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Preparation, Characterization, and Fluoride Adsorption Performance of Inorganic Composite Adsorbents

Abstract : Groundwater with too high a fluoride concentration is still a persistent public-health issue, and adsorption is the most popular remediation pathway due to its simplicity and scalability. Single-component adsorbents, however, suffer from low capacity, low pH range, and potential releases of metals, and from interference by other co-existing anions. To overcome such limits, inorganic composite adsorbents, such as combinations of metal oxides, metal hydroxides, layered double hydroxides (LDHs), calcium phosphates, magnetic or granular supports, have been developed. Literature published between 2018 and 2026 is reviewed and it is seen that (i) routine methods of composite preparation such as co-precipitation, hydrothermal and soft-template synthesis, calcination, doping and in-situ coating, are connected to the structure; (ii) characterization tools are linked to structure to function; and (iii) adsorption performance, mechanisms, selectivity, regeneration and real-water validation. Recent reported capacities range from approximately 15 mg F^-/g for LDH functionalized carbon fiber to approximately 204 mg F^-/g for a Mg–Fe–Ce ternary oxide and the addition of rare-earth (La, Ce) and Zr components generally enhances affinity and near-neutral performance. However, performance drops significantly when using real groundwater, phosphate is a constant competitor and there are too few long-term column data. Future work priorities are discussed such as selectivity engineering, shaped media, and standardized reporting and life-cycle assessment.

Keywords : *Fluoride; Adsorption; Composite Adsorbent; Metal Oxide; Layered Double Hydroxide; Hydroxyapatite; Characterization; Water Treatment.*

1. Introduction : Fluoride is the naturally occurring anion found in the groundwater, which is leached out from the minerals that contain it. It is known that at low level

consumption, dental enamel is protected, while high level consumption for an extended period results in dental and skeletal fluorosis (Kumar et al., 2019; Costa et al., 2024). The WHO guideline value for fluoride in drinking water is 1.5mg/L with a note that a lower guideline value for fluoride in drinking water may be appropriate in areas where total fluoride intake is high (World Health Organization [WHO] 2022). In some aquifers of India and China, fluoride concentration is 8–30mg/L (Cai et al., 2018b), which is a priority for community and household supply defluoridation.

Considering the available technologies, adsorption is considered to be an attractive method because of its low cost, simple operation and potentially regenerated (He et al., 2020; Gai & Deng, 2021). A multitude of sorbents have been studied and tested over the years, ranging from minerals to biomass, metal oxides to carbon materials, and the literature has been reviewed several times (Kumar et al., 2019; He et al., 2020; Gai & Deng, 2021; Costa et al., 2024). All the studies suggest composite formation and control of crystalline phase, microstructure and active sites are effective approaches to enhance defluoridation (Gai & Deng, 2021).

The appeal of composites is that they have complementary roles for each of the components. First, the earliest and most widely used fluoride adsorbents are the aluminum oxides and hydroxides, which have a very large surface area; however, aluminum is easily leached in water, especially at low pH (Wei et al., 2022). Rare-earth elements (REE) have a higher affinity with fluoride, however, they are expensive and it is a logical design to combine them with inexpensive metals (Wei et al., 2022; Xie et al., 2024). Layered, phosphate-based and magnetic architectures impart anion-exchange properties, near-neutral operating pH or easy separation (Li et al., 2020; Su et al., 2025; Zhang et al., 2025).

Table 1: Fluoride concentration benchmarks relevant to adsorbent design

Benchmark	Value (mg/L)	Source and comment
WHO guideline value for drinking water	1.5	WHO (2022); a lower local value may be appropriate if intake is high
Typical artificial fluoridation range	0.5–1.0	WHO (2022); lower than the guideline value
Environmentally relevant groundwater range	2–12	Used as the test range for Ca–Al–CO_3 LDH by Wei et al. (2020)
High-fluoride groundwater in some locations	8–30	Reported for parts of India and China (Cai et al., 2018a)

Studies conducted at very high initial fluoride concentrations overestimate practical performance as adsorbents need to reduce the fluoride to a concentration of less than or equal to 1.5 mg/L, which is much less than several to tens of mg/L.

Scope and Approach of This Review : This review is aimed at inorganic composite adsorbents, i.e., substances consisting of at least two different inorganic phases (metal oxides, hydroxides, LDHs, calcium phosphates or inorganic support and inorganic coating) that are blended together to make a fluoride binding solid. When the active fluoride-binding phase is inorganic, then hybrids made up of carbon and polymer parts are included. Studies published between 2018 and 2026 were considered and preference was given to studies providing details on adsorption synthesis and structural characterization and quantitative adsorption data. As the conditions vary greatly from study to study, values are reported and interpreted with caution.

2. Fluoride Removal Technologies and the Case for Composite Adsorbents : The adsorption, membrane filtration, electrocoagulation, photocatalysis, and ion exchange (Arab et al., 2024) are means by which fluoride can be removed. Nanomaterial based sorbents like iron nanoparticles, alumina nanoparticles, and zirconium nanoparticles are often suggested, however frequent

regeneration and replacement of the adsorbents are required in such instances and high fluoride concentrations and competing minerals are the major challenges for groundwater remediation in this context (Arab et al., 2024). The main routes are compared qualitatively in Table 2.

