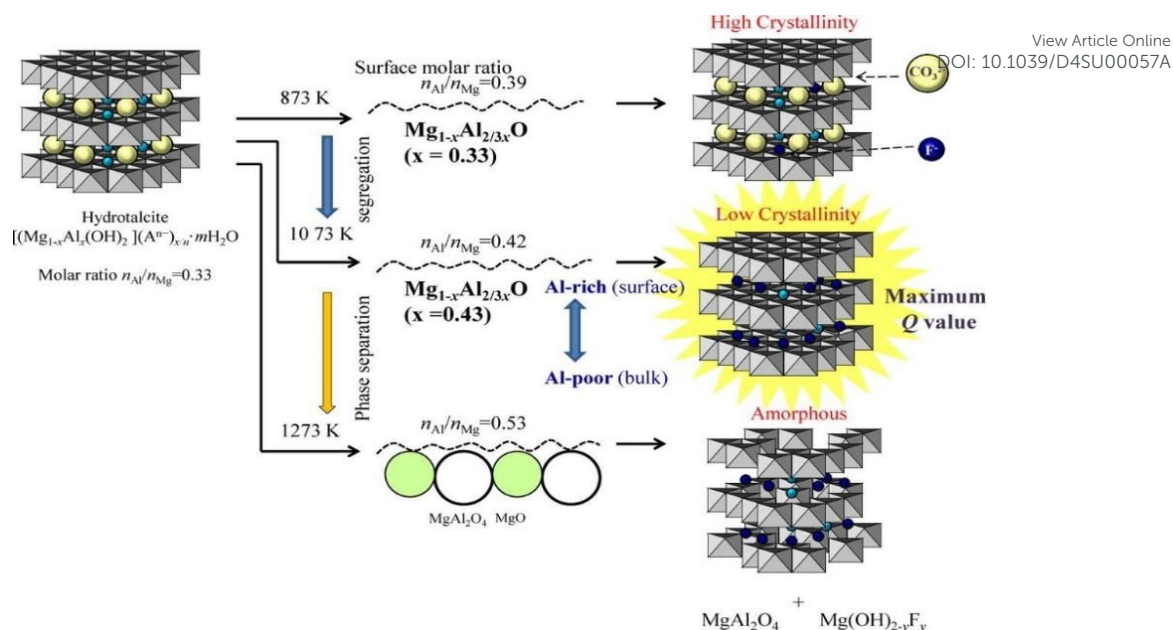
Fig. 6 Effect of calcination temperatures on the structure of LDH.[67] Copyright 2014, Elsevier.

restored into MgAl-LDH structure after being exposed to aqueous fluoride ions, whereas the other types of MMOs did not show a similar behavior.[80, 111]

Compounding pretreatment of LDH can improve the subsequent MMO morphology and fluoride ion adsorption capacity. For example, MgFe-LDH loaded on chitosan prepared by the co-precipitation method had the specific surface area of about 16.38 m^2/g before activation, while the specific surface area after thermal activation was 116.98 m^2/g with the theoretical maximum fluoride removal capacity of 27.56 mg/g, mainly because the dispersion of carbon inhibited the aggregation of MMO.[87]

The core/shell/shell mesoporous MgAl-LDH composite was synthesized with magnetic Fe_3O_4 microspheres as the core, SiO_2 as the inner layer, and MgAl-LDH as the outer layer. It had a large specific surface area and a good mesoporous structure with a theoretical maximum fluoride ion removal capacity of 28.51 mg/g after thermal activation at 350°C (Fig. 7).[62]

4.7 Summary

In summary, in order to improve the fluoride ion removal ability, LDH can be modified *via* morphology control, acid etching, rare earth element doping, anion exchange, heterocoagulation and thermal activation. Statistics were conducted on the fluoride ion removal effects of each modification method, and it is observed that although morphology control modification is the simplest, the fluoride ion
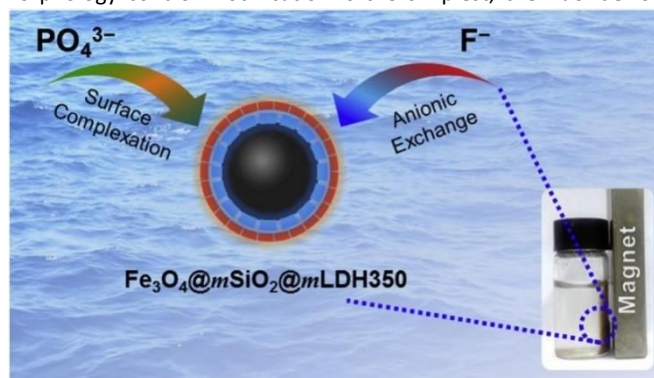

Fig. 7 Fe_3O_4@mSiO_2@mLDH350 composite adsorbent.[57] Copyright 2020, Elsevier.

removal is generally weak (Fig. 8). By compounding LDH with other materials, the fluoride ion removal capacity is not significantly improved, but the composite adsorbent can have properties that the LDH component does not have, expanding the application fields of LDH. The fluoride removal performance derived from rare earth element doping method is significantly improved compared to morphology control, indicating the great potential of this method. Anion exchange modification has a more obvious improvement effect than RE doping and heterocoagulation, but the number of studies is small, which may be due to the difficulty of anion exchange. There are many studies on thermal activation modification, and the fluoride ion removal effect is also more obvious than that of morphology control. However, thermal activation needs to be carried out at high temperature and consumes more energy. In addition, it is noted that the fluoride ion removal ability of thermal

