



Review

Bentonite-Based Composites in Medicine: Synthesis, Characterization, and Applications

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Abstract: One of the most interesting and poorly studied carriers of medicinal substances is the polymer clay composite material (PCCM). Bentonite clays are used in pharmacy for the manufacturing of various dosage forms, as well as in the adsorption of drugs to slow their release. Polymer–clay nanocomposites have demonstrated significantly improved properties compared to pure polymers. A review of recent scientific advances has shown promising results regarding the application of polymer–clay materials in medicine and bioengineering, particularly in the development of carrier sorbents with prolonged action for controlled drug release. As a result, interest in polymer–clay systems is steadily growing and gaining momentum. This paper focuses on the structure and properties of bentonite clays, including their sorption, ion exchange, binding, and rheological properties. The methods for preparing intercalated and exfoliated nanocomposites, such as radical intercalative polymerization in situ on clay surfaces, are reviewed. Furthermore, the improved efficacy and exposure times of PCCMs, combined with their enhanced bactericidal properties, are analyzed for the creation of universal and multifunctional preparations for medical use.

Keywords: bentonites; polymer composites; montmorillonite; organoclay; sorption properties; clay modification; intercalated nanocomposites; exfoliated nanocomposites



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1. Introduction

The search for effective treatments for chronic, slow-healing wounds is of both fundamental and applied interest, particularly in the development of universal, multifunctional medical formulations containing multiple active pharmaceutical ingredients (APIs) with synergistic therapeutic effects. Some of the most promising yet underexplored carriers for such APIs are polymer–clay composite materials (PCCMs).

In recent years, bentonite clays have been increasingly utilized in pharmaceutical applications, including the formulation of various dosage forms and the adsorption of drugs to control and prolong their release. PCCMs have demonstrated significantly enhanced properties compared to pure polymers. Layered silicate clays such as bentonite

are frequently used as fillers in polymer composites due to their large specific surface area, cation exchange capacity, low cost, and biocompatibility.

The introduction of organic or inorganic components into polymer matrices enables the creation of composite materials with a broad range of functional properties. Composite materials combine natural or synthetic components with a polymer matrix, resulting in materials that exhibit the ideal physical and chemical properties of each component [1]. Depending on the intended application, different polymers are used as the matrix. The matrix serves as a binder, holding and transferring loads to the reinforced materials, which can range from organic to inorganic, in polymer composites [2].

Polymer composites incorporating clay-based materials occupy a prominent position and are gaining increasing attention due to the tightening of environmental regulations. This trend has spurred a growing demand for natural, cost-effective clay minerals. Among the most promising for polymer and natural fiber modification are nanoclays such as montmorillonite, organoclay, saponite, and halloysite. Bentonite clays also fall into this category, offering a range of practically valuable properties, including their sorption capacity, ion exchange ability, high binding efficiency, and favorable rheological behavior.

The use of modified bentonite—particularly that treated with silver ions or silver nanoparticles—can significantly enhance the functional performance of the resulting polymer composite materials (PCMs) by imparting bactericidal properties [3]. Special emphasis is placed on environmentally friendly (“green”) synthesis approaches for silver nanoparticles, particularly their biosynthesis via the reduction of silver salts using plant extracts [4,5].

To achieve a substantial improvement in the properties of polymer nanocomposites, it is essential to ensure the uniform dispersion of silicate nanoparticles within the polymer matrix. A fundamentally novel application of such materials lies in the development of therapeutic films, which are applied as dressings to skin, wounds, burns, and mucous membranes.

Natural bentonites are employed as fillers in these systems. A special place is occupied by compositions of polymers with clay materials, which are gaining prominence due to increasingly stringent environmental legislation. This has created a growing need for natural, inexpensive clay materials. Nanoclays, such as montmorillonite, organoclay, saponite, and halloysite, are particularly promising in modifying polymers and natural fibers. Bentonite clays, which possess a range of practically significant properties, including sorption abilities, ion exchange, high binding capacities, and rheological properties, are also included in this category.

Bentonite clays have a wide range of applications, including the preparation of molding mixtures, iron ore pellets, and drilling muds. They are also used as insulating materials in hydraulic structures, as well as for the clarification of wines, solutions, and oils to remove harmful impurities [6–12].

Environmental protection measures have been developed utilizing bentonite clays from the Urangai deposit (Republic of Kazakhstan) and products derived from sulfur-containing waste utilization [13,14]. The effective use of bentonite clays, which possess a high sorption capacity and a rich microelement composition, can help to address environmental problems and improve public health [15–18].

2. Structure and Properties of Bentonite Clays

Kazakhstan is home to several deposits of bentonite clays, including Chardara (South Kazakhstan), the Karagie Depression (Mangyshlak Peninsula), Kushmurun, Verkhne-Ubaganskoe (Kustanay region), and Andreevskoe (Zhetysu region). Additionally, zeolite deposits are found in the eastern, southern, and other regions of Kazakhstan. In Eastern Kazakhstan, the Primanrak group of natural aluminosilicate deposits is confined to Upper Cretaceous and Palaeogene sediments. The southern part of the Zaisan Basin is home to the

Tagan, Manrak, and Dinosaur deposits of bentonite clays, as well as the Taizhuzgen deposit of zeolites [13]. The natural bentonite clays and zeolite deposits in East Kazakhstan offer several advantages, including high adsorption properties, confirmed by extensive research; accessibility, with deposits located close to consumers; a low cost, compared to reagents used in wastewater treatment technology; and resistance to the temperatures and climatic conditions encountered during transport, storage, and operation. Despite numerous studies on the development of polymer–clay composite materials (PCCMs) based on bentonite clays and polymers, the problem of creating unique, non-toxic medical composites that combine multiple functions remains relevant. Reducing the toxicity of existing drugs, increasing their efficacy and exposure times, and improving their microbicidal properties is of fundamental and applied interest in the development of universal and multifunctional drugs for medical use.

Bentonites are finely dispersed systems whose composition can be expressed by the general formula “ $\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot n\text{H}_2\text{O}$ ”. The primary rock-forming component in bentonite clays, which determines their structure and physicochemical characteristics, is montmorillonite. Minerals of the montmorillonite group (smectites) exhibit almost all the properties of natural nanoscale particles. Bentonites can be easily dispersed in water to form a colloidal state, and they possess an increased binding capacity, high exchangeable base capacity, sorption, and catalytic activity [19,20]. In terms of the cation complex composition, bentonites are classified into three categories: alkaline, alkaline-earth, and mixed bentonites. The classification of bentonites according to their predominant cation composition and genesis is presented in Table 1. Notably, most bentonite deposits worldwide contain alkaline-earth bentonites, whereas high-quality alkaline bentonites have a limited distribution, primarily concentrated in volcanogenic–sedimentary deposits [15].

Table 1. Classification of bentonites.

