The Academic
International Journal of Multidisciplinary Research

An Online Peer Reviewed / Refereed Journal
Volume 4 | Issue 10 | October 2026
ISSN: 2583-973X (Online), SJIF IF(2026): 5.6
Website: www.theacademic.in

Synthesis of Iron-Based Inorganic Composites for Defluoridation of Drinking Water

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DOI : https://doi.org/10.5281/zenodo.24461932

ARTICLE DETAILS

Research Paper

Received: 31-10-2026

Accepted: 05-11-2026

Published: 20-11-2026

Keywords:

Fluoride; Defluoridation; Iron Oxide; Composite Adsorbents; Co-Precipitation; Drinking Water; Magnetic Nanoparticles

ABSTRACT

In drinking water, excess fluoride (mainly geogenic) affects an estimated 200 million people all over the world with dental and skeletal fluorosis. Adsorption is generally regarded as the most viable defluoridation technique for decentralised supplies and iron based inorganic materials are considered to be attractive due to their abundance, low cost and versatile nature. This review summarizes the synthesis methods of iron-based composites for fluoride removal, including co-precipitation, the preparation of binary and trimetal oxide composites, the doping method, the preparation method using magnetic core and shell structure, and using granulation for column use. Synthesis variables that are related to surface hydroxyl density and surface charge control the uptake of electrostatic attraction and ligand exchange. It is widely suggested in the literature that a combination of iron with aluminium, cerium or titanium or magnetic cores have superior capacity, selectivity and separability when compared with a single iron oxide and that granulation eliminates the hydraulic restriction of fine powders. The problems that remain are related to pH dependence, interference from coexisting anions, regeneration, secondary contamination and lack of pilot-scale data using actual groundwater. Special emphasis is placed on the interaction

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between precipitation pH, metal ratio, ageing and shaping and how it affects performance and on matching the type of material for the various uses of household, community or centralised use. Comparative tables, schematic figures and interpretations provided, key research gaps identified and future priorities identified for development of scalable, low cost and sustainable materials outlined.

1. Introduction

Safe drinking water is still one of the major public health issues and fluoride is one of the most common geogenic contaminants. It can be incorporated into groundwater primarily by weathering of primary rocks and by dissolution of fluoride-bearing minerals, and groundwater containing high fluoride concentrations usually has low calcium and high bicarbonate concentrations [1]. The occurrence of high fluoride is not a local phenomenon but is revealed by regional survey, as in the case of China where elevated levels of arsenic, fluoride and iodine in groundwater have been compiled [2]. It is estimated that approximately 200 million people worldwide, primarily in 25 countries, are at risk of fluorosis, India and China being the biggest affected countries [1]. The fluoride paradox in health is that low doses of fluoride protects against dental caries, while high doses (chronic) cause dental and skeletal fluorosis [1,3]. Also systematic appraisals emphasize that food and other food supplements also contribute to the total exposure and make it difficult to draw the relationship between fluoride in drinking water and the incidence of fluorosis [3]. Therefore, control of fluoride in the water supply is essential but not always adequate, and must be achieved using methods that are cost-effective in rural/peri-urban communities most impacted.

Several different defluoridation techniques have been evaluated such as coagulation and precipitation, ion exchange, membrane processes, electrochemical treatment and adsorption [4–6]. Of these, adsorption is typically considered to be the most economical and efficient [7] and comprehensive reviews list the adsorbents investigated so far [8,9]. The best results and highest capacities have been obtained for metal oxides and metal hydroxides within the adsorbent families, particularly those in nano-form [7]. Iron-based materials are central elements in this group: the surfaces of iron and aluminium hydroxides, for instance magnetite and gibbsite, are considered to be the most important solid surfaces in water for the adsorption of fluoride [10]. However, single iron oxides usually lack the capacity, selectivity and mechanical properties that are necessary for field use.

2. Fluoride in Drinking Water: Occurrence, Health Effects and Guideline Values

There are some differences in the guideline values for fluoride as this takes in to account the risk of fluorosis and the need to prevent caries. The most common international reference guideline value is 1.5 mg/L recommended by WHO [7,10]. There are also several authorities that use different numbers, and the regulatory values of several of these are summarised in Table 1 and shown on Figure 1, along with indicators of the scale of the health burden.

Table 1: Fluoride guideline values and indicators of population exposure

Parameter / authority	Value	Remark
WHO guideline value	1.5 mg/L	Most widely adopted international reference [7,10]
China, national drinking-water standard	1.0 mg/L	Stricter than the WHO value; relevant to large endemic regions [2]
US EPA, enforceable limit	4.0 mg/L	Upper regulatory limit aimed at preventing skeletal effects
US EPA, non-enforceable limit	2.0 mg/L	Advisory level aimed at preventing dental fluorosis
US HHS, recommended level	0.7 mg/L	Recommended level for caries prevention in community water
Population at risk (global)	≈200 million, ≈25 nations	India and China worst affected [1]

The range of values in the regulations is nearly an order of magnitude (0.7–4.0 mg/L) and this is understood to be due to the different priorities of the regulatory authorities concerned. The implication in practice is that if a material is to be used in defluoridation in more than one regulatory setting, then it is necessary to have it reduce typical groundwater concentrations to 1.5 mg/L or lower, preferably to 1.0 mg/L or below. The population data indicate that a problem exists in the countries with high population density, and in these countries, centralized treatment is often not available, favoring simple low cost adsorption systems.