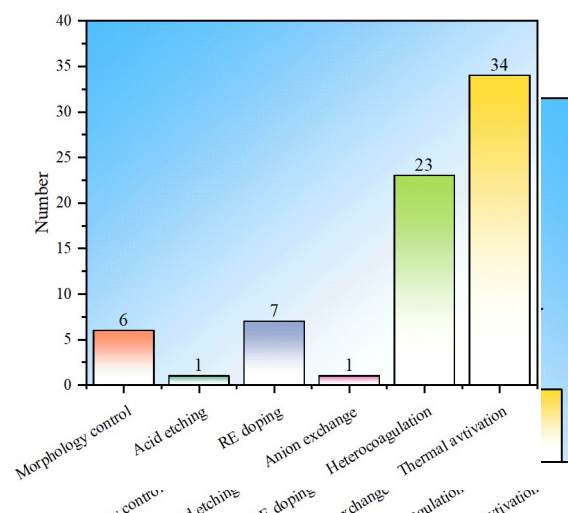activation modification has a wide range, mainly because the fluoride

Fig. 9 Statistical histogram of the number of studies on modification of LDH-based adsorbents (All LDH-based adsorbents including heterocoagulated or MMO samples)

while there are only few studies on acid etching and anion exchange, indicating that these methods may have some limitations. This result well demonstrates the popularity of various modification methods in the research of LDH-based fluoride ion adsorbent.
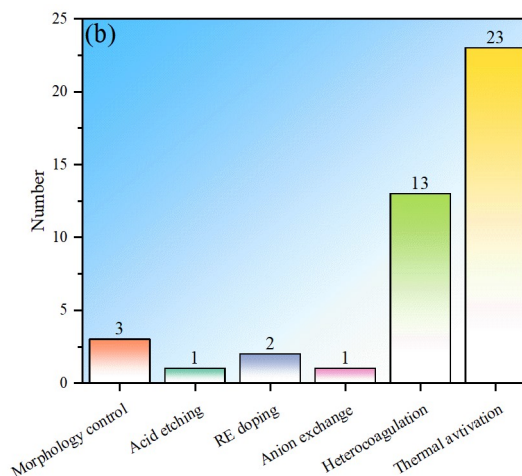

...ide removal performance corresponding to different modification methods (b) the number of studies corresponding to different modification methods (Only LDHs by single modification are counted. There is only one study on acid etching, anion exchange modification and rare earth element doping, respectively, therefore error bars are not included)

ion removal performance is not only related to the modification method, but also related to the structure and morphology of starting LDH.

Statistics on the number of modifications among LDH-based fluoride ion adsorbents were conducted (Fig. 9). It can be seen that the distribution of the number of studies involving multiple modifications is the same as that of single modification, and the thermal activation method is still the most studied, which once again shows that the thermal activation process is easy to implement. Compounding modification is also widely studied, mainly due to people's expectations for performance expansion and improvement by other "good" materials that have advantages in certain aspects. There are only a few studies on morphology control, indicating that the modification effects of this conventional methods are limited;

5. Factors affecting fluoride ion adsorption

The adsorption of fluoride ions by LDH and its derivative MMO will be affected by several factors such as pH, temperature, adsorbent dose or competitive effect of coexisting anions. This section summarizes the general rules regarding these influencing factors. It should be noted that after statistics of existing research results, it was found that the impact of environmental factors on most LDH and MMO has roughly the same trend, so they are discussed together here.

5.1 pH

The effect of pH on the adsorption of fluoride ions is mainly through its effect on the surface charge of LDH. Generally speaking, as the pH decreases, the fluoride ion removal ability of LDH increases (Fig. 10).[75,112] This phenomenon is similar to some other adsorbents such as alumina, hydroxyapatite, and activated carbon. This can be explained by the fact that when pH < pH_{pzc} (pH at zero point potential), the surface of LDH is protonated, resulting in a positive charge on the surface, which is conducive to the adsorption of fluoride ions through electrostatic interaction. This process can be expressed as shown in Equation 3 and 4.

$$\equiv MOH(s) + H^+(ap) \leftrightarrow \equiv MOH_2^+(s) \qquad （3）$$
$$\equiv MOH_2^+(s) + F^-(aq) \leftrightarrow \equiv MF(s) + H_2O \qquad （4）$$
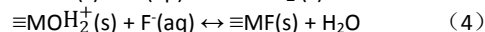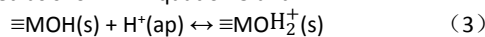
Low pH may also lead to structure dissolution and release of metal ions which leads to the formation of precipitates if the corresponding fluoride or anionic salt is insoluble. For example, LaFeMg-LDH will release La and Mg under acidic conditions and complex with fluoride ions to form a precipitate.[24] However, too low pH may destroy the LDH structure, thereby reducing the fluoride ion adsorption efficiency.
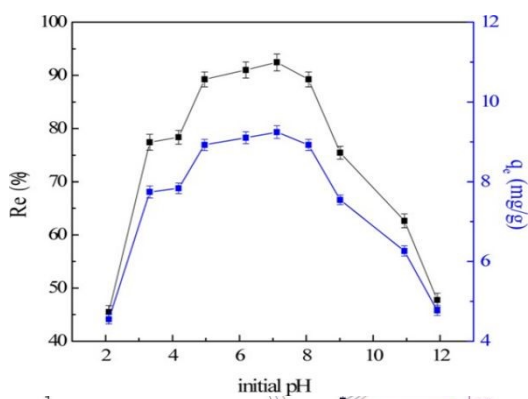
Fig. 12 Effect of initial pH (V = 50 mL, T = 25 ± 1°C, C0= 10 mg/L, Re is removal percentage；qe is equilibrium adsorption capacity).[64] Copyright 2016, John Wiley and Sons.
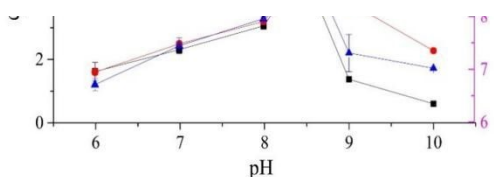