Type of Bentonite	Chemical Composition	Physicochemical Properties	Application	Features	References
Alkaline bentonites	Main components: montmorillonite, $\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot n\text{H}_2\text{O}$	Ability to swell repeatedly in aqueous solution	Used in the manufacture of drilling fluids, as binders, for the production of catalysts	Used in the production of enterosorbents to remove heavy metals and radionuclides from the body	[12,18]
Alkaline-earth bentonites	Montmorillonite with high content of alkaline-earth cations	High adsorption and catalytic properties, high free surface energy	Used in the chemical and petrochemical industry for filtration, purification, bleaching, and refining of oils and fats	Environmentally friendly, high adsorption capacity	[12]
Mixed bentonites	Combination of alkaline and alkaline-earth components	May have properties characteristic of both alkaline and alkaline-earth bentonites	They are used in various fields depending on their composition	Includes properties of both categories, used in different industries	[12]

Alkaline bentonites, whether natural or modified, can swell repeatedly in aqueous solutions, making them suitable for use in the manufacture of drilling muds. Additionally,

they possess binding abilities and plasticity, which enable their use as binders. Sodium-free montmorillonites are also utilized in the production of catalysts. Furthermore, alkaline montmorillonites from the 12th horizon of the Tagan deposit (East Kazakhstan region, Republic of Kazakhstan) serve as raw materials for producing enterosorbents, which are capable of removing heavy metal ions and radionuclides from the human body [21].

Alkaline-earth bentonites, in an air-dry state, exhibit high adsorption and catalytic properties due to their high free surface energy. As a result, they are utilized in the chemical and petrochemical industries for various applications, including filtration, purification, bleaching, and refining oils and fats. A notable characteristic of bentonite clay as a natural material is its complete environmental safety. The crystal lattice of montmorillonite comprises two outer silica–oxygen tetrahedrons and an alumina–oxygen octahedral mesh between them. These layered packets are loosely bound together, with interlayer distances ranging from 9.6 Å to 30 Å [16]. The packets have free space between them, allowing exchangeable cations and water molecules to penetrate and causing swelling upon wetting.

The specific surface area of montmorillonite is large, ranging from 600 to 800 m²/g, and it contains isomorphically substituted ions. This combination of properties results in the high cation exchange capacity of bentonites, typically between 80 and 150 mmol eq/100 g of air-dry clay [22,23]. The three-layer package of montmorillonite has a negative charge due to the substitution of trivalent iron and aluminum with two-valent magnesium atoms (Figure 1). The unique structure of the crystal lattice of montmorillonite, the primary mineral component of bentonite, explains its significant swelling capacity, high binding capacity, and notable adsorption and catalytic activity. Exchangeable ions can be removed from bentonite by soaking it in aqueous acid solutions at a temperature close to 95 °C, followed by acid washing. This treatment reduces the cation exchange capacity while increasing the specific surface area and specific pore volume of the modified bentonite [24,25]. The acid modification of bentonite has a profound impact on its morphological, textural, catalytic, colloidal, and rheological properties [26–31]. In a dry state, as well as during slight swelling, lamellar crystals of bentonite form aggregates known as “stacks”. As swelling progresses, these ordered stacks give way to disordered plates.

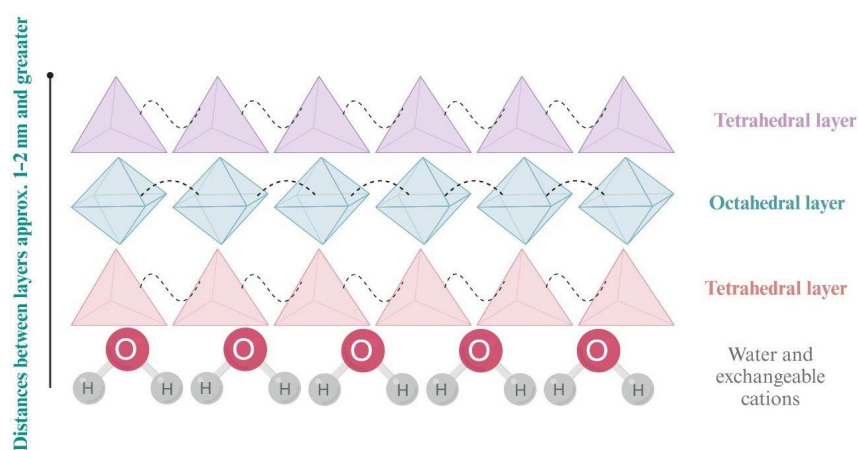


Figure 1. Schematic representation of the layered structure of bentonite.

The rheological properties of bentonite are significantly influenced by factors such as the clay concentration, temperature, pH, and presence of electrolytes [32]. Higher bentonite concentrations generally lead to increased viscosity and gel strength due to enhanced interparticle interactions. The temperature affects the viscosity of bentonite suspensions, with higher temperatures typically resulting in lower viscosities due to increased thermal energy and reduced interparticle attraction. The pH of the surrounding medium influences the surface charge of bentonite particles, affecting their dispersion and aggregation

behavior [33]. Furthermore, the type and concentration of electrolytes present can significantly alter the rheological properties of bentonite suspensions by influencing the electrical double layer surrounding the clay particles, which affects interparticle repulsion and attraction forces [34]. The optimization of bentonite's properties often involves a multifaceted approach, carefully considering the impacts of these parameters to achieve the desired performance in specific applications [35]. Modifying bentonite with micro- and nano-sized particles can significantly enhance soil stabilization by improving the strength of untreated soil materials [36].

3. Influence of Bentonite Clay Composition on Its Practical Application

The chemical composition of bentonite clay has a profound impact on its physicochemical characteristics and applications. Montmorillonite, the primary mineral component of bentonite, is characterized by its high cation exchange potential and swelling ability. These distinctive properties make bentonite an indispensable material in various technologies, including wastewater treatment, the manufacture of high-quality ceramics, and pharmaceutical applications, where material purity is critical [37]. The ratio of sodium, calcium, magnesium, and other ions present in the mineral structure significantly influences these characteristics. Variations in bentonite's composition, particularly in its montmorillonite content, determine its effectiveness in different applications. Table 2 illustrates how the chemical composition of bentonite affects its key properties, which in turn determine its suitability for various industrial and biomedical applications. For instance, sodium-rich montmorillonite enhances the adsorption capacity of the clay, increasing its value as an adsorbent [38]. Furthermore, the additional purification of bentonite increases its montmorillonite content, rendering it suitable for pharmaceutical and cosmetic applications where high purity is essential [37].

One of the primary applications of bentonite is wastewater treatment, which holds considerable significance in the context of sustainable societal development. In the construction industry, the pozzolanic properties of bentonite, attributed to its silicate content, can improve the quality of cement and ceramic materials, contributing to more stable structures [39]. This is attributed to the large surface area of montmorillonite and its ability to undergo ion exchange, which facilitates the effective adsorption of pollutants [40].