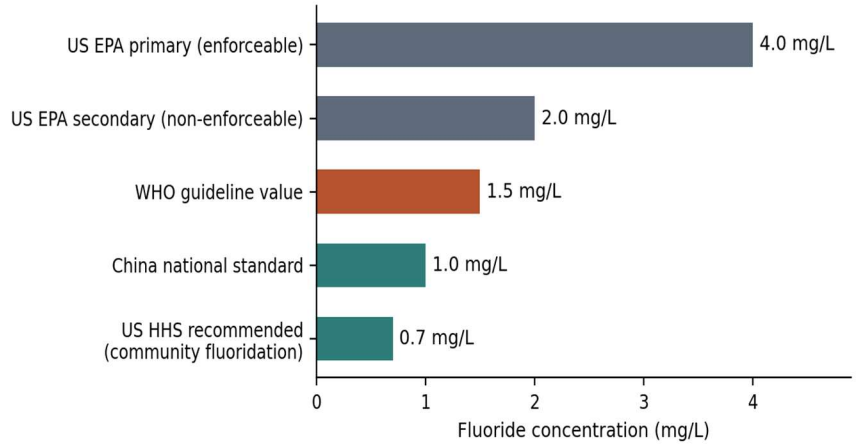

Figure 1: Fluoride concentration limits and recommended levels in drinking water. Values are taken from the regulatory figures listed in Table 1.

In India, dental fluorosis at average fluoride levels of 0.5 ppm, skeletal and crippling skeletal fluorosis at 0.7 and 2.8 ppm respectively have been reported indicating that other factors, such as nutrition, total fluoride intake and local water chemistry, influence individual susceptibility to fluorosis [1]. In addition to the several exposure pathways mentioned by Kabir et al. [3], this further justifies a conservative approach for defluoridation systems, which will have to be able to comfortably reduce the fluoride levels below the guideline value.

3. Defluoridation Technologies and the Case for Adsorption

Although over 35 countries have reported excess fluoride in drinking water, there are few effective and sustainable methods for removing fluoride, especially in the developing world where the challenge is most severe [6]. The most common defluoridation techniques in fluoride endemic areas include coagulation and adsorption/ion-exchange processes, while membrane processes ensure good water quality, but require higher technology and higher costs; electrochemical processes are excellent removers of fluoride, but have high energy requirements. The main approaches are compared in Table 2.

Table 2: Comparison of the main defluoridation technologies

Technology	Principle	Advantages	Limitations
Coagulation / precipitation	Dosing of metal salts or lime to form fluoride-bearing	Widely practised in endemic regions [6]	Sludge generation and dose control; residual metal in treated water

	flocs or precipitates		is a concern
Adsorption / ion exchange	Fluoride binds to surface sites of a solid or is exchanged for another anion	Low cost, simple operation and a wide range of available adsorbents [7]	Often requires pH adjustment; co-existing ions can interfere [7]
Membrane processes	Pressure-driven separation (e.g., nanofiltration, reverse osmosis)	Good product-water quality [6]	"Higher technology and higher cost"; unsuited to many rural settings [6]
Electrochemical methods	Electrocoagulation or electrolytic generation of coagulant in situ	Excellent fluoride removal [6]	Energy-intensive [6]

The comparison gives the reason why the defluoridation by adsorption is preferred for research on community scale as it is simple to operate and cost of capital is low. Its drawbacks (pH sensitivity and co-ion interference) are characteristics of the adsorbent surface and can be mitigated by materials design. This is the main reason of studying the composite iron-based adsorbents by tuning the composition and structure to increase the selectivity and capacity.

In general, there are three steps in the process of fluoride adsorption on a solid: transport of fluoride molecules from the bulk solution to the surface of the solid material at the solution-solid interface in the boundary layer; adsorption of fluoride molecules on the solid material surface; for porous solid, transfer of fluoride molecules to the interior of the particle by intraparticle diffusion [7]. The suitability of practical use, which is determined by the adsorption capacity, fluoride selective, regenerability and cost, while the efficiency of removal always depends on raw water quality (i.e. initial fluoride concentration, pH, temperature, contact time and adsorbent dose) [7]. When iron phases are used together with biopolymers, related reviews are relevant to the use of alternative sorbents like chitosan derivatives and composites [16].

4. Iron-Based Adsorbents: Chemical Rationale and Classification

Surface chemistry is the basis of the iron(III) (hydr)oxides affinity for fluoride. The surface of hydrated iron oxide contains amphoteric hydroxyl groups which are protonated/deprotonated depending on the pH,

resulting in a positive surface charge below the point of zero charge and a negative surface charge above the p.z.c. A small, hard fluoride anion can replace the surface OH groups and bind in the form of inner-sphere Fe–F bonds. A mechanistic study of γ-Fe_2O_3 nanoparticles suggests the removal of fluoride occurs via dehydroxylation, in which hydroxyl groups are replaced by fluoride ions; direct interaction between fluoride and nanoparticles has been confirmed by FTIR [10]. The effects of surface charge and hydroxyl groups in adsorption for Fe–Al–Ce hydrous oxides have been studied explicitly and the adsorption sites have been characterized, as well as the resulting fluorine complex species [17] and [12].