Table 2: Qualitative comparison of major defluoridation technologies

Technology	Advantages	Limitations	Suitability
Coagulation / precipitation	Low chemical cost; simple	Sludge; residual ions; limited polishing	Large plants, high F^- streams
Membrane processes	High rejection	Energy, fouling, concentrate disposal	Centralized supplies
Ion exchange	High efficiency; rapid kinetics	Poor selectivity; regeneration waste	Industrial polishing
Adsorption (single oxide)	Simple, regenerable, low cost	Narrow pH window, modest capacity, leaching	Household / community filters
Adsorption (composite)	Higher capacity, selectivity, stability	Synthesis complexity; rare-earth cost; scale-up data scarce	Community systems; field filters

Composites move the adsorption trade-off towards more uptake per mass with tolerance of near neutral pH and shapeable forms, but come with the cost of synthesis complexity and a lack of long-term field evidence. Arab et al. (2024), Kumar et al. (2019) and Gai and Deng (2021) synthesized the sources.

3. Classification of Inorganic Composite Adsorbents : Inorganic composites can be classified into two groups based on their composition and their architecture. The principal families and representative studies are summarized below in Table 3.

Multimetal (mixed) oxides : The use of Fe in combination with Al, La, Ce or Zr in an oxide makes use of the different roles they play. The optimum composition of La–Fe–Al ternary oxides prepared by inter-doping and calcination was found to achieve the highest fluoride removal rate (up to 99.78%) and density functional calculations indicated the presence of three significant adsorption sites (La, Fe and Al), with the order of adsorption as follows: $La_2O_3 > Al_2O_3 > Fe_2O_3$ (Xie et al., 2024). The same study also summarizes a ternary oxide of Mg–Fe–Ce that has a capacity of 204 mg/g with a wide range of optimal pH (4.0–5.5) and that still functions at pH 7 (Xie et al., 2024). Co-precipitation prepared magnetic Fe_3O_4–ZrO_2 exhibited the highest performance for Fe/Zr = 1:1 (Águila-Martínez et al., 2025) and mesoporous ZrO_2 fibers have been extensively investigated for the mechanism (Yu et al., 2018). In order to improve the fluoride ability of host oxides, rare-earth elements (RE) and Zr are commonly doped in oxides (Cai et al., 2018a).

Layered double hydroxides and LDH hybrids : LDHs are lamellar compounds consisting of metal hydroxide layers that are positively charged and counterbalanced by anions that can be exchanged between the layers. Untreated, calcined or microwave treated Ca–Al–CO_3 LDHs were successfully used to remove fluoride in the synthetic groundwater solutions, with 6.7–8.4 mg/g of fluoride removed at the pH of groundwater solutions (Wei et al., 2020). Doping of La into Li/Al LDH resulted in improved uptake and stability at pH 5–9 (Cai et al., 2018b), and the confinement of La-doped Li/Al LDH in a polystyrene anion-exchange bead resulted in a millimeter-sized composite with a stable performance in the pH range 4–9 (Cai et al., 2018a). Magnetic separation and mesoporous MgAl-LDH layer (Li et al., 2020), Fe_3O_4@mSiO_2@mLDH composites were combined.Fe_3O_4@mSiO_2@mLDH composites were combined with magnetic separation (Li et al., 2020) and mesoporous MgAl-LDH (Zhang et al., 2019).

Calcium phosphate and hydroxyapatite composites : Hydroxyapatite (HAP) is easily

synthesized, low cost, performs best at neutral and near neutral pH level, which most defluoridation materials cannot overcome, and Fluoride is removed by surface adsorption, ion exchange and electrostatic interaction (Rathnayake et al., 2022). Some of the composite strategies used include alum doping (Varma et al., 2024), decoration with carbon nanotubes (Tang et al., 2018), and in situ growth of aluminum-substituted HAP on granular charcoal (Bera et al., 2023). Amorphous calcium phosphate particles (ACP) with surface area of 200-330 m2/g are converted to fluorapatite (FAp) presence of fluoride (Su et al., 2025).

Magnetic and MOF-derived inorganic hybrids, and coated media : A magnetic efficiency of 93% was obtained for the hydrothermally synthesized magnetic Fe_3O_4@La–Zr–MOF composites for both phosphates and fluoride recovery (Zhang et al., 2025). The coating of cheap volcanic rock with Zr (Zr-coated pumice and ZrO_2-coated scoria) has been studied in a fixed-bed column as a way to practical media (Geleta et al., 2021, 2022).