According to studies, changes in the sodium and calcium concentrations of montmorillonite have a strong impact on its sorption capacity, swelling behavior, and thermal stability, among other characteristics. Interestingly, the sodium form of montmorillonite has a greater swelling capacity and better sorption capabilities than the calcium version. Due to these characteristics, sodium montmorillonite is especially well suited for use in water filtration systems, food packaging, and medical applications. Furthermore, by giving gas molecules a convoluted path, montmorillonite significantly improves the mechanical and barrier qualities of polymer matrices, increasing the film's impermeability [41].

Modifying montmorillonite with organic compounds, such as quaternized ammonium salts, increases its compatibility with non-polar polymers, thereby expanding its range of applications. Organophilic montmorillonite is widely applied in packaging materials to enhance the barrier properties and polymer compatibility [41]. Furthermore, modifying montmorillonite with silver nanoparticles and other bioactive components enables the creation of materials with antimicrobial properties, which are actively used in medical and food technologies, including the development of intelligent packaging [41].

The addition of bentonite to starch bioplastics significantly affects their physicochemical and mechanical properties, expanding their potential applications in food packaging. Increasing the bentonite concentration to up to 1.5% leads to substantial improvements in the tensile strength and elastic modulus, attributed to the uniform distribution of ben-

tonite particles in the bioplastic matrix and the formation of hydrogen bonds between montmorillonite and starch molecules [42]. The addition of bentonite also reduces moisture absorption and increases the resistance to water degradation. A concentration of 1.5% is optimal for minimizing water absorption and maximizing degradation in soil due to the intercalated structure of montmorillonite, which enhances the moisture tolerance and environmental degradability of bioplastics [42].

Table 2. Influence of chemical composition of bentonite on its properties and applications.

Scope of Application	Influence of Chemical Composition	Notes	Reference
Pharmaceutical industry	High purity of montmorillonite, high adsorption capacity	It is used in excipients (tablets, capsules) and for skincare (cleansing masks, creams).	[29]
Cosmetics industry	High adsorption capacity, biocompatibility	It is used to create safe and environmentally friendly cosmetic products (masks, skin creams).	[29]
Wastewater treatment	Large surface area, ion exchange capacity	Used for removal of heavy metals and organic pollutants.	[33]
Construction industry	Silica and aluminosilicate content	Improves the strength of cement and ceramic materials, reduces the ecological footprint by replacing cement clinkers.	[31]
Ceramics production	Increased strength, improved structure	Improves crack resistance, lowers firing temperature, increases production efficiency.	[32]
Manufacture of refractory materials	Interaction with industrial waste	Creation of refractory materials with improved mechanical characteristics.	[34]
Food industry	High adsorption capacity, interaction with polymers	Used for packaging (controlled release of bioactive components), wine clarification.	[30]
Nanocomposites for packaging	Improved barrier and mechanical properties, high stability	Used to create packaging with improved properties, extends the shelf life of products.	[37]
Modified bentonites	Organic modification (quaternized ammonium salts)	They increase the compatibility with non-polar polymers used in active packaging with antimicrobial properties.	[36]
Applications in bioplastics	Improved durability, reduced water absorption	The addition of bentonite improves the mechanical properties and moisture resistance in bioplastics.	[35]
Pharmaceutical industry	High purity, adsorption capacity, biocompatibility	Purified bentonite is used to create excipients and remove toxins and heavy metals.	[29]

The pharmaceutical industry extensively utilizes purified bentonite due to its biocompatibility and ability to uniformly release active ingredients. For instance, purified bentonite has been successfully employed as an excipient in dosage forms such as tablets and capsules, leveraging its high adsorption and swelling capacities as a suitable carrier for medical applications [37]. These properties have also been exploited in the development of cosmetic products, including cleansing masks and skin creams, where bentonite

serves as a safe and environmentally friendly base [37]. Research on the modification of bentonite by incorporating silver and copper nanoparticles has demonstrated that such additives enhance the antimicrobial properties of bentonite, expanding its applications in food packaging, where the controlled release of bioactive components and improved barrier properties are crucial [43].

The high purity of montmorillonite significantly enhances the effectiveness of bentonite in pharmaceutical applications, such as the creation of excipients and cleansing masks. Notably, purified bentonite with low impurity content exhibits an increased adsorption capacity, making it ideal for the removal of toxins and heavy metals [37].

4. Modification of Bentonite Clays

Particles of the clay mineral bentonite have a layered structure, characterized by plate thicknesses of up to 1 nm and lateral sizes of up to several tens of nanometers. Incorporating filler particles into a polymer base can enhance the physical, mechanical, and operational characteristics of composite materials, particularly by increasing their sorption parameters. Thus, modifying clays can substantially improve their properties, opening up opportunities for their use in medicine, even if the original material has limited characteristics [44,45].

To enhance the sorption properties, materials used for purifying solutions containing heavy metal ions undergo various modifications [46], resulting in the increased specific surface area and porosity of bentonites. When modifying sorbents by grafting chemical functional groups onto their surfaces, the porous structure of the material remains unchanged, while the chemical nature of its surface is altered by fixing the modifying agent on its active centers in amounts typically not exceeding 1–5% of the sorbent's mass. So-called semi-synthetic sorbents have been developed, which are composite materials prepared from natural mineral raw materials through chemisorption modification with organic or inorganic compounds, the deposition of simple or complex oxides, or other treatments [47–49]. This process yields sorbents with distinct surface properties and porous structures differing from those of the original mineral, combining the beneficial properties of both the original mineral and synthetic sorbents. Research [50,51] has shown that the most effective methods of modifying natural materials involve electromagnetic influences (IR and UV treatment) and acid activation. However, acid activation is associated with the use of aggressive reagents, requires chemically resistant equipment, and generates additional effluents that incur disposal costs. Similarly, more advanced modification techniques, such as microwave, ultrasonic, and acid treatments, as reported by Buntin and Agliullin [52], enhance the adsorption capacity of the material by increasing the structural homogeneity and specific surface area. Modifying alkaline-earth bentonite using stabilized nanodisperse hydrosols of silicon and aluminum oxides, combined with ultrasonic and microwave treatment, significantly improves its adsorption properties. The combined methods of bentonite modification using nanotechnology substantially increase its adsorption characteristics, rendering the material more versatile and competitive.

The surfactant treatment of bentonites, as demonstrated in [53], can enhance the textural and chemical properties of such clays. By increasing the specific surface area and modifying the active centers of the clay, its applications can be expanded into various fields due to its improved characteristics. The modification of the surfaces of bentonite clays enables the expansion of existing application areas for the material. Specifically, introducing various types of metal particles into the clay composition allows for the creation of materials with unique properties [54–57]. For instance, the intermolecular space can be utilized to grow silver nanoparticles. The metal atoms combine to form nanoparticles, which bind to the layers of the clay material itself. As a result of this bonding, the silver is trapped between the layers, preventing the formation of low-activity conglomerations or aggregation. The

formation of such nanoparticles is based on the mechanism of spontaneous cation exchange, which does not require complex chemical reactions [57–59]. The main factors regulating the antibacterial activity of nanomaterials are summarized in Figure 2. Furthermore, modifying bentonite with zinc and copper ions not only improves its physicochemical properties and alters its composition but also significantly enhances its antibacterial activity [60]. The properties obtained make such clays suitable for the pharmaceutical and cosmetic industries, as evidenced by their high efficacy against fungi and bacteria. Similar results were reported by Bui Quang Cu et al. [61], who found that modification with silver nanoparticles not only enhanced the antibacterial properties of bentonite but also inhibited a wide range of pathogens, including *Staphylococcus aureus* and *Escherichia coli* [62,63].