Iron supplementation is not always best. There were some reports that a Fe–Ti bimetallic oxide has Langmuir adsorption capacity of 47.0mg/g, which is very high compared to the Langmuir adsorption capacities of Fe oxide or Ti oxide pure adsorbents reported [7]. Other surveys also suggest that the binary and trimetal oxides/hydroxides are good candidates for fluoride removal [7]. The observations lead to the classification in Figure 2, whereby the iron-based adsorbents are not classified according to their individual composition, but by their structural concept.

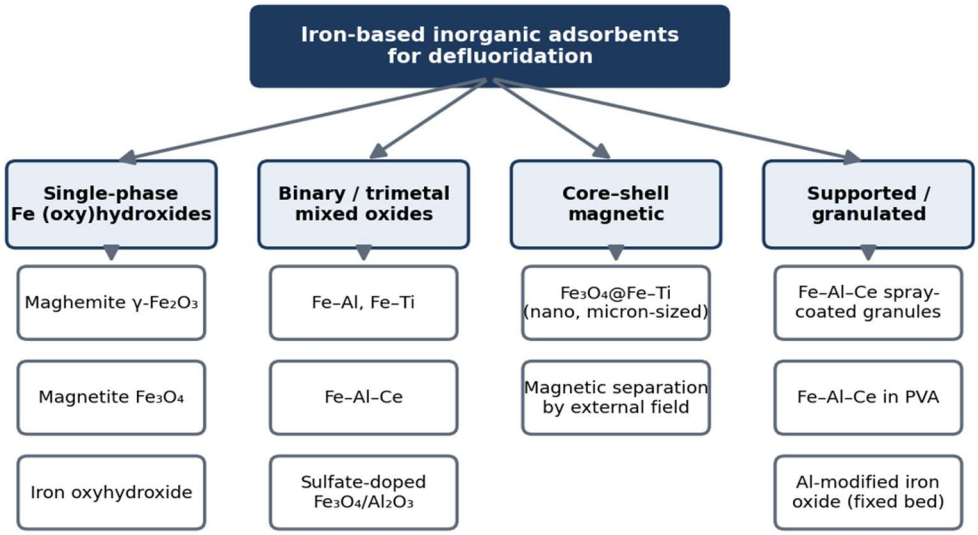

Figure 2: Classification of iron-based inorganic adsorbents for fluoride removal, with representative examples from the cited literature [10,11,13,15,18–20].

There are four families. Single-phase iron (oxy)hydroxides, such as maghemite [10] and iron oxyhydroxide nanoparticles [18], are the simplest to make. The introduction of a second (binary) or third (trimetal) metal to change the surface charge and hydroxyl density and stability, as in Fe–Al–Ce [11] and sulfate-doped Fe_3O_4/Al_2O_3 [19] has also been done. Core–shell magnetic composites are magnetic composites that are

magnetized using an active shell and a magnetic core to allow separation of the components from an external magnetic field [14,15]. Finally, the active powder can be shaped into particles suitable for the fixed-bed operation by supported or granulated composites [13,20].

5. Synthesis Strategies for Iron-Based Inorganic Composites

A generic wet-chemical workflow is outlined in Fig. 3, and is followed in most of the preparations described below. The differences are mainly in the type of co-precursor, the pH, temperature schedule, and the post-synthesis shaping treatment.

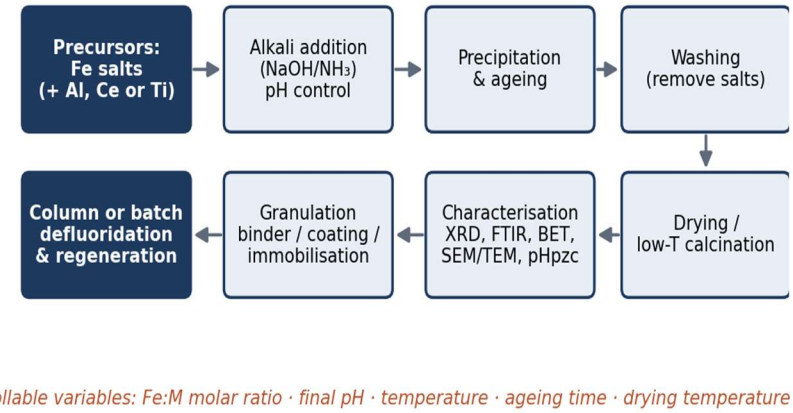

Figure 3: Generalised workflow for the synthesis, characterisation and deployment of iron-based composite adsorbents

5.1 Co-precipitation of iron oxides and oxyhydroxides

Co-precipitation is the most commonly used method as it requires only simple equipment and mild conditions. Magnetic iron oxide nanoparticles are typically prepared by precipitation of ferrous and ferric ions in alkaline medium, subsequent centrifugation, washing with a number of times with deionised water and ambient drying [10]. Particles were prepared as described in this way and found to have a surface area of 16.5 ± 2.5 m^2/g by the Sears' method [10] which showed that they aggregated to 5–20 nm in the atmosphere. There was also a rapid removal of fluoride, with approximately 95 ± 3% being removed in the first 15 min, and uptake was higher at lower pH [10]. The same solution-based methods have been used to prepare iron oxyhydroxide nanoparticles that have also been used to remove fluoride [18].