Fig. 10 Effect of initial pH on the F− removal by Ca–Al–CO₃ LDH and its modified products. (Initial F- = 10 mg/L, adsorbent dose = 1 g/L, T = 25 ± 1 °C, q_e is equilibrium adsorption capacity).[75] Copyright 2020, Elsevier.

When pH > pH$_{pzc}$, hydroxylation (deprotonation) occurs on the surface of LDH, so the negative charge density increases, which is not conducive to the adsorption of fluoride ions through electrostatic force; in addition, high concentration of hydroxides in the solution will lead to competition with fluoride ions for adsorption sites, which will subsequently reduce the adsorption of fluoride ions. For example, when the ambient pH was above 9, the adsorption capacity of LDH decreased (Fig. 11). It can be seen from the potential-pH dependence relationship that when the pH was in the range of 2 - 5, the zeta potential of MgAl-MMO was completely positive, but the peracid would cause the layered structure to be destroyed, and the adsorption efficiency would be reduced. In the pH range of 6 to 9, the zeta potential was close to zero, corresponding to higher adsorption efficiency of fluoride ions.[64]

5.2 Temperature

The impact of temperature changes on the fluoride ion removal effect of LDH can be analyzed using the Langmuir and Freundlich isotherm models which can be used to calculate the theoretical maximum fluoride removal capacity of LDH. The adsorption mechanism of fluoride ions on the adsorbent surface can also be further determined. By analyzing the pseudo second-order rate constant of the fluoride ion adsorption reaction of MgAl-MMO at several different temperatures of 30°C, 40°C, 50°C, and 60°C, it was found that the fluoride ion removal rate increased with temperature (Fig. 12).[13] This phenomenon is explained by the increased active sites of the fluoride, which in response increased interaction of the number of active sites present at the surface of the adsorbent.[64] Some research results on carbonate-type LDH show different trends. For example, the equilibrium adsorption capacity of CO₃²⁻ type CaAl-LDH and MMO derivative decreased with temperature, indicating that the adsorption of LDH and MMO is an exothermic process.[75, 112]

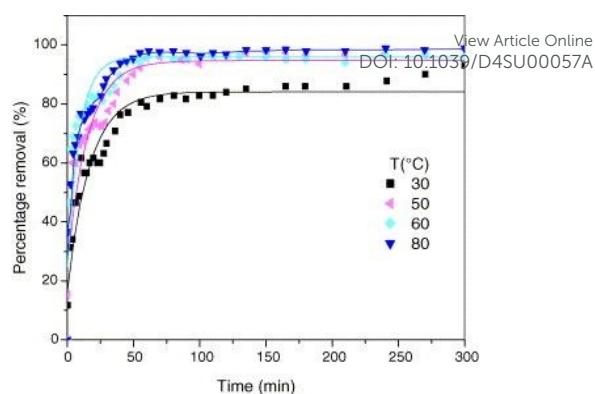Fig. 11 Relationship between the percentage removal of fluoride ions and the time for various temperatures (V = 1.8 L, pH = 6.0, F− = 50 mg/L，adsorbent mass = 2.0 g).[13] Copyright 2006, Elsevier.

5.3 Dosage

The dosage is the key to efficient and economical utilization of LDH. Generally, as the amount of adsorbent increases, the total number of active sites available for adsorption increase, so the fluoride ion removal efficiency also increases. For example, for carbonate-type CaAl-LDH, when the adsorbent dosage increased from 0.1 g/L to 2 g/L, the removal rate significantly increased from 20% to 90%.[112] However, the equilibrium adsorption capacity of LDH decreased (Fig. 13).[64] This can be explained by the fact that the increase of LDH adsorbent can lead to incomplete dispersion of particles in the aqueous solution, resulting in the adsorption sites on the adsorbent not being fully exposed and the adsorption of fluoride ions being limited. When the fluoride ion adsorption capacity generated by adding LDH is greater than the total amount of fluoride ions in the solution, the equilibrium adsorption capacity will continue to decrease. At this time, it is meaningless to continue to increase the dose of adsorbent. Therefore, when selecting the adsorbent dose, a comprehensive evaluation should be carried out based on the final removal target of fluoride ions and the cost of the adsorbent. In practice, a certain dosage before reaching the equilibrium adsorption capacity is usually selected, which can ensure better adsorption efficiency and not excessive adsorbent dosage.
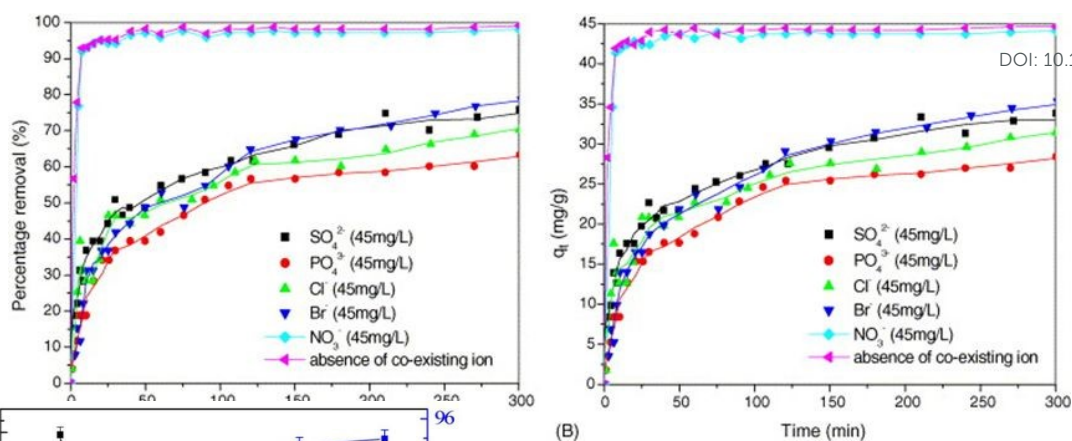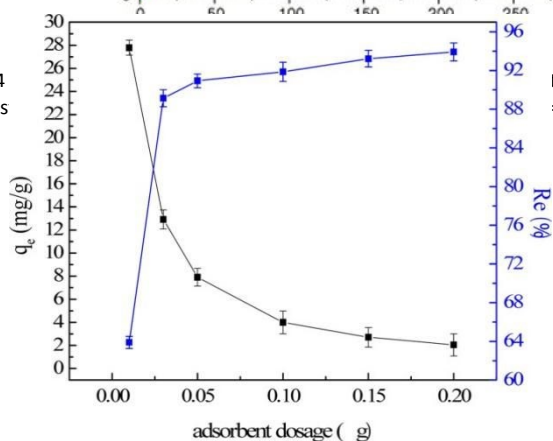
5.4 Coexisting anions