Table 3: Families of recent inorganic composite adsorbents and representative studies

Family	Typical composition	Common preparation	Representative studies
Mixed / ternary oxides	La–Fe–Al; Mg–Fe–Ce; Fe_3O_4–ZrO_2; ZrO_2 fibers	Inter-doping and calcination; co-precipitation	Xie et al. (2024); Águila-Martínez et al. (2025); Yu et al. (2018)
LDHs and LDH hybrids	Ca–Al, La–Li–Al, MgAl on Fe_3O_4@SiO_2, LDH/carbon fiber	Co-precipitation; hydrothermal; soft-template; doping	Wei et al. (2020); Cai et al. (2018a, 2018b); Li et al. (2020); Zhang et al. (2019)
Calcium phosphate / HAP	Al-HAp, alum-HAP, HAP-CNT, Cit-ACP	Co-precipitation; in-situ growth	Varma et al. (2024); Tang et al. (2018); Bera et al. (2023); Su et al. (2025)
Magnetic MOF-derived hybrids	Fe_3O_4@La–Zr–MOFs	Hydrothermal	Zhang et al. (2025)
Coated media	Zr-coated pumice; ZrO_2-coated scoria	Surface coating	Geleta et al. (2021, 2022)

Most recent high performers are either multimetal oxides that maximise the affinity per site, or shaped and magnetic hybrids that maximise handling and recovery. Granulated or coated multimetal oxides have both of these properties. This is a compilation by the author of the cited studies.

4. Preparation Methods : The synthesized route affects the phase composition, crystallinity, surface area, pore structure and surface hydroxyl density, all of which impact fluoride uptake. The method of preparation of composite adsorbents is usually co-precipitation, hydrothermal or impregnation method (Wei et al., 2022). The following Figure 1 summarizes a generic workflow.

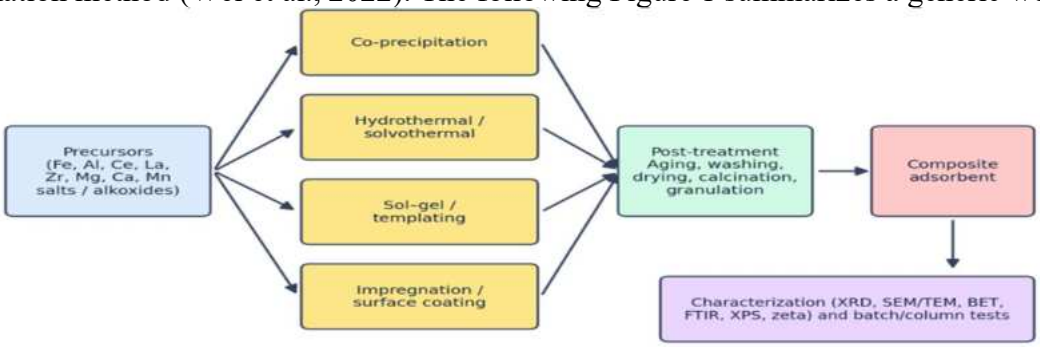


Figure 1: Generalized workflow for preparing and evaluating inorganic composite fluoride

adsorbents. Source: original schematic by the author, adapted conceptually from the preparation approaches described in Gai and Deng (2021), Wei et al. (2022) and He et al. (2020).

Co-precipitation and doping : The most common route is co-precipitation in which the metal salts are hydrolysed using base addition, due to easy equipment and mixing. Ferric magnetic nanoparticles (Fe_3O_4–ZrO_2) were prepared by co-precipitation method and the Fe/Zr molar ratio used as the parameter of interest (Águila-Martínez et al., 2025). Biomimetically prepared Alum doped hydroxyapatite particles were obtained by co-precipitation and these particles were washed and air dried at 650 °C (Varma et al., 2024) and citrate stabilised amorphous calcium phosphate particles were obtained by mixing the calcium chloride solution with sodium citrate and then calcined at various temperatures (Su et al., 2025). La-substituted Li/Al LDH has a larger interlayer distance and more exchangeable sites, which are due to doping (Cai et al., 2018a).

Hydrothermal and soft-template synthesis : The hydrothermal treatment makes it possible to control the architecture and increase the crystallinity. The Fe_3O_4@La–Zr–MOF composite was prepared by hydrothermal process (Zhang et al., 2025). The Fe_3O_4@mSiO_2@mLDH system of core/shell/shell was synthesized using a soft-template hydrothermal method to form a Fe_3O_4 core with a mesoporous SiO_2 shell and then coated with a mesoporous MgAl-LDH shell, resulting in surface areas of 73, 168 and 137 m^2/g for the three composites studied (Li et al., 2020). The bamboo fibers were selected as the source material for obtaining LDH/biomass carbon fiber, which was prepared by the combination of sol–gel, carbonization and hydrothermal processes (Zhang et al., 2019).

Calcination : The process of calcination transforms precursors into oxides (and adjusts crystallinity). Ferric chloride, aluminum sulfate and lanthanum oxide were inter-doped and calcined at 600 °C prior to the synthesis of the ternary oxide, La–Fe–Al (Xie et al., 2024). The calcination temperature is usually higher for increased crystallinity, however it might be lower for decreasing the surface hydroxyl density and thus the temperature must be optimized for each system.

In-situ growth, coating and shaping : Filters made from powder is hard to use in columns, so recent work is done by growing or coating the active phase on a granular support. HAP with Al in the lattice structure was synthesized in situ at room temperature on to commercial granular wood charcoal with size range 0.5–3.0 mm, which were selected for packing in the bed (Bera et al., 2023). Granular media (Geleta et al., 2021, 2022) can be made of inexpensive materials like pumice or scoria coated with zirconium or ZrO_2. When LDH is immobilized in a polystyrene anion-exchange bead, a stable material is obtained which is a few millimeters in size (Cai et al., 2018a). Table 4 shows the methods compared.