There are controllable variables in co-precipitation such as the Fe^{2+}/Fe^{3+} ratio, the final pH, temperature, ageing time and the rate of base addition. These are related to crystallinity, particle size and hydroxyl density, and hence capacity. Strategies for subsequent reduction developed in this section, however, to take into account the tendency to aggregation of fine particles (with high external area) that is presented above and that makes solid–liquid separation difficult.

5.2 Binary and trimetal oxides

A simple method of increasing the capacity is to incorporate aluminium, titanium or cerium into the iron oxide framework. The Fe–Al–Ce trimetal oxide reported by Wu et al., was described as a novel adsorbent with strong fluoride removal performance [11] and its adsorption property was explained by the role of the surface charge and surface hydroxyl groups [17] and the identification of the adsorption sites and the complex species of fluorine formed [12]. One typical argument for the use of these materials is that the disparate metals provide the desired properties, namely a stable, easily precipitated framework in the case of iron, hydroxylated sites of high affinity for fluoride in the case of aluminium and cerium. The Langmuir capacity of the Fe–Ti system was measured (47.0 mg/g) higher than that of the pure oxides [7] and the overall conclusion for the review stated that binary and trimetal oxides are particularly interesting [7].

The novel absorbent—sulfate doped Fe3O4/Al2O3 nanoparticles—with fluorides affinity and magnetic separability was developed for the treatment of drinking water [19]. The effect of pH and Fe:Al ratio has also been investigated for the arsenate and fluoride analogues of binary iron–aluminium oxides and compared to aluminium oxyhydroxide and iron oxyhydroxide, respectively, and has been reported as being a critical synthesis parameter [7].

5.3 Magnetic core–shell composites

Nanoparticles have a high surface area, but are hard to hold in a treatment unit. Magnetic nanoparticles are an answer to this problem to a certain extent and the factors that are important for their sustainable use in environmental applications has been reviewed [21]. Zhang et al. developed a magnetic core–shell composite nanoadsorbent for removal of fluoride from drinking water and subsequently developed a micron-sized Fe_3O_4@Fe–Ti composite, with a larger particle size making it easier to handle and separate, and the shell providing fluoride binding sites [14, 15]. The same group [22] reported an increase in capacity by careful control of precipitation conditions without addition of a second metal, a separate high capacity iron oxide adsorbent.

5.4 Granulation, immobilisation and column-ready forms

The use of nanopowders in fixed bed directly has some problems such as high pressure drop and loss of fines. Methods of granulation investigated include spray coating in a fluidised bed [13] and porous polyvinyl alcohol [20] immobilisation.

Fe–Al–Ce Hydroxide Nano-adsorbent. The performance of Al-Fe oxides has also been evaluated with the model solution containing 4 mg/L fluoride in a fixed-bed reactor with actual drinking water at 1 mL/min flow rate for different doses of the adsorbent (2, 4 and 6 g) [7]. Any exposed surface of the material that is exposed will reduce mechanical strength, therefore the choice of binder or support must ensure that no active sites will be lost and no contaminants added.

5.5 Other wet-chemical routes

In addition to direct co-precipitation, iron oxide nanomaterials can be synthesized using sol–gel, hydrothermal/solvothermal process, and plant-extract mediated ("green") reduction/precipitation. These methods are well known for iron oxides in general, but the fluoride specific investigations reviewed here are mostly based on solution preparations by wet chemical methods [10,11,18,19]. Under hydrothermal and solvothermal conditions, increasing temperature and pressure typically promotes crystalline phases with less surface defects, which can enhance the stability and magnetic response, but may reduce the number of reactive hydroxyl groups, which as mentioned above, are involved in the control of fluoride binding. While the precipitation method has been the most popular defluoridation process due to its scalability and low cost, the finer control over the particle size or the use of benign reagents in the sol–gel and green routes has never been compared systemically with the precipitation method for defluoridation. This is one of the places where it would be useful to have some like-for-like studies.

5.6 Influence of synthesis parameters on adsorbent properties

The usefulness of a synthetic method will depend on how the final substance will react to the reaction conditions. The pH of precipitation, metal ratio, product ageing and shaping each impart a distinct characteristic on the product, as illustrated by Table 4 (below). These relationships are assembled in Table 3 and are directional relationships as expected from colloid and surface chemistry and from the studies cited; they can only be considered design hypotheses for each new material and should not be regarded as rules for all materials.

Table 3: Expected influence of synthesis variables on adsorbent properties and fluoride uptake

Synthesis variable	Primary effect on the solid	Consequence for fluoride uptake	Evidence / comment
Precipitation pH	Controls nucleation, phase and surface hydroxylation	Alters surface charge and reactive hydroxyl density	Surface charge and hydroxyl groups govern adsorption [17]
Fe : second-metal ratio	Sets composition and phase mixture	Determines site type and capacity	Ratio examined for Fe–Al binary oxides [7]
Choice of second metal	Changes hardness, charge and stability of surface sites	Higher capacity than single oxides is possible	Fe–Ti capacity exceeded pure oxides [7]; Fe–Al–Ce [11]
Ageing time and temperature	Crystallinity and particle growth	Higher crystallinity may reduce site density	General colloid chemistry; test per system
Washing and drying	Removes residual salts; sets hydration state	Residual ions can block sites; over-drying lowers hydroxyl content	Washing and drying are standard steps [10]
Magnetic core or shell	Adds separability; shell controls surface chemistry	Retains capacity while enabling recovery	[14,15,21]
Granulation binder / support	Mechanical integrity and pore access	Some loss of accessible surface; improved column hydraulics	[13,20]

The highlight in the table is that the capabilities of an element depend on a number of interdependent decisions. The chemistry of the surface is affected by the precipitation pH and composition, and the physical

state of the surface is affected by ageing and drying, while shaping affects mass transfer. Optimisation requires multivariate experimental designs as opposed to one-variable-at-a-time scans because the optimal pH for one composition could be suboptimal for the other.