Fig. 14
co-exis   the adsorption time (A), the adsorption loading of fluoride and the time (B), for various
                                                           = 2.0 g).[13] Copyright 2006, Elsevier.

Fig. 13 Effect of adsorbent dosage (V = 50 mL; T = 25 ± 1°C; C_0 = 10 mg/L; q_e is equilibrium adsorption capacity).[64] Copyright 2016, John Wiley and Sons

The influence of other coexisting anions on the removal of fluoride ions is mainly manifested in the competitive adsorption with fluoride ions.[66, 113] By studying the interference effects of sulfate, phosphate, chloride, bromide and nitrate on the adsorption of fluoride ions on MgAl-MMO, it was found that the order of influence of these anions was PO_4^{3-} > Cl^- ≈ SO_4^{2-} > Br^- >> NO_3^- (Fig. 14), mainly because anions with high charge density have a stronger affinity for LDH and are more easily adsorbed; the significant impact of chloride ions may be due to its low molar mass, leading to that its molar concentration is higher than other anions when the concentration being controlled in mg/L.[13] In addition, for carbonate CaAl-LDH without thermal activation, the anions such as Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^- have almost no significant impact on the adsorption of fluoride ions.[75]

5.5 Time

Time-dependent adsorption kinetics can provide information on adsorption rate, adsorption performance, mass transfer mechanism, etc. The adsorption trends of different LDH samples are fast at the beginning and then gradually reach equilibrium, but the specific analysis needs to be fitted with a kinetic model.

At present, many adsorption kinetic models have been proposed.[114-116] Nevertheless, only a few models have been applied in the fluoride adsorption of LDHs. The pseudo-first-order (PFO)[117] and the pseudo-second-order (PSO)[118] kinetic models are the most widely used in the study of LDH adsorption of fluoride ions; in addition, the Elovich model[119] and the intraparticle diffusion (IP) model[120] are also often used. Both the PFO and PSO models are empirical models. People often summarize the adsorption mechanism that conforms to

the PFO model as physical adsorption, and the adsorption mechanism that conforms to the PSO model as chemical adsorption. However, in recent years, some scholars have put forward different views.[114-115] For example, Wang and Guo pointed out that the PFO model is applicable when the initial solute has a high concentration, when there are fewer active sites on the adsorbent, and/or in the initial stage of fluoride ion adsorption; while the PSO model is applicable when the initial solute has a low concentration, when there are abundant active sites on the adsorbent, and/or in the final stage of fluoride ion adsorption.[115] The Elovivh model is an empirical model based on heterogeneous surface adsorption, whose fitting effect on the entire adsorption process is usually good.[115] The most commonly used intra-particle diffusion model is the Weber & Morris (W&M) model, which is mainly based on the assumption that intrapore diffusion is the rate-determining step.[105]

According to our statistics (Table 1), the defluorination of most LDH materials is more in line with the PSO kinetic model, indicating that the rate-limiting step of adsorption is the adsorption of surface-active sites in the final stage of fluoride ion adsorption, which may be due to the replacement of divalent ions by trivalent ions in the brucite structure, resulting in a large number of positively charged active sites on the material surface. In the future, more nonlinear regression models can be tried for the fluoride adsorption kinetics of LDH, and the physical meaning can be further clarified. At the same time, more statistical parameters should be used to evaluate the fitting effect.[115]

