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Recent Advances in Antibacterial Metallic Species Supported on Montmorillonite Clay Mineral: A Review

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Abstract: This review provides information on the latest advances in inorganic materials with antimicrobial properties based on a metallic species immobilized on the clay mineral montmorillonite realized between the years 2015 and 2023. This class has shown many promising results compared to certain organic agents. Montmorillonite in natural and/or modified forms is a good platform for the storage and release of metallic species, and several researchers have worked on this mineral owing to its cation exchange capacity, low cost, biocompatibility, and local availability. The preparation methods and the properties such as the antibacterial, antifungal, and toxicological activities of this mineral are discussed. The main characteristics of this antibacterial class for the elimination of pathogenic bacteria were examined and the known weak points of its antimicrobial application are discussed, leading to suggestions for further research.

Keywords: clay minerals; montmorillonite; nanocomposite; antibacterial activity; pathogenic bacteria; metallic species

1. Introduction

Diseases caused by pathogens such as bacteria, fungi, viruses, and protozoa are disturbingly on the rise, and the increasing frequency of their resistant strains has increased researchers' efforts to develop efficient, non-toxic, inexpensive, and strong inhibitory materials for disinfection. These antimicrobial materials can be broadly divided according to their chemical composition: organic and inorganic agents. Organic antibacterial agents have been widely utilized due of their strong inhibitory effects on bacterial growth [1–4]. However, these compounds suffer from many problems such as low thermal stability, high cost, toxicity, and a short shelf life, which limit their applications in this field. In recent years, inorganic materials have been targeted as very particular alternatives by virtue of their prospects as antibacterial agents. Several studies have suggested that clay-based nanocomposites are effective, biocompatible, inexpensive, and stable materials for treating various pathogens [5–13].

Generally, metallic nanoparticles have a good bacteriostatic effect resulting from their large surface/volume ratio, allowing them to contact the bacterial cell in a desirable manner [14–18]. Recently, metallic ions, metal nanoparticles, and metal oxides based on silver [19–21], gold [22], copper [23], cerium [24,25], iron [26], cobalt [27], copper oxide [28,29],



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). zinc oxide [30–32], nickel oxide [33], tin oxide [34], manganese oxide [35], nickel hydroxide [36], and magnetite [37] have been applied in various fields, especially in medicine, dentistry, the pharmaceutical industry, food packaging, coatings, the paint industry, and biology. Recently, the growing concerns about microbial infections and their resistance have increasingly pushed researchers to develop powerful new antimicrobial agents that are stable and sustainable. Several researchers have shown that the antibacterial effect of nanoparticles depends on their size, shape, distribution in the matrix, morphology, surface functionalization, and physical and chemical stability [14,38,39]. In addition, the use of these antibacterial metal nanoparticles has shown many interesting advantages compared to organic antibacterial materials, and among the important advantages is the diversity of their preparation methods by physical, chemical, and even biological processes. These nanoparticles can be easily fabricated using green methods, which have an advantage for human health and our ecosystem. These antimicrobial nanoparticles are very important materials for fundamental research with a wide range of applications, due to their remarkable characteristics, which are represented by their nanometric size, their large specific surface area, and their physical and chemical stability. When using these pure particles alone, many problems can arise, such as their complexation, precipitation, and agglomeration, and they can even react with other compounds present in the reaction medium, thus leading to a decrease in their reactivity. To overcome these disadvantages, researchers have supported them in appropriate matrices such as clays [5,34,40], zeolites [41–44], mesoporous materials [45–48], and polymers [49–54].

