

Review

Hydroxyapatite–Clay Composites: Mineralogical Control, Environmental Remediation, and Biomedical Applications

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Abstract

Hydroxyapatite (HAp)–clay composites have attracted increasing interest as multifunctional materials for environmental remediation and biomedical applications owing to the complementary physicochemical properties of calcium phosphate and clay minerals. However, the influence of clay mineralogy on composite formation, interfacial interactions, and functional performance remains insufficiently integrated into existing application-oriented reviews. This review critically examines HAp–clay composites from a mineralogical and structure–function perspective, focusing on how clay crystal structure, morphology, layer charge, surface and interlayer chemistry, and chemical modification influence composite formation, reactivity, and functionality. Environmental applications are evaluated for the removal of heavy metals, radionuclides, fluoride, dyes, and pharmaceutical contaminants, with particular attention to adsorption mechanisms, solution chemistry, and limitations in cross-study comparisons. Biomedical applications are discussed in relation to bone tissue engineering, implant coatings, mineralization, and therapeutic delivery. The analysis highlights the distinct roles of expandable layered montmorillonite, tubular halloysite, and fibrous palygorskite in controlling HAp distribution, interfacial organization, and composite architecture. Montmorillonite provides exchangeable interlayer cations and tunable interlayer environments, whereas halloysite offers tubular surfaces and internal lumens for particle organization and functional loading. Both minerals can provide nanoscale confinement through different structural environments. The reviewed evidence indicates that composite performance depends not only on the constituent mineral phases but also on modifying species, preparation routes, and application-specific conditions. Further systematic investigations using well-characterized clay minerals and standardized experimental conditions are required to establish reliable mineralogy–interface–structure–function relationships for the rational design of HAp–clay composites.

Keywords: Hydroxyapatite; Clay minerals; Halloysite; Montmorillonite; Environmental remediation; Bone tissue engineering; Biomineralization; Structure–function relationships

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1. Introduction

Hydroxyapatite (HAp), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is a calcium phosphate mineral widely investigated in environmental and biomedical materials because of its pH-dependent stability, surface reactivity, ion-exchange behavior, biocompatibility, and compositional similarity to the inorganic mineral component of bone. In environmental systems, HAp can immobilize metal ions, radionuclides, fluoride, and other contaminants through mechanisms including ion exchange, surface complexation, electrostatic interactions, and dissolution–precipitation [1]. In biomedical materials, its osteoconductivity and ability to participate in bone-like mineral formation support its use in scaffolds and implant-related composites [2]. However, HAp alone may be limited by particle aggregation, brittleness, limited mechanical integrity, difficult recovery of fine powders from treated water, and restricted control over porosity and interfacial organization.

Clay minerals provide structurally diverse inorganic phases that can complement HAp, but their relevant properties depend strongly on mineral identity. Smectite-group minerals such as montmorillonite possess expandable 2:1 layers, permanent layer charge, and exchangeable interlayer cations; halloysite combines a 1:1 aluminosilicate structure with tubular morphology and chemically differentiated inner and outer surfaces; kaolinite provides a non-expandable 1:1 layered structure; and palygorskite/attapulgite exhibits a fibrous, channel-containing architecture. These mineralogical differences influence layer charge, ion-exchange behavior, interlayer accessibility, particle morphology, and related physicochemical properties [3].

Combining HAp with these clay minerals can therefore generate different interfacial and functional responses rather than a single generic "HAp–clay" effect [4]. Depending on mineralogy, composite architecture, and preparation route, the clay phase may provide charged or exchangeable sites, structural reinforcement, porosity, nanoscale confinement, or surfaces for HAp organization, whereas HAp contributes calcium-phosphate surface chemistry, apatite-forming functionality, and affinity toward selected ionic species. Organic functionalization can alter clay surface and interlayer properties [5], while interactions between HAp surface ions and organic functional groups provide additional routes for tailoring HAp interfaces [6]. The contributions of these modifiers should therefore be distinguished from the intrinsic properties of the constituent mineral phases.

This distinction is particularly important because reported improvements in adsorption, mechanical properties, bioactivity, or cellular response are often described as synergistic even when the individual contributions of HAp, the clay mineral, and modifying species have not been experimentally resolved. Direct mechanistic evidence illustrates this complexity. For example, biomineralization studies using amino-acid-modified SWy-2 montmorillonite showed that HAp formation within the modified interlayer environment was accompanied by changes in montmorillonite basal spacing and in the structure of the resulting apatite [7]. Molecular-dynamics simulations further indicated that HAp–montmorillonite interactions were mediated predominantly by intercalated aminovaleric-acid molecules rather than solely by direct contact between the two inorganic phases [8]. These findings suggest that HAp–clay interactions can depend strongly on interlayer chemistry and modifying species and may involve reciprocal structural changes rather than simple physical mixing.

Direct comparison among published HAp–clay systems is further complicated by differences in clay source and mineral purity, HAp/clay ratio, synthesis route, modification procedure, particle dimensions, solution chemistry, contaminant speciation, competing ions, temperature, adsorbent dosage, material architecture, and testing protocols. Consequently, reported performance should be interpreted within the specific mineralogical and experimental context of each system rather than as an intrinsic property of a broadly defined HAp–clay composite.

A mineralogy-centered analysis is therefore required to connect clay-mineral structure with HAp–clay interfacial organization and resulting material function. This review critically examines HAp–clay composites within a mineralogy–interface–structure–function framework, with particular emphasis on the contrasting roles of expandable montmorillonite, tubular halloysite, non-expandable kaolinite, and fibrous palygorskite/attapulgite. Natural clay-rich materials such as bentonite are considered separately from individual clay minerals because their properties depend on smectite content, accessory phases, and sample-specific mineralogical composition.

Environmental applications are evaluated for the removal of heavy metals, radionuclides, fluoride, dyes, and emerging organic contaminants, with attention to removal mechanisms, solution chemistry, regeneration, and limitations of cross-study comparison. Biomedical applications are assessed in relation to bone-tissue engineering, orthopedic materials, implant coatings, therapeutic functionality, and mineralization. Preparation and characterization approaches are subsequently considered to clarify how synthesis route and processing conditions affect HAp formation and/or distribution, interfacial organization, phase composition, crystallinity, morphology, and porosity. Finally, current limitations and research needs are identified to support the transition from empirical formulation toward mineralogy-informed design of HAp–clay composites for environmental and biomedical applications.

2. Clay Mineralogy and HAp–Clay Interfacial Organization

The formation and interfacial organization of HAp–clay composites depend on the structural characteristics of the constituent clay minerals and the mineralogical composition of natural clay-rich materials. This section examines how layered montmorillonite, kaolin-group minerals (kaolinite and halloysite), and fibrous palygorskite differ in their interactions with HAp, considering mineral-specific surface chemistry, interlayer accessibility, morphology, and modification state. Natural bentonite is discussed separately as a smectite-rich clay material rather than an individual clay mineral. Particular attention is given to distinguishing experimentally demonstrated interfacial interactions from mechanisms inferred from established mineralogical characteristics.

2.1. Bentonite and Montmorillonite

Bentonite is a natural clay-rich material commonly dominated by smectite minerals, particularly montmorillonite, although its mineralogical composition varies among deposits and individual samples. In HAp-containing composites, montmorillonite may influence interfacial organization through its negatively charged layers, exchangeable interlayer cations, and expandable interlayer environment. These features can affect the distribution of calcium-containing species, the accessibility of reactive sites, and the organization of HAp during composite preparation. However, the extent of these effects depends on mineral purity, surface modification, synthesis conditions, and the resulting composite architecture.

Experimental studies have demonstrated the application-specific performance of bentonite- and montmorillonite-based HAp composites. Choudhury et al. [9] reported improved Pb(II) uptake by a glutaraldehyde-crosslinked bentonite–HAp composite compared with its individual components. Hokkanen et al. [10] investigated a HAp–bentonite–nanocellulose composite for the removal of Cd(II), Ni(II), and phosphate, highlighting the involvement of multiple surface functionalities and the influence of solution conditions. Fernando et al. [11] reported that *in situ* synthesis of an HAp–montmorillonite composite increased the montmorillonite basal spacing from 11.38 to 11.61 Å, while the specific surface area increased from 46.4 m² g^{−1} for neat HAp to 78.98 m² g^{−1} for HAp–MMT. These structural and textural differences were accompanied by higher experimental

fluoride uptake for HAp–MMT (14.90 mg g^{-1}) than for neat HAp (7.32 mg g^{-1}), and the in situ synthesized composite also outperformed a physically mixed HAp/MMT system under the investigated conditions. Collectively, these studies indicate that composite performance depends on mineralogical characteristics, additional modifiers, preparation routes, and interfacial organization rather than on the presence of bentonite or montmorillonite alone.

Acid activation, mechanochemical treatment, surfactant functionalization, and modification with metal cations or other inorganic and organic species can alter the surface chemistry, porosity, and ion-exchange behavior of bentonite [12–14]. When such modified materials are incorporated into HAp-containing composites, the resulting interfacial interactions and functional properties may also be affected by the modification procedure and introduced species.

Among the bentonite deposits considered in the reviewed literature, the Tagan deposit in East Kazakhstan provides an example of a natural smectite-rich clay material. Characterization of selected Tagan bentonite samples reported montmorillonite contents of 75.5%–88% and specific surface areas of $94\text{--}104 \text{ m}^2 \text{ g}^{-1}$ [15], whereas another study reported approximately 73 wt.% smectite together with quartz (22.5 wt.%), feldspar (2.3 wt.%), and calcite (1.2 wt.%) in the investigated Taganskoe bentonite [16]. Although these findings indicate a broadly smectite-rich composition, the reported values should not be directly equated because they refer to different samples and mineralogical characterizations. Accordingly, the mineralogical composition and physicochemical characteristics of the specific bentonite sample or batch should be reported when evaluating HAp–clay composite preparation and performance.

Natural Tagan bentonite has been evaluated for Mn(II) and V(IV) sorption [17], while natural and mechanically activated material has been studied for the treatment of multi-component mine wastewater [18]. Modified or mechanically activated Tagan-bentonite-based complex sorbents have also been investigated for chromium-containing and heavy-metal-bearing industrial effluents [19,20]. In another study, Cs(I) and Sr(II) sorption by Taganskoe bentonite was related to characteristics of its smectite fraction, including cation-exchange behavior and layer charge [16].

Although these studies demonstrate the sorption potential of natural and modified Tagan bentonite, they do not provide direct evidence of the interfacial structure or adsorption performance of Tagan-derived HAp composites. Such properties require experimental evaluation of the final HAp-containing material.

Unlike natural bentonite, which contains a variable assemblage of mineral phases, purified or well-characterized montmorillonite provides a more compositionally controlled system for investigating HAp–clay interfacial interactions. Its expandable inter-layer environment can be modified by exchangeable cations, amino acids, polymers, or other introduced species, potentially influencing HAp nucleation, distribution, and interfacial organization. However, the resulting effects must be interpreted in relation to the specific modification and synthesis conditions rather than attributed solely to pristine montmorillonite [7,8,21–23].

Experimental evidence illustrates the importance of this distinction. Studies of amino-acid-modified SWy-2 montmorillonite demonstrated changes in basal spacing and apatite structure during HAp formation, while molecular-dynamics simulations indicated that intercalated organic molecules can mediate important HAp–montmorillonite interactions [7,8]. These findings provide a specific example of modification-dependent interfacial organization, although further experimental studies are needed to establish how such structural changes influence the functional performance of HAp–montmorillonite composites.

2.2. Kaolin Group Minerals

Kaolin-group minerals provide non-expandable 1:1 aluminosilicate structures that differ fundamentally from the expandable 2:1 architecture of smectites. Among the kaolin-group minerals considered in HAp-containing materials, kaolinite and halloysite are particularly relevant, but their different particle morphologies and surface environments can lead to distinct roles in composite formation. Their contributions should therefore be interpreted according to the specific mineral, particle morphology, purity, and preparation conditions rather than generalized to the kaolin group as a whole [23–28].

Kaolinite is a non-expandable 1:1 clay mineral with limited interlayer accessibility under conventional conditions. In HAp-containing systems, its contribution is therefore expected to arise predominantly from external mineral surfaces, particle organization, and its role as a structural or ceramic component rather than from the expandable interlayer processes characteristic of montmorillonite. Kaolinite and kaolinite-rich materials have been incorporated into HAp-based composites investigated for fluoride, dye, pharmaceutical, and heavy-metal removal [23–33]. For example, a HAp/white-clay composite prepared from predominantly kaolinite-containing clay with quartz and illite admixtures exhibited an increase in BET surface area from 18 to 63 m² g^{−1} after HAp incorporation and achieved complete U(VI) removal under the reported kinetic-test conditions, compared with 78% for the parent clay [32]. These results illustrate the functional importance of composite architecture and HAp incorporation, although the individual contributions of kaolinite, accessory minerals, and HAp cannot be fully separated. Accordingly, the reported performance should not be attributed to kaolinite mineralogy alone.

Halloysite also belongs to the kaolin group but commonly occurs with a tubular morphology and an internal lumen, creating interfacial environments that differ from those of platy kaolinite. Its outer and inner surfaces are chemically differentiated, while tube dimensions, lumen accessibility, mineral purity, and surface chemistry can vary among halloysite sources. In HAp-containing composites, this morphology can provide high-aspect-ratio reinforcement, external surfaces for calcium-phosphate association, and a lumen that may be exploited for loading functional or therapeutic species. For example, TEM/EDS characterization of a halloysite-directed calcium-phosphate composite confirmed the association of calcium-phosphate mineral phases with halloysite nanotubes, providing direct evidence of HNT-associated mineralization [34]. Other studies have demonstrated modification of scaffold architecture, mechanical reinforcement, and therapeutic-carrier functionality in halloysite-containing composite systems [35–40]. Nevertheless, the individual contributions of halloysite curvature, lumen chemistry, external surface chemistry, and mineral purity to HAp nucleation and organization remain incompletely resolved.

The contrasting morphologies and surface environments of kaolinite and halloysite demonstrate that kaolin-group minerals should not be regarded as functionally interchangeable HAp supports. Their specific contributions to HAp organization and composite performance should be evaluated through mineralogical and interfacial characterization rather than inferred solely from their shared 1:1 aluminosilicate structure.

2.3. Fibrous Clay Minerals

Fibrous clay minerals provide a mineralogical architecture distinct from both expandable smectites and non-expandable kaolin-group minerals. Palygorskite, also commonly referred to as attapulgite in the applied literature, is characterized by an elongated fibrous morphology and a channel-containing structure that can provide accessible external surfaces and porous pathways. In HAp-containing materials, these characteristics may influence particle organization, HAp distribution, rheological behavior, porosity, and mass transfer; however, the magnitude of these effects depends on mineral source, purity, particle dimensions, composite composition, and processing conditions.

Palygorskite/attapulgite has been incorporated into HAp-containing materials investigated for both environmental and biomedical applications [41–43]. In the HAp-modified attapulgite system investigated for U(VI) removal [41], the fibrous porous mineral phase served as a support for HAp and was associated with reduced HAp agglomeration and improved accessibility of reactive sites. The resulting material exhibited rapid U(VI) uptake involving multiple pathways, including ion exchange, complexation, dissolution–precipitation, and electrostatic interactions. These observations support a structural role of the fibrous clay carrier, although the individual contributions of clay morphology, surface chemistry, and HAp to the overall removal performance cannot be completely separated.