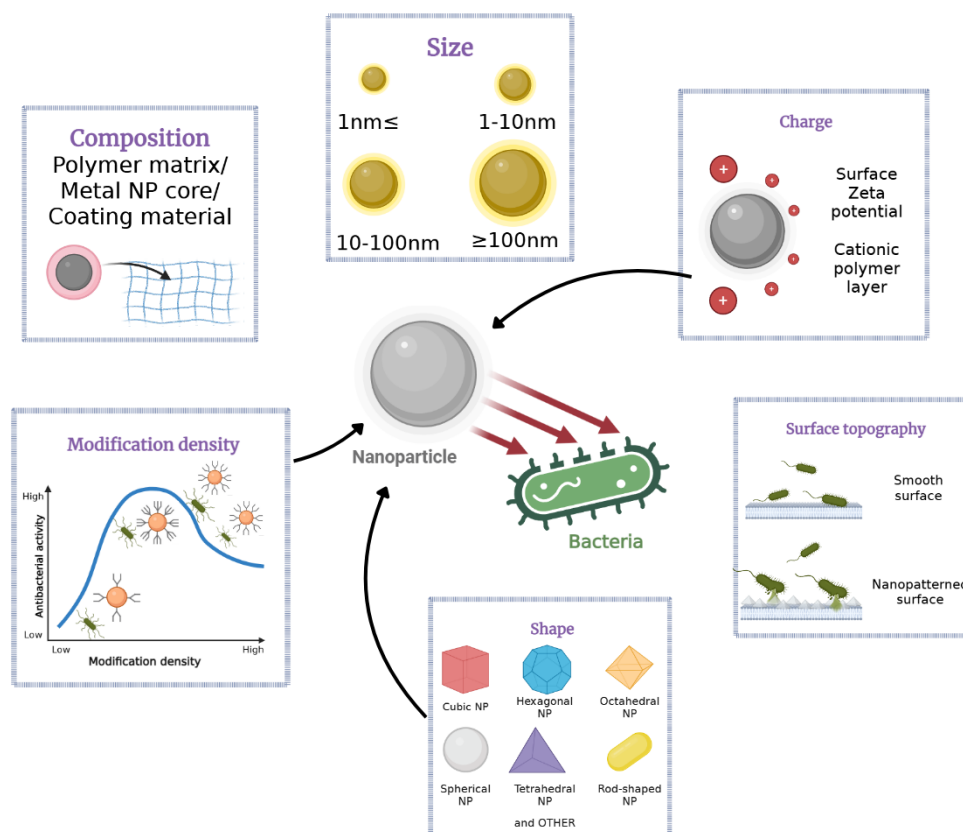


Figure 2. Main factors regulating the antibacterial activity of nanomaterials.

The modification of clay minerals is a critical strategy in enhancing their functional properties in various applications. Among the available approaches, physical, chemical, and biological modification techniques each offer distinct advantages and limitations that must be carefully considered when selecting the optimal method. In particular, chemical and physical methods, commonly used for the synthesis of nanoparticles, tend to be costly and potentially hazardous, especially in medical applications. Consequently, the biosafety and environmental sustainability of metallic nanoparticle production—which is rapidly expanding in the medical field—remain pressing concerns. At the same time, the selection of optimal reducing agents, solvents, pH conditions, and stabilizers for the synthesis of nanoparticles with targeted properties still requires thorough investigation. The antibacterial efficacy of modified bentonites obtained through various approaches is summarized in Table 3, while a comparative analysis of different bentonite modifications is presented in Table 4.

Physical modification techniques, while offering simplicity and reduced environmental impacts, often fall short in achieving the robust interfacial adhesion attained by chemical

methods [64]. The selectivity of adsorption targets in physical modification is limited compared to the precision offered by chemical approaches, where surface functional groups can be tailored to the specific characteristics of the adsorbed components [65]. This can result in non-specific interactions and reduced efficiency in targeted adsorption applications [66].

In contrast, chemical modification provides enhanced specificity and strong interfacial adhesion due to the ability to fine-tune the surface chemistry of the material. However, it is not without drawbacks. A significant disadvantage arises from the environmental concerns associated with the use of chemical reagents and the generation of potentially hazardous byproducts [67]. The multistep nature of chemical modification—including the synthesis of functional reagents, their grafting onto the clay surface, and subsequent purification—increases the production costs and complexity [68]. Moreover, such processes often require harsh conditions, such as elevated temperatures or corrosive environments, which may degrade the clay structure and compromise its functional properties. Consequently, despite its effectiveness, chemical modification demands careful consideration of the environmental impacts, energy consumption, and waste management strategies.

Table 3. Antibacterial activity of modified bentonites.

Type of Bentonite	Chemical Composition	Physicochemical Properties	Application	Features	References
Modification with silver nanoparticles	Introduction of silver nanoparticles into the intermolecular space of clay	Improvements in physical and chemical properties, increase in specific surface area	Suppression of a wide range of pathogens, including <i>Staphylococcus aureus</i> and <i>Escherichia coli</i>	Silver is retained between the clay layers through cation exchange	[53]
Modification using copper and zinc ions	Introduction of copper and zinc ions into the structure of bentonite	Improvements in adsorption and mechanical properties	Increased antibacterial activity against fungi and bacteria	Used in the pharmaceutical and cosmetic industries	[52]
Modification with surfactants	Grafting of chemical functional groups on the surface of bentonite	Increase in specific surface area and porosity	Increased antibacterial activity, improved textural properties	Increased adsorption characteristics, broadened application areas	[54]
Combined methods (ultrasound, microwave treatment)	Microwave and ultrasonic treatment with the addition of nanodispersed silicon and aluminum oxides	Increased specific surface area, improved homogeneity of the structure	Improved adsorption efficiency and antibacterial properties	Used to improve the adsorption characteristics and versatility of the material	[44]
Chemisorption modification	Introduction of organic or inorganic compounds	Improvements in surface nature and porous structure	Increased ability to sorb heavy metals and organic pollutants, improved mechanical properties	The technique improves the sorption properties and antibacterial activity	[38–40]

Table 4. Comparative table of antibacterial activity of different modifications of bentonite.