Several supporting substrates for these antimicrobial nanoparticles have been developed in recent years such as grapheme [55], diatomite [56], zeolites [57–59], polysaccharides [60–62], hydrated layered polysilicates [63–67], mesoporous materials [68,69], and double-layered hydroxides [70,71] for the preparation of the bacteriostatic hybrids' components. Consequently, the resulting composites generate a synergistic effect between the support and the metal to eliminate a variety of pathogenic microorganisms. Additionally, silver species loaded on organic or inorganic carriers as hybrid composites are the most-popular and the most-effective antibacterial materials, on account of their excellent bacteriostatic characteristic [66,72–75], and several studies have shown that these composites are very effective at killing different types Gram-positive and Gram-negative bacteria, as well as fungi [20,76,77]. Most of these supports present a handicap either in their availability, their preparation, their stability, their high costs, their biodegradability, or their toxicity, e.g., graphene and its modified forms have been shown to be effective at capturing bacteria from contaminated water, but they are very expensive to prepare. Special attention has been paid to silver species loaded on montmorillonite as the carrier, which is superior in terms of safety and long-term antibacterial effectiveness when compared with other materials. Figure 1 presents a diagram of the numerous scientific publications on antibacterial materials based on zinc, copper, silver, and other metallic species, which are supported on montmorillonite for antimicrobial applications. More than 50 scientific publications have been produced during the period from 2015 to 2023 on silver and montmorillonite as a precursor for the preparation of antibacterial composites. Silver has been used on account of its high activity and low bacterial resistance [78]. When bacteria approach silver particles, positively charged silver ions are formed due to Coulomb gravity. The silver ions attract the sulfhydryl group on the enzyme protein of the bacteria, leading afterwards to the loss in the activity of the bacteria and, then, its death [79,80].

Clay minerals are relatively abundant in nature, biocompatible, and non-toxic to the environment and humans, as well as have good physical and chemical stability [7,81,82]. This class of solids has been widely used for medicinal applications throughout human history in view of their characteristics of adsorbing and fixing viruses, bacteria, and other harmful substances [76,83–88]. They have been used as a mineral remedy for ailments such as diarrhea, dysentery, tapeworms, hookworms, wounds, and abscesses [83,89,90]. They have been used for the elimination of fungi, viruses, and Gram-negative and Gram-positive bacteria, due to their high cation exchange capacity, high surface area, high swelling

capacity, high water dispersibility, stability, and non-toxic properties [91–93]. Without any modification, the negative charge on their surfaces allows the exchange of positively charged antimicrobial substances. Their combinations with antimicrobial metallic species constitute an important class of composites known by the name inorganic–clay hybrids. The clay also acts as a protective agent for the nanoparticles, as a stabilizer (prevents aggregation and dissolution), and as a suitable surface for homogeneous dispersion.



Figure 1. Number of articles based on antibacterial metallic species supported on montmorillonite (based on Scopus database searches).

The most-common clay used for the fabrication of this class of antibacterial materials is montmorillonite [94]. This mineral is the main component of bentonite; its deposits mostly develop from the weathering of volcanoclastic rocks [95]. It is extensively used in the medicine and biological fields owing to its excellent intrinsic properties; it has been specifically used as an adsorbent, dispersant, suspender, coagulant, and filler [96–99]. Montmorillonite belongs to the group of smectites with a 2:1 layer structure, which is formed by coordination bonds between silicon (Si⁴⁺) and oxygen atoms with one octahedral sheet in between, which is formed by either Mg²⁺ or Al³⁺ coordinated with oxygen atoms and some hydroxyl (OH) groups on the cleavage sites [100]. With isomorphic substitutions using Si^{4+} , Mg^{2+} , and Al^{3+} atoms, negative charges can be created all over the layers, which are neutralized by cations such as Na⁺, K⁺, Ca²⁺, and in some cases, Mg²⁺. These charges have the ability to fix positive substances in the interlayer space [72]. In addition, the Si–OH and Al–OH groups can react with silane coupling agents, giving rise to hybrid organoclays [72,101]. Several studies have been carried out using montmorillonite in a modified or unmodified form with the aim to prepare antimicrobial agents. Due to this, particular attention has turned toward these solids and their nanocomposite counterparts. Recently, montmorillonite supporting spherical SnO₂ nanoparticles having a particle size of less than 10 nm showed good antibacterial activity against a Gram-positive bacterial strain [34]. Another study attributed the antibacterial activity of chitosan/AgNP-bentonite composite beads against Staphylococcus aureus and Pseudomonas aeruginosa bacteria to the AgNPs species loaded in the bentonite [67]. Chitosan-based nanocomposites containing bentonite-supported silver and zinc oxide nanoparticles have also been used for water disinfection with a bacteria removal efficiency of 78%. Furthermore, leaching tests have demonstrated that nanocomposite-based montmorillonite is stable and, consequently, could be effectively used as an antibacterial material for water disinfection [102]. Recently, new antibacterial paper nanocomposites stabilized by montmorillonite have shown excellent antimicrobial activity against several types of bacteria: Escherichia coli, Pseudomonas aeruginosa, Aspergillusniger, Staphyloccocus aureus, and Bacillus subtilis [103]. Giraldo et al. [72] also reviewed the main montmorillonite and silver incorporation strategies for the preparation of a potential antibacterial material with prolonged antibacterial activity.