Biomedical studies provide further evidence that fibrous clay architecture can contribute to composite-level properties. For example, nanoattapulgite incorporated into HAp-containing scaffold systems has been associated with changes in rheology, printing behavior, scaffold architecture, mechanical performance, and biological response [42,43]. However, these systems contain multiple functional components, and the observed outcomes cannot be attributed exclusively to attapulgite morphology. Contributions from HAp, polymeric phases, mineral-derived ions, scaffold architecture, and processing conditions must also be considered.

Thus, palygorskite/attapulgite provides a distinct fibrous and channel-containing alternative to layered clay minerals in HAp-containing composites. Its potential contribution lies primarily in its morphology, accessible surfaces, porous architecture, and ability to participate in composite organization. Nevertheless, direct comparisons with smectite- or kaolin-group minerals under matched synthesis and testing conditions remain limited, and the respective contributions of clay morphology, mineral chemistry, ion release, and HAp interfacial interactions require further experimental resolution.

The mineralogy-dependent pathways through which layered montmorillonite, tubular halloysite, and fibrous palygorskite/attapulgite may influence HAp interfacial organization and subsequent environmental or biomedical functionality are summarized schematically in Figure 1. The illustrated relationships are conceptual and system-dependent.

To distinguish measured mineralogical characteristics from general mineral-based interpretations, Table 1 summarizes, where reported in the original studies, clay mineral composition and purity, cation-exchange characteristics, exchangeable-cation information, and modification state, while explicitly identifying parameters that were not reported.

The comparison in Table 1 highlights that clay-mineral selection for HAp-containing composites should be based on specific structural and chemical characteristics rather than broad mineral-group classifications. Smectites provide expandable charged interlayers, kaolin-group minerals offer contrasting layered and tubular architectures, and palygorskite provides a fibrous, channel-containing structure. However, their functional contributions depend on mineral purity, modification state, HAp distribution, preparation conditions, and the target application. Accordingly, mineralogy-dependent effects should be distinguished from those attributable to HAp, modifying species, and processing history, with mechanistic interpretations supported by characterization of the investigated composite.

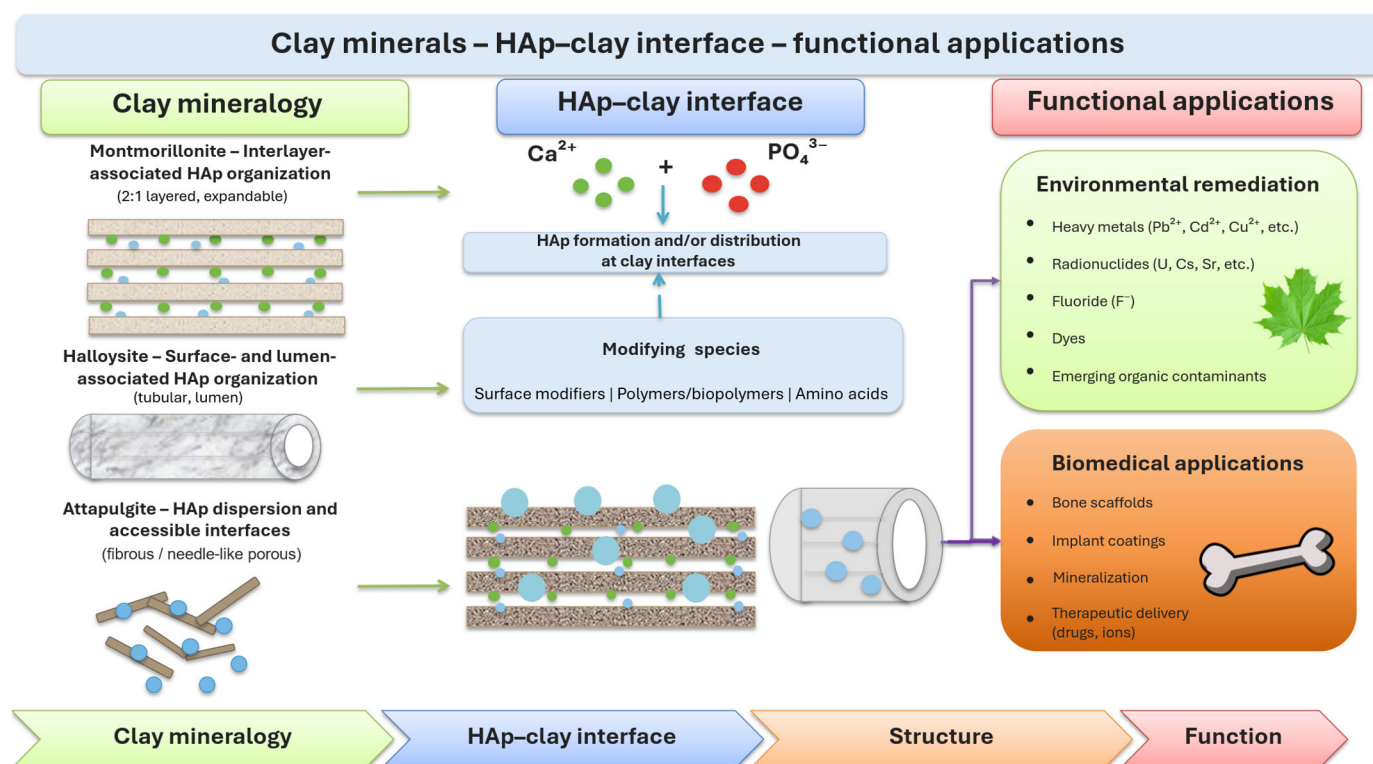


Figure 1. Schematic representation of mineralogy-dependent interfacial organization and structure–function relationships in HAp–clay composites.

Table 1. Mineralogical characteristics of clay minerals and clay-rich materials relevant to HAp–clay composite formation and functionality.

Clay Material/Mineral	Structure and Morphology	Mineral Composition/Purity	CEC/Exchangeable Cations	Modification State	Mineralogical Implication for HAp–Clay Interaction	Evidence Basis/Ref.
Bentonite (natural smectite-rich clay material)	Natural clay-rich material commonly dominated by expandable 2:1 smectite minerals; not a single mineral species.	Variable mineral assemblage. Tagan samples: 75.5%–88% montmorillonite [15]; another Taganskoe sample: ~73 wt.% smectite with quartz, feldspar, and calcite [16].	CEC is largely associated with the smectite fraction in the investigated smectite-rich materials; values depend on sample composition and require measurement.	Natural, mechanically activated, or chemically modified, depending on the investigated material.	The smectite fraction provides charged expandable layers and exchangeable cations that may influence HAp association and organization. Accessory minerals, purity, and processing conditions can modify the resulting interface.	Direct mineralogical characterization of Tagan bentonite [15,16]; implications for HAp-containing composites are inferred and require direct experimental validation.
Montmorillonite (MMT)	Expandable 2:1 phyllosilicate with permanent layer charge,	Purified/reference MMT or MMT-	Exchangeable interlayer cations are intrinsic to MMT; study-	Pristine or modified; reported systems include amino-acid-	Permanent layer charge and exchangeable interlayer cations	Direct evidence of interlayer reorganization and modifier-

	exchangeable interlayer cations, and layered particle morphology.	containing material, depending on the study; quantitative mineral purity frequently NR.	specific CEC and cation composition frequently NR.	modified, surfactant-modified, and organomodified MMT.	enable ion exchange and intercalation. In selected modified-MMT systems, interlayer modifiers mediate Ca^{2+} /phosphate interactions and influence HAp nucleation and organization.	mediated HAp interactions in selected modified-MMT systems; extrapolation to other MMT systems remains inferred [7,8].
Kaolinite/kaolinite-rich clay	Non-expandable 1:1 layered aluminosilicate with limited interlayer accessibility under conventional conditions.	Source-dependent. The white clay investigated by Broda et al. [32] contained predominantly kaolinite with quartz and illite admixtures.	Study-specific CEC and exchangeable-cation composition NR in the HAp/white-clay study.	Unmodified clay precursor in the representative HAp/white-clay system.	The non-expandable structure favors HAp association with accessible external surfaces rather than interlayer incorporation. Accessory minerals and synthesis conditions may influence composite behavior.	Clay mineral composition characterized by XRD; external-surface HAp association is a mineralogy-based interpretation rather than a directly established mechanism [32].
Halloysite (HNT)	1:1 aluminosilicate, commonly exhibiting tubular morphology with an internal lumen and chemically differentiated inner and outer surfaces.	Natural or commercial HNT, depending on the study; quantitative mineral purity frequently NR.	Study-specific CEC and exchangeable-cation composition NR in most reviewed HAp–HNT studies.	Pristine or surface/polymer-functionalized, depending on the composite; HNT may also serve as a therapeutic nanocarrier.	Tubular morphology provides external surfaces and an internal lumen that may contribute to reinforcement, therapeutic loading, and HAp organization. The relative contributions of lumen chemistry, surface properties, and curvature remain system-dependent.	Tubular morphology, scaffold effects, and HNT-associated calcium-phosphate mineralization are experimentally supported in selected systems; specific contributions of lumen chemistry, curvature, and individual surfaces remain partly inferred [34–40].
Palygorskite (attapulgite, ATP)	Fibrous Mg–Al phyllosilicate with elongated particles and a channel-containing structure.	Natural palygorskite or nanoattapulgite, depending on the study;	Study-specific CEC and exchangeable-cation composition generally NR in the reviewed HAp–ATP studies.	Unmodified or incorporated into multicomponent HAp systems; additional	Fibrous morphology and channel-containing architecture may influence HAp distribution,	Effects on scaffold architecture, rheology, and functional performance are experimentally supported

quantitative mineral purity and accessory-mineral content frequently NR.	modification depends on the study.	accessible porosity, rheology, and mass transfer. The individual contributions of clay morphology, mineral chemistry, and HAp remain system-dependent.	in selected systems; the individual contributions of morphology, mineral-derived ions, and HAp interactions remain incompletely resolved [41,43].
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Note: CEC, cation-exchange capacity; NR, not reported in the original study. Bentonite is classified here as a natural clay-rich material rather than an individual clay mineral. Quantitative mineralogical and compositional parameters are reported only when explicitly provided in the cited studies and should not be interpreted as universal values for the corresponding mineral or clay-rich material. Structure–property relationships are considered directly supported when the relevant mineralogical, compositional, or interfacial characteristics were experimentally established in the investigated system. Relationships inferred from established mineralogical characteristics but not directly demonstrated in the corresponding HAp–clay composite are identified as proposed or inferred.

3. Environmental Applications of Hydroxyapatite–Clay Composites

Hydroxyapatite–clay composites have been investigated as multifunctional materials for the removal of inorganic and organic contaminants from aqueous media. Their removal performance depends on the physicochemical properties of HAp and the specific clay mineral or clay-rich material, as well as composite architecture, modification state, target-contaminant chemistry, and solution conditions. Depending on the system, HAp may contribute ion-exchange, surface-complexation, and precipitation-related pathways, whereas clay minerals may provide charged external surfaces, exchangeable cations, accessible interlayer sites in expandable minerals, and structural support. Additional modifying components can introduce further binding sites or alter the accessibility of existing ones. Consequently, contaminant removal may involve several simultaneous processes, including ion exchange, surface complexation, electrostatic interactions, precipitation, hydrogen bonding, and physical adsorption. The relative importance of these mechanisms should be established for each investigated material rather than inferred solely from its nominal HAp–clay composition.

3.1. Heavy Metal Removal

Heavy metals represent an important class of contaminants investigated using hydroxyapatite–clay composites because of their persistence, potential toxicity, and environmental mobility. Depending on the specific contaminant, clay mineralogy, composite composition, and experimental conditions, the combination of HAp with clay minerals may provide complementary removal pathways, including ion exchange, surface complexation, electrostatic interactions, and precipitation of sparingly soluble metal-containing phosphate phases. In multicomponent systems, additional materials such as nanocellulose, activated carbon, biochar, and manganese ferrite may further influence adsorption behavior, structural stability, regeneration, and material handling. However, improvements in removal performance cannot be attributed exclusively to HAp–clay interactions without appropriate comparisons with the individual components. The representative experimental results and material-specific mechanisms reported in the reviewed studies are summarized in Table 2.

Table 2. Comparative performance of hydroxyapatite–clay composites for heavy metal removal.

Heavy Metal	Composite Composition/Modification	Clay Mineral	Maximum Removal Performance	Optimum Conditions	Dominant Removal Mechanism	Key Advantages	Key Studies
Pb(II)	Bentonite–HAp nanocomposite; glutaraldehyde-cross-linked; HAp/clay ratio NR	Bentonite	Langmuir $q_{\max} = 346 \text{ mg g}^{-1}$; Pb removal $\approx 99\%$	pH 7; 30 °C	Langmuir isotherm; pseudo-second-order kinetics; physisorption + chemisorption	High adsorption capacity; RSM optimization; simple synthesis	[9]
Cd(II)	HAp–bentonite–nanocellulose (CHA–BENT–NCC); HAp formed in situ; 3.0 g bentonite + 3.2 g NCC used in synthesis; final HAp/clay ratio NR	Bentonite	$q_{\max} = 10.34 \text{ mmol g}^{-1}$ ($\approx 1162 \text{ mg g}^{-1}$)	Optimized pH, contact time, temperature and initial concentration	Freundlich isotherm	Five regeneration cycles; validated using real mine water	[10]
Ni(II)	HAp–bentonite–nanocellulose (CHA–BENT–NCC); HAp formed in situ; 3.0 g bentonite + 3.2 g NCC used in synthesis; final HAp/clay ratio NR	Bentonite	$q_{\max} = 29.46 \text{ mmol g}^{-1}$ ($\approx 1729 \text{ mg g}^{-1}$)	Optimized pH, contact time, temperature and initial concentration	Freundlich isotherm	Five regeneration cycles; multi-functional composite; real mine water validation	[10]
Pb(II)	Activated-carbon/illitic-clay pellets coated twice with a 2–3 wt.% HAp nanoparticle suspension; final HAp loading NR	Illitic clay	$q_{\max} = 56 \text{ mg g}^{-1}$	pH 6	Langmuir isotherm; pseudo-second-order kinetics	Pelletized adsorbent; reusable; fixed-bed application	[44]
Co(II), Ni(II), Zn(II)	Clay ceramic substrate modified with nano-HAp; HAp content NR	Clay (ceramic substrate)	Maximum reported biosorption amount $\approx 57.21 \text{ mg}$; biosorption efficiency $\approx 72\%$ (biofilm–ceramic reactor system)	pH 5.8; 22 °C	Biofilm-mediated biosorption on nano-HAp-modified ceramic substrate; individual contribution of HAp not isolated	Continuous reactor; inexpensive ceramic support; high mechanical stability	[45]
Cr(VI)	MnFe ₂ O ₄ –HAp/kaolinite/biochar; 0.3 g kaolinite + 0.3 g biochar; HAp and	Kaolinite	Langmuir $q_{\max} = 343.05 \text{ mg g}^{-1}$	pH 3.0; contact time = 60 min; T = 60 °C; adsorbent dose = 0.1 g;	Ion exchange + electrostatic interactions + surface complexation + chemical precipitation	Waste-derived biochar; multi-component adsorbent;	[46]

	MnFe ₂ O ₄ formed in situ; final HAp/clay ratio NR			isotherm C ₀ = 300–1000 mg L ⁻¹		high model-derived Cr(VI) capacity	
Cu(II)	MnFe ₂ O ₄ –HAp/vermiculite/biochar; 0.3 g vermiculite + 0.3 g biochar; HAp and MnFe ₂ O ₄ formed in situ; final HAp/clay ratio NR	Vermiculite	q _{max} = 261.87 mg g ⁻¹	pH 5.0; contact time = 50 min; T = 60 °C; adsorbent dose = 0.1 g; isotherm C ₀ = 300–1000 mg L ⁻¹	General-order kinetics; Redlich–Peterson isotherm	Multifunctional nanocomposite; rapid adsorption; green synthesis	[46]
Ni(II)	MnFe ₂ O ₄ –HAp/vermiculite/biochar; 0.3 g vermiculite + 0.3 g biochar; HAp and MnFe ₂ O ₄ formed in situ; final HAp/clay ratio NR	Vermiculite	q _{max} = 230.34 mg g ⁻¹	pH 7.0; contact time = 30 min; T = 50 °C; adsorbent dose = 0.1 g; isotherm C ₀ = 300–1000 mg L ⁻¹	General-order kinetics; Redlich–Peterson isotherm	Multifunctional nanocomposite; rapid adsorption; green synthesis	[46]

Approximate values in mg g⁻¹ were calculated by the authors of this review from the original adsorption capacities reported in mmol g⁻¹ to facilitate comparison among studies.