It is important to note that the selection of the dopant is important. High-valent metals, such as La, Ce and Zr, can form strong bonds with fluoride, and increase the ratio of reactive M–OH sites, as demonstrated by the increase in hydroxyl fraction and specific La–F interaction observed in the case of La-doped LDH (Cai et al., 2018a). The optimal composition is usually an empirical compromise, such as the La:Fe:Al of 1:2:3 in Xie et al. (2024) or the Fe:Zr ratio of 1:1 in Águila-Martínez et al. (2025), and should be verified with phase and elemental analysis. Residual counter-ions and structural water are also known to be strongly affected by washing and drying.

Table 4: Comparison of preparation methods for inorganic composite adsorbents

Method	Strengths	Weaknesses	Examples

Co-precipitation	Simple, scalable, good mixing	Often amorphous; washing and drying sensitive	Fe_3O_4–ZrO_2; alum-HAP; Cit-ACP
Hydrothermal / soft-template	Crystallinity; architecture control	Energy, autoclaves, batch size	Fe_3O_4@mSiO_2@mLDH; Fe_3O_4@La–Zr–MOFs
Calcination / inter-doping	Oxide formation; synergy between metals	Thermal cost; may lower hydroxyl density	La–Fe–Al oxides
In-situ growth / coating	Granular, column-ready media	Pore blockage; coating durability	Al-HAp on charcoal; Zr-coated pumice
Doping into beads or layers	Selectivity and stability	Multistep; cost of dopant	LaLiAl-LDH@201

None of the routes is better. It is based on the objective (capacity: precipitation/hydrothermal, cautious drying), handling/recovery (coating, beads/ magnetic core) or simplicity of the process.

5. Characterization of Composite Adsorbents : Characterization confirms the mechanism and is a link between the synthesis conditions and the adsorption behaviour. Technique and interpretation of results used in the recent studies are given in Table 5.

Table 5: Characterization techniques and their interpretation in fluoride adsorption studies

Technique	Information obtained	Interpretation relevant to fluoride uptake
XRD	Crystalline phases, interlayer spacing	Expanded interlayer distance after La doping indicates more exchangeable sites (Cai et al., 2018a); post-adsorption phase change evidences fluorapatite formation (Su et al., 2025)
SEM / TEM with EDS	Morphology, element distribution	TEM-EDS confirms La incorporation into LDH (Cai et al., 2018a); FE-SEM-EDS supports HAP and alum-HAP morphology (Varma et al., 2024)
N_2 sorption (BET)	Surface area, pore size	Cit-ACP of 200–330 m^2/g versus 60–160 m^2/g for blank ACP (Su et al., 2025); mesoporous LDH composites of 73–168 m^2/g (Li et al., 2020)
XPS	Oxidation states, bonding	Evidence of La–F interaction and increased M–OH fraction (Cai et al., 2018a); F binding on core–shell ACP (Su et al., 2025)
Zeta potential	Surface charge versus pH	Changes before and after uptake, combined with XRD and XPS, support the Cit-ACP to fluorapatite transformation (Su et al., 2025)
DFT calculation	Adsorption sites and energies	Identifies La, Fe and Al sites and their relative affinity for HF and F^- (Xie et al., 2024)
Magnetic and recovery tests	Separability, reuse	Magnetic recovery efficiency of 93% for Fe_3O_4@La–Zr–MOFs (Zhang et al., 2025)

There should be converging evidence (such as XRD, XPS and zeta potential) for a convincing mechanical claim, as uptake can be due to electrostatic attraction, ligand exchange, anion exchange or precipitation. The data were compiled by the author from the cited studies.

The most informative fresh and spent adsorbent pairs are. XRD, XPS and zeta potential results before and after fluoride removal for Cit-ACP indicated that the core–shell structure led

to the combination of fluoride in solution and calcium in the shell to promote transformation of the core to fluorapatite (Su et al., 2025). The XRD, SEM-EDS, TEM-EDS and XPS measurements have indicated successful incorporation of La ions into the LDH beads, increased interlayer spacing and a particular interaction between La and F for La-doped LDH beads (Cai et al., 2018a). Computational tools are now used in conjunction with experiments: In the case of La–Fe–Al oxides, the contribution of each metal site was rationalized with the help of density functional calculations (Xie et al., 2024).

6. Fluoride Adsorption Performance :

Reported capacities and structure–performance relationships : Capacity values reported must be interpreted with care because they strongly rely on the test conditions (initial concentration, pH, dose, temperature). Despite this, recent studies reported a clear spread with 15.21 mg/g for LDH on biomass carbon fiber (Zhang et al., 2019), 28.51 mg/g for Fe_3O_4@mSiO_2@mLDH (Li et al., 2020), 105 mg/g at 303 K for Al-HAp on granular charcoal (Bera et al., 2023) and 204 mg/g for a ternary oxide of Mg-Fe-Ce as summarized by Xie et al. (2024).