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Through these studies described above and the others that will also be mentioned in this review, montmorillonite and antibacterial metallic-species-based nanocomposites have attracted much attention from researchers over the last five years. This review focused on a group of inorganic antimicrobial materials based on antibacterial metallic species and montmorillonite as the inorganic carrier. In addition, an assessment of the most-promising antimicrobial properties of these composites is presented, as well as the most-effective materials are discussed, providing a viewpoint about the possible directions for actual applications.

2. Structural Features of Montmorillonite

The surface area of montmorillonite is the key factor that allows it to accommodate metallic species, as well as to adsorb microorganisms in its interlayer space [104]. The schematic structure of the 2:1-type clay mineral is presented in Figure 2. Montmorillonite belongs to the family of 2:1 smectite minerals. Due to its swelling characteristic, its specific surface area is higher than other types of minerals such as the 1:1-type. It is composed of one octahedral sheet between two tetrahedral sheets, which forms an interlayer thickness of 1 nm [100]. The substitutions of Si⁴⁺ in the tetrahedron sheet by Al³⁺ or those of Al³⁺ in the octahedron sheet by Fe²⁺ occur in this group of minerals [105]. This results in a negative surface charge all along the sheet, allowing the easy exchange of cations such as Na⁺, K⁺, H⁺, Ca²⁺, and Mg²⁺. These characteristics provide it a higher charge density, a large surface area, and an elevated swelling capacity. Table 1 presents the values of the typical parameters of montmorillonite.



Figure 2. Structure of the Na-montmorillonite (2:1 type) of clay minerals.

Table 1. Representation values of typical parameters of montmorillonite such as cation exchange capacity, surface area, porosity structure, and point of zero charge.

Parameter	Value	References
Basal spacing (Å)	10–13	[106,107]
Typical thickness (mm)	2	[108]
Exchange capacity (mEq/100 g)	80-120	[106]
Specific surface area (m^2/kg)	164.79	[109,110]
Micropore surface area (m ² /g)	38.48	[111]
External surface area (m^2/g)	126.31	[111]
Total pore volume (cm^3/g)	0.271	[112]
Average pore size (Å)	64.74	[113,114]
Point of zero charge (pH _{pzc})	8.0	[115]

The acidity, such as the Brønsted and Lewis types, in clays considerably increases their adsorption capacity. The Brønsted acidity originates from the hydrogen ions of the water molecules present on the clay's surface, which is due to the substitution of Si⁴⁺ by Al³⁺, while the Lewis acidity is created either from the exposed trivalent cations, mostly Al³⁺ at the edges, or Al³⁺ arising from the rupture of the Si–O–Al bonds, or through the dehydroxylation of some Brønsted acid sites [107].

3. Classification of Antibacterial Composite Materials

Antibacterial materials based on inorganic or organic substances have been widely studied for various characteristics such as mechanical, chemical, or thermal stability, potential activity against different types of bacteria, as well as long-term antibacterial effectiveness [116–118]. This category of materials can be classified into three main groups: inorganic–inorganic, organic–inorganic, and organic–organic materials [117,119]. Based on this, clay-based antibacterial materials can also be classified into two categories: (i) inorganic–clay antibacterial materials and (ii) organoclay hybrids (Figure 3) [117,120]. The inorganic–clay compounds include metal or metal oxides supported on clay, while the organic–clay hybrid supports antibacterial organic compounds such as quaternary ammonium compounds, antibiotic drugs, fungicides, and other bacteriostatic organic agents. Therefore, each material has its own concept, history, architecture, and properties. In this review, we only discuss inorganic clay materials. These materials are considered the most-popular due to the fact that they have unique properties, molecular selectivity, hyper-functional activity, and preparations based on abundant substances, and these composite materials have also shown a non-toxic characteristic. The use of layered materials such as montmorillonite, as a carrier for metal oxides, has become the subject of intensive research due to their effective catalytic and antibacterial activities, despite that natural clay minerals, such as kaolinite, montmorillonite, and vermiculite, have no antibacterial effect [121,122]. Some clays have been found to have good antibacterial activities against various bacteria when an antibacterial agent is intercalated or adsorbed on their surfaces. Several studies have shown that these inorganic materials based on clays and oxides such as TiO₂, ZnO, Ag₂O, and SnO₂ have very good antimicrobial activities, especially in water disinfection [34,123,124]. Another study by Ugwuja et al. [83] showed interesting results: they prepared several clay minerals modified by inorganic substances for the elimination of harmful pathogens present in water. The last class of antibacterial composite materials are those that contain only organic substances [125]. Several fabricated materials based on quaternary ammonium, antibiotic, and fungicide molecules have been immobilized on a polymer or biopolymer matrix to test their antimicrobial activities [126–130].