Pb(II) is a frequently investigated target ion in HAp–clay systems, reflecting both its environmental relevance and the strong affinity of Pb species for phosphate-bearing sorbents. For example, the glutaraldehyde-crosslinked bentonite–HAp nanocomposite reported by Choudhury et al. [9] exhibited a Langmuir-derived maximum adsorption capacity (q_{max}) of 346 mg g⁻¹ at 30 °C. This value represents the model-derived capacity for Pb(II) under the conditions of that particular study and should not be interpreted as the highest adsorption capacity among all HAp–clay composites reviewed here. Direct ranking against capacities reported for Cd(II), Ni(II), or other target ions is not appropriate because the studies differ substantially in composite composition, initial concentration, pH, adsorbent dosage, temperature, contact time, and adsorption models. Accordingly, the values summarized in Table 2 are best interpreted within each contaminant–material system rather than as a universal ranking of sorption performance.

The incorporation of nanocellulose into hydroxyapatite–bentonite composites enabled efficient simultaneous removal of Cd(II), Ni(II), and phosphate while maintaining adsorption performance over repeated adsorption–desorption cycles and demonstrating successful application to real mine wastewater. These findings indicate a transition from simple laboratory adsorbents toward multifunctional composite materials with enhanced operational stability.

More recent developments have emphasized engineering design and sustainability. Pelletized activated carbon–clay composites coated with hydroxyapatite improved mechanical handling, regeneration capability, and suitability for fixed-bed adsorption systems while maintaining high Pb(II) adsorption capacity. Similarly, hydroxyapatite-modified ceramic biofilm reactors extended the application of clay-based composites from conventional batch adsorption to continuous industrial wastewater treatment, illustrating the increasing importance of reactor-scale design and process integration.

The latest generation of hydroxyapatite–clay composites combines natural clay minerals with waste-derived biochar and magnetic phases to produce multifunctional green nanocomposites. Manganese ferrite-doped hydroxyapatite/kaolinite/biochar and hydroxyapatite/vermiculite/biochar composites exhibited exceptionally high adsorption capacities toward Cr(VI), Cu(II), and Ni(II), reaching 343.05 mg g^{−1} for Cr(VI). The reported adsorption behavior may reflect the combined contributions of biochar surface functional groups, HAp-associated phosphate chemistry, clay mineral adsorption sites, and manganese ferrite components. However, the relative importance of these contributions requires component-specific experimental verification.

High adsorption capacities were reported for both the BT–HAp nanocomposite and MnFe₂O₄–HAp/biochar–clay systems, although their performance arises from fundamentally different material architectures and removal mechanisms. The former combines bentonite and hydroxyapatite within a cross-linked composite architecture, whereas the latter incorporates additional functional phases, including biochar and manganese ferrite. Their reported adsorption performance should therefore be interpreted in relation to the specific composite composition, contaminant chemistry, and experimental conditions rather than attributed to a universally established synergistic mechanism.

Beyond the comparison of adsorption capacities presented in Table 2, recent studies reveal a clear evolution in the design philosophy of hydroxyapatite–clay composites. Early investigations primarily focused on maximizing adsorption efficiency through binary hydroxyapatite–clay systems, whereas subsequent developments introduced additional functional components to improve regeneration, mechanical stability, and process applicability. As summarized in Table 3, these advances reflect a progressive transition from laboratory-scale adsorbents toward multifunctional and application-oriented composite materials.

Table 3. Representative design strategies of HAp–clay composite systems for heavy-metal removal.

Design Strategy	Composite Design	Primary Design Objective	Representative Study
Binary HAp–clay composites	HAp + Bentonite	High adsorption capacity	[9]
Biopolymer-reinforced HAp–clay composites	HAp + Bentonite + Nanocellulose	Regeneration and real wastewater	[10]
Engineered/pelletized HAp-based adsorbents	Pelletized ACC-HAp	Mechanical stability and handling	[44]
Reactor-integrated HAp–clay systems	Biofilm ceramic reactor	Continuous treatment	[45]
Multifunctional hybrid nanocomposites	Biochar + Clay + MnFe ₂ O ₄ + HAp	Multifunctionality and green synthesis	[46]

As summarized in Table 3, HAp–clay composites for heavy-metal removal can be grouped according to distinct material-design strategies rather than a strict chronological sequence. These strategies range from relatively simple HAp–clay combinations to biopolymer-reinforced, engineered, reactor-integrated, and multifunctional hybrid systems incorporating activated carbon, biochar, or magnetic components. Importantly, the increasing architectural complexity is not necessarily associated with higher adsorption capacity alone; instead, different design strategies address additional requirements such as structural stability, regeneration, material recovery, process integration, and applicability under practical treatment conditions. This comparison therefore highlights a shift in design priorities from adsorption performance as an isolated metric toward the broader engineering functionality of HAp–clay composite systems.

3.2. Radionuclide Removal

Radionuclide contamination of aquatic environments presents significant environmental challenges because radionuclide mobility and potential risks depend on chemical speciation, environmental conditions, and exposure pathways. Although clay minerals have been investigated for the immobilization of Cs(I) and Sr(II), the HAp–clay composite studies examined in this review provide more extensive quantitative information for U(VI). Accordingly, the present section focuses primarily on U(VI) removal. Uranium(VI) speciation and mobility are strongly influenced by pH, carbonate and phosphate concentrations, and other solution components. Depending on the composite composition and experimental conditions, U(VI) immobilization may involve ion exchange, surface complexation, electrostatic interactions, and precipitation of sparingly soluble uranium-containing phosphate phases.

Recent studies have progressively moved from relatively simple HAp–clay systems toward structurally and chemically tailored composites based on bentonite, montmorillonite, attapulgite, and kaolinite-rich clays. Surface functionalization with cationic surfactants, control of clay morphology and interlayer accessibility, and suppression of HAp particle agglomeration have been employed to enhance uranium uptake. However, direct comparison of reported adsorption capacities requires caution because U(VI) speciation and removal efficiency are strongly influenced by pH, temperature, carbonate and phosphate concentrations, competing ions, and the adsorption model used to derive the reported capacity. The principal quantitative results and mechanistic characteristics of representative HAp–clay systems are summarized in Table 4.

Table 4. Comparative performance of hydroxyapatite–clay composites for U(VI) removal.

Radio-nuclide	Hydroxyapatite–Clay Composite	Clay Mineral	Functional Modification/Synthesis	Adsorption Performance	Experimental Conditions	Adsorption Model/Dominant Mechanism	Key Advantages and Limitations	Ref.
U(VI)	CTAB-modified hydroxyapatite–bentonite (CTAB–HAp–Bent)	Bentonite	CTAB functionalization; one-step hydrothermal synthesis	$q_e \approx 108.19 \text{ mg g}^{-1}$; removal $\approx 89.09\%$	pH 8.0; U(VI) = 50 mg L^{-1} ; $[\text{CO}_3] = 2 \text{ mmol L}^{-1}$; $[\text{P}] = 1.5 \text{ }\mu\text{mol L}^{-1}$	PSO; Langmuir; Br^- anion exchange + $-\text{OH}$ coordination	Specifically evaluated in phosphate–carbonate media; phosphate promoted whereas carbonate suppressed uptake; regeneration not reported	[47]
U(VI)	CTAB-modified montmorillonite–hydroxyapatite (CMH)	Montmorillonite	CTAB modification + HAp; hydrothermal/in situ synthesis	Reported U(VI) adsorption capacity = 678.6 mg g^{-1} ; U(VI) removal $>99\%$ under the specified low-concentration conditions	pH 5.0; 298 K; U(VI) = 10 mg L^{-1} for reported $>99\%$ removal	PSO; Langmuir; electrostatic interaction + ion exchange + complexation	Very high capacity; ion-interference resistance; 96.2% adsorption efficiency after five cycles; actual wastewater/pilot-scale validation not established	[48]
U(VI)	Hydroxyapatite-modified	Attapulgite	HAp deposition; one-step	$q_{\text{max}} = 387.27 \text{ mg g}^{-1}$	Equilibrium $\approx 20 \text{ min}$	Ion exchange + complexation + dissolution–	Rapid uptake; porous fibrous carrier	[41]

		attapulgit (HAP/ATP)	(palygor- hydrothermal skite) synthesis		precipitation + electrostatic ad- sorption	suppresses HAp agglomeration; regeneration and real-wastewater validation not re- ported	
U(VI)	Hydroxyap- atite/white clay nanocomposite (HAp/white clay)	White clay (pre- domi- nantly kaolinite; quartz and illite admix- tures)	HAp incorpo- rated by wet synthesis; fi- nal HAp/clay ratio NR	Langmuir- Freundlich A = 570.8–669.9 mg g ⁻¹ (295– 323 K); 100% removal un- der kinetic- test condi- tions	pH 2–10 in- vestigated; equilibrium ≈ 180 min; ad- sorption in- creased with temperature	Freundlich, Langmuir- Freundlich and D–R; ion ex- change + HAp- assisted uranyl- phosphate pre- cipitation	High model ca- pacity and com- plete removal under favorable conditions; re- generation and real-wastewater validation not re- ported [32]

Note. Adsorption capacities are reported according to the terminology and models used in the original studies. Experimental equilibrium capacities (q_e) and model-derived maximum capacities (q_{max} or A) should not be interpreted as directly equivalent. Differences in pH, uranium speciation, temperature, competing ions, and solution composition should also be considered when comparing adsorption performance among studies.

Among the investigated HAp–clay systems, smectite-based composites demonstrate the importance of surface and interlayer modification for controlling U(VI) uptake. CTAB functionalization of HAp–bentonite enabled efficient U(VI) removal under phosphate–carbonate conditions, yielding an equilibrium adsorption capacity of approximately 108.19 mg g⁻¹ and a removal efficiency of about 89% [47]. More importantly, this study demonstrated that adsorption performance is strongly governed by aqueous uranium speciation: phosphate promoted U(VI) uptake, whereas carbonate and increasing alkalinity suppressed adsorption. In contrast, the CTAB-modified montmorillonite–HAp composite (CMH) exhibited a substantially higher reported maximum capacity of 678.6 mg g⁻¹ and maintained 96.2% adsorption efficiency after five cycles [48]. The enhanced performance of CMH was associated with increased interlayer accessibility, greater porosity, and a higher abundance of functional binding sites, enabling electrostatic interactions, ion exchange, and complexation. However, the numerical difference between [47] and [48] should not be interpreted as a direct ranking of the two materials because the adsorption experiments were conducted under substantially different solution chemistries and U(VI) speciation conditions.

The results obtained for fibrous attapulgite further demonstrate that high U(VI) removal does not require an expandable smectite matrix. HAp-modified attapulgite (HAP/ATP) exhibited a maximum adsorption capacity of 387.27 mg g⁻¹ and reached equilibrium within approximately 20 min [41]. In the investigated HAP/ATP system, the fibrous and porous attapulgite phase was reported to support HAp distribution and limit particle agglomeration, potentially improving the accessibility of reactive sites [41]. Accordingly, U(VI) immobilization proceeds through multiple pathways, including ion exchange, complexation, dissolution–precipitation, and electrostatic adsorption. This behavior highlights a different design strategy from CTAB-functionalized smectites: rather than relying predominantly on interlayer and surface-charge modification, HAP/ATP exploits the morphology and porosity of the clay carrier to improve HAp dispersion and mass transfer.

A further mechanistic distinction is evident for the HAp/white clay nanocomposite [32]. The white clay consisted predominantly of kaolinite with quartz and illite

admixture, while HAp incorporation increased the BET surface area from 18 to 63 m² g^{−1}, thereby providing a more developed interface for U(VI) immobilization.

The composite achieved complete U(VI) removal under the kinetic-test conditions after approximately 180 min, compared with 78% for the unmodified white clay. The reported Langmuir–Freundlich capacity increased from 570.8 mg g^{−1} at 295 K to 669.9 mg g^{−1} at 323 K, confirming the favorable effect of temperature on uranium uptake. Importantly, U(VI) removal in this system cannot be described solely as conventional surface adsorption. Ion exchange involving hydroxyl groups contributes to uranyl binding, while the HAp component promotes immobilization through the formation of sparingly soluble uranyl-phosphate species. The near-complete removal observed over favorable pH conditions was associated with precipitation of a uranium-containing phosphate phase on the adsorbent surface.

Taken together, the studies summarized in Table 4 demonstrate that the efficiency of HAp–clay composites for U(VI) removal is governed by a combination of clay mineral structure, HAp dispersion, surface functionalization, uranium speciation, and solution chemistry, rather than adsorption capacity alone. Smectite matrices provide expandable interlayers and ion-exchange sites that can be further tailored through surfactant modification [47,48], whereas fibrous attapulgite facilitates rapid mass transfer and suppresses HAp agglomeration [41]. Kaolinite-rich clay, despite its comparatively low intrinsic cation-exchange capacity, can serve as an effective structural support for HAp and thereby facilitate strong uranium immobilization through phosphate-associated processes [32]. These findings indicate that the clay component should not be regarded merely as an inert carrier. Its mineralogical structure and surface chemistry may influence the accessibility of reactive sites and the relative contributions of U(VI) removal pathways, together with HAp-associated phosphate chemistry, surface modification, and solution conditions.

Key implication:

The available evidence indicates a transition from adsorption-dominated U(VI) removal toward deliberately engineered multi-mechanistic immobilization in HAp–clay composites. Surface-charge modification, control of interlayer accessibility, suppression of HAp agglomeration, and exploitation of phosphate-driven precipitation provide complementary strategies for improving uranium sequestration. Consequently, adsorption capacity alone is insufficient for identifying the most effective radionuclide sorbent; aqueous speciation, competing ions, immobilization mechanism, regeneration behavior, and long-term stability must also be considered when evaluating practical performance.

Research gap: Despite the high U(VI) removal capacities reported for several HAp–clay composites, most studies remain based on controlled batch experiments. Direct validation in real uranium-contaminated waters is still limited, and systematic information on long-term radionuclide retention, desorption under changing geochemical conditions, continuous-flow operation, and structural stability after repeated use remains insufficient. Regeneration has been demonstrated for CMH [48], but comparable cycling data are lacking for several other promising systems summarized in Table 4. Future research should therefore move beyond maximizing model-derived adsorption capacities toward evaluating radionuclide immobilization under realistic multicomponent water chemistry and long-term operating conditions.