Type of Modification	Additives/Methods Used	Target Bacteria/Fungi	Antibacterial Activity	Comments	References
Initial bentonite	Without modification	<i>Staphylococcus aureus</i> , <i>Escherichia coli</i>	Moderate activity against some pathogens	The main properties of bentonite are adsorption and physicochemical characteristics, without obvious antibacterial activity.	[38]
Silver modification	Silver nanoparticles (Ag)	<i>Staphylococcus aureus</i> , <i>Escherichia coli</i> , fungi	High activity against a wide range of bacteria and fungi	Modification with silver nanoparticles significantly improves antibacterial properties by preventing pathogen aggregation.	[47,49–51]
Copper modification	Copper nanoparticles (Cu)	<i>Staphylococcus aureus</i> , <i>Escherichia coli</i>	High activity against bacterial pathogens	Activates antibacterial activity through copper ionization mechanisms.	[52]
Modification with zinc	Zinc nanoparticles (Zn)	<i>Staphylococcus aureus</i> , <i>Escherichia coli</i>	Increased activity against Gram-positive and Gram-negative bacteria	Zinc improves physicochemical properties and enhances bactericidal action.	[52]
Surface modification (surfactants)	Surfactants	<i>Escherichia coli</i> , <i>Staphylococcus aureus</i>	Moderate activity	Modification with surfactants improves the chemical and textural properties of clays, which enhances their adsorption capacity.	[50]
Microwave treatment + SiO ₂ /Al ₂ O ₃ nanoparticles	Microwave processing, silicon and aluminum oxide nanoparticles	<i>Escherichia coli</i> , <i>Staphylococcus aureus</i>	Very high activity against a wide range of bacteria and fungi	Increased porosity and improved structure through microwave treatment, and the addition of nanoparticles improves the antibacterial properties.	[44]
Ultrasonic treatment + modification with SiO ₂ /Al ₂ O ₃	Ultrasonic treatment, silicon and aluminum oxide nanoparticles	<i>Staphylococcus aureus</i> , <i>Escherichia coli</i> , fungi	Very high activity against various pathogens	Ultrasonic treatment increases the homogeneity of the structure and its porosity, which enhances its antibacterial activity.	[44]
Surfactant modification	Surfactant treatment, silver and copper nanoparticles	<i>Escherichia coli</i> , <i>Staphylococcus aureus</i> , fungi	Average activity	Treatment with surfactants improves the interaction between the clay and additives, improving its adsorption properties and antibacterial activity.	[55]

Biological modification techniques, while promising in their eco-friendliness and biocompatibility, are often constrained by their sensitivity to environmental factors and the complexity of biological systems. Biological modification processes are often slow compared to chemical or physical methods, requiring extended incubation periods for microorganisms to effectively modify the clay structure [69]. The stability of biologically

modified clays can be a concern, as the incorporated biological agents may be susceptible to degradation or deactivation under certain environmental conditions [70].

To enhance the sorption capacity and absorption of polyvalent metal ions, the polymer matrix is subjected to modification, particularly through the introduction of fillers. Incorporating bentonite fillers into the polymer matrix improves the mechanical characteristics of materials, preserves their shapes when sorbing liquids, and expands the application areas of composites based on them [58,71,72]. Modifying bentonite clays significantly enhances their physical and chemical characteristics, thereby broadening their potential applications in various industries. The chemical composition and montmorillonite content determine the key properties of bentonite, including its sorption capacity, cation exchange potential, and swellability. Combined modification techniques, such as reactant activation, ultrasonic treatment, and nanoparticle introduction, enable increased adsorption capacities, improved mechanical and antimicrobial properties, and the customization of the material to meet the demanding requirements of the pharmaceutical, construction, and food industries. These improvements render bentonite clays more versatile and capable of fulfilling modern performance and sustainability criteria. According to some authors, achieving the homogeneous dispersion of nanofillers in the polymer matrix is a crucial step in obtaining intercalated structures. Turri, Alborghetti, and Levi reported that obtaining a nanocomposite requires first achieving the good delamination of the clay in the polymer matrix [73]. Clay delamination leads to the formation of a homogeneous dispersion consisting of individual nanometer-sized plates.

To produce fillers with controlled porosity and microstructural properties, bentonites undergo a decationization process, which involves the removal of alkali metal cations from the interlayer spaces. This modification facilitates the subsequent incorporation of silver nanoparticles. One approach to obtaining composite materials involves the radical intercalative polymerization of in situ monomers on the surfaces of clay fillers [3,74,75]. In this process, polymerization proceeds within the galleries, causing the clay particles to gradually swell, eventually exfoliate into discrete layers, and ultimately form a more homogeneous material with the uniform distribution of the mineral throughout the polymer matrix. The continuous phase in composites can be any synthetic polymer, such as polyacrylamide, polycarboxylic acids, or polyhydroxyethylacrylates. It has been reported [76] that chemically crosslinked gels based on bentonite clay from the Manirak deposit and non-ionogenic (polyhydroxyethylacrylate and polyacrylamide) and ionogenic (polyacrylic and polymethacrylic acid) polymers were synthesized through the process of the preliminary intercalation of monomers in an aqueous suspension of bentonite. The sorption capacity of polymer–clay composites with respect to Pb^{2+} , Zn^{2+} , and Ni^{2+} cations was evaluated. The results showed that increasing the temperature of the medium and the content of bentonite clay in the composite favored the sorption process. Additionally, clay composite carriers of polycarboxylic acids, polyhydroxyethylacrylate, and polyacrylamide were obtained through radical polymerization with and without the intercalation process [4,5,77]. In the presence of bentonite particles in situ, the formation of different nanocomposite structures is possible, ranging from intercalated to exfoliated (Figure 3). When embedded in the interpackage space of bentonite plates, the intercalated polymer strengthens the structure and enhances the sorption characteristics of the entire polymer composition.

Changing the distance between clay layers via the intercalation of long chains or grafting of different functional groups transforms the hydrophilic properties of clay into hydrophobic ones, opening up possibilities to obtain new and interesting properties. Clay modification is currently of great interest in creating polymer nanocomposites with improved mechanical, thermal, and barrier properties, making them promising for applications in automotives, packaging, construction, and electronics [78–80]. However, clay

nanolayers tend to agglomerate, forming tactoids that can offset the benefits of a single component. Due to the incompatibility of hydrophilic clays and hydrophobic engineering polymers, separating these tactoids into separate monolayers becomes even more challenging.

Unlike pure polymers or conventional micro- and macroscopic composite materials, the proper distribution of nanostructures in the polymer matrix is critical in improving the material performance [78,79,81]. Conventional polymer–clay composites consist of a polymer matrix with dispersed clay particles. The primary purpose of adding clay to the polymer is to enhance its mechanical, thermal, and barrier properties. Polymer–clay composites can be produced through various methods, including extrusion, injection molding, in situ polymerization, and others. A key factor influencing the properties of the composite is the degree of dispersion and interaction between the polymer and clay particles.