Figure 3. Classification of antibacterial composite materials.

4. Some Important Properties of the Antibacterial Metallic Species Loaded on Montmorillonite

Montmorillonite $(Al_{2-x}Mg_x(Si_4O_{10})(OH)_2 \cdot (Na_x \cdot nH_2O))$ is a 2:1 phyllosilicate. Its host layer constitutes an octahedral metal–oxygen sheet, which is confined by two adjacent tetrahedral [SiO₄] sheets, these forming a sandwich-like structure with a thickness of 0.96 nm. Isomorphic substitutions in the octahedral (Al³⁺ by Mg²⁺) and tetrahedral (Si⁴⁺ by Al³⁺) sheets result in the negative surface charge, which is neutralized by sodium cations and crystal water molecules and can be further exchanged with other cations, e.g., K⁺, Na⁺, Ca²⁺, Mg²⁺, and H⁺, or even organic tetra-alkyl ammonium groups [131]. Montmorillonite has an ecological nature and is abundant, inexpensive, non-toxic, and thermally stable, making it a very good candidate compared to other supports for the design and fabrication of antibacterial materials [132]. The montmorillonite sheets' particles are plate-shaped, typically 1 nm in thickness and $0.2-2 \ \mu m$ in diameter. Due to its cost effectiveness, as well as its good compatibility with most polymers [133], it has been utilized in various fields such as laboratory research, as well as in industry for manufacturing commercial products. This layered silicate is a promising support for nanoparticles with excellent hydrophilicity, a good adsorption ability, a large specific surface area, and a stable physicochemical property [134]. Consequently, various researchers have expounded on the benefits of these interesting properties and the application of montmorillonite and its modified forms in diverse fields. Their negative surface charge can be modified with cationic surfactants, and these can be used as solid carriers and as antibacterial agents [101]. The interaction forces between the guest antibacterial substance and the clay sheets' surface can delay drug release. This feature can be favorable when the slow and controlled desorption of the bactericidal compound has a positive effect on its therapeutic action. Montmorillonite modified with Tris [2-(dimethylamino)ethyl]amine was evaluated for antibacterial activities against multi-drug-resistant strains, and the resulting composite was able to absorb different microorganisms onto the surface and, accordingly, acted as a very effective antibacterial agent [135]. Montmorillonite can strengthen polymers and provide them with various characteristics such as antimicrobial activity, facilitated recovery, electrical and/or thermal conductivity, chemical and thermal stability, targeted delivery, compatibility, and biodegradability [133]. Various modification methods of montmorillonite offer it a variety of properties that can have several fields of application.