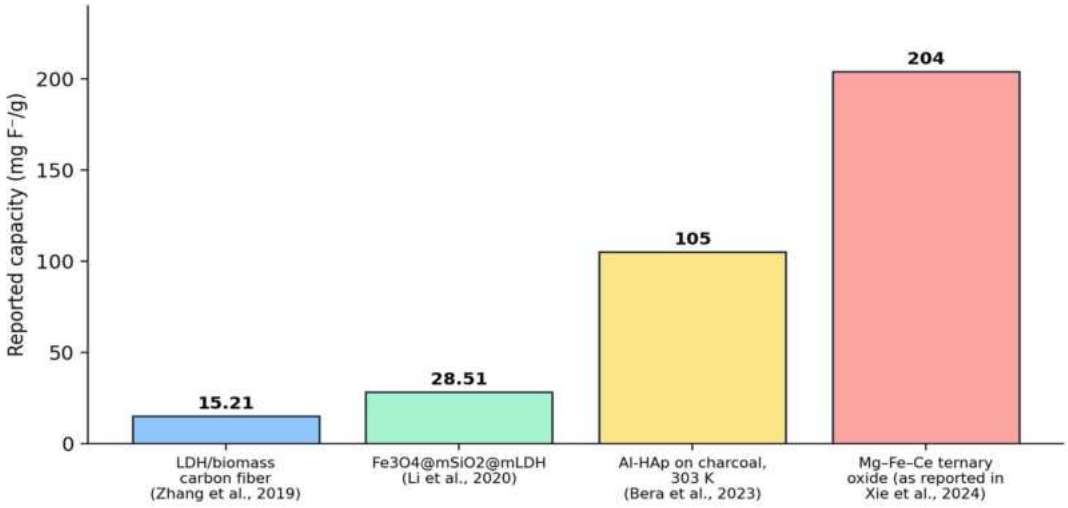


Figure 2: Reported fluoride adsorption capacities of selected recent inorganic composites. Source: data compiled by the author from Zhang et al. (2019), Li et al. (2020), Bera et al. (2023) and Xie et al. (2024); values are as reported under each study's own conditions and are not strictly comparable.

The ordering is in accordance with the hypothesis that the rare-earth-containing multimetal oxides have more reactive sites per mass than LDH or carbon-supported hybrids, whereas the latter have practical advantages like magnetic recovery or granular form. Selected composites and their reported behavior is summarized in table 6.

Table 6: Selected recent inorganic composite adsorbents and reported fluoride adsorption behavior

Adsorbent	Preparation	Reported performance and key findings	Source
La–Fe–Al ternary oxide	Inter-doping; calcination	Removal rate up to 99.78% at optimal ratio; La, Fe, Al adsorption sites by DFT	Xie et al. (2024)
Mg–Fe–Ce ternary oxide (summarized)	Not detailed here	204 mg/g; optimal pH 4.0–5.5; effective at pH 7	Xie et al. (2024)

Fe_3O_4@mSiO_2@mLDH	Soft-template hydrothermal	28.51 mg F^-/g and 57.07 mg PO_4^{3-}/g; Langmuir; magnetic separation; recovery with $NaNO_3$–NaOH	Li et al. (2020)
Fe_3O_4@La–Zr–MOFs	Hydrothermal	93% magnetic recovery; wide pH range; ion exchange, electrostatic, surface complexation	Zhang et al. (2025)
Fe_3O_4–ZrO_2	Co-precipitation	Best at Fe/Zr 1:1; NO_3^-, Cl^-, SO_4^{2-} negligible; HCO_3^-, CO_3^{2-}, PO_4^{3-} reduce removal	Águila-Martínez et al. (2025)
LaLiAl-LDH@201	La doping in LDH inside D201 beads	Stable at pH 4–9; column working capacity about twice that of undoped bead; >98% desorption with NaOH + NaCl	Cai et al. (2018a)
Ca–Al–CO_3 LDH	Untreated, calcined or microwave	6.7–8.4 mg/g at groundwater pH; higher below pH 8	Wei et al. (2020)
Al-HAp on charcoal	In-situ, room temperature	105 mg/g at 303 K; column tests with real groundwater	Bera et al. (2023)
Alum-doped HAP	Biomimetic co-precipitation	Up to 83% versus 74% for HAP at pH 2; pseudo-second-order; Langmuir	Varma et al. (2024)
Cit-ACP	Citrate-stabilized precipitation	200–330 m^2/g; conversion to fluorapatite	Su et al. (2025)
LDH/biomass carbon fiber	Sol–gel, carbonization, hydrothermal	15.21 mg/g; higher than Al_2O_3/carbon fiber	Zhang et al. (2019)

The ability to operate near a neutral pH, be multimetal or rare earth in composition, or be regenerated, are all attributes of high performance. Values are reported and are dependent on experimental conditions.

Adsorption mechanisms : Fluoride uptake by inorganic composites is mainly achieved through electrostatic attraction, ligand (ion) exchange/complexation and hydrogen bonding (Wei et al., 2022), as well as through anion exchange in the case of layered composites and precipitation or conversion to fluorapatite in calcium phosphates (Figure 3). In the case of La-doped LDH beads, the enhanced anion exchange capacity of the embedded LDH and the specific La-F interaction were found to be responsible for the improved uptake, respectively (Cai et al., 2018a). The fluoride and phosphate removal mechanisms of Fe_3O_4@La–Zr–MOFs are ion exchange, electrostatic interaction and surface complexation (Zhang et al., 2025), while the fluoride removal mechanisms of HAP-based materials are surface adsorption, electrostatic interaction and ion exchange (Rathnayake et al., 2022). Optimum ranges are because the contribution of each mechanism changes as pH changes.