Table 4: Summary of synthesis routes for iron-based fluoride adsorbents

Route	Typical procedure	Example materials	Strengths	Limitations
Co-precipitation	Mixing Fe^{2+}/Fe^{3+} (± other metal salts) with base; ageing, washing, drying [10]	γ-Fe_2O_3 [10]; iron oxyhydroxide [18]	Simple, scalable, mild conditions	Aggregation; fine powders hard to separate
Mixed-metal co-precipitation	Co-precipitating Fe with Al, Ce or Ti precursors	Fe–Al–Ce [11]; Fe–Ti [7]	Higher capacity than single oxides [7]	Ratio and pH control critical; costly Ce
Doping	Introducing anions or a second oxide into a magnetic phase	Sulfate-doped Fe_3O_4/Al_2O_3 [19]	Combines affinity with magnetic recovery	More complex preparation
Core–shell construction	Forming an active shell on a magnetic core	Fe_3O_4@Fe–Ti [15]; core–shell nano-adsorbent [14]	Magnetic separation; tunable shell	Multi-step; shell stability
Granulation / immobilisation	Spray coating, polymer embedding, binder shaping	Fe–Al–Ce granules [13]; Fe–Al–Ce in PVA [20]	Suitable for fixed-bed columns	Reduced accessible surface; binder effects

The table depicts a progression of synthetic complexity, in parallel, the progression of practicality. Simple co-precipitation provides reactive yet challenging powders, mixed-metal and doped materials increase capacity, magnetic construction allows for recovery, and granulation allows for continuous operation. There is no single path that is best for all, rather the type of filter should be based on the deployment scenario, and powders or magnetic separation is acceptable for batch household units, but not for community filters.

6. Characterisation and Structure–Property Relationships

The adsorption behaviour is correlated with the synthesis conditions via characterization. For the γ-Fe_2O_3 study, the particles were characterised by X-ray diffraction and transmission electron microscopy, direct interaction with the fluoride was demonstrated by the FTIR, and the infrared frequencies and interatomic distances were modelled using density functional theory calculations [10]. For Fe–Al–Ce hydrous oxides, the adsorption sites and the species of fluorine complexes have been characterised, allowing for direct evidence of the binding mode [12]. Table 5 summarises the common techniques used to guide the design of defluoridation adsorbents.

Table 5: Characterisation techniques and their relevance to fluoride adsorbents

Technique	Information obtained	Relevance to defluoridation
X-ray diffraction (XRD)	Crystalline phase and crystallite size	Confirms phase (e.g., maghemite vs. magnetite) and amorphous character, which affects site density [10]
Electron microscopy (SEM/TEM)	Particle size, morphology, aggregation	Reveals aggregation (≈5 nm to 5–20 nm) that reduces effective area [10]
FTIR / Raman spectroscopy	Surface functional groups; changes after fluoride uptake	Evidence of hydroxyl displacement and direct fluoride interaction [10]
N_2 physisorption (BET)	Specific surface area and porosity	Normalises capacity per unit area; e.g., 16.5 ± 2.5 m²/g reported for γ-Fe_2O_3 [10]
Point of zero charge / zeta	Surface charge as a function of	Predicts pH window for electrostatic

potential	pH	attraction [17]
Surface-sensitive spectroscopies	Adsorption sites and fluorine complex species	Identifies binding mode of fluoride [12]

The most informative combination is the surface charge data and the spectroscopic evidence of surface complexes, as these two account for the pH dependence and selectivity of an adsorbent. Surface area alone is an inadequate indicator: a high surface area, but aggregated material or hydroxyl deficient material will not be as effective as a lower surface area material with more hydroxyl groups as is suggested by the Fe–Al–Ce studies [17].

7. Adsorption Mechanisms and Influencing Factors

Typically two mechanisms are proposed. In the pH range below the pH of the point of zero charge, the protonated surface electrostatically attracts fluoride, and then the fluoride displaces OH groups on the surface via ligand exchange, forming inner-sphere complexes [10,17]. This sequence is shown as follows in Figure 4. The proposed dehydroxylation pathway for the process of removal of fluoride from γ-Fe_2O_3 agrees with the spectroscopic detection of fluorine complex species in Fe–Al–Ce hydrous oxides [12].