5. Antibacterial Metallic Species

Nanoparticles have good antibacterial and antifungal properties due to their large surface/volume ratio, providing a desirable contact with the bacterial cell [15,17,76,136]. In recent years, metallic nanoparticle species based on silver, gold, copper, zinc, and titanium have been applied in various fields such as medicine, dentistry, the pharmaceutical industry, and biology [63,137–143]. With the growing concerns about bacterial infections, antibiotic resistance, and the side effects caused by antibiotics [143], there is a growing need to develop new stable and potent antimicrobial agents. For this, several studies have developed antibacterial materials based on metal oxides, such as copper oxide (CuO) [91], zinc oxide (ZnO) [92], silver cations (Ag⁺) [144], silver oxide (Ag₂O) [15], zero-valence-state silver nanoparticles (Ag^0) [145], and titanium oxide (TiO_2) [94], which have been used as agents either directly or incorporated into a solid support. While their combination has proven a good solution, the resulting antibacterial material has a promising antimicrobial characteristic with low toxicity. Recently, a study was reported by Ozdemir et al. [91] in which they suggested that Na–montmorillonite has no antibacterial activity against S. aureus and E. coli bacteria. While modified montmorillonite using cationic/anionic surfactants and Cu^{2+}/Zn^{2+} has shown a synergistic effect of the ions against both bacteria, it has been confirmed that their toxicity was reduced. Bimetallic nanoparticles based on copper and silver were evenly distributed on the montmorillonite's surface with particle sizes of 10.1 ± 1.7 nm. The release rate of the Cu and Ag ions was higher with the antimicrobial action of bimetallic NPs depending on the concentration of the materials concerned and their stability in the medium [146]. Among the inorganic antibacterial agents, there is chlorine and its compounds, which are agents mainly used in water treatment owing to their effectiveness and low cost. However, their additions alter the taste of the water and react with the constituents present in the medium, and this results in the formation of byproducts that are carcinogenic. In addition, bacteria can develop strong resistance against these agents. The TiO_2 -nanoparticle-based materials are some of the most-commonly used materials for photocatalytic antibacterial applications in view of their low cost, chemical stability, and non-toxic characteristics [147].

The utilization of these metal species alone as an antibacterial agent likely will present challenges with much inconvenience. The major concerns are the unknown post-release health effects of their use. Their accumulation also poses a problem for the environment. Their performance in the laboratory is not guaranteed until they are used in real applications. The precipitation, agglomeration, and complexation phenomena can decrease or weaken their antibacterial activity. Another disadvantage of using these species is their effects on non-target microorganisms.

6. Various Preparation Processes of Antibacterial Metallic Species Supported on Montmorillonite

Microbial infections in everyday life, and especially in hospitals and clinics, often present potentially serious or even fatal situations, especially in immune-compromised patients. To minimize this, there is a need to develop low-cost, easy-to-prepare, non-toxic biomaterials with excellent antimicrobial properties. Nanocomposite materials have been part of this line of research for some time. The smectites have excellent properties, often chosen to reinforce and enhance solids in numerous studies for the elaboration of antimicrobial nanocomposites. Montmorillonite alone has no antimicrobial properties [148], but is capable of absorbing microorganisms due to its large specific surface area and excellent adsorption capacity, while the incorporation of substances into its lamellar spaces make it antibacterial and/or antifungal depending on the nature of the guest substances used. Composites based on metallic species (cations, oxide, or zero valence state) supported on a montmorillonite matrix can be synthesized using several direct or indirect methods, and their preparation is still based on techniques such as intercalation using an ion exchange process, γ-irradiation, hydrothermal synthesis, chemical reduction methods, polyol reduction methods, solvo-thermal methods, electroless plating, hydrothermal synthesis, the sol–gel process, and ultra-sonication [6,149]. The most-reported modification process of montmorillonite using these antibacterial metal species is either by a simple ion exchange method or by organic surfactants, which can provide a higher specific area to host more metal species. The guest metallic particles' size plays a determining role in the antimicrobial behavior. Due to this, several studies have been realized with the aim to optimize their dimensions [144,145,150,151]. As described previously, the variety of reduction methods either by chemical salts, solvents, bacteria, plant extracts, UV and MW irradiation, or thermal treatment have all had an effect on the shape, size, and distribution of the particles on the surface [145,150,152]. Very interesting studies have been carried out in this area; in the rest of this part, some of them will be mentioned. Roy et al. contributed a very informative work: they reported a comparative study on the synthesis and the antibacterial, antifungal, and toxicological behaviors of silver and copper nanoparticles deposited on a montmorillonite matrix using different reduction media [145]. They realized four different ways for reducing the silver and copper metals present on the montmorillonite surfaces (two chemical routes and two physical routes), as presented in Figure 4i. TEM micrographs of the hybrids of silver or copper nanoparticles deposited on montmorillonite are presented in Figures 4ii and 4iii, respectively. From the TEM images, the four reduction processes successfully reduced the silver and copper cations to zero valence states. The size of the nanoparticles dispersed on the clay sheets was strongly reliant on the type of reducing agent used. The smallest diameter of silver and copper nanoparticles was obtained by reduction using borohydride (NaBH₄), while the largest mean nanoparticles diameter was obtained by a thermal process (calcination of the clays). As a result, the authors claimed that montmorillonite had no antimicrobial activity, confirming that the bactericidal action was entirely contributed by the silver and copper species supported on the montmorillonite sheets. The smaller-diameter nanoparticles exerted a toxic effect on the bacteria due to their instability and high reactivity.