5.6 Summary

The environmental factors such as pH value, temperature and dosage have basically the same impact on the fluoride removal performance of LDH and MMO materials. The optimal adsorption pH range is between 5 and 8. Too high or too low pH is not conducive to the adsorption of fluoride ions. This is mainly because such pH range can find the best balance between the structure stabilization of the adsorbent and the competitive adsorption of hydroxide groups. The effect of temperature on LDH and MMO is usually that the adsorption capacity increases as the temperature increases, but different structures may also show abnormal behaviour. The influence of adsorbent dose is that as the adsorbent dose increases, the fluoride ion removal efficiency gradually reaches equilibrium, while the adsorption capacity gradually decreases. Therefore, when selecting the adsorbent dose, the cost of the adsorbent and the fluoride ion removal target must be considered comprehensively by determining a certain value before the equilibrium adsorption capacity. The effects of coexisting anions on LDH-based fluoride removal materials are different. The known research reports show that high-valence anions hinder the fluoride removal performance of MMO more than low-valence anions, but have little effect on some intrinsic LDH. However, this rule is also closely related to the material itself, and more cases may be needed for further verification.
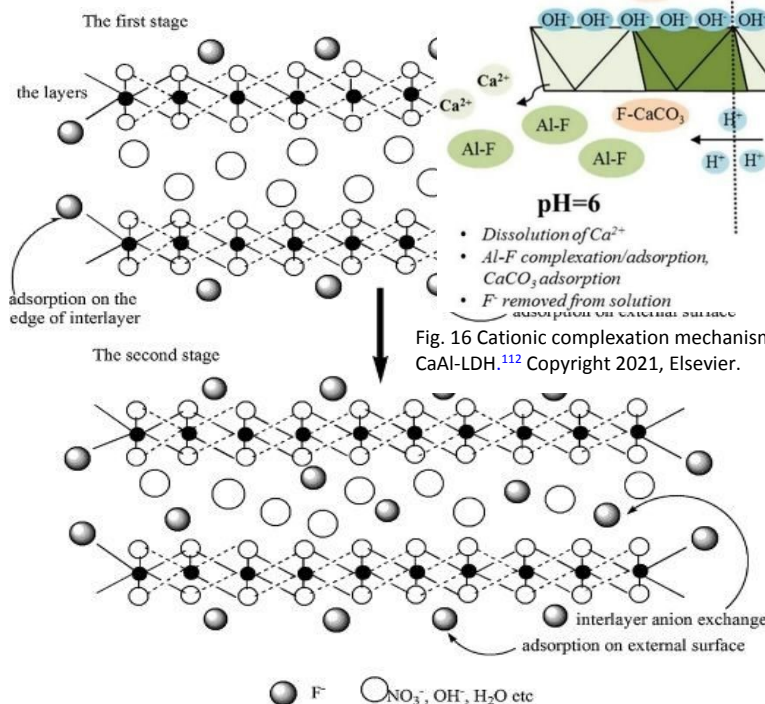
6 Adsorption mechanism

composites (Section 6.2), and finally summarize the adsorption mechanism of MMO (Section 6.3). It is worth noting that the adsorption mechanisms obtained by adsorption kinetics analysis (e.g., physical adsorption, chemical adsorption) are macroscopic, while the adsorption mechanisms discussed here are intuitive and atomic level. At the end of each microscopic mechanism section, its corresponding macroscopic category is also given.

6.1 Intrinsic adsorption mechanism

6.1.1 Anion exchange

When the affinity between existing interlayer anions and LDH layer is lower than that between fluoride ions and LDH layer, such as Cl^- or NO_3^-, fluoride ions can be adsorbed through ion exchange. The fluoride ion removal mechanism of this type for LDH, such as nitrate-based MgCaAl-LDH, is that fluoride ions are first adsorbed on the outer surface and edge of the LDH particles, and then are exchanged with NO_3^-, thereby achieving good fluoride ion adsorption (Fig. 15).[38] NiFe-LDH containing Cl^- anion has the similar fluoride removal mechanism.[20] Due to the strong affinity between CO_3^{2-} and the
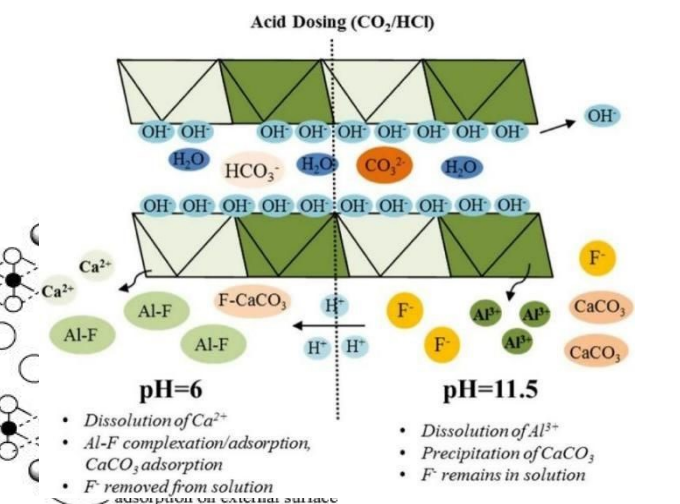

Fig. 16 Cationic complexation mechanism for the removal of fluoride ions by CaAl-LDH.[112] Copyright 2021, Elsevier.

Fig. 15 The anion exchange mechanism for the removal of fluoride ions by $Mg_{2.5}Ca_{0.5}Al-NO_3-LDH$.[38] Copyright 2012, Elsevier.