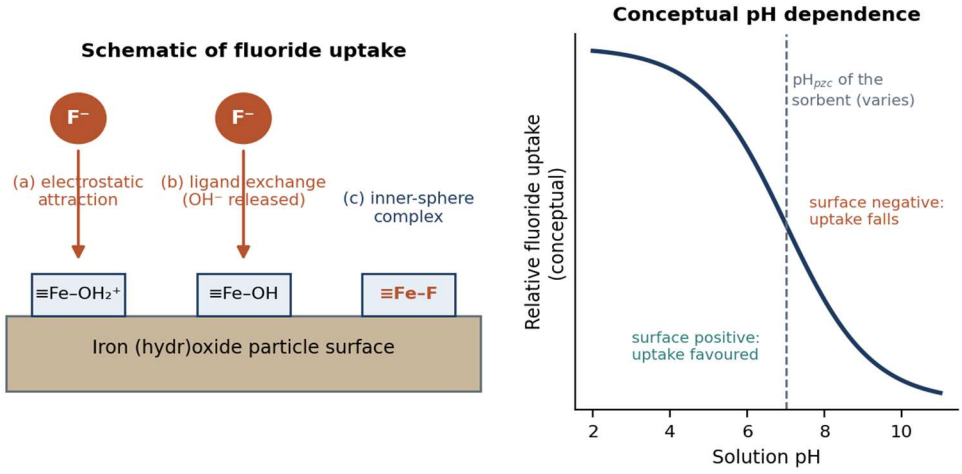

Figure 4: (Left) Schematic of electrostatic attraction and ligand exchange of fluoride on an iron (hydr)oxide surface. (Right) Conceptual trend of fluoride uptake with pH; the curve is illustrative only and not experimental data, and the pH of zero charge differs between materials

Table 6: Key factors affecting fluoride removal by iron-based adsorbents

Factor	Reported or expected effect	Design implication
Solution pH	Uptake was greater at lower pH on γ-Fe_2O_3 [10]; adsorbents often need pH adjustment [7]	Tune pH of zero charge through composition so that neutral pH operation is possible
Contact time	Rapid initial uptake: ≈95 ± 3% within 15 min on γ-Fe_2O_3 [10]	Short empty-bed contact time is feasible for fine materials; granules need longer
Initial concentration and dose	Removal efficiency depends on initial fluoride concentration and adsorbent dose [7]	Report capacity at defined concentration and dose for comparability
Temperature	Listed among the variables controlling efficiency [7]	Test at realistic ambient ranges, not only at 25 °C
Co-existing ions	Co-ions occupy active sites and reduce effective capacity under real conditions [7]	Evaluate in real groundwater, not only in synthetic NaF solutions
Surface charge and hydroxyl content	Control fluoride adsorption on Fe–Al–Ce [17]	Select dopants and precipitation pH that maximise reactive hydroxyl sites

Table 6 indicates that the same factors affecting performance in the lab (pH, dose, co-ions) are the ones that most frequently impact performance in real waters. The lesson for synthesis is that the optimization must be performed under realistic conditions: A material that works well in the test with a single solute may fail in the presence of competing anions; this is of little or no use in practice. These tests should be accompanied by isotherm and kinetic modelling, typically using Langmuir and Freundlich equations, so as to allow results from various laboratories to be correlated.

7.1 Regeneration, reuse and fate of the fluoride-laden waste

If a defluoridation adsorbent can be reused, or if its cost is sufficiently low that it can be disposed of safely after just one use, it will be economical. In other metal-hydroxide systems, the solution pH has been shown to affect desorption, presumably by the competition between the hydroxide ion and the adsorbate for surface sites that reverses the ligand-exchange step [7], and regeneration of the metal-oxide adsorbents is often attempted by increasing the pH. Ligand exchange releases hydroxide when it is adsorbed [10] and adsorption and regeneration are effectively the reverse of one equilibrium; the best adsorbents in terms of capacity may be those that are the most difficult to regenerate. The balance between strong binding and easy removal is seldom measured in the studies referred to and should be specifically addressed in future studies, such as repeated adsorption/desorption cycles, capacity loss and metal dissolution measurements.

7.2 Equilibrium and kinetic modelling

Batch data can be fit to equilibrium and kinetic models to quantify the adsorbents. The most common isotherms used for interpretation of equilibrium data are the Langmuir isotherm and the Freundlich isotherm, and the most common kinetic equations used for interpretation of kinetic data are the pseudo-first order equation and pseudo-second order equation; these have been used in the Fe–Ti case, for which a Langmuir capacity of 47.0 mg/g was reported [7]. Table 8 shows the standard forms and the typical interpretation of their meaning. The interpretation of a model should always be correlated with the spectroscopic data - FTIR and complex-species analysis discussed in Section 6 [10,12] - that is independent from the model.

Table 8: Common adsorption models used to interpret fluoride uptake data

Model	Standard form	Parameters	Typical interpretation
Langmuir isotherm	$q_e = q_m \cdot K_L \cdot C_e / (1 + K_L \cdot C_e)$	q_m: maximum capacity (mg/g); K_L: affinity constant	Monolayer coverage on uniform sites; source of reported capacities such as 47.0 mg/g [7]
Freundlich	$q_e = K_F \cdot C_e$^(1/n)	K_F: capacity factor;	Heterogeneous surfaces, as

isotherm		n: heterogeneity	expected for mixed-metal oxides
Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	k_1: rate constant (1/min)	Diffusion-limited uptake at early times
Pseudo-second-order	$t/q_t = 1/(k_2 q_e^2) + t/q_e$	k_2: rate constant (g/mg·min)	Often associated with surface chemisorption
Intraparticle diffusion	$q_t = k_id \cdot t\text{^}0.5 + C$	k_id: diffusion rate; C: boundary-layer term	Pore diffusion contribution, relevant for granules [7]

The table illustrates the important difference between granulated materials and powders with respect to kinetic analysis. Uptake of nanoparticles is rapid and often occurs in a matter of minutes [10] which indicates that the surface reaction is the dominant process while for granules, there is also the contribution from intraparticle diffusion, consistent with the three-step description of adsorption presented before [7]. Therefore, it is important that these parameters, both isotherm and kinetic, be reported at stated conditions for scale-up to be carried out.