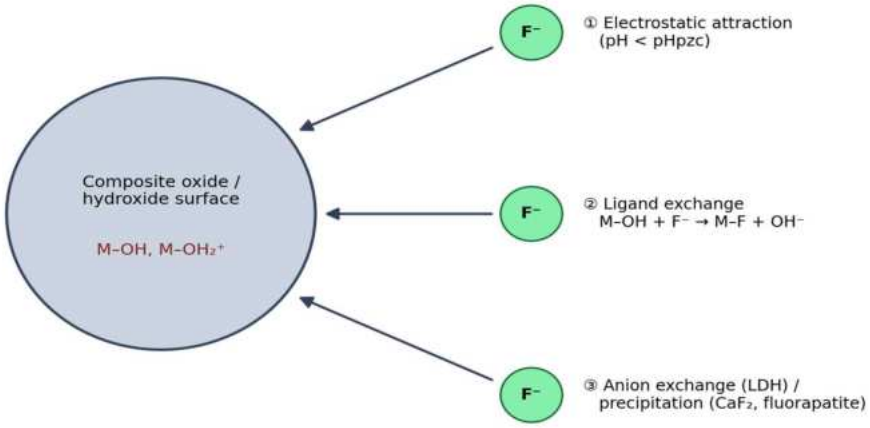


Figure 3: Principal fluoride uptake mechanisms on inorganic composite adsorbents.
Source: original schematic by the author, based on mechanisms described in Wei et al. (2022), Cai et al. (2018a), Su et al. (2025) and Zhang et al. (2025).

Effect of pH and co-existing anions : Surface charge and fluoride speciation are controlled by the solution pH. Aluminum-based phases tend to leach and release fluoride ions under acidic conditions (Wei et al., 2022) and Ca–Al–CO_3 LDH exhibits greater fluoride removal ability below pH 8 (Wei et al., 2020). The pH of the optimum performance of LDH beads is in the range of 4–9 (Cai et al., 2018a), the optimum pH for HAP is neutral and near-neutral (Rathnayake et al., 2022), and the optimum pH of the Mg–Fe–Ce ternary oxide is 4.0–5.5 (Xie et al., 2024). However, Optima differ, as alum doped HAP was able to remove up to 83% in batch tests at pH 2 (Varma et al., 2024). The typical behavior of amphoteric oxide composites is depicted in Figure 4.

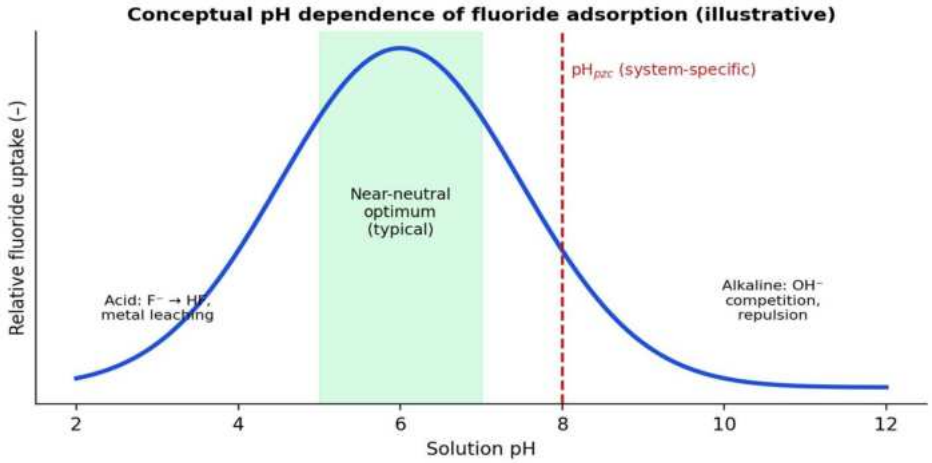


Figure 4: Conceptual pH dependence of fluoride adsorption on amphoteric metal oxide composites.
Source: author's schematic based on trends reported by Cai et al. (2018a), Wei et al. (2022), Rathnayake et al. (2022) and Xie et al. (2024).

When there are multiple anions competing, they vie for sites. The standard magnetic Fe_3O_4–ZrO_2 is pretty much unaffected by nitrate, chloride and sulfate while bicarbonate, carbonate and phosphate decreased removal (Águila-Martínez et al., 2025). Phosphate is a

common competitor as it forms inner sphere complexes with metal hydroxyl groups similar to fluoride, and some designs have been specifically designed to target both ions, like Fe_3O_4@$mSiO_2$@mLDH (Li et al., 2020) and Fe_3O_4@La–Zr–MOFs (Zhang et al., 2025). However, if only fluoride needs to be removed, phosphate selectivity is the most important design issue.