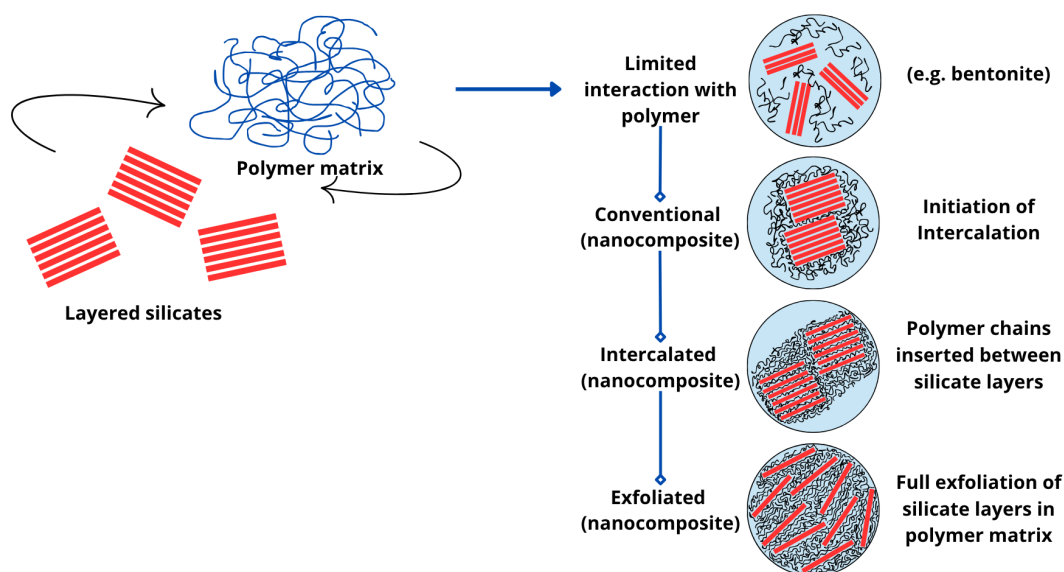


Figure 3. Formation of nanocomposites based on layered silicate and polymer.

Well-dispersed and intercalated or exfoliated clay particles can significantly improve the composite's properties compared to pure polymers [78,79,82]. Various methods based on physical adsorption and chemical modification have been developed to enhance the dispersibility of clay. Studies have shown that, when obtaining montmorillonite/polymer nanocomposites, only well-exfoliated and well-dispersed montmorillonite nanolayers in the polymer matrix can significantly improve the properties of nanocomposites. Factors such as the montmorillonite sources, organic modifiers, polymers, and exfoliation methods and conditions affect this process.

The exfoliation of montmorillonite and the subsequent improvements in the properties of nanocomposites are closely related to the interaction between the polymer matrix and the montmorillonite nanolayers. This interaction depends on the degree of exfoliation and the content and distribution of the nanolayers in the composite. Nanocomposites with well-exfoliated montmorillonite nanolayers exhibit significantly improved mechanical and barrier properties, as well as enhanced thermal and fire resistance [78,82,83].

Physical adsorption, determined by thermodynamic standards, enhances the physical and chemical properties of composites without modifying the clay structure. However, it has the disadvantage of weak interactions between adsorbed molecules and the clay. In contrast, chemical modification, which involves applying polymers or functional groups to the clay surface or ion exchange with organic cations or anions, improves the interaction between the clay and modifiers, resulting in better composites.

Intercalated nanocomposites are materials in which polymer chains are inserted between clay layers, increasing the distance between them and improving the compatibility with the polymer matrix. Conventional polymer–clay composites typically exhibit limited property improvement due to insufficient clay dispersion and weak interactions between the components. In these conventional composites, the clay particles are not uniformly distributed, and agglomeration often occurs, reducing the improvement in the properties compared to pure polymers. Exfoliated nanocomposites, where the clay layers are completely delaminated and dispersed in the polymer, exhibit the best mechanical and barrier properties, as well as resistance to heat and fire, due to the high degree of interaction between the polymer and clay layers [78–80,83].

Nanocomposite materials based on clays (montmorillonite, synthetic hectorite, and fluorhectorite) and poly(methyl methacrylate) were prepared by heterocoagulation. Initially, an emulsion of poly(methyl methacrylate) (PMMA) was obtained through emulsion polymerization, which was then mixed with an aqueous suspension of clay [84,85]. To obtain exfoliated structures, various methods have been employed in the preparation of PMMA–clay-based nanocomposite materials, including solution mixing [86,87], melt intercalation [88,89], and in situ polymerization [75,89]. The melt intercalation method offers several advantages over in situ polymerization or exfoliation methods. Firstly, it is environmentally acceptable due to the absence of organic solvents. Secondly, it is compatible with current industrial processes, such as extrusion and injection molding. Furthermore, it has been shown that modifying the melt mixing conditions can alter the nanocomposite structure [89,90]. In general, polymer/silicate layered nanocomposites can be categorized into three distinct types:

- (1) Intercalated nanocomposites, where polymer chains are inserted into the layered silicate structure in a regular pattern, with repeating spacing of several nanometers, regardless of the polymer-to-clay ratio [80];
- (2) Flocculated nanocomposites, where intercalated and stacked silicate layers are flocculated to some extent due to the hydroxylated edge interactions of the silicate layers [80];
- (3) Exfoliated nanocomposites, where individual silicate layers are completely separated and randomly dispersed in a continuous polymer matrix [91–93].

Exfoliated polymer–clay nanocomposite membranes are particularly favored due to their good macroscopic properties, mainly attributed to the interfacial area of the clay particles [94]. However, achieving the complete exfoliation of the clay structure is challenging, and most polymer–clay nanocomposite membranes exhibit regions where both intercalated and exfoliated structures coexist [95]. The degree of exfoliation depends on various factors, including the surface chemistry of the clay particles and the processing conditions [92,93,95]. To improve the affinity of the clay to the polymer matrix, the surface of natural clay is often treated organically, and the organic component also influences the degree of dispersibility of the clay.

The organic polymer matrix is typically composed of polypropylene [96], polyethylene [75], polyethylene terephthalate [97], polyurethane [98], polystyrene [99], polyamide [99], or polyolefin [100], among others [75,101]. Biopolymers, such as cellulose, starch, plastics derived from maize, and polylactic acid, have gained attention due to their eco-friendly and renewable nature, making them ideal for medical and pharmaceutical applications [102–104]. For instance, biofilms have become an important tool in modern medicine, offering unique properties such as biocompatibility, low toxicity, and minimal immunogenicity [105]. Recent studies have demonstrated that biofilms based on collagen, polycaprolactone, chitosan, alginate, and polylactic acid can accelerate wound healing due to their antimicrobial properties and ability to stimulate cell proliferation [106]. These

features make them suitable for use in medical and pharmaceutical products, providing protection and support to damaged tissue.

Therapeutic films designed for application to the skin, wounds, burns, and mucosal surfaces represent an advanced class of pharmaceutical dosage forms [29–31]. The sustained-release effect in such systems is achieved through the immobilization of local anesthetics and antibiotics onto polymer-based carriers, ensuring controlled delivery and prolonged pharmacological action.