Figure 4. (i) Preparation methods; (ii,iii) TEM micrographs and histogram of metallic nanoparticle– montmorillonite hybrids. Reproduced with permission from [145].

Because of their small particle size, they can be difficult to recover from solutions, if not supported on another matrix such as polymers or biopolymers. For this, another attractive study was realized Roy et al. [148], in which they prepared nanocomposite antimicrobial agents based on zinc cations and zinc oxide supported on montmorillonite and polyethylene (HDPE). Figure 5i shows the schematic preparation process of the Zn–montmorillonite and ZnO–montmorillonite materials. TEM images of the prepared materials are presented in Figure 5ii. Spherically shaped ZnO nanoparticles supported by the montmorillonite sheets were observed with a mean particle diameter of about 20 nm. The bactericidal

results of these materials are exhibited in Figure 5iii. The authors concluded that the Zn–montmorillonite material presented a better antibacterial and antifungal activities than the ZnO–montmorillonite material, as the zinc cations were relatively mobile compared to the ZnO nanoparticles.



Figure 5. (i) Preparation methods; (ii) TEM micrographs and histogram of zinc oxide–montmorillonite nanocomposite; (iii) zones of inhibition. Reproduced with permission from [148].

7. Characterizations of the Antibacterial Metallic Species Loaded on Montmorillonite Composites

The most-beneficial techniques that have been used to prove montmorillonite's modification, as well as dispersion and the content and the forms of metallic species on the clay surface are generally XRD, TEM, and XPS analyses.

Figure 6 presents the XRD and TEM analyses of the antibacterial nanocomposites based on silver carbonate and silver nanoparticles stabilized on a montmorillonite matrix [153]. As depicted in Figure 6i, the XRD patterns for the Ag–montmorillonite nanocomposites exhibited the characteristics peaks of metallic silver. The diffraction of the d-spacing (d_{001}) was shifted to a lower degree, due to an increase in the interlayer distance, which could be attributed to the intercalation of silver and Ag₂CO₃ nanoparticles into the montmorillonite galleries. From the XRD, it can be concluded that the presence of the characteristic peaks corresponded to the metallic species and the change in the interlayer distance (d_{001}), suggesting the formation of a metallic–montmorillonite composite.



Figure 6. (i) XRD and (ii) TEM analyses of Ag–montmorillonite and Ag₂CO₃–montmorillonite nanocomposites. Reproduced with permission from [153].

TEM images of Ag–montmorillonite nanocomposites are exhibited in Figure 6ii. By varying the media treatments of the reaction, the mean diameters of the silver nanoparticles changed. This change was detected by the resolution of the TEM analysis. It can be observed that, for each sample, the silver nanoparticles' size was varied. For example, the sample that was treated with ethylene glycol showed a dispersion of small spherical silver nanoparticles with a mean diameter of around 2–3 nm. The other samples showed nanoparticles with mean diameters in the ranges of 7–9 and 15–50. This variety in particle sizes both influenced and was responsible for the antibacterial activity. It has been reported that the antibacterial property was related to the nanoparticles' size and their dispersion throughout the clay.

The XPS technique helped to confirm the metallic species that existed on the clay's surface. Figure 7 presents the elemental dot mapping and XPS spectrum of the SnO₂-montmorillonite composite. As can be seen from Figure 7i, the SnO₂ nanoparticles supported by the montmorillonite displayed a good and homogeneous distribution of SnO₂ on the clay support. Several studies have shown that the good distribution of particles on a lamellar structure has a favorable effect on the antibacterial activity [29]. XPS analysis provides the chemical oxidation state of the metal. Figure 7ii presents the XPS spectra of the SnO₂-montmorillonite composite. The two peaks of binding energy (B.E.) localized at 490 and 498.2 eV were attributed to $(Sn_3d_{5/2})$ and $(Sn_3d_{3/2})$, respectively, showing the existence of Sn⁴⁺ in the SnO₂ nanoparticles. The SnO₂ nanoparticles loaded on the montmorillonite sheets were tested against *S. aureus* and *P. vulgaris* bacteria and showed positive results. The presence of metallic oxide particles with their high surface area was the effect responsible for the enhanced chemical and biological properties of the composite.