Isotherms, kinetics and thermodynamics : Typically, equilibrium data are used to determine Langmuir models and Freundlich models and kinetics are used to determine pseudo-first-order models and pseudo-second-order models (Figure 5). For Fe_3O_4@$mSiO_2$@mLDH, the adsorption isotherm fitted was Langmuir isotherm and for alum doped HAP, the adsorption isotherm that best described the adsorption was Langmuir isotherm with spontaneous and endothermic adsorption.For Fe_3O_4@$mSiO_2$@mLDH, Langmuir isotherm was the best fit adsorption isotherm and for alum doped HAP, pseudo-second order kinetic and Langmuir isotherm with spontaneous and endothermic adsorption best described the adsorption. Pseudo-second-order fits have come to be interpreted as a sign of chemisorption, which is in agreement with the mechanism of ligand exchange, but a good fit does not constitute proof of a mechanism and should be backed up with spectroscopic evidence. Costa et al. (2024) state that all of these factors (including temperature, particle size, pH, adsorbent mass, and co-existing ions) have to be taken into account when engineering a design.

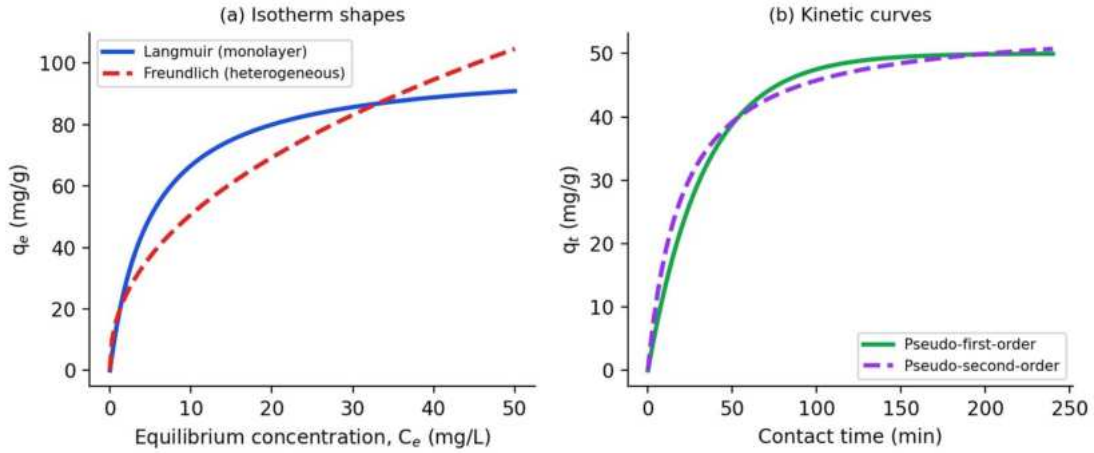


Figure 5: Conceptual shapes of (a) Langmuir and Freundlich isotherms and (b) pseudo-first-order and pseudo-second-order kinetic curves.
Source: generated by the author from standard model equations with arbitrary parameters, for illustration only.

Table 7: Interpretation of common adsorption model outcomes

Model / parameter	Example in recent studies	Interpretation
Langmuir (qmax, KL)	Fe_3O_4@$mSiO_2$@mLDH; alum-HAP (Li et al., 2020; Varma et al., 2024)	Monolayer coverage on similar sites; qmax allows capacity ranking
Freundlich (KF, 1/n)	Commonly paired with Langmuir	Surface heterogeneity; 1/n < 1 suggests favorable adsorption
Pseudo-second-order	Alum-HAP (Varma et al., 2024)	Rate controlled by surface reaction (chemisorption-like)
$\Delta G° < 0$	Alum-HAP (Varma et al., 2024)	Spontaneous uptake

$\Delta H° > 0$	Alum-HAP (Varma et al., 2024)	Endothermic; capacity rises with temperature

Conditions (pH, dose, ionic strength) must be reported with the parameters for the parameters to have meaning and values from different studies cannot be ranked without this context.

Regeneration and reusability : Cost-effectiveness is a requirement for regeneration. The fluoride ions (Cai et al., 2018a) and the phosphate ions (Li et al., 2020) loaded on the composites were recovered with a $NaNO_3$–NaOH solution to allow the composites to be recycled. The problem of separation in powders is solved by magnetic recovery of 93% for Fe_3O_4@La–Zr–MOFs (Zhang et al., 2025). Repeated regeneration, however, may result in a loss of active phase over time, and therefore, over-cycle leaching and capacity should always be provided.

Effect of dose, initial concentration and temperature : The removal efficiency and loading depends on the adsorbent dose and initial concentration. As the dose increases, the percentage removal increases but the capacity per gram decreases once the water is exhausted, therefore there needs to be an optimization of the dose in relation to the remaining target concentration (WHO, 2022): 1.5 mg/L. The higher initial concentrations increase loading until sites are saturated and so the maximum capacities are typically determined at concentrations much higher than those found in groundwater; therefore, the 2–12 mg/L range was tested by Wei et al. (2020). In the case of endothermic uptake (such as alum doped HAP) better performance is obtained at high temperature and this is relevant for hot climates. The designs should be tested with low initial concentrations of the designs, the realistic temperature and the representative ionic strength.