Aerogels have recently garnered significant attention in the drug delivery field due to their high loading capacity. These porous materials play a crucial role in biomedicine, serving as efficient systems for the encapsulation and delivery of organic molecules [107,108]. Additionally, nanoclays have been reported to increase the mechanical strength of biopolymers, attributed to the strong interfacial interaction between the polymer matrix and clay, which alters the morphology of the polymer matrix [109,110].

5. Practical Use of Polymer Composite Materials in Medicine

The use of bentonite in medicine and pharmacology is promising. Available data testify to its exceptional efficiency for therapeutic purposes, mainly for external applications, due to its finely dispersed structure. The ion exchange properties of montmorillonite are successfully utilized in medical practice. For example, fillers based on montmorillonite and montmorillonite with a hydroxyapatite layer, which has remineralizing potential, are used to create composite materials for dental fillings [26,27,89,92,111].

The increasing medical interest in bentonite, a montmorillonite clay that has long been used for its therapeutic qualities, has been brought to light by recent clinical and preclinical research. Significant therapeutic effects were shown by a new bentonite complex on burn wounds in vivo. In vitro, it reduced inflammation by downregulating COX-2 signaling and promoted skin regeneration through increased collagen production, cell proliferation, and angiogenesis [112]. Furthermore, a controlled study showed that a bentonite cream was noticeably more successful than calendula in hastening the healing of infant diaper dermatitis, resulting in quicker and more complete lesion recovery [113]. Although more research is necessary to guarantee its safety and broaden its therapeutic applications, these results, in addition to bentonite's known antibacterial and antioxidant qualities, support its potential as a promising biomedical agent [114].

Biopolymers are widely used to develop drug formulations, such as hydrogels, aerosols, and nanoparticles. Due to their properties, they provide nutrition and targeted drug delivery, as well as controlling the release, stability, and bioavailability of active substances, which can improve the therapeutic effect and minimize pathological effects. Their use in modern medicine opens up new opportunities for the treatment of various diseases [102,104]. Clay minerals are employed as carriers for bactericidal agents. Various methods are used to produce modified clay minerals, and composites derived from clay minerals and other materials can be used as novel bactericidal materials to exert bactericidal action [83,115]. When developing polymer–clay composites for medical applications, several factors must be considered: their suitability for medical use, their ability to gel, the presence of functional groups for drug binding, and their intercompatibility. Therapeutic compositions of bentonite clay with alchidine and richlocaine, combined with various polymers [116–118], such as arabinoxylan, chitosan, guar gum, and xyloglucan, have been obtained [119]. It has been observed that clay minerals can enhance the bactericidal capacity through various modification methods, including the thermal [120,121], acid [122], or inorganic modification of metals [83,121] or metal oxides [121] and organic [121,123] and composite modification [121]. These modifications increase the surface area, improve the mineral porosity and dispersion, and enhance the overall thermal stability and mechanical

strength of the material [124,125]. The clay minerals primarily used for the modification and preparation of bactericidal materials are montmorillonite, kaolinite, halloysite, and vermiculite. Organically modified clay minerals are incorporated into the organopolymer matrix to enhance the physicochemical properties and bactericidal activity of the materials [83,115,120,126]. These materials are mainly utilized to produce antibacterial cotton wipes, cotton discs, and films from nanofibers. Clay minerals are also employed as fillers in composites to enhance the thermal and mechanical stability of nanomaterials, typically at the nanoscale.

Due to the poor compatibility of clay minerals with organic molecules, organic compounds are often used to modify clay minerals, increasing their dispersibility in organic solvents and ensuring compatibility with subsequent organic compounds. Organomodification frequently employs anionic and cationic surfactants (quaternary ammonium salts and hybrid compounds being the most common) [127–130] to modify the surface properties of the clay, altering the surface electrical properties and surface hydrophobicity [130,131] or introducing organics into the interlayer to create hydrophobicity between layers [131,132]. The high compatibility of organomodified clays and polymers makes them ideal materials for improving the properties of polymer matrices, and they are widely used as precursors for bactericidal materials. The properties of composite bactericidal materials are influenced by the size scale of the different components and the degree of mixing between the various phases [133]. To improve the distribution of clay particles in the polymer matrix, the ultrasonic treatment of bentonite clay was performed [134]. Bentonite-based multicomponent ointments containing levomycetin, methyluracil, metronidazole, and streptocide have demonstrated high antimicrobial activity [135,136]. In this case, the ion exchange properties of clay facilitate the sorption of harmful substances and the simultaneous saturation of the skin with microelements. The intermolecular space of bentonite can be utilized for the introduction of silver nanoparticles [137]. The authors of [138] reviewed the preparation and antibacterial activity of chitosan-based nanocomposites containing silver and zinc oxide nanoparticles on a bentonite base for water disinfection. Chitosan–bentonite nanocomposites were investigated for use as films in wound healing [139]. Other researchers have studied the electrokinetic properties and antimicrobial activity of biodegradable chitosan/organobentonite composites [140], taking into account the effects of the electrolyte pH, surfactants, and temperature. Sodium bentonite composites with chitosan were tested against various bacteria and fungi, demonstrating increased antimicrobial activity with increasing ζ -potential values. The antimicrobial effects observed were either stronger than or equivalent to those of controls.

The authors of [141] explored the possibility of using sodium bentonite as an excipient in slow-release tablets. In [142], a dispersed bentonite powder with silver ions was used to obtain an antimicrobial preparation by compounding it with a 0.5–2% alcoholic solution of a block copolymer of polydimethylsiloxane and polyurethane, with viscosity of 10,000 to 45,000 Pa·s at 110 °C, at a weight ratio of 1:(100–200). The antimicrobial material was found to be biocompatible with animal and human body fluids and tissue. Modifying the surface of bentonite clay expands its application areas. Introducing a modifier, such as bentonite, during the development of polymer composite materials (PCMs) enhances not only the physical and mechanical characteristics of the composite, including its strength, elasticity, and preservation of its shape in the swollen state, but also increases the sorption capacity of hydrogel compositions. Furthermore, using modified bentonite—for example, with silver ions or nanoparticles—significantly expands the operational capabilities of the created PCMs, imparting bactericidal properties [143]. The antibacterial properties of silver are attributed to the interaction of silver ions with the negatively charged bacterial cell wall. Silver nanoparticles exhibit the most effective antimicrobial properties [144–146].