Understanding the adsorption mechanism is the key for optimization the fluoride ion adsorption performance of LDH and MMO, and the adsorption mechanism can be indirectly evaluated by fitting the fluoride ion adsorption kinetic model.[121, 122] Because LDH and MMO have different structures and surface properties, when classifying and summarizing the adsorption mechanisms, we first summarize the fluoride ion adsorption mechanism of LDH (Section 6.1), and then discuss the adsorption mechanism of LDH-based heterocoagulated

brucite layer, the relevant synthesis or modification should strictly control the environmental atmosphere. Although anion exchange does not change the structure of the brucite layer, it does change the physical phase of LDH including brucite layer and interlayer anions. Therefore, the anion exchange mechanism is essentially chemical adsorption. In kinetic analysis, anion exchange should conform to the intraparticle diffusion (IP) model (corresponding to interlayer diffusion), but actually, it is found that the rate-controlling step is not

IP diffusion but external surface adsorption.[20,38] This contradiction needs to be further clarified.

6.1.2 Cationic complexation

Some metal cations such as Ca, Al, Mg, etc. have a greater affinity to fluoride ions. When LDH contains these metal cations, their complexation with fluoride can be used to remove fluoride ions. For example, MgCaFe-LDH will release part of Ca^{2+} during the fluoride ion adsorption process, which will form fluorite. Therefore, the fluoride ion removal mechanism of this type of LDH can be explained by the adsorption of fluoride ions on the surface of LDH and the reaction with Ca^{2+} released from LDH.[40] By studying the metal ion concentration and fluoride ion concentration in solutions at different pH, it was found that carbonate-type CaAl-LDH also has a similar fluoride removal mechanism. Specifically, Al^{3+} leaching from LDH would occur at an alkaline pH of 11.5. At this point, fluoride ions will not complex with metal ions; but when some acids other than carbonic acid were added to make the solution acidic, fluoride ions would complex with Al^{3+} metal ions to achieve a reduction of fluoride ion concentration. In addition, if CO_2 acidification is used in this process, $CaCO_3$ will be formed, and fluoride ions can be further removed by surface adsorption to this cationic compound (Fig. 16).[112] Cationic complexation is obviously a chemical adsorption, and the PSO model usually has a better fitting effect on kinetic analysis.[40,112] However, the explanation of the adsorption mechanism cannot obtain more contribution from the kinetic results, but is mainly obtained through the characterization of the adsorbent before and after adsorption and leaching tests.[40,112]

6.1.3 Hydroxyl exchange

The hydroxyl groups in LDH are distributed on the outer and interlayer surfaces. The exchange between surface hydroxyl groups and fluoride ions is a common adsorption mechanism observed for LDH. However, the exchange of interlayer hydroxyl groups and fluoride ions has not been clearly experimentally proven. Nuclear magnetic resonance (NMR) technique and DFT calculations have been used to study the affinity of MgAl-LDH adsorption sites with fluoride ions at different positions. The results show that the base and edge binding sites of LDH are potential sites for fluoride ion adsorption, but it is difficult to form suitable adsorption sites between layers due to the steric hindrance, electrostatic repulsion, and hydrogen bonding effect of water molecules.[45] Hydroxyl exchange involves the breaking and reconstruction of chemical

active site adsorption type,[115] but the specific physical image is mainly obtained through experimental detection or DFT simulation.[45]
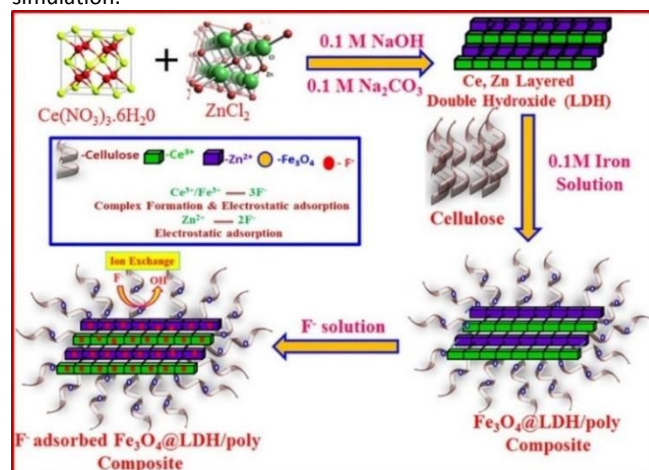

Fig. 17 Heterophase synergistic mechanism for fluoride ion removal by Fe₂O₃@LDH/poly composite.[25] Copyright 2018, Elsevier.

6.1.4 Polar adsorption of brucite layer

Due to the electropositive nature, the LDH layer directly attracts negatively charged fluoride ions through Coulomb attraction. This process is a physical adsorption. This behavior will exist in any brucite layer in LDH. However, this adsorption process is reversible, unstable, and has no selectivity for anions. In the study of LDH fluoride ion removal, replacing divalent metal ions with monovalent metal ions in LDH layer, or increasing the content of trivalent ions in LDH layer, can improve the positive charge density of the LDH layer. In the specific study of fluoride ion removal performance, the fitting of the pseudo first-order kinetic equation may indirectly give some clues regarding mechanism for the fluoride ion removal process of LDH. Such studies can be found in the literature.[23, 34, 87] Polar adsorption of brucite layers is the easiest adsorption mechanism to understand. It is mainly derived from the Coulomb force between the positively charged brucite layer and the negatively charged fluoride ions and belongs to physical adsorption. In kinetic analysis, relevant support can be obtained through an adsorption model with physical significance.[115]
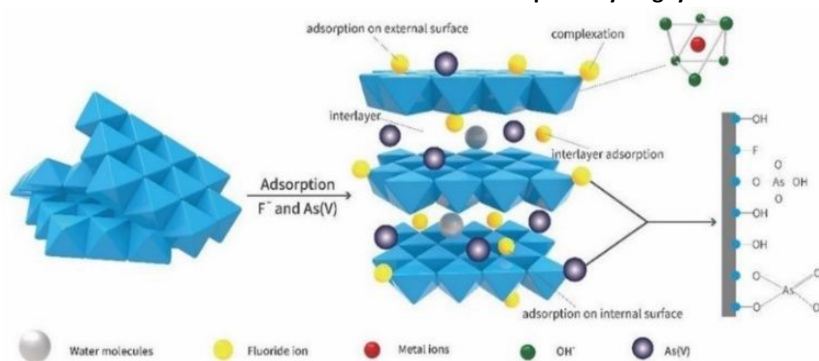
6.2 Heterophase synergy