3.3. Fluoride Removal

Fluoride contamination of drinking water represents an important environmental and public-health challenge, particularly in regions where groundwater contains naturally elevated fluoride concentrations. Hydroxyapatite is of interest for defluoridation because fluoride can interact with its hydroxyl-containing apatite structure through F[−]/OH[−] substitution, while additional immobilization pathways may involve surface interactions

and the formation of fluoride-containing calcium phases. Incorporation of HAp into clay-containing materials may provide structural support, modify accessible surface sites and porosity, and facilitate the fabrication of mechanically stable filtration media. However, these effects depend on clay mineralogy, HAp loading, synthesis route, sintering conditions, and the architecture of the resulting composite.

The development of HAp–clay materials for fluoride removal has progressively evolved from sintered clay–HAp composites toward nanostructured adsorbents, post-formed materials, and point-of-use ceramic filtration devices. Early work on sintered clay–HAp systems demonstrated that fluoride uptake is strongly influenced by HAp loading, sintering temperature, porosity, and contact time [49], whereas subsequent studies explored structural enhancement through montmorillonite exfoliation [11], calcined-kaolin/HAp post-forming [29], and multifunctional HAp-doped ceramic water filters [50]. These studies also demonstrate that adsorption capacity alone is insufficient for assessing practical defluoridation performance because adsorbent form, hydraulic behavior, mechanical stability, regeneration, and treated-water quality become increasingly important as materials progress toward filtration applications. The principal adsorption and engineering characteristics of representative HAp–clay systems are summarized in Table 5.

Table 5. Comparative performance of hydroxyapatite–clay composites for fluoride removal.

HAp–Clay System	Clay Matrix	Preparation/Material Design	Fluoride-Removal Performance	Relevant Conditions	Adsorption Model/Mechanism	Practical Performance/Reusability	Key Advantages and Limitations	Ref.
Sintered clay–HAp composite (C–HA)	Redart clay (predominantly illite and kaolinite)	Clay/HAp with sawdust as pore former; C:HA ratios 90:10–75:25; sintered at 500–900 °C; frustum-shaped filters at ~861 °C	Fluoride uptake increased with HAp content; at $C_0 = 2.5$ mg L ⁻¹ , filtration reduced F ⁻ to 0.265 ± 0.043 mg L ⁻¹ (75:25) and 0.157 ± 0.015 mg L ⁻¹ (80:20)	Batch adsorption: 0.25 g/30 mL, 24 h; filtration tested at F ⁻ = 2.5 and 20 mg L ⁻¹	Freundlich; heterogeneous adsorption; F ⁻ /OH ⁻ exchange, fluorapatite formation and CaF ₂ formation at higher F ⁻ concentration; intraparticle/pore diffusion	Proof-of-concept point-of-use filter; simultaneous F ⁻ and E. coli removal	Early demonstration of engineered C–HA filtration; performance depends on HAp loading, porosity and sintering; filtrate pH increased to ~11–12.4; long-term operation not established	[49]
HAP–MMT nanocomposite	Montmorillonite	Wet chemical in situ precipitation; HAP:MMT = 1:1	Experimental $q_e = 14.9$ mg g ⁻¹ ; Freundlich-derived capacity reported by authors = 16.7 mg g ⁻¹	Optimum pH ≈ 5; equilibrium ≈ 30 min; adsorption investigated at 27–60 °C	Freundlich; PSO; OH ⁻ /F ⁻ ion exchange + interactions with Ca ²⁺ sites, enhanced by MMT intercalation/exfoliation	Gravity filtration at 1.5 mg L ⁻¹ F ⁻ ; breakthrough volume = 1600 mL g ⁻¹ ; three regeneration cycles	High surface accessibility, rapid adsorption and flow-through validation; competing anions reduce uptake; regeneration performance decreased 55 → 43 → 37%	[11]
Post-formed calcined-	Calcined kaolin	Biogenic HAp from bovine bone; CK:HAP = 75:25; alkali	$q_e = 1.54$ mg g ⁻¹ ; 77% removal at pH 3 for post-formed CK75	pH 3 for maximum reported CK75 performance;	Freundlich for post-formed composite; electro-static at-	Molded/tablet form improves practical handling and adsorption relative to	Engineered macroscopic form; however, relatively low experimental capacity;	[29]

kao-lin/HAp (CK75)		activation/geo-polymerization and post-forming	pH 2–12 investigated	traction + OH [−] /F [−] ion exchange	corresponding CK75 powder	increasing HAp content reduced hardness and fluoride exposure induced microcracking; regeneration/column tests not reported
HA-doped ceramic water filter (Clay–HA CWF)	Redart clay	Clay:saw-dust:HAp = 30:50:20 (weight ratio); hydraulic pressing; air-drying for 6 d; sintering at 850 or 900 °C for 5 h	Fluoride LRV = 2.02 ± 0.15 (Clay–HA; reported in Ref. [50]).	$C_0 = 5\text{--}20$ mg L ^{−1} (isotherm tests); filtration: 5 L solution, 6 h.	Freundlich isotherm; proposed F [−] /OH [−] substitution in HAp and possible electrostatic contribution from the clay phase	Simultaneous fluoride and bacterial removal; lower fluoride removal than BP-doped CWFs; [50] fluoride adsorption decreased at higher HAp crystallinity after sintering at 900 °C

Note. Fluoride-removal performance is reported according to the metrics used in the original studies. Batch adsorption capacities, model-derived capacities, log-reduction values (LRVs), breakthrough volumes, and filtration concentrations are not directly equivalent and should not be used for simple numerical ranking. Differences in adsorbent form, initial fluoride concentration, pH, contact time, sintering conditions, and flow configuration should be considered when comparing the reported systems. HAp/clay ratios and component contents are reported as provided in the original studies; NR denotes compositional information not reported by the original authors.

The early sintered C–HA system reported by Yakub and Soboyejo [49] established an important transition from powdered fluoride adsorbents toward engineered HAp–clay filtration media. Fluoride uptake generally increased with HAp content, while the heterogeneous adsorption behavior was adequately described by the Freundlich model. Mechanistically, fluoride immobilization involved F[−]/OH[−] exchange and fluorapatite formation, with CaF₂ formation becoming increasingly relevant at higher fluoride concentrations. Kinetic analysis further indicated an important contribution from intraparticle/pore diffusion, demonstrating that the porous architecture of the ceramic composite participates directly in controlling mass transfer. Importantly, proof-of-concept filtration reduced an initial fluoride concentration of 2.5 mg L^{−1} to approximately 0.16–0.27 mg L^{−1}, depending on the clay:HAp ratio, while simultaneously removing microbial contamination.

This device-oriented concept was subsequently extended in HAp-doped ceramic water filters [50], where the interplay between adsorption, hydraulic performance, and mechanical stability became particularly evident. The filters combined Redart clay, sawdust, and HAp to generate micro-/nanoporous structures capable of simultaneous fluoride and bacterial removal. Lower-temperature sintering favored fluoride uptake, whereas higher-temperature treatment improved mechanical properties but reduced adsorption performance, illustrating a clear processing–performance trade-off. The resulting filters achieved practical flow rates of approximately 1.4–2.2 L h^{−1} and were estimated to treat at least 40 L of water per day, demonstrating the potential of HAp–clay composites for point-of-use treatment rather than batch adsorption alone [50].

A different strategy was demonstrated for the HAp–MMT nanocomposite [11], where enhancement of fluoride adsorption was achieved primarily through nanoscale

structural modification rather than macroscopic filter design. In the HAp–MMT system investigated in ref. [11], HAp incorporation was associated with increased surface accessibility and interlayer spacing, which may have contributed to the experimentally observed improvement in fluoride uptake. Rapid adsorption, with near-equilibrium behavior within approximately 30 min, was attributed to improved accessibility of hydroxyl and Ca^{2+} -associated binding sites resulting from MMT intercalation and exfoliation. Particularly importantly, the material was also evaluated under gravity-flow conditions, yielding a breakthrough volume of 1600 mL g^{-1} for water containing 1.5 mg L^{-1} fluoride. Thus, ref. [11] provides a useful bridge between nanoscale adsorption enhancement and flow-through validation.

In contrast, the calcined-kaolin/HAp system [29] highlights the importance of adsorbent formability and mechanical handling rather than maximizing fluoride uptake alone. Post-forming through alkali activation converted the powdered CK/HAp mixture into a macroscopic adsorbent, with the CK75 composition reaching approximately 1.54 mg g^{-1} and 77% fluoride removal at pH 3. Although this capacity was considerably lower than that reported for HAp–MMT [11], the study addressed a practical limitation of powdered sorbents by developing mechanically handleable forms. However, increasing HAp content reduced hardness, and fluoride exposure induced microcracking, revealing a trade-off between chemical functionality and structural durability. This comparison demonstrates that incorporation of HAp does not universally enhance fluoride uptake; its effectiveness depends strongly on clay mineralogy, processing route, and the structural role of HAp within the composite.

Taken together, the studies summarized in Table 5 demonstrate that the development of HAp–clay defluoridation materials involves a progressive shift from adsorption-centered optimization toward integrated materials and device engineering. In the investigated HAp–MMT system, increased surface and interlayer accessibility was associated with improved fluoride uptake [11], whereas the kaolin-based system demonstrated the potential of post-forming approaches for producing shaped adsorbents with improved handling [29]. Sintered clay–HAp systems [49,50], in turn, demonstrate the feasibility of incorporating fluoride-binding functionality directly into porous point-of-use filters. However, these advantages introduce additional design constraints, including hydraulic resistance, mechanical integrity, sintering-induced changes in HAp reactivity, regeneration efficiency, and control of treated-water chemistry. Consequently, the most suitable HAp–clay material cannot be identified solely from its maximum adsorption capacity; practical selection requires simultaneous consideration of adsorption kinetics, operating concentration, flow performance, reusability, structural stability, and water-quality outcomes.

Key implication: The available studies indicate that the design of HAp–clay materials for fluoride removal requires balancing adsorption performance with engineering functionality. Increasing accessible HAp sites and optimizing clay–HAp interfaces can enhance fluoride uptake, whereas shaping, sintering, and pore engineering enable transition toward practical filtration devices but may simultaneously alter adsorption efficiency and mechanical stability. Therefore, future HAp–clay defluoridation systems should be optimized as integrated adsorption–filtration materials rather than evaluated solely as high-capacity sorbents.

Research gap: Despite substantial progress from batch adsorbents toward point-of-use filtration systems, several barriers remain before HAp–clay materials can be widely implemented for drinking-water defluoridation. Regeneration remains insufficiently investigated or progressively loses efficiency, as observed for HAp–MMT [11], while long-term breakthrough behavior and service life have rarely been established. The early C–HA filter [49] also produced a substantial increase in filtrate pH, reaching approximately

11–12.4, demonstrating that high fluoride removal does not necessarily guarantee acceptable treated-water quality. Mechanical degradation and microcracking represent additional concerns for shaped systems [29], whereas sintering conditions create a trade-off between adsorption performance and mechanical strength in ceramic filters [50]. Future studies should therefore prioritize long-term continuous-flow testing, regeneration and safe disposal, mechanical durability, performance in real groundwater containing competing ions, and systematic monitoring of treated-water chemistry.

3.4. Removal of Organic Contaminants

Organic contaminants, including synthetic dyes and pharmaceutical residues, represent an important class of water pollutants because of their chemical persistence, structural diversity, and potential environmental impacts. Their removal by HAp–clay composites depends on pollutant molecular structure, ionization state, solution pH, composite composition, and the availability of accessible surface sites. Depending on mineralogy, the clay component may contribute charged external surfaces, hydroxyl-containing groups, and, in expandable clay minerals, exchangeable interlayer cations. HAp provides calcium-, phosphate-, and hydroxyl-associated surface functionalities, while additional organic modifiers may introduce further adsorption sites or alter surface charge. Consequently, removal may involve electrostatic interactions, ion exchange, hydrogen bonding, surface complexation, and other system-dependent pathways. The relative contributions of these mechanisms should be evaluated for each investigated pollutant–composite system.

Studies of organic-contaminant removal by HAp–clay materials have evolved from relatively simple binary composites for dye adsorption [30,51] toward polymer-integrated and thin-film systems with improved multifunctionality and reusability [52–54]. More recent investigations of antibiotics have further demonstrated the importance of contaminant speciation, clay cation-exchange capacity, competing ions, and water-matrix composition [31,55,56]. In particular, the transition from tetracycline adsorption on HAp–clay composites [56] to oxytetracycline removal in treated wastewater [31] and molecular-level analysis of ciprofloxacin adsorption on mesoporous Hydroxyapatite@Montmorillonite [55] illustrates the increasing mechanistic and application-oriented complexity of this research area. Representative adsorption characteristics and practical limitations of HAp–clay systems for organic-contaminant removal are summarized in Table 6.

Table 6. Comparative performance of hydroxyapatite–clay composites for the removal of organic contaminants.

Contaminant	HAp–Clay System	Clay/Composition/Modification	Adsorption Performance	Relevant Conditions	Isotherm/Kinetics	Main Removal Mechanism	Practical Aspects/Limitations	Ref.
Methylene blue (MB)	Bentonite-like clay/HAp (C–HA)	Bentonite-like clay (BT6, Tam Bo deposit); 5 g clay; HAp formed in situ by chemical precipitation at Ca:P = 1.67; final HAp/clay ratio NR	Langmuir $q_m = 175.44$ mg g ^{−1} at 298 K; kinetic experimental $q_e = 72.08$ mg g ^{−1}	pH 4–12; equilibrium ≈ 20 –40 min; 298–333 K	Langmuir; PSO	Electrostatic attraction, clay interlayer ion exchange, Lewis acid–base interactions and H-bonding; external/internal diffusion	High MB capacity; $q_m \approx 1.28 \times$ clay and $17.8 \times$ HAp; regeneration and real-wastewater tests not reported	[51]

Methylene blue (MB)	BTHAAAlg/BT HAGel	Commercial bentonite (BT); HAp:BT = 1:1 (0.5 g:0.5 g); 2.0 g alginate or gelatin biopolymer matrix	43.70 mg g ⁻¹ (BTHAAAlg); 47.50 mg g ⁻¹ (BTHAGel)	C ₀ = 100 mg L ⁻¹ ; dosage = 0.1 g/50 mL; contact time = 40 min; optimum pH = 11	Langmuir; PSO + intraparticle diffusion	Langmuir; pseudo-second-order and intraparticle diffusion; electrostatic attraction and hydrogen bonding	Reusable up to five cycles; adsorption/removal efficiency decreased progressively	[52]
Indigo carmine (IC)	HAP-CTS-Mt thin film		Langmuir q _m = 243.18 mg g ⁻¹ (isotherm); kinetic experimental q _e = 99.87 mg g ⁻¹	Isotherm C ₀ = 10–200 mg L ⁻¹ ; kinetic/optimization tests: C ₀ = 20 mg L ⁻¹ ; dose = 0.2 g L ⁻¹ ; equilibrium ≈ 90 min	Langmuir; PSO	Charge-dependent electrostatic interactions; adsorption favored below pH _{PZC} = 6.24	Thin-film architecture; 3 regeneration cycles; acidic stability of chitosan is a concern	[53]
Methyl orange (MO)	HAP-CTS-Mt thin film	Na-montmorillonite + chitosan; HAp:Mt = 1:1 (0.4375 g:0.4375 g); 3.5 g CTS; mixed/intercalated thin-film composite	Langmuir q _m = 137.50 mg g ⁻¹ (isotherm); kinetic experimental q _e = 96.65 mg g ⁻¹	Isotherm C ₀ = 10–200 mg L ⁻¹ ; kinetic/optimization tests: C ₀ = 50 mg L ⁻¹ ; dose = 0.5 g L ⁻¹ ; equilibrium ≈ 60 min	Langmuir; PSO	Charge-dependent electrostatic interactions; adsorption favored below pH _{PZC}	Same film removes anionic and cationic dyes; 3 regeneration cycles; real-wastewater/flow validation not reported	[53]
Methylene blue (MB)	HAP-CTS-Mt thin film		Langmuir q _m = 168.52 mg g ⁻¹ (isotherm); kinetic experimental q _e = 47.92 mg g ⁻¹	Isotherm C ₀ = 10–200 mg L ⁻¹ ; kinetic/optimization tests: C ₀ = 20 mg L ⁻¹ ; dose = 0.2 g L ⁻¹ ; equilibrium ≈ 60 min	Langmuir; PSO	Charge-dependent electrostatic interactions; MB adsorption favored above pH _{PZC}	Demonstrates charge-responsive multifunctionality; reusable for 3 cycles	[53]

Note. Adsorption performance is reported according to the metrics and experimental conditions used in the original studies. Experimental equilibrium capacities (q_e), Langmuir-derived maximum capacities (q_m or q_{max}), and other reported maximum adsorption values are not necessarily directly equivalent. Direct numerical ranking should therefore be interpreted cautiously because pollutant structure and speciation, initial concentration, pH, temperature, adsorbent dose, composite composition, and water-matrix chemistry differ among studies. For ref. [31], values obtained in distilled water, competing-ion medium, and treated wastewater are reported separately to illustrate the influence of matrix complexity.