7. Practical Considerations: Real Water, Column Operation, Cost and Sustainability :

From synthetic solutions to real groundwater : Actual water performance can be vastly different than that in synthetic solution. The AACP adsorbent was found to be more effective at removing fluoride in synthetic solution with a 65.4% reduction, compared to 38.6% in groundwater samples from Rio Grande do Sul, Brazil (de Oliveira et al., 2024). In order to make a comparison between adsorbents, it is very important to have both laboratory and real treatments done (Chiavola et al., 2022). The good news is that La-doped LDH beads have been tested with actual fluoride contaminated groundwater in a fixed-bed column; the working capacity of the La doped bead was almost double that of the undoped bead, and Al-HAp on charcoal was tested with actual contaminated groundwater and a pore-diffusion model for breakthrough (Cai et al., 2018a; Bera et al., 2023).

Fixed-bed operation and shaping : Since powders will give high head loss and are difficult to hold, granular media is necessary. Coated volcanic rocks (Geleta et al., 2021, 2022), granular charcoal-supported Al-HAp (Bera et al., 2023) and bead-supported LDH (Cai et al., 2018a) are practical responses. Breakthrough-curve data, throughput in terms of bed volume before the effluent reaches 1.5 mg/L, and the regeneration efficiency with repeated cycles are much less reported and are required for a fair assessment.

Cost and environmental aspects : The Fe-, Al- and Ca-based phases are low-cost materials while the La-, Ce- and Zr-based phases are expensive; hence the low-level doping is an attractive option when it provides a disproportionate gain (Cai et al., 2018a; Wei et al., 2022). The coating of low-cost geomaterials with Zr (Geleta et al., 2021, 2022) and the mixing of La with lower cost metals (Xie et al., 2024) are based on this principle. The eluates produced during alkaline regeneration contain fluoride ions, and leaching of Al ions should be proven to be negligible (Wei et al., 2022). There are very few examples in the fluoride literature that consider life-cycle assessments including the synthesis energy and regeneration waste and the adsorbent lifetime.

8. Critical Discussion, Challenges and Future Perspectives : Several themes emerge. First, while a multimetal composition is known to improve performance, the majority of the data available are from synthetic NaF solutions in batch mode, and the decrease in real water (de Oliveira et al., 2024) highlights the need for more data. Second, there is no consensus on the phosphate selectivity. Thirdly, questions have been raised about the cost and sustainability of the use of rare earths. Fourth, Shaping is key to the transformation of powder to usable filters but mechanical durability and hydraulic data are limited. Last, the inconsistent reporting calls for a meta-analysis of the HAP materials using the partition coefficient instead of the maximum capacity; according to Rathnayake et al. (2022), the latter is too strongly dependent on the initial loading. Table 8 provides an overview of the key challenges.

Table 8: Key challenges and recommended research directions

Challenge	Evidence in literature	Recommended direction
Phosphate and carbonate interference	Reduced removal by HCO_3^-, CO_3^{2-}, PO_4^{3-} (Águila-Martínez et al., 2025)	Design selective sites (La, Zr); test in real water
Lower performance in real water	65.4% versus 38.6% removal (de Oliveira et al., 2024)	Validate with groundwater; compare lab and real conditions (Chiavola et al., 2022)
Metal leaching and stability	Al leaching under acid (Wei et al., 2022)	Report leaching data; Zr or Fe substitution
Shaping and scale-up	Coated media and granular composites (Geleta et al., 2021, 2022; Bera et al., 2023)	Column tests, mechanical strength, hydraulic data
Cost of rare earths	La, Ce and Zr widely used (Xie et al., 2024)	Low-dose doping; life-cycle and cost analysis
Reporting inconsistency	Capacity depends on conditions (Rathnayake et al., 2022)	Standardized protocols; report pH, dose, ionic strength

There are four priorities that may be identified. (1) Selectivity engineering: Systematic comparison of dopants in phosphate- and carbonate-rich solutions, using spectroscopic evidence of site-specific binding. (2) Process relevant testing: column testing with real groundwater, reporting throughput in bed volume, residual metal concentrations and regeneration over many cycles. (3) Low energy precipitation and minimal rare-earth materials usage, plus strong coatings, scalable and greener synthesis. (4) Data transparency: standardizing pH, dose, temperature, and ionic composition and synthesis details, which would enable pooling of results in meta-analysis and machine learning modelling, e.g. as used for La–Fe–Al oxides (Xie et al., 2024). Advances in this direction would transform laboratory evidence to reliable defluoridation systems at the community level.

9. Conclusions : Recently developed inorganic composite adsorbents are a definite improvement over the single oxides. Multimetal oxides based on La, Ce or Zr, LDH-based, calcium phosphate composites and shaped or magnetic hybrids have capacities ranging from approximately 15 to approximately 204 mg/g, a wider pH range and better regenerability. These should be related with adsorption via combined characterization (XRD, XPS, zeta potential and computation) and linked with synthesis route, calcination and doping control surface hydroxyl density, porosity and stability. Mechanisms are either electrostatic attraction or ligand exchange, anion exchange

or conversion to fluorapatite in the case of calcium phosphates. Limitations of phosphate selectivity, real groundwater performance, long-term column data, and leaching control & leaching life cycle assessment exist. The challenge is to fill these gaps: whether laboratory composites can become technologies that can defluoride water at field scale.

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