Various methods are employed to produce silver nanoparticles through the reduction of silver salts. Different synthesis types are utilized, with the most common being chemical, electrochemical, ultrasonic, biochemical, and irradiation-based methods [147]. Considerable attention is focused on “green” technology for the production of silver nanoparticles via bioremediation using extracts from medicinal plants [148–151]. Silver can be incorporated into medicines and wound coatings in the form of soluble salts, colloidal solutions with fine dispersibility, or silver compounds with proteins. However, these compounds tend to disintegrate quickly, resulting in a lack of prolonged action and effective bactericidal activity. When exposed to air, water, or wounds, silver oxidizes to form silver oxides, creating an oxide film. Over time, silver is released into the solution as ions, providing a dose-dependent effect [152–156]. It is essential to note that the biosafety and environmental friendliness of metal nanoparticle production, which is increasingly used in the medical industry, remain pressing concerns. These concerns necessitate the careful selection of non-toxic, optimal reducing agents, solvents, and stabilizers that consider the pH environment to obtain nanoparticles with the desired properties. In a previously reported work, composites synthesized from polyetherimide with added bentonite were investigated [157]. Thermogravimetric analysis revealed that the decomposition temperature of the polyester nanocomposite increased from 514.2 °C to 551.2 °C for the composition containing 20 wt.% of bentonite. Additionally, the glass transition temperature rose from 174 °C to 210 °C for the filled samples.

Hydrogels are widely used in medicine due to their unique performance characteristics. Their applications include the production of sanitary and hygienic products (e.g., disposable napkins, towels, personal care items) and targeted drug delivery systems in pharmacology [158–162]. In [143], the influence of the bentonite concentration and crosslinking agent on the equilibrium swelling degree of the polymer composition during swelling in distilled water at 25 °C was investigated. It was found that increasing the bentonite share to 5 wt.% led to an increase in the equilibrium swelling degree values, attributed to the hydrophilicity and sorption abilities of bentonite itself. Conversely, increasing the proportion of the crosslinking agent resulted in a decrease in the equilibrium swelling degree values.

Furthermore, increasing the proportion of bentonite beyond 5 wt.% led to a decrease in the swelling values of the polymer material. This decrease is explained by the increased average effective number of physical mesh nodes in the interaction of the polymer chains with the growing total surface area of the modified bentonite particles, consequently limiting chain mobility during the formation of the surface layer [128,148–150]. Notably, in the high dispersibility range (at $d < 0.25$ mm), increasing the proportion of mineral-containing filler in the concentration range of 1–5 wt.% led to a significant increase in the equilibrium swelling degree values compared to the unfilled sample (1.5–3 times). Conversely, with the decreasing dispersibility of the filler (particle size 0.5–0.25 mm), increasing the bentonite share to 5 wt.% resulted in a decrease in the equilibrium swelling degree.

The study of swelling processes in physiological solutions revealed that the equilibrium swelling degree values sharply decreased to 10–20 g/g in the presence of metal ions in aqueous salt solutions, attributed to the polyelectrolyte suppression effect [163]. A similar effect was observed for the equilibrium swelling degree in amino acid solutions [164,165].

A study of the influence of the nature and ionic strength of the solution on the kinetic parameters of the swelling of mineral-containing moisture-absorbing acrylic composites revealed that the values of the rate constants and swelling rates of polymeric bentonite-filled composites were 20–40% higher than those of unmodified acrylic crosslinked copolymers [135]. Thus, the polymer composite material (PCM) based on a bentonite modifier improves not only the physical and mechanical characteristics of the composite, such as the

strength, elasticity, and preservation of its shape in the swollen state, but also the sorption capacity of the obtained compositions.

As summarized in Table 5, modified clay-based materials and biopolymers are widely applied in various medical and pharmaceutical fields due to their biocompatibility, sorption capacity, and controlled-release properties.

Table 5. Overview of applications of modified clay materials and biopolymers in medicine and pharmacology.

Study Area	Material	Modification Method and Role of Modifier	Application	Physicochemical Properties and Biological Activity	References
Application of bentonite in dentistry	Montmorillonite	Hydroxyapatite layers	Dental fillings	Resistance to exposure, biocompatibility	[23,24,70,91,149]
		Remineralization, ion exchange with Ca^{2+}		Increased remineralization of teeth	
Biopolymers for drug delivery	Hydrogels, nanoparticles	Formation of hydrogels, nanocomposites	Medicines	Increased bioavailability, stability	[92,93]
		Improving drug delivery and release		Targeted delivery of active ingredients	
	Montmorillonite, kaolinite, halloysite	Thermal, acidic, organic modification	Antibacterial materials (bandages, wipes)	Increased surface area, improved porosity, thermal stability	[94,99,150]
		Improved bactericidal properties		Increased bactericidal activity	
Modification of bentonite clays for creation of polymer composites	Bentonite	Surfactants, crosslinking agents	Medicine, pharmaceuticals	High sorption capacity, improved mechanical properties	[105–108]
		Increased compatibility with polymers, improved properties		Improved properties when interacting with polymers	

Although bentonite-based composites have significant benefits for biomedical and environmental remediation applications, further research is necessary to fully understand their drawbacks, particularly with regard to ecotoxicity and biocompatibility. The greatest health risk linked to bentonite is occupational inhalation, especially because some types of the material contain respirable crystalline silica (RCS). Although some types, including calcium and sodium bentonites, have shown excellent efficacy in toxin adsorption and minimal acute toxicity, there is still a lack of long-term safety data, particularly for non-occupational exposure [166–169]. There are also issues with bentonite’s assimilation of nanosilver. Despite improving antibacterial qualities, nanosilver introduces intricate toxicity pathways. According to the available data, nanosilver can impact several bodily systems, such as the digestive, reproductive, and respiratory systems, mostly by causing inflammation or releasing silver ions [170]. There are still questions, nevertheless, about the degree of absorption of nanosilver, its changes in physiological settings, and the relative contributions of intact nanoparticles and silver ions to the observed harmful effects. Because little is known about nanosilver’s permanence, capacity for bioaccumulation,

and interactions with ecosystems, the environmental hazards are also substantial. Future research must prioritize intergenerational toxicity assessments, sophisticated nanoparticle characterization in pertinent biological media, and thorough environmental impact evaluations to guarantee safe deployment, especially in biomedical and environmental contexts. These actions are necessary to responsibly recognize the limitations of bentonite-based nanocomposites while balancing their advantages.

An analysis of the scientific publications in the field of developing polymer–clay composite materials highlights the need for further research, as there remains a fundamental and applied interest in creating universal and multifunctional preparations for medical use.

6. Conclusions

Bentonite-based composites demonstrate significantly enhanced physical and mechanical properties, including improved strength, elasticity, and structural integrity even in the swollen state. Incorporating bentonite into polymer matrices not only increases their swelling capacities and sorption abilities but also contributes to improved antimicrobial properties. The modification of clay minerals with bactericidal agents, such as silver or copper nanoparticles, further boosts their efficacy against a broad spectrum of microorganisms. These properties make bentonite-based materials highly promising for biomedical applications, particularly for sustained antimicrobial action through controlled ion release.

However, the full potential of clay minerals—especially in the biomedical field—remains underexplored. Future research should focus on the development of multifunctional polymer–clay composites that combine sorption, membrane, antimicrobial, and catalytic activity. Such materials hold promise for use in wound healing, drug delivery, tissue engineering, and other areas of medicine and pharmacology. Moreover, expanding the study of clay modification and hybridization with biologically active components can lead to the creation of next-generation, smart biomedical materials with tailored performance characteristics.

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