Fig. 18 MMO hydration mechanism for fluoride ions adsorption by MgFeLa-MMO.[28] Copyright 2018, American Chemical Society.

bonds, and therefore belongs to chemical adsorption. The kinetic model involved in this adsorption mechanism should mainly be
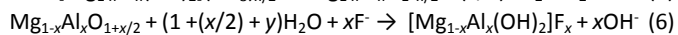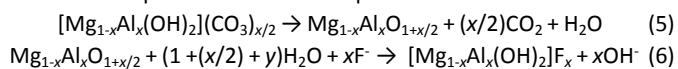
When LDH is compounded with other materials, the fluoride removal mechanism not only involves the intrinsic adsorption mechanism of

LDH, but also the adsorption by the materials compounded with LDH. Therefore, the adsorption mechanism of such materials should be comprehensively considered. For example, the fluoride ion removal mechanism using compounding of cellulose and ZnCe-LDH involves the exchange between fluoride ion and hydroxyl group on the cellulose surface.[25] The fluoride ion removal mechanism is shown in Fig.17. When LDH is compounded with some metal oxides, the compounded metal oxides can provide more active sites for the adsorbent, such as non-thermal plasma (NTP) modified CeO_2/MgFe-LDH, in which CeO_2 was further enhanced by MgFe-LDH's adsorption capacity.[86] The LDH/Al_2O_3 compounding material with hierarchical structure prepared by template directional synthesis had a theoretical maximum capacity of 58.7 mg/g due to the cooperative adsorption of fluoride ions by Al^{3+} in Al_2O_3 and LDH.[57] Heterophase synergy mainly relies on the adsorption of other phases to improve the defluorination performance or other additional properties of LDH. Different added phases bring different defluorination mechanisms. Therefore, in the kinetic analysis, it is necessary to combine the added phase type and select the appropriate kinetic model for specific discussion.

6.3 MMO hydration

During the rehydration process of the MMO material, fluoride ions are inserted into the space between LDH layers as interlayer anions. After thermal activation of MgAl-LDH at 500 ℃, LDH decomposed into a mixed oxide of magnesium and aluminum (MgAl-MMO). The interlayer carbonate was decomposed and released. When MgAl-MMO was rehydrated, fluoride ions enter the layer as compensating anions.[13] The process is shown in Equation 5 and 6.

$$[Mg_{1-x}Al_x(OH)_2](CO_3)_{x/2} \rightarrow Mg_{1-x}Al_xO_{1+x/2} + (x/2)CO_2 + H_2O \quad (5)$$
$$Mg_{1-x}Al_xO_{1+x/2} + (1 + (x/2) + y)H_2O + xF^- \rightarrow [Mg_{1-x}Al_x(OH)_2]F_x + xOH^- \quad (6)$$

In addition to entering the structure as an interlayer anion during hydration, fluoride ions can also replace part of the hydroxyl groups to achieve the restoration of the brucite-like layered structure. For example, when MgFeLa-MMO co-adsorbed arsenate and fluoride, the addition of La increased the affinity of the brucite layer towards fluoride ions. On the one hand, fluoride ions act as interlayer anions to compensate for the charge imbalance of the LDH layer; on the other hand, fluoride ions replaced hydroxyl groups to maintain the structural integrity of the brucite layer. In addition, fluoride ions can also be adsorbed on the outer surface of the material.[28] The overall fluoride ion adsorption mechanism is shown in Fig. 18. MgFe-MMO also exhibits a similar fluoride ion adsorption mechanism.[19] However, it must be pointed out that some current studies suggest that fluoride ions are mainly adsorbed on the outer surface of LDH.[123] The current MMO hydration mechanism involves the entry of fluoride ions into the interlayer and the replacement of fluoride ions for hydroxyl groups,[28] which is a chemical adsorption. The PSO model is usually better for kinetic analysis, but the adsorption mechanism is mainly obtained through characterization of the adsorbent before and after adsorption and DFT simulation,[19, 28] because kinetic analysis cannot provide adsorption details.

6.4 Summary

The fluoride ion removal mechanisms of LDH-based adsorbents can be divided into three major categories: intrinsic adsorption,

heterophase assisted adsorption, and MMO hydration adsorption. The intrinsic adsorption does not significantly change the brucite layer structure. In this case LDH interacts with fluoride ions through direct adsorption of lamellar polarity, interlayer anion replacement, partially dissolved cation complexation, surface hydroxyl exchange. The heterophase assisted adsorption involves the use of the adsorption capacity or dispersion ability of other heterophase. MMO hydration adsorption mainly refers to fluoride ions which are inserted into the interlayer space and replace part of the hydroxyl groups, when MMO is reconstructed to LDH. At present, the adsorption behavior of fluoride ions is mainly studied through kinetic and thermodynamic experiments, assisted by other characterization methods. However, because fluoride ions and hydroxyl groups are similar in nature and ionic radius, most experimental results and characterization methods are difficult to provide direct evidence, especially the interlayer hydroxyl exchange mechanism, requires further investigation. In addition, it should be pointed out that the analysis of adsorption kinetics can only obtain some adsorption mechanism information with macroscopic significance, and its connection with the specific microscopic adsorption mechanism needs to be further strengthened.