For dye removal, the results summarized in Table 6 demonstrate that the contribution of HAp and clay depends strongly on both adsorbent architecture and dye charge. In the relatively simple bentonite-like clay/HAp composite [51], the Langmuir capacity for methylene blue reached 175.44 mg g⁻¹, exceeding those of both the parent clay and HAp.

However, the substantially greater intrinsic affinity of the clay toward MB compared with neat HAp indicates that the clay phase remains a major contributor to cationic-dye adsorption. A similar clay-mineralogy dependence was demonstrated in [30], where composites prepared using the same eggshell-derived HAp followed the performance order HAP-BENT > HAP-HNT > HAP-KAO. These findings indicate that HAp incorporation alone does not determine organic-dye uptake; the surface charge, ion-exchange characteristics, and structure of the clay phase remain critical.

Polymer integration introduces a different design strategy. The HAP-CTS-Mt thin film [53] exhibited adsorption toward both anionic and cationic dyes, with Langmuir capacities of 243.18, 137.50, and 168.52 mg g⁻¹ for indigo carmine, methyl orange, and methylene blue, respectively. Its adsorption behavior was strongly charge-dependent: anionic dyes were favored below the point of zero charge, whereas cationic MB adsorption increased under conditions where the surface became negatively charged. Thus, incorporation of chitosan and formation of an intercalated thin-film architecture broadened the functional range of the material rather than simply maximizing adsorption of a single dye. The BTHACS [54] and BTHAAlg/BTHAGel [52] systems similarly illustrate a shift toward biopolymer-assisted hybridization, with regeneration reported for up to five cycles. Notably, their reported MB capacities were lower than that of the simpler C-HA system [51], indicating that increasing composite complexity does not necessarily produce a proportional increase in adsorption capacity. Instead, biopolymer incorporation may provide other operational benefits, including recoverability, reuse, and improved material handling.

Antibiotic adsorption presents a more complex physicochemical problem because the molecular charge of tetracycline-class and fluoroquinolone antibiotics varies with solution pH. Consequently, adsorption cannot be interpreted solely in terms of a fixed adsorbent surface charge. The early HA-C study [56] demonstrated a tetracycline uptake capacity of 76.02 mg g⁻¹ and identified cation exchange and surface complexation as major mechanisms. The substantially greater capacity and cation-exchange capacity of HA-C compared with the HAp-pumice composite highlighted the importance of the aluminosilicate phase and established clay ion-exchange properties as a key design parameter for antibiotic adsorption.

This concept was extended in the oxytetracycline study [31], where several HAp-aluminosilicate materials were evaluated under increasingly complex solution conditions. Although HA-NC exhibited a Langmuir-derived capacity of 61.46 mg g⁻¹ in distilled water, the corresponding values decreased to 28.88 mg g⁻¹ in the presence of competing ions and 32.17 mg g⁻¹ in treated municipal wastewater. For this specific oxytetracycline-adsorbent system, the approximately twofold reduction in Langmuir-derived capacity indicates that adsorption performance measured in distilled water may not be representative of performance in more complex aqueous matrices. This observation should not be generalized to all antibiotic-HAp-clay systems without comparable experimental evidence. The results also reinforce the importance of cation exchange, hydrogen bonding, and surface complexation while showing that dissolved ions and organic matter can compete effectively for available adsorption sites.

A more detailed molecular-level interpretation was provided for ciprofloxacin adsorption on mesoporous HAP@Mt [55]. The composite exhibited a Langmuir-derived maximum adsorption capacity of 91.18 mg g⁻¹, close to the experimentally reported uptake of 89.28 mg g⁻¹, and showed higher ciprofloxacin removal than either pristine montmorillonite or HAp under the investigated conditions. These findings indicate improved composite-level performance, although the individual contributions of the mineral phases and their interfacial interactions require further differentiation. The enhanced performance was associated with the mesoporous architecture and increased specific surface area,

while adsorption involved a combination of electrostatic interactions, hydrogen bonding, hydrophobic effects, and $n-\pi$ electron donor–acceptor interactions. Importantly, Monte Carlo and DFT calculations supported the experimentally observed pH dependence by demonstrating particularly favorable interactions of ciprofloxacin with HAP@Mt under near-neutral conditions.

Ref. [55] also demonstrates that mechanistic optimization can be combined with regenerability. Desorption reached 99.1% using 1.0 M NaOH, while ciprofloxacin removal remained above 78.5% after four adsorption–desorption cycles. Nevertheless, these results were obtained under controlled batch conditions, and validation in real wastewater and continuous-flow systems remains necessary.

Taken together, the studies summarized in Table 6 demonstrate that the adsorption mechanisms of organic contaminants by HAP–clay composites depend strongly on pollutant chemistry and speciation. For cationic dyes such as methylene blue, the reviewed studies frequently identify electrostatic attraction and ion exchange involving the clay phase, with HAP providing complementary surface functionality and structural modification. Polymer incorporation can broaden charge selectivity and improve regeneration or handling, but does not necessarily increase adsorption capacity. For ionizable antibiotics, adsorption may involve pH-dependent molecular speciation together with ion exchange, surface complexation, hydrogen bonding, hydrophobic interactions, and donor–acceptor interactions. Importantly, the available studies do not provide sufficiently matched experimental conditions to establish that antibiotics as a class are more sensitive to competing solutes or water-matrix composition than dyes. However, a pronounced matrix effect was directly demonstrated for oxytetracycline adsorption on HA–NC [31], for which the Langmuir-derived capacity decreased from 61.46 mg g^{−1} in distilled water to 28.88 mg g^{−1} in the presence of competing ions and 32.17 mg g^{−1} in treated municipal wastewater. Therefore, the effectiveness of HAP–clay composites toward organic contaminants should be interpreted in relation to the specific pollutant–material system, clay mineralogy, HAP surface chemistry, composite architecture, pollutant speciation, and solution composition.

Key implication: HAP–clay composites offer a versatile platform for organic-contaminant removal because the two mineral phases can provide complementary adsorption environments that can be further tuned through polymer incorporation and structural engineering. However, the function of HAP differs among pollutant classes: for some cationic dyes, clay-mediated electrostatic attraction and ion exchange may dominate, whereas for ionizable pharmaceuticals the combined HAP–clay interface enables more diverse, speciation-dependent interactions. Consequently, future material design should prioritize pollutant-specific interfacial chemistry and operational functionality rather than pursuing adsorption capacity alone.

Research gap: Despite promising adsorption capacities and increasing mechanistic understanding, most HAP–clay studies on organic contaminants remain based on single-solute batch experiments. Direct evidence from real textile or pharmaceutical wastewater is limited, with ref. [31] representing an important exception by demonstrating a substantial decline in oxytetracycline adsorption in treated wastewater compared with distilled water. Regeneration has been investigated for several polymer-containing dye adsorbents and HAP@Mt [55], but long-term cycling, structural stability, continuous-flow operation, and safe management of contaminant-loaded or spent adsorbents remain insufficiently addressed. In addition, competitive adsorption among dyes, antibiotics, natural organic matter, and inorganic ions should be systematically investigated because these interactions may substantially alter adsorption mechanisms and capacity under realistic treatment conditions. Future studies should therefore integrate real-water validation, multi-component adsorption, long-term regeneration, column-scale testing, and assessment of

contaminant desorption or secondary release before practical implementation can be reliably evaluated.

Overall, the available evidence demonstrates that the performance of hydroxyapatite–clay composites is governed not by a single universal adsorption mechanism but by the interplay between clay mineralogy, HAp surface chemistry, composite architecture, contaminant speciation, and operating conditions. For heavy metals, HAp-assisted precipitation, ion exchange, and surface complexation dominate, while recent material development increasingly emphasizes regeneration, multifunctionality, and process integration. Radionuclide removal is particularly sensitive to aqueous speciation and benefits from deliberately engineered multi-mechanistic immobilization pathways. In fluoride treatment, the research focus has progressively shifted from adsorption capacity toward shaped adsorbents and point-of-use filtration, where hydraulic and mechanical properties become equally important. For organic contaminants, adsorption is governed by pollutant-specific molecular interactions, ranging from clay-mediated electrostatic attraction and ion exchange for dyes to speciation-dependent complexation, hydrogen bonding, and donor–acceptor interactions for pharmaceuticals. Collectively, these findings indicate that future HAp–clay systems should be designed as application-specific multifunctional materials in which adsorption efficiency is optimized together with regeneration, structural durability, water-matrix tolerance, hydraulic performance, and long-term contaminant immobilization.

4. Biomedical Applications of Hydroxyapatite–Clay Composites

4.1. Bone Tissue Engineering and Orthopedic Applications

Bone tissue engineering represents one of the most promising biomedical application areas for HAp–clay composites because it exploits the complementary characteristics of a bone-mimetic calcium phosphate phase and structurally diverse clay minerals. HAp provides chemical similarity to the mineral component of bone and contributes osteoconductive and apatite-forming functionality, whereas clay minerals can modify mechanical properties, scaffold microarchitecture, interfacial interactions, mineral nucleation, and therapeutic loading. When incorporated into polymeric matrices, these inorganic phases can therefore generate hierarchical composites that more closely reproduce the structural and functional complexity of native hard tissues. More broadly, inorganic particle–polymer composites offer opportunities to regulate mechanical, structural, and biological properties simultaneously, although long-term safety and particle–cell interactions remain important translational considerations [57].

Importantly, the biomedical function of the clay phase depends strongly on its mineralogical structure and morphology. The mineralogical distinctions outlined in Section 2 translate directly into different biomedical functions. Halloysite primarily provides reinforcement, nanoscale confinement, and therapeutic-carrier functionality, whereas montmorillonite contributes interfacial reinforcement through intercalation/exfoliation and modification of polymer–mineral organization. Clay-derived phases may also contribute indirectly, as illustrated by bentonite-derived wollastonite [58]. These distinct roles underpin the development of porous scaffolds, hierarchical hard-tissue materials, implant coatings, and additively manufactured therapeutic devices summarized in Table 7.

Table 7. Comparative structure–function characteristics of HAp–clay-based composites for biomedical applications.

HAp–Clay System	Clay/Architecture	Application	Key Structural/Mechanical Outcome	Key Biological/Functional Outcome	Clay Role/Evidence Limitation	Ref.
PCL/HA vs. PCL/HNT porous scaffolds	Halloysite nanotubes (HNT); tubular 1:1 clay mineral; commercial HNT, average tube length ≈800 nm	Bone tissue engineering	HA or HNT separately incorporated at 1, 5, and 10 wt.% into PCL/PEO (50:50) matrix; co-extrusion and supercritical-N ₂ gas foaming. HNT more strongly affected rheology, pore architecture, and mechanical properties than HA at comparable loading.	Low HNT loading supported hMSC proliferation and osteogenic differentiation	HNT provides tubular reinforcement and modifies scaffold microarchitecture; biological response depended on HNT loading and resulting pore architecture. HNT and HAp were evaluated in separate scaffold series; therefore, a direct HAp–HNT interfacial synergy was not demonstrated.	[37]
PCL/HA/HNT composites; curcumin-loaded PCL/HA/HNT composite	Halloysite nanotubes (HNT); tubular; commercial HNT (Sigma-Aldrich)	Bone-tissue engineering/re- sorbable fixation materials/drug-delivery functionality	20 wt.% HA with 2.5, 5.0, or 7.5 wt.% HNT; optimal formulation: PCL/20 wt.% HA/7.5 wt.% HNT. Components were twin-screw extruded and injection molded; HNTs were additionally lumen-loaded with curcumin for functionalization.	Combined HA/HNT incorporation substantially improved mechanical and thermal properties; HNT lumen provided a route for curcumin loading. Curcumin-functionalized HNTs reduced mechanical performance relative to the non-loaded PCL/HA/HNT composite.	HNT provides tubular reinforcement and a lumen for therapeutic loading. Mechanical enhancement of the combined HA/HNT system was directly measured; however, curcumin loading promoted HNT aggregation and reduced mechanical properties, and therapeutic/biological efficacy of curcumin release was not directly demonstrated in vivo.	[36]
3D-printed PCL–HA–HNT–gentamicin composite	Halloysite nanotubes (HNT); tubular; commercial HNT	Local antibiotic delivery/prevention of fracture-related infection	PCL containing 20 wt.% HA + 2.5 wt.% HNT; 2 or 5 wt.% gentamicin sulfate (GS); hot-melt extrusion followed by fused-filament-fabrication 3D printing. HA/HNT incorporation increased tensile and flexural elastic moduli.	Burst GS release followed by sustained release for 14 days; 2 and 5% GS composites completely killed <i>S. aureus</i> ex vivo; 5% GS substantially prevented infection in vivo.	HNT is incorporated as a nanofiller within the PCL–HA matrix; however, the antimicrobial effect was attributable to released gentamicin rather than to HNT or HA. The device was evaluated as an antibiotic-release system rather than as an independently load-bearing fixation plate, and the in vivo endpoint was limited to 3 days.	[38]
HNT-directed CaP composite (C–P–H; CPH@P)	Halloysite nanotubes (HNT); tubular clay with chemically differentiated inner/outer surfaces	Biomineralization/enamel-like structural	CaP mineralization occurred on HNT surfaces; TEM/EDS directly confirmed CaP associated with HNT, while HRTEM revealed nanoscale CaP associated with the HNT structure. CPH@P composites contained 40.56–72.39 wt.%	High stiffness and hardness together with antibacterial activity against <i>S. aureus</i> and <i>S. mutans</i> ; L929 cell viability remained high over the tested concentration range.	Direct TEM/EDS and FTIR evidence supports HNT-associated CaP mineralization and HNT–CaP interfacial coordination. However, exact starting HNT composition could not be established from the information reported in the original study [34]; mechanistic interpretations involving	[34]