8. Comparative Performance of Representative Materials

The ability of an adsorbent to remove a pollutant varies with initial concentration, pH, dose, and temperature and water matrix [7] and thus direct numerical comparison of adsorbents is hard to perform. Table 7 thus collects representative materials and the results that could be confirmed in the sources cited, without trying to rank them.

Table 7: Representative iron-based adsorbents and verified key findings

Material	Form / route	Key finding reported	Source
γ-Fe_2O_3 nanoparticles	Co-precipitation; ≈5 nm	≈95 ± 3% fluoride removal in first 15 min; higher uptake at	[10]

		lower pH	
Fe–Ti bimetallic oxide	Binary oxide	Langmuir capacity 47.0 mg/g, higher than pure Fe or Ti oxide	[7]
Fe–Al–Ce trimetal oxide	Hydrous trimetal oxide	Novel adsorbent with high removal performance; adsorption sites and fluorine complexes characterised	[11,12]
Sulfate-doped Fe_3O_4/Al_2O_3	Doped magnetic nanoparticles	Fluoride removal from drinking water with magnetic separability	[19]
Fe_3O_4@Fe–Ti	Micron-sized core–shell	Magnetic composite designed for drinking-water fluoride removal	[15]
Al-modified iron oxides	Fixed-bed column	Tested on 4 mg/L fluoride solution and real drinking water at 1 mL/min	[7]
Granulated Fe–Al–Ce	Spray-coated or PVA-immobilised	Granulation routes developed for column use	[13,20]

Three conclusions follow. First, composites typically have better properties than single oxides, the best of which is perhaps the Fe–Ti case [7] that has been studied most thoroughly. Second, the ability to achieve almost complete removal in minutes [10] demands to overcome the separation and shaping problems, and magnetic and granulated designs provide a solution to these challenges [13,15]. Third, evidence is heterogeneous: the evidence comes from a variety of initial concentrations and doses, matrices, and the capacities reported cannot be ranked without standardised testing. Numerical capacities have not been included numerically when it was not possible to trace them back to a verified source.

8.1 Matching materials to deployment scenarios

The two synthesis routes outlined in section 5 and the evidence provided in table 7 can be converted into practical guidance by asking the following question: where will the adsorbent be used? Figure 5 is a

conceptual selection logic, not a validated decision tool, but an interpretive aid that was created from the studies cited. For household or small batch units, magnetic composites [14,15,19] are of interest, since there is no need for a recovery column. Granulated or immobilised materials [13,20] are preferred in community filters as they will not fines loss and can be operated as a fixed bed. The binary oxides Fe–Ti [7] do not require rare earth additions and are the more cost-effective option where cost takes precedence, while the larger plants might be able to afford the trimetal oxides [11] along with a regeneration loop.

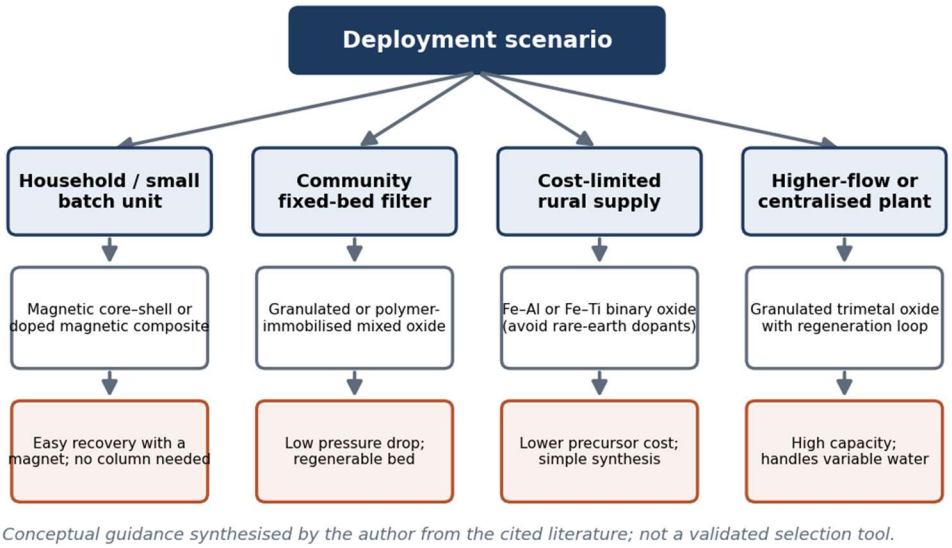

Figure 5: Conceptual guide for matching iron-based composite types to deployment scenarios

Table 8: Strengths and trade-offs of iron-based composite types for field deployment