7. Conclusion and outlook

This work provides a comprehensive review of the research progress of LDH materials for fluoride ion adsorption in water. The content is arranged according to the logical line of category, synthesis, modification, environmental factors, and adsorption mechanism. Statistical histograms on all LDH studies involved in fluoride removal (that is, including LDH as a component phase and intermediates) are made at the end of each section to show the research hotspot distribution of this field.

Among binary LDHs, LDH composed of aluminum as a trivalent metal is the most studied type of fluoride ion removal LDH with high performance; LDH with Fe as a trivalent metal which can reduce the risk of Al ion dissolution to a certain extent, show good fluoride ion removal performance as well, but the number of studies currently is small; LDH with Cr or rare earth elements as a trivalent metal does not show better performance than other binary LDH, and the cost is higher. Ternary LDH with/whithout RE elements show excellent fluoride ion removal performance and large control space over the synthesis parameters, so LDH with multi-metal components is worthy of in-depth study in the future.

Due to the simplicity of the synthesis method, co-precipitation and urea-assisted methods are currently mainly used for the synthesis of LDH original defluorination agents. In comparison, the LDH obtained by the co-precipitation method, which stabilizes the pH value within a smaller range through constant alkali control, has better performance; while the urea method has unique advantages in preparing some special morphology. Similarly, co-precipitation and urea methods are also the most important synthesis methods of LDH in LDH-based fluoride scavengers (including LDH compounded with other phases, and LDH derivatives), and will continue to attract research attention in the future. Although the hydrothermal method can obtain samples with good performance, more experiments are needed to verify it. In addition, the hydrothermal method has higher

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requirements on equipment than the co-precipitation method, which must be considered in actual production. Microemulsion is an important method for synthesizing monodispersed nanomaterials, but the adsorption capacity of the LDH synthesized in the examples is relatively low, which may be due to the type of material selected. In the future, new LDHs can be synthesized to further verify the effect of this method.

Among the existing modification methods, morphology control is the simplest, but its effect on the fluoride removal is very low; after compounding LDH with other materials, the fluoride ion removal capacity of the material is not high, but the final material may possess new properties not observed for raw LDH；after rare earth element doping of LDH's the fluoride removal performance is significantly improved compared to morphology control approach. Acid etching and anion exchange of LDH are the most effective modification methods, but the number of studies is small and further verification is needed. Thermal activation modification is the most studied method, and the fluoride ion removal effect is relatively good, but the balance between energy cost and performance should be considered in future research.

The optimal adsorption pH range of most LDH-based adsorbents is between 5 and 8. A pH that is too high or too low is not conducive to the adsorption of fluoride ions; as the temperature increases, the adsorption capacity of fluoride ions increases, but some structures may show abnormal behavior. As the adsorbent dose increases, the fluoride ion removal rate gradually reaches equilibrium, while the adsorption capacity gradually decreases. The coexisting high-valent anions improve the fluoride removal effect of MMO more than low-valent anions, but have little effect on some intrinsic LDH. The reasons for these inconsistencies need to be analyzed in conjunction with specific materials in the future.

The existing fluoride removal mechanisms of LDH-based adsorbents include intrinsic adsorption, heterophase assisted adsorption and MMO hydration adsorption. Intrinsic adsorption does not significantly change the structure of the brucite-like layer, mainly through lamellar polarity, interlayer anion exchange, complexation of partially dissolved cation, surface hydroxyl exchange, etc. Heterophase assisted adsorption utilizes the adsorption capacity or dispersion capacity of other phases; MMO hydration adsorption mainly utilizes the memory effect in the recovery process of LDH structure. At present, there are still few detailed studies on each adsorption mechanism, and direct evidence is still lacking.

Therefore, through a summary of previous research, several key points for future research on LDH-based adsorbents are proposed: (1) to synthesize high-efficiency fluoride-removing LDH by optimizing the ratio of multi-metallic components; (2) use hydrothermal or microemulsion method to synthesize different LDH nanomaterials to further verify the effect of these methods; (3) further test the modification effect of acid etching; (4) develop a low-cost modification process and expand the application scope of LDH, such as using multiple modification processes to jointly improve the fluoride removal performance of LDH, and study the possible synergistic effects between different modification methods; (5) conduct targeted analysis on the influence of environmental factors that are inconsistent with the general rules, based on the structure and morphological characteristics of LDH itself; (6) use more new

methods such as in-situ observation and computer simulation[76] to further reveal the microscopic mechanism of LDH defluorination; (7) study the chemical stability of LDH structures during fluoride adsorption to prevent the release of harmful ions into treated waters and wastewaters; (8) in addition, due to the needs of sustainable development of human society, special attention should be paid to the recycling of LDH in future research. Through these efforts, it is expected to develop fluoride ion adsorption materials with low cost, good fluoride removal effect, low secondary pollution, and easy recycling.

Author Contributions

Li Sun writing investigation, formal Analysis, original draft. Jinan Niu conceptualization, supervision, writing – review & editing. Hongpeng Liu investigation, formal Analysis. Fangfang Liu formal Analysis, visualization. Arianit A. Reka writing – review & editing. Jakub Matusik writing – review & editing. Peizhong Feng resources, funding acquisition, project administration.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Data availability

This review is based on the existing research and literature. No primary research results, software or code have been included and no new data were generated or analysed as part of this review.