		mate- rial/anti- micro- bial function- ality	inorganic phase depend- ing on formulation.		spatial confinement should therefore be distinguished from directly observed inter- facial mineralization.
Chitosan– HNT–HA electro- phoretically de- posited films	Halloysite nanotubes (HNT); tubu- lar; commer- cial HNT (Al- drich)	Biomed- ical im- plant coat- ings/cor- rosion protec- tion	EPD from 0.1–0.5 g/L chitosan solutions con- taining up to 0.6 g/L HNT and 1.0 g/L HA; representative chitosan– HNT–HA films were de- posited from 0.5 g/L chi- tosan + 0.6 g/L HNT + 1.0 g/L HA. Monolayer, multilayer, and func- tionally graded films were obtained.	Composite films im- proved corrosion re- sistance of stainless- steel substrates in simulated physiologi- cal solution.	Chitosan directly enabled dis- persion, charging, and co- deposition of HNT and HA; XRD and SEM confirmed in- corporation of both phases. Biomedical evaluation was limited to materials character- ization and corrosion testing; direct cell, osteogenic, drug- release, or in vivo perfor- mance was not demonstrated. [39]
HNT– HA–hya- luronic acid (HYH) films	Halloysite nanotubes (HNT); tubu- lar; commer- cial HNT (Al- drich)	Biomed- ical im- plant coat- ings/po- tential con- trolled drug de- livery	Anodic EPD of HNT– HA–HYH composite films at room tempera- ture; sodium hyalu- ronate (HYNa) served as dispersing, charging, and film-forming agent for HNT and HA. Film composition and deposi- tion yield were tunable.	Proposed for biomed- ical implant coatings and controlled drug- delivery applications; direct cellular, osteo- genic, or in vivo eval- uation was not re- ported.	HNT provides the tubular clay component and potential nanocontainer functionality, whereas HA provides the cal- cium-phosphate bioactive phase. EPD and composite- film formation were experi- mentally demonstrated, but therapeutic loading/release and biological performance were proposed rather than di- rectly validated in this study. [40]
Mg ²⁺ /Gd ³⁺ - substi- tuted HAp/starc h/wollas- tonite (MHAP/St arch/WST) retained as an coating on Ti	Bentonite-de- rived wollas- tonite (WST); bentonite used as sili- cate precur- sor and not intact clay phase	Orthope- dic im- plant coat- ing/bone regener- ation	WST synthesized from bentonite by alkaline treatment and calcina- tion; 15% WST added to the MHAP/starch com- posite. MHAP contained Mg ²⁺ and Gd ³⁺ substi- tuted for Ca ²⁺ ; the com- posite was electropho- retically deposited on Ti.	Composite coating showed apatite for- mation in SBF, 11.25% degradation after 7 days, and enhanced MG-63 cell viability, ALP activity, and Ca mineralization rela- tive to HAP/MHAP controls.	Bentonite served only as a precursor for WST; therefore, the biological and mechanical responses cannot be at- tributed directly to intact ben- tonite. The final response re- flects the combined effects of WST, Mg ²⁺ /Gd ³⁺ -substituted HAp, and starch; in vivo bone regeneration was not evalu- ated. [58]
CTS– OMMT– HAP– ZrO ₂ hy- brid nano- compo- sites (CMZH I– III)	Organically modified montmorillo- nite (OMMT); layered clay; CTAB-modi- fied	Bone-tis- sue engi- neer- ing/or- thopedic implant material	CTS/OMMT/HAP–ZrO ₂ compositions: 90/5/5, 85/10/5, and 80/15/5 wt.% (CMZH I–III); HAP–ZrO ₂ phase con- tained 98 wt.% nano- HAP + 2 wt.% nano- ZrO ₂ . XRD/TEM indi- cated partially exfoliated OMMT in the CTS ma- trix.	Improved tensile and rheological proper- ties, antibacterial ac- tivity, blood compati- bility, and MG-63 cy- tocompatibility; CMZH I (90 wt.% CTS/5 wt.% OMMT/5 wt.% HAP–ZrO ₂) showed the most fa- vorable combined performance among	OMMT directly affected me- chanical behavior, swelling, antibacterial activity, and cell response; however, the sys- tem contains CTS, CTAB- modified MMT, HAP, and ZrO ₂ , so individual contribu- tions cannot be fully isolated. Antibacterial effects may partly arise from the quater- nary-ammonium modifier [59]

			the tested formula- tions.	rather than from montmoril- lonite itself.
CS-OM- HA po- rous com- posite scaffold	CTAB-modi- fied montmo- rillonite (OM); lay- ered clay	Non- load- bearing bone tis- sue engi- neering scaffold	OM = 10 wt.% and HA = 10 wt.% relative to chi- tosan; HA Ca/P = 1.67; microwave-assisted gas foaming followed by freeze-thawing and freeze-drying. CTAB modification increased MMT basal spacing; XRD indicated exfolia- tion of OM in the CS- OM-HA matrix. Inter- connected pores >100 µm were obtained.	Improved tensile properties and bioac- tivity; reduced swell- ing and degradation; altered protein ad- sorption; non-cyto- toxic toward MG-63 osteoblast-like cells. Intended for non- load-bearing bone-tis- sue engineering.
3D-print- ed PVA/COL /ATP/HA scaffolds	Nanoatta- pulgite (ATP); fi- brous/acicu- lar Mg-rich clay; 150–500 nm; unmodi- fied	Vascu- larized bone re- genera- tion/bon- e-defect repair	ATP:HA = 3:0, 2:1, 1:1, and 0:3 (<i>w/w</i>); corre- sponding PVA:COL:ATP:HA = 40:30:30:0, 40:30:20:10, 40:30:15:15, and 40:30:0:30. ATP im- proved ink rheology, printing fidelity, and wet-state compressive strength; ATP and HA incorporation was con- firmed by XRD/FTIR and elemental analysis.	ATP provides fibrous rein- forcement and releases Mg ²⁺ ; ATP-containing scaffolds di- rectly showed improved printability, mechanical per- formance, osteogenesis, and vascularization. However, the relative contributions of ATP morphology, Mg/Si-related chemistry, ion release, and in- teractions with HA were not independently resolved.

Note. The systems summarized in Table 7 differ in composition, architecture, fabrication, and validation level and therefore should not be ranked directly by individual mechanical or biological metrics. Proposed clay-specific contributions are distinguished from effects that cannot be separated from those of HAp, organic modifiers, polymer matrices, or other composite components.

The studies summarized in Table 7 demonstrate that halloysite is the most extensively explored clay mineral in biomedical HAp-containing systems, largely because its tubular morphology provides functions beyond conventional particulate reinforcement. In PCL-based porous scaffolds, HNT influenced not only mechanical reinforcement but also rheology and pore architecture, with the biological response strongly dependent on nanotube loading [61]. This finding illustrates an important structure–function relationship: the biomedical effect of the clay phase cannot be inferred from its intrinsic biocompatibility alone because clay-induced changes in scaffold architecture may indirectly regulate cell infiltration and osteogenic response.

Combining HAp and halloysite within the same polymer matrix introduces additional multifunctionality. In PCL/HA/HNT composites, HNT contributed mechanical reinforcement and simultaneously provided tubular loading sites for curcumin; however, therapeutic loading promoted nanotube aggregation and reduced mechanical performance [36]. This system therefore illustrates a recurring design trade-off in multifunctional HAp–clay materials: enhancement of therapeutic functionality may alter clay dispersion and interfacial reinforcement, and these functions cannot be optimized independently.

More recent work indicates that halloysite can play an even more active role by controlling HAp formation itself. In the biomineralization-inspired system reported in [56], HNT acted as a nanoscale template for calcium-phosphate nucleation and assembly, while poly(acrylic acid) regulated precursor formation and subsequent maturation toward highly crystalline HAp. The resulting hierarchical composite combined favorable mechanical properties with antibacterial activity, pH-responsive Ca^{2+} release, and preliminary cytocompatibility. This study is mechanistically important because halloysite functions not merely as a reinforcing filler or carrier but as a mineralization-directing template that influences the organization and maturation of the calcium-phosphate phase.

The mineralization-directing behavior reported in [34] can be viewed as an advanced development of earlier observations that HNT-containing surfaces promote apatite formation. For example, CS/HNT coatings deposited on titanium developed carbonated HAp around the nanotubes after five days in simulated body fluid, whereas the corresponding chitosan coating showed no comparable apatite deposition [35]. However, SBF-induced apatite formation should be interpreted as evidence of *in vitro* apatite-forming ability rather than direct proof of cellular biocompatibility or osseointegration. Together, these studies suggest an evolution from empirical observation of HNT-induced mineral deposition toward deliberate use of tubular clay morphology to control HAp nucleation, crystallization, and hierarchical assembly.

Halloysite has also been incorporated into electrophoretically deposited HAp-containing coatings, where its tubular morphology and surface-charge characteristics contribute to dispersion and spatial organization of the composite layer [39,40]. These studies demonstrate the feasibility of producing monolayer, multilayer, and functionally graded HAp–HNT architectures and further suggest potential carrier functionality of HNT within therapeutic implant interfaces. However, the available evidence remains predominantly materials-level; direct osteogenic responses, long-term coating stability, controlled therapeutic release, and *in vivo* osseointegration require further validation.

The therapeutic potential of halloysite-containing HAp composites was translated into a more application-oriented system by Guarch-Pérez et al. [38]. A 3D-printed PCL/HAp/HNT composite loaded with gentamicin provided sustained antibiotic release and demonstrated antibacterial efficacy in *ex vivo* and *in vivo* infection models. Importantly, the antimicrobial effect was associated with gentamicin rather than with the unloaded HAp/HNT composite itself. Moreover, the device was not designed for independent mechanical fracture stabilization, and the *in vivo* endpoint was limited to three days. Thus, ref. [38] represents a transition from proof-of-concept HNT drug-carrier functionality [36] toward an additively manufactured and *in vivo*-tested therapeutic device, although not yet a fully integrated load-bearing and bone-regenerating implant.

Comparison of halloysite- and montmorillonite-containing systems demonstrates that clay morphology and mineral structure govern the mode by which the clay phase contributes to biomedical performance. Halloysite primarily exploits its one-dimensional tubular geometry: it modifies rheology and pore formation [37], provides mechanical reinforcement [36], offers an internal lumen for therapeutic loading [36,38], and can act as a nanoscale template for calcium-phosphate nucleation and HAp assembly [34]. By contrast, montmorillonite contributes through its two-dimensional layered structure and interlayer chemistry. Organic modification expands the interlayer environment and improves compatibility with polymer matrices, enabling intercalation or partial exfoliation and extensive polymer–silicate interfacial interactions [59,60]. Consequently, halloysite is particularly suited to nanocontainer and mineralization-template functions, whereas montmorillonite is especially effective as an interfacial and matrix-reinforcing phase. These distinctions indicate that clay minerals should not be treated as interchangeable “nanoclay” additives in biomedical HAp composites; their morphology, surface

chemistry, interlayer accessibility, and modification state determine fundamentally different structure–property relationships.

The CS-OM-HA scaffold [60] provides a relatively direct example of complementary HAp–montmorillonite functionality, in which organomodified MMT contributes interfacial and polymer-matrix reinforcement while HAp provides complementary bioactivity. Although the resulting porous scaffold showed improved mechanical and biological properties relative to the corresponding controls, its strength remained insufficient for load-bearing applications and validation was limited to *in vitro* testing. The more complex CTS-OMMT-HAp-ZrO₂ system [59] further improved mechanical and multifunctional performance through partial OMMT exfoliation and incorporation of an additional ceramic phase. However, this increased compositional complexity also makes it difficult to distinguish the individual contributions of montmorillonite, its organic modifier, HAp, and ZrO₂.

Fibrous clay minerals provide a third mineralogical route to biomedical functionality. Ma et al. [43] demonstrated that nanoattapulgite incorporated into 3D-printed PVA/collagen/HAp scaffolds improved ink rheology, printing fidelity, and wet-state mechanical integrity while simultaneously enhancing osteogenic and angiogenic responses. In a rabbit tibial defect model, ATP/HAp-containing scaffolds promoted both new-bone formation and vascularization relative to HAp-containing controls. These findings extend the structure–function relationships identified for tubular halloysite and layered montmorillonite to fibrous clay architectures. However, the respective contributions of ATP morphology, Mg/Si-containing mineral functionality, HAp, and the overall scaffold architecture remain incompletely resolved.

Organic modification of montmorillonite requires particular attention when interpreting biomedical performance. Alkylammonium modification can improve clay dispersion and compatibility with polymer matrices and may facilitate intercalation or exfoliation, but the modifier itself can also influence surface properties, antimicrobial behavior, and biological response. Therefore, biological or antibacterial effects observed for OMMT-containing composites should not automatically be attributed to the montmorillonite mineral itself. Distinguishing intrinsic clay-mineral effects from modifier-induced functionality is essential when evaluating biomedical performance and when comparing organoclays with pristine or naturally occurring clay minerals [59,60].

A conceptually different strategy was reported in [58], where bentonite was not retained as an intact clay phase but served as a low-cost silicate precursor for wollastonite, which was subsequently incorporated into an HAp-containing coating on titanium. This approach broadens the role of clay resources in biomedical HAp materials from direct structural components to precursors of bioactive secondary mineral phases. However, because the final system contains wollastonite rather than intact bentonite and includes multiple functional components, the specific contribution of the original clay resource to the resulting biomedical performance cannot be isolated.

Taken together, the studies summarized in Table 7 demonstrate a progressive broadening of design strategies in biomedical HAp–clay composites. Relatively simple systems incorporate clay and HAp into polymer matrices or composite coatings [39,40], whereas other approaches exploit clay-dependent control of scaffold architecture, mechanical properties, and biological response [37,43,60]. Additional functionality has been introduced through therapeutic loading, ceramic reinforcement, and surface or interlayer modification [36,59]. More application-oriented systems extend these concepts toward additive manufacturing and *in vivo* antimicrobial validation [38], while mineralization-directed designs demonstrate that the clay phase can actively influence HAp nucleation and hierarchical organization [34]. Collectively, these studies show that the clay phase can function not only as a reinforcing component but also as an interfacial regulator,

nanocarrier, mineralization-directing template, or contributor to scaffold-level biological functionality, depending on its mineralogy and composite architecture.

These studies also demonstrate that increasing compositional or architectural complexity does not automatically improve biomedical performance. Higher clay loading may increase stiffness while compromising pore interconnectivity and cellular response [37]; therapeutic loading may promote aggregation and reduce mechanical performance [36]; and incorporation of multiple functional phases can broaden material functionality while making the contributions of individual components more difficult to distinguish [58,59]. Consequently, optimization of HAp–clay biomedical composites should balance mechanical, architectural, biological, and therapeutic requirements rather than maximize any single material property.

Key implication: Biomedical performance in HAp–clay composites depends on the mineralogy, morphology, and modification state of the clay phase rather than on the generic incorporation of “nanoclay.” Tubular halloysite, layered montmorillonite, and fibrous attapulgite provide distinct routes to reinforcement, interfacial organization, mineralization, therapeutic delivery, and control of scaffold architecture, while clay-derived phases can provide additional bioactive functionality. Accordingly, the clay component should be selected according to the intended structure–function relationship and evaluated together with the complementary bone-related mineral functionality provided by HAp.