Composite type	Main strength	Main trade-off	Best-suited use
Single iron (oxy)hydroxide nanoparticles	Simple synthesis; rapid uptake [10]	Aggregation and difficult separation	Laboratory studies; base material for composites
Binary oxide (e.g., Fe–Ti, Fe–Al)	Capacity above that of pure oxides [7]	Needs ratio and pH optimisation	Cost-limited batch or column systems
Trimetal oxide (Fe–Al–Ce)	High-performance trimetal design [11]	Rare-earth content raises cost	Higher-demand or centralised treatment

Magnetic core–shell / doped magnetic	Recovery with an external magnet [15,19]	Multi-step synthesis; shell durability	Household and small batch units
Granulated / immobilised composite	Suited to fixed beds [13,20]	Binder may mask active sites	Community filters and plants

It is obvious from the table that there is no one-size-fits-all best composite. The binding, ease of recovery, hydraulic compatibility and cost forces the design in a variety of ways, and the synthesis path must be selected to balance the most important penalty in the intended application. One important consequence of this is that research reports include information about the intended deployment scenario (what was used to measure the capacity) so that the capacity data can be compared with the appropriate benchmark.

8.2 Cost and sustainability considerations

The advantage of adsorption is that it is economical, however, the cost of the iron-based composite will need to be considered, such as the precursors used, number of synthesis steps, solvent usage, energy consumption, and the number of reusages. While the interest on binary systems is due to the low cost of iron and aluminium salts, the interest on granulation processes is due to granulation processes that allow the use of a small quantity of active nano-adsorbent with an efficient result [13]. Energy intensity also is important: less demanding than hydrothermal treatment or high temperature calcination, but more crystalline products may be more durable in service. The cost per cubic metre of treated water at a given outlet concentration would be a fair comparison, taking into account regeneration and disposal costs, which is normally not reported in the literature on laboratory-scale systems and would be beneficial for decision makers in endemic areas [6].

9. Challenges and Research Gaps

1. pH dependence: Natural waters, which tend to be near neutral, make it difficult to favor adsorption, but materials with a higher Point of Zero Charge (PZC) or less pH-sensitive binding would be required.

2. Competing anions: Effective capacity is affected by co-ions in real treatment conditions [7] and selectivity should be shown in the groundwater matrix.

3. Regeneration and reuse: Although the practical systems demand stability of capacity for repeated cycles, regeneration chemistry and the fate of the concentrated fluoride waste stream do not usually get detailed evaluation. [8]

4. Cost of the dopants and their sustainability: Adding rare-earth elements like cerium to increase capacity is also expensive [11] and needs to be considered in a techno-economic analysis.

5. Secondary contamination and safety: Treatment of water that is designed to dissolve the iron, aluminium or cerium, and to release magnetic nanoparticles or binder components, should be monitored for dissolution of these materials as well as for the release of nanoparticles or binder components, particularly magnetic nanoparticles, which pose questions of sustainable use that have been examined in the environmental literature [21].

6. Scale-up: The majority of studies are still conducted on a batch scale; granulation and column studies are relatively rare [13, 20] and pilot-scale tests on real water are scant.

7. Standardised reporting: There are no common test conditions, making it difficult to compare with the literature [7].

10. Future Perspectives

First, synthesis needs to be oriented towards deployment: magnetic architectures or granulated architectures [13,15] matching household, community or industry architectures for treatment. Secondly, the use of biopolymer matrices like chitosan where the derivatives and composites have been covered as carriers for fluoride removal [16] could give mechanically strong and low cost carriers when used in combination with iron phases. Third, wider recent reviews [8,9] suggest that there is a need for systematic comparison of the composition ratios of the adsorbents; and, statistical experimental design can be used to replace one factor at a time optimisation of Fe:M ratio, pH and ageing. Fourth, life cycle and cost information should be provided with the performance information to enable ranking materials by sustainability as well as capacity. Last, field trials in endemic areas and long term monitoring of metal leaching/regeneration performance are necessary to ensure that the laboratory success is translated to public-health benefits [6].Last but not least is data transparency. If the complete set of experimental conditions (initial concentration, pH, dose, water matrix, regeneration protocol, and temperature) and the synthesis conditions provided in Table 3 were provided together and with the data, then a meta-analysis might be possible and eventually quantitative structure–performance models. Many of the Fe–Al–Ce and magnetic Fe–Ti systems have been used in

various studies and have been seen to be recurring in the literature [11,15] and hence a limited number of well characterised materials as common reference adsorbents could be adopted by the laboratories.

11. Conclusions

Among the most versatile inorganic composites that can be used for the removal of fluoride from drinking water are iron based. Simple co-precipitation delivers reactive iron (oxy)hydroxide; incorporation of aluminium, titanium or cerium enhances capacity and selectivity; magnetic core-shell construction allows for easier recovery; granulation or immobilisation allows powders to be used in fixed-bed. The common theme is the control of surface charge and hydroxyl, controlling electrostatic attraction and ligand exchange. The major challenges to widespread use are pH sensitivity, anion interference, regeneration, and the cost of dopants, and the absence of pilot-scale experience with real waters. The future will be determined by materials which combine scalable synthesis with standardised testing, real water matrices and sustainability evaluation, to bring these materials from the laboratory to communities in need.

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