Research gap: Despite substantial progress in mechanical reinforcement, scaffold fabrication, biomineralization, and therapeutic functionality, evidence supporting clinical translation of HAp–clay biomedical composites remains limited. Most studies rely on physicochemical characterization, simulated-body-fluid testing, or in vitro cell models, while in vivo validation remains comparatively scarce, although it now includes short-term antimicrobial evaluation [38] and vascularized bone regeneration in a rabbit tibial defect model [43]. Long-term fate and safety of the clay phase also require greater attention, particularly for organomodified montmorillonite, where modifier-related effects must be distinguished from intrinsic clay-mineral functionality, and for halloysite, where persistence, degradation, and dose-dependent responses should be established for the final composite. Future studies should integrate rigorous mineralogical characterization with standardized mechanical and biological testing, long-term degradation and inflammatory assessment, and clinically relevant in vivo models. Direct comparison of different clay minerals under otherwise matched HAp/polymer compositions would be particularly valuable for establishing robust mineralogy–structure–biological-function relationships.

4.2. Mineralogical Control of HAp–Clay Interactions in Biomedical Composites

The application-level comparisons discussed above demonstrate that biomedical performance depends strongly on clay mineralogy. At the mechanistic level, these differences arise from the distinct nanoscale environments provided by individual clay minerals, including their crystal structure, morphology, layer charge, interlayer accessibility, surface chemistry, and modification state. Halloysite and montmorillonite provide particularly well-studied examples of how contrasting mineral architectures can regulate HAp nucleation and interfacial organization through fundamentally different pathways.

For halloysite, available evidence indicates a surface- and morphology-directed mineralization pathway. HNT-containing surfaces can promote apatite formation [35], while biomineralization-inspired systems demonstrate that tubular halloysite can participate more directly in calcium-phosphate nucleation, assembly, and maturation toward HAp [34]. These observations support a mineralization-directing role for HNT beyond conventional reinforcement or carrier functionality. However, the respective contributions of the

external siloxane surface, aluminol-containing lumen, nanotube curvature, and nanoscale confinement remain insufficiently resolved.

A fundamentally different mineralization pathway has been demonstrated for montmorillonite. Ambre et al. [7] used SWy-2 Na-montmorillonite modified with 5-aminovaleric acid to create chemically active interlayer environments for in situ HAp mineralization. In this system, modification of the expandable MMT galleries was not simply intended to improve polymer compatibility. Instead, the intercalated amino acid provided functional sites capable of mediating mineral nucleation. FTIR evidence indicated interactions between modifier-derived carboxylate groups and Ca^{2+} , consistent with chelate formation and the creation of probable nucleation sites for apatite [7]. Mineralization was accompanied by a decrease in the MMT basal spacing from 12.81 to 12.30 Å, demonstrating that HAp formation reorganized the modified interlayer environment rather than occurring independently of the clay structure. The resulting apatite also exhibited shifts in XRD reflections and phosphate vibrational bands relative to conventionally synthesized HAp, indicating that nanoconfinement and interfacial chemistry affected the developing HAp structure [7].

Molecular-dynamics analysis subsequently provided a mechanistic interpretation of these observations [8]. The model explicitly accounted for the T–O–T structure and layer charge of SWy-2 MMT and showed that protonated 5-aminovaleric acid replaced interlayer Na^+ and became strongly associated with the charged clay surfaces. Experimentally, the Na exchange capacity decreased from 40.54 meq/100 g for Na-MMT to 0.96 meq/100 g after organic modification, supporting extensive replacement of interlayer Na^+ by the protonated modifier [8]. Molecular simulations further showed that, despite different initial orientations, the aminovaleric-acid molecules tended to adopt orientations approximately parallel to the MMT surfaces, demonstrating that the clay galleries actively organize the modifier rather than merely accommodating it.

Importantly, the simulations identified the organic modifier as the principal molecular bridge between MMT and HAp. For the perpendicular OMMT–HAp configuration, the calculated total non-bonded interaction energies were −1511 kcal/mol for HAp–aminovaleric acid and −1609 kcal/mol for MMT–aminovaleric acid, compared with −557 kcal/mol for the direct MMT–HAp interaction. A similar relationship was obtained for the parallel configuration, where HAp–modifier and MMT–modifier interactions were −1746 and −1937 kcal/mol, respectively, compared with only −202 kcal/mol for direct MMT–HAp interaction. Thus, HAp interacts with the clay predominantly through the chemically organized aminovaleric-acid interface rather than through simple direct contact between two inorganic phases.

The molecular interaction pattern was more complex than a single Ca^{2+} –carboxylate linkage. Attractive Ca–COOH interactions supported the experimentally proposed chelation mechanism, whereas particularly strong NH_3^+ – PO_4^{3-} attraction demonstrated that the amino functionality also participates in organization of the developing mineral interface [8]. At the same time, phosphate groups experienced strong attractive and repulsive interactions with MMT and neighboring modifier groups. These interactions provide a molecular explanation for the phosphate-band shifts previously observed by FTIR and demonstrate that the local environment of phosphate in biomineralized HAp differs from that in conventional HAp. The simulations also reproduced the experimentally observed tendency toward contraction of the organically modified galleries after HAp formation: the OMMT model had a calculated basal spacing of 14.08 Å, whereas the perpendicular and parallel OMMT–HAp configurations decreased to 13.92 and 13.08 Å, respectively. Thus, HAp–clay interactions in this system are reciprocal: MMT interlayer chemistry controls HAp nucleation, while mineral formation simultaneously reorganizes the modifier conformation and clay interlayer structure.

The structural consequences of this nanoconfined mineralization extend beyond basal-spacing changes. TEM–EELS analysis of the same biomineralized HAPclay platform demonstrated rounded apatite morphologies distinct from conventional synthetic HAP and revealed subtle differences in the local electronic environments of Ca and P [62]. Changes in Ca outer-shell transitions and P-L_{2,3} near-edge features indicated that the clay-controlled mineralization environment influenced the electronic structure of the resulting apatite. These findings are particularly significant when considered together with the molecular-dynamics results of [8]: the strong electrostatic and non-bonded interactions predicted around Ca and PO₄ species provide a plausible molecular basis for the altered local environments detected experimentally by EELS. Nevertheless, these differences should be interpreted as modifications of local coordination and electronic structure within biomineralized HAP rather than evidence for formation of an entirely different calcium-phosphate mineral phase.

The biological relevance of this mineralogical control was subsequently investigated using the same in situ HAPclay platform incorporated into chitosan/polygalacturonic-acid matrices [63]. Human mesenchymal stem cells adhered to the HAPclay-containing scaffolds, exhibited osteogenic differentiation, and formed mineralized extracellular matrix and Alizarin-Red-positive nodules even in the absence of conventional osteogenic supplements [63]. Particularly importantly, changing the order in which HAPclay interacted with the two biopolymers altered scaffold microstructure and cellular organization despite an unchanged nominal HAPclay content. This observation extends the mineralogical argument from composition to interface formation: the biological expression of a clay–HAP system depends not only on the mineral phases present but also on how processing determines exposure and organization of the mineral–polymer interfaces.

Taken together, refs. [7,8,63,64] provide an unusual multiscale case study linking clay mineral structure to biological performance. The sequence can be described as MMT layer charge and interlayer accessibility → amino-acid intercalation and molecular organization → modifier-mediated Ca/phosphate interactions → HAP nucleation and altered lattice/local electronic environment → processing-dependent composite architecture → osteogenic cellular response. However, this sequence should not be interpreted as proof that the altered HAP electronic structure itself causes osteogenic differentiation. The electronic-structure differences identified in [64] coexist with the favorable hMSC response observed for the same biomineralized mineral platform [63], but a direct causal relationship has not yet been demonstrated.

Comparison of halloysite and montmorillonite therefore reveals two distinct routes by which clay mineralogy can regulate HAP-containing biomedical composites. Halloysite primarily exploits its one-dimensional tubular morphology, surface heterogeneity, and nanoscale confinement to regulate mineral assembly, composite rheology, pore structure, and therapeutic loading [34–38]. Montmorillonite, by contrast, exploits its expandable 2:1 layered structure, permanent layer charge, exchangeable interlayer cations, and chemically modifiable galleries to organize intercalated molecules and create tailored environments for HAP nucleation [7,8,59,63,64]. In the amino-acid-modified MMT system, the clay does not simply provide a surface for apatite deposition; its charged interlayer structure organizes the modifier that subsequently mediates the HAP–clay interface. In halloysite, mineralization control appears to be more strongly associated with tubular geometry and surface-mediated assembly. Thus, both clay minerals can function as mineralization-directing components, but the underlying mechanisms are fundamentally different.

This distinction also demonstrates why the broad term nanoclay is inadequate for mechanistic interpretation of biomedical HAP–clay composites. Tubular halloysite and expandable smectites differ in layer topology, charge origin, swelling behavior, accessible

surface environments, and response to organic modification. Consequently, replacing one clay mineral with another cannot be assumed to preserve HAp nucleation behavior or biological functionality. Even within a single mineral group, layer charge, isomorphic substitution, exchangeable cation composition, particle dimensions, purity, and modification chemistry may alter the HAp–clay interface. Mineralogical characterization should therefore be treated as a design requirement rather than simply as compositional identification.

Key implication: The reviewed biomedical studies demonstrate that HAp–clay composite functionality depends on mineral-specific interfacial organization rather than on clay incorporation alone. Crystal structure, layer charge, surface and interlayer chemistry, morphology, and modification state can influence HAp nucleation, composite architecture, and subsequent biological responses. However, these effects must be distinguished from the contributions of organic modifiers, polymer matrices, and processing conditions. Accordingly, rational biomedical composite design requires mineralogical characterization and experimentally supported evaluation of the relationships between interfacial structure and functional performance.

Research gap: Despite increasingly detailed evidence for mineralogy-dependent HAp–clay interactions, direct structure–function comparisons among different clay minerals remain scarce. In particular, the relative contributions of clay morphology, layer charge, isomorphic substitution, interlayer cation composition, surface hydroxyl chemistry, organic modification, and nanoconfinement to HAp nucleation and crystal development have rarely been isolated under otherwise identical synthesis conditions. For organomodified MMT, the biological response cannot yet be separated unequivocally from the effects of the organic modifier, altered HAp structure, ion release, scaffold microarchitecture, and polymer–mineral interface. Similarly, the respective contributions of the external surface, lumen chemistry, and curvature of halloysite to HAp mineralization remain insufficiently resolved. Future studies should combine well-characterized reference clay minerals with controlled HAp synthesis, molecular simulations, advanced spectroscopic and diffraction methods, quantitative dissolution/ion-release measurements, and standardized osteogenic models. Direct comparisons of tubular, expandable layered, fibrous, and non-expandable clay minerals under matched experimental conditions would be particularly valuable for establishing causal mineralogy–interface–HAp structure–biological function relationships.

5. Preparation and Characterization of Hydroxyapatite–Clay Composites

The preparation route is a critical determinant of the structure and functionality of HAp–clay composites because it governs not only HAp phase composition, crystallinity, particle morphology, and size, but also the mode and extent of interfacial contact between HAp and the clay mineral. HAp and HAp-based composites can be prepared using a broad range of synthesis and processing routes, including wet-chemical precipitation, hydrothermal and sol–gel processes, mechanochemical treatment, and microwave-assisted approaches [1,2,62]. When these approaches are extended to clay-containing systems, synthesis history additionally governs the spatial organization and physicochemical nature of the HAp–clay interface. Consequently, materials containing nominally similar HAp and clay components may exhibit substantially different properties depending on whether the phases are generated together, assembled from preformed particles, or subjected to subsequent thermal or mechanical treatment. This distinction is particularly important for mineralogy-informed interpretation because clay crystal structure, surface chemistry, exchangeable cations, and interlayer accessibility can influence Ca^{2+} localization and subsequent calcium-phosphate nucleation.

The relationships between preparation route, HAp–clay interfacial organization, resulting material characteristics, and functional performance are summarized schematically in Figure 2. Although individual preparation methods differ in processing conditions and degree of structural control, they regulate HAp formation and/or spatial distribution relative to the clay phase and thereby influence phase composition, Ca/P ratio, crystallinity, morphology, specific surface area, porosity, and interfacial organization.

Wet-chemical precipitation and in situ precipitation are among the most relevant routes for preparing HAp–clay composites. In a conventional precipitation process, soluble Ca^{2+} and phosphate precursors are reacted under controlled pH, followed by aging, filtration, washing, drying, and, where required, calcination. When precipitation is performed in the presence of dispersed clay particles, HAp nucleates and grows directly within the clay-containing reaction environment rather than being synthesized separately and subsequently blended with the mineral phase. This in situ configuration can increase interfacial contact and promote a more homogeneous distribution of calcium-phosphate particles over accessible clay surfaces. Its principal advantages are relatively simple aqueous processing, compositional control, and the possibility of regulating HAp nucleation through pH, precursor concentration, Ca/P ratio, temperature, aging time, and clay loading. Conversely, these same variables make the method sensitive to synthesis conditions. In HAp precipitation, parameters such as reagent addition rate, reaction temperature, stirring rate, ripening time, initial Ca concentration, solvent composition, dispersant, and drying conditions can influence phase composition, purity, crystallinity, crystallite or particle size, particle-size distribution, morphology, and dispersibility [65–68]. Inadequate control of Ca/P stoichiometry may additionally promote the formation of secondary calcium-phosphate phases [66].

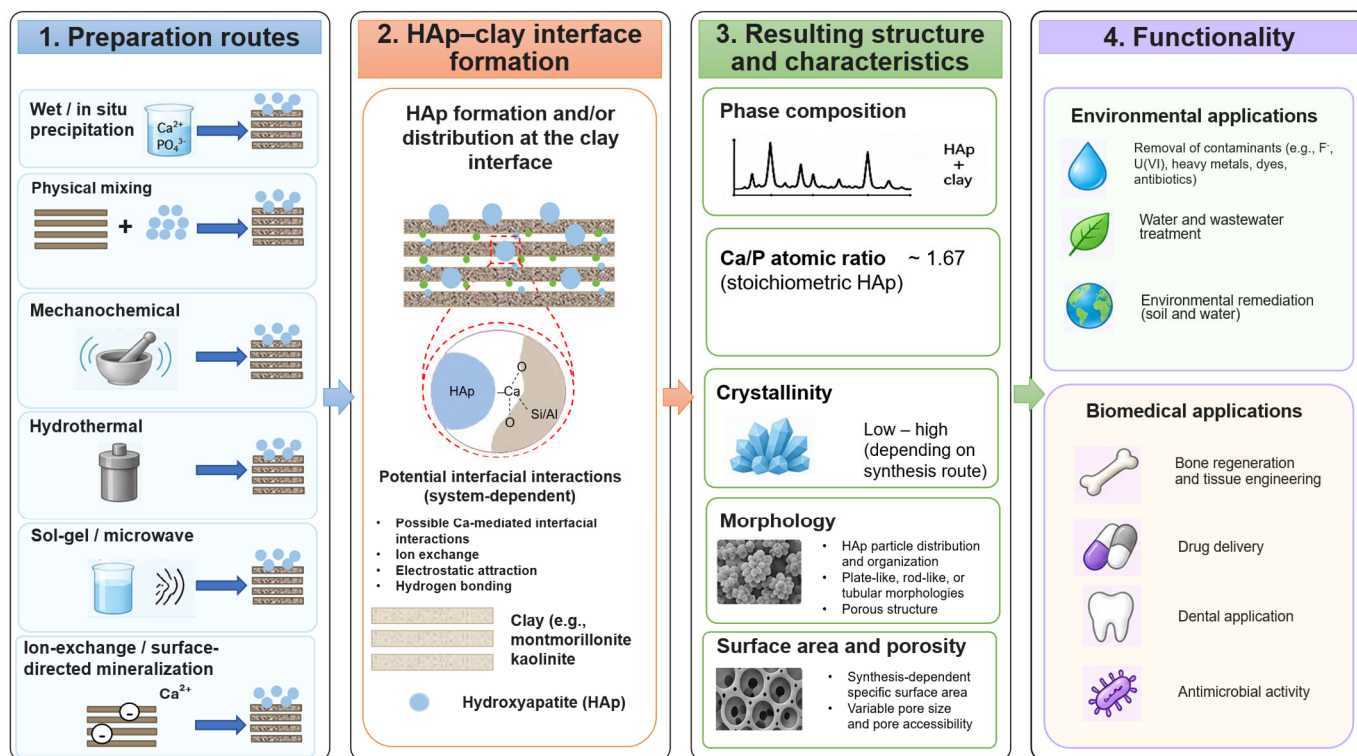


Figure 2. Preparation–interface–structure–function relationships in HAp–clay composites.

Precipitation-based synthesis has been directly applied to clay-containing HAp systems. Ersan et al. [56] prepared hydroxyapatite/clay composites for tetracycline removal from aqueous solution, providing an application-specific example of a precipitation-based

HAp–clay adsorbent. Such studies demonstrate the practical applicability of precipitation-based routes to environmental HAp–clay adsorbents and complement studies in which HAp is synthesized separately and subsequently combined with the clay phase.

The importance of distinguishing in situ formation from post-synthesis blending is illustrated by reported HAp–clay systems. HAp has been combined with kaolinite, bentonite, halloysite, montmorillonite, and other clay minerals through precipitation-based or wet-chemical routes, while other studies have used separately synthesized HAp followed by physical incorporation of the clay phase. In the latter approach, preparation is experimentally straightforward but interfacial organization is governed primarily by mixing and subsequent thermal treatment rather than by clay-directed HAp nucleation. For example, Annan et al. synthesized HAp from eggshell-derived CaO by wet precipitation at pH 10, followed by aging, drying, and calcination; the resulting HAp was subsequently mixed with halloysite, kaolinite, or bentonite at clay contents corresponding to 10%–20% of the HAp mass and dried at 110 °C [30]. This approach therefore represents post-synthesis physical assembly rather than true in situ HAp mineralization on the clay. Such distinctions are important when comparing reported composite performance because similar labels such as “HAp–bentonite” may describe fundamentally different interfacial architectures.

Mechanochemical processing provides an alternative route in which mechanical energy generated during grinding or milling promotes intimate mixing and modification of the physicochemical properties of the constituent phases. Depending on the starting materials, mechanochemical treatment may be applied to preformed HAp-containing mixtures or incorporated into multistep processing routes involving calcium-phosphate precursors. Compared with conventional solution-based synthesis, mechanochemical processing can reduce solvent requirements and facilitate intimate contact between the constituent phases. At the same time, intensive milling may modify particle size, surface and textural properties, crystallinity, and structural order; therefore, milling conditions require careful control to preserve the desired phase composition and functionality of the final composite. The applicability of this approach to clay-containing HAp systems has recently been demonstrated for yellow clay/HAp-based composites prepared by a mechanochemical route [69].

Hydrothermal processing offers greater control over HAp crystallinity and morphology. In this route, calcium and phosphate precursors are reacted in an aqueous medium at elevated temperature and autogenous or externally controlled pressure, generally in an autoclave. Hydrothermal conditions can produce HAp with different particle sizes and morphologies, depending on precursor chemistry, pH, temperature, pressure, and reaction time [70,71]. This capability is advantageous where crystal morphology and phase purity are critical, particularly for biomedical composites. The principal limitations include the requirement for pressure-resistant equipment and comparatively demanding control of temperature, pressure, and reaction time [70,71]. For clay-containing systems, hydrothermal processing can additionally promote HAp formation in close association with mineral surfaces or accessible interfacial regions, as demonstrated for hydrothermally prepared montmorillonite–HAp and attapulgite–HAp composites [41,48]. Consequently, both the calcium-phosphate and clay phases should be characterized after synthesis to establish the resulting mineralogical and interfacial structure.

Sol–gel and microwave-assisted approaches provide additional routes for controlling HAp formation. Sol–gel processing relies on hydrolysis, condensation, and gelation of Ca- and P-containing precursors and can provide good compositional homogeneity and control of particle or crystallite dimensions, but it generally requires more elaborate precursor chemistry and subsequent drying and thermal treatment. Microwave-assisted synthesis provides rapid and volumetric heating and can substantially shorten reaction times, while

microwave–hydrothermal combinations can further regulate nucleation and crystal growth. These approaches are well established for HAp synthesis, although their application to mineralogically well-characterized HAp–clay systems remains less systematic than conventional precipitation-based routes. The available HAp literature confirms precipitation, sol–gel, microwave-assisted, hydrothermal, and microwave–hydrothermal synthesis as established routes [1,2]. Accordingly, their advantages should be interpreted in relation to the required composite architecture rather than ranked universally as intrinsically superior or inferior methods.

Ion-exchange-assisted or surface-directed mineralization is particularly relevant from a clay-mineralogical perspective. Expandable 2:1 clay minerals such as montmorillonite possess permanent layer charge and exchangeable interlayer cations, providing chemically distinct environments for Ca^{2+} uptake and subsequent phosphate interaction. Depending on clay pretreatment and interlayer accessibility, this can favor HAp nucleation at clay surfaces or within modified galleries and can produce interfaces that differ fundamentally from those obtained by simple mechanical mixing [7,8,72]. Organomodification adds another level of control because functional groups introduced into the interlayer can participate directly in HAp–clay interactions [7,8,73]. Consequently, the preparation method cannot be separated from clay mineralogy: the same synthesis route may generate different HAp distributions and interfaces in expandable layered, non-expandable layered, tubular, and fibrous clay minerals.

Irrespective of the synthesis route, control of HAp phase composition and stoichiometry is essential. Stoichiometric HAp has a Ca/P atomic ratio of approximately 1.67, whereas calcium-deficient or substituted apatites can exhibit different surface charge, solubility, and reactivity [74]. In clay-containing reaction media, additional complexity arises because negatively charged surfaces and, in expandable minerals, exchangeable interlayer sites can provide chemically distinct environments for Ca^{2+} localization and subsequent calcium-phosphate nucleation, as demonstrated particularly for modified montmorillonite systems [7,8]. Moreover, precursor chemistry and thermal treatment can influence the phase composition and stability of HAp relative to other calcium-phosphate phases [66,75]. Therefore, nominal precursor stoichiometry alone is insufficient to establish the composition of the final HAp phase, and direct mineralogical and chemical characterization of the resulting composite is required. Natural-clay variability further complicates reproducibility because mineral purity, accessory phases, exchangeable cations, and surface chemistry may vary among deposits and even among batches from the same source.

Characterization of HAp–clay composites should therefore be designed to establish both constituent phases and their interface rather than merely confirm the presence of HAp. Because HAp properties depend strongly on phase composition, morphology, and microstructure, these characteristics should be controlled and verified during both synthesis and subsequent processing [76]. X-ray diffraction (XRD) is essential for identifying crystalline HAp and clay phases, detecting secondary calcium phosphates or thermally induced phases, and estimating crystallite dimensions or phase fractions where appropriate. Fourier-transform infrared spectroscopy (FTIR) provides complementary evidence for phosphate, hydroxyl, silicate/aluminate, carbonate, and modifier-related functional groups and can reveal changes associated with composite formation. SEM and TEM provide information on particle morphology, HAp distribution, aggregation, clay architecture, and interfacial organization, while EDS/EDX supports local elemental identification and mapping. BET gas sorption is useful for quantifying specific surface area and pore characteristics, whereas particle-size analysis and zeta-potential measurements provide information relevant to dispersion and surface-charge-dependent interactions [9,76]. The need for this complementary approach is demonstrated by individual HAp–clay studies; for example, BT–HAp materials have been characterized by XRD, FTIR, FESEM/EDX,

TEM/HRTEM, and BET because no single technique can independently resolve phase identity, morphology, elemental composition, crystallinity, and textural properties [9]. In another example, Annan et al. primarily used XRD and FTIR to characterize the synthesized HAp before its incorporation with the clay phases, illustrating the variable depth of mineralogical characterization across the literature [30].

For biomedical HAp–clay materials, structural characterization should be complemented by porosity, mechanical, degradation, and biological measurements, because architectural parameters required for tissue integration may be accompanied by changes in mechanical performance [2,77–80]. Processing conditions can additionally influence the mechanical integrity and interfacial performance of HAp-based materials; for example, the properties, adhesion, and cohesion of plasma-sprayed HAp coatings depend on the technological parameters used during coating fabrication [81]. HAp ceramics themselves exhibit an inherent trade-off between biological architecture and mechanical performance, and processing temperature can alter densification and phase stability [82]. Dense and porous HAp are therefore not functionally interchangeable, and their processing conditions must be interpreted in relation to the intended application.

For environmental adsorbents, characterization before and after contaminant uptake is particularly valuable because changes in phase composition, surface chemistry, elemental distribution, or solution chemistry can distinguish adsorption from ion exchange, surface complexation, or dissolution–precipitation mechanisms.

Overall, no single preparation route is universally optimal for HAp–clay composites. The selection of synthesis and processing conditions should account for clay mineralogy, modification state, the intended HAp–clay interfacial organization, and the target application. Reliable comparison among composites requires reporting the mineralogical composition and purity of the clay material, HAp/clay ratio, phase composition, Ca/P ratio where available, crystallinity, morphology, surface area, porosity, and relevant processing parameters. Such characterization is essential for distinguishing mineralogy-dependent effects from differences arising from synthesis history and composite architecture.

6. Conclusions

Hydroxyapatite–clay composites have developed from relatively simple combinations of two low-cost mineral phases into multifunctional materials with increasingly controlled interfacial chemistry, hierarchical structure, and application-specific performance. The studies reviewed here indicate that the functional performance of these composites cannot always be explained by the properties of HAp or the clay component considered independently. Instead, their properties emerge from interactions among HAp, clay mineral surfaces or interlayers, modifiers, and, where present, polymeric phases. Consequently, the mineralogical characteristics of the clay phase—including layer structure, morphology, surface chemistry, layer charge, cation-exchange capacity, swelling behavior, and susceptibility to intercalation or surface modification—represent fundamental design variables for HAp–clay composites.

In environmental remediation, combining HAp with clay minerals can integrate the strong affinity of calcium-phosphate phases for selected ionic contaminants with the high surface area, ion-exchange properties, porosity, and structural versatility of clays. The resulting composites have been investigated for the removal of heavy metals, radionuclides, fluoride, dyes, and emerging organic contaminants. Across these applications, adsorption commonly involves multiple concurrent mechanisms, including surface complexation, ion exchange, electrostatic interactions, precipitation or dissolution–reprecipitation, and interactions with surface functional groups. Modification of the clay phase can further alter surface charge and accessibility, as illustrated by surfactant-modified bentonite and montmorillonite systems. However, the reported adsorption capacities should not be

interpreted independently of experimental conditions, because pH, contaminant speciation, ionic strength, competing ions, adsorbent dosage, and solution composition can substantially change apparent performance. The most convincing future advances will therefore require a shift from optimization in simplified batch systems toward mechanistically resolved testing in multicomponent and environmentally realistic waters.

Biomedical applications reveal an equally important but different expression of HAp–clay complementarity. HAp provides a bone-related calcium-phosphate phase, whereas clay minerals can regulate mechanical reinforcement, scaffold architecture, mineral nucleation, interfacial organization, and therapeutic delivery. Importantly, these functions depend on clay mineral structure rather than on the generic incorporation of a “nanoclay” phase. Tubular halloysite can influence rheology and pore formation, provide an internal compartment for therapeutic agents, and participate in the organization of calcium-phosphate mineralization. Expandable montmorillonite operates through a different mineralogical mechanism: its permanent layer charge, exchangeable interlayer cations, and accessible galleries permit intercalation and chemical functionalization, enabling the interlayer environment to participate directly in HAp nucleation and composite organization. These differences demonstrate that clay minerals with contrasting structures should not be considered interchangeable fillers in biomedical HAp composites.

Particularly significant are studies demonstrating that HAp–clay interactions can be reciprocal rather than simply additive in selected chemically modified montmorillonite systems. In amino-acid-modified montmorillonite, the chemically organized interlayer environment directs HAp nucleation, while mineral formation simultaneously reorganizes the modified clay structure [7,8]. Molecular simulations indicate that this interaction is mediated predominantly through the intercalated organic modifier rather than through direct contact between HAp and MMT [8]. Complementary nanoscale and biological studies further show that clay-controlled mineralization is associated with changes in apatite morphology and local electronic structure [64] and with favorable osteogenic responses in HAp/clay-containing scaffolds [63]. Together, these findings illustrate how clay mineralogy and interfacial organization can propagate across multiple structural scales toward functional biological outcomes, although direct causal links between specific mineral-structural changes and osteogenic response remain to be established.

A central conclusion of this review is that clay mineralogy should be treated as an active design parameter rather than merely as a source of inexpensive support or reinforcement. However, the functional contributions of individual clay minerals must be distinguished from those of HAp, organic modifiers, polymers, and secondary phases. Such differentiation is essential for establishing reliable mineralogy-dependent structure–property relationships.

Despite the substantial progress summarized in this review, several limitations continue to restrict translation of HAp–clay composites. Natural clay variability and incomplete mineralogical characterization complicate comparison among studies, while differences in synthesis procedures, HAp/clay ratios, particle dimensions, modification routes, and testing protocols further limit quantitative cross-study evaluation. Environmental studies require greater emphasis on realistic contaminant concentrations, competing species, continuous-flow operation, regeneration, and management of contaminant-loaded materials. Biomedical studies require long-term degradation and ion-release measurements, assessment of inflammatory and immune responses, standardized osteogenic testing, and substantially more *in vivo* evidence for bone regeneration and osseointegration. In both fields, increasingly complex multicomponent formulations may improve apparent functionality while simultaneously making it more difficult to identify the contribution of the clay mineral itself.

Preparation conditions further influence HAp–clay composite structure and performance by controlling phase composition, particle distribution, and interfacial organization. Accordingly, reproducible comparisons require consistent reporting of clay mineralogy and purity, modification state, HAp/clay composition, and relevant structural and processing parameters. This information is essential for separating mineralogical effects from those introduced by synthesis and subsequent treatment.

Future progress should therefore move toward mineralogy-informed and mechanism-driven design. Well-characterized reference clay minerals should be compared under matched synthesis and testing conditions, with particular attention to layer charge, exchangeable cations, surface hydroxyl chemistry, interlayer accessibility, particle morphology, and mineral impurities. Advanced diffraction and spectroscopic characterization, microscopy, molecular simulations, and quantitative interfacial analyses should be integrated with application-level testing to connect clay structure with HAp nucleation, interfacial energetics, adsorption or biological response. Such an approach could establish predictive mineralogy–interface–structure–function relationships, allowing the clay phase to be selected deliberately for a required function rather than empirically incorporated into a composite. This transition from composition-based formulation to mineralogically controlled materials design is likely to be central to the development of the next generation of HAp–clay composites for environmental remediation and biomedical applications.

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Abbreviations

BT–HAp—bentonite–hydroxyapatite; CHA–BENT–NCC—hydroxyapatite–bentonite clay–nanocellulose; ACC–HAp—activated carbon–clay pellets coated with hydroxyapatite; TK–NC—MnFe₂O₄-doped hydroxyapatite/kaolinite/biochar; TV–NC—MnFe₂O₄-doped hydroxyapatite/vermiculite/biochar; qmax—maximum adsorption capacity.

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