Figure 7. (i) Elemental dot mapping of Al, Si, O, and Sn on the surface of montmorillonite. (ii) XPS spectrum of the SnO₂ nanoparticles. Reproduced with permission from [34].

8. Applications Fields of Clay Minerals

Clays are widespread, more-easily available, and low-cost chemical substances. Both in their native state and in numerous modified forms, clays are versatile materials that have a wide range of applications [7,154,155]. Just as it can be molded into any shape, its micro-structure can be modified to suit the needs of chemists depending on the application to be achieved. Several applications of these materials and their composite counterparts are mentioned in Figure 8. As shown in this figure, we can say that the application fields of these materials are very wide, apart from some of them, which are still limited. Clay minerals are receiving more attention in industrial applications, such as being used as a raw material in construction. Clay minerals rich in silica are used for the manufacture of Portland cement and of several ceramic products. Kaolinite is the most-suitable for the manufacture of white Portland cement [156]. Clays that have high potassium content are used as agro mineral additives to enhance soil fertility. Montmorillonite and kaolinite are exploited in pesticide preparations as diluents to enhance the dispersion of the toxicant and keep the pesticide on the plants. They have also been used for centuries in pharmaceutical preparations of intestinally adsorbed drugs and other therapeutically useful applications. Food packaging films and plastic surface modifications are further fields of application. The addition of clay particles to plastics leads to improved strength, barrier, and abrasion properties, excellent surface qualities, low thermal expansion, and very good flow properties and treatment [157]. Their applications in the environmental field for water treatment are due to their good dispersion and their high adsorption capacity [7,158]. They can also be used to reduce and eliminate bad odors and bad tastes from water and also to soften water.



Figure 8. Various applications of clay minerals.

8.1. Clay Minerals in Water Disinfection

Montmorillonite is a type of clay mineral that has been studied for its potential applicability in water disinfection and purification processes. While it may play a role in water treatment, it is important to note that it is not a standalone method for complete water sterilization, especially for water contaminated with pathogenic microorganisms. Instead, clay minerals including montmorillonite can be used as a part of a multi-step water treatment process. The mechanism of montmorillonite's role in water disinfection primarily involves adsorption, a process in which molecules or particles adhere to the surface of the clay mineral. Here is how it can contribute to water treatment:

Adsorption of impurities: Montmorillonite has a high surface area and a net negative charge, which makes it attractive for adsorbing various impurities present in water. These impurities can include organic matter, heavy metals, and some pathogens.

Pathogen removal: Montmorillonite can potentially adsorb certain pathogens such as bacteria and viruses to its surface due to its physical and chemical properties. However, it may not be highly effective in removing all types of pathogens, especially if they are not strongly attracted to the clay's surface.

Heavy metal removal: Montmorillonite can be particularly effective in removing heavy metal ions from water. The negatively charged surface of montmorillonite can attract and bind positively charged heavy metal ions, helping to reduce their concentration in the water.

Adsorption of organic compounds: It can also adsorb organic compounds, which can improve the water's aesthetic quality and reduce the presence of some potential contaminants.

However, it is important to note that montmorillonite alone may not provide complete water sterilization or disinfection, especially for water sources that are heavily contaminated with pathogenic microorganisms. To achieve effective water disinfection, multiple treatment steps are typically necessary such as coagulation and flocculation, filtration, disinfection, and montmorillonite treatment.

Prior to using montmorillonite, the coagulation and flocculation processes are often employed to clump together suspended particles, including pathogens, making them easier to remove. After flocculation, water is usually passed through a filter to physically remove larger particles and microorganisms. This is a critical step in achieving pathogen removal. Following filtration, a disinfection step is required to kill or inactivate any remaining pathogens. Common disinfection methods include chlorination, UV treatment, ozone treatment, or other chemical disinfectants. Montmorillonite can be used as a supplementary treatment step to adsorb any residual impurities and improve water quality further.

Montmorillonite can play a beneficial role in water treatment by adsorbing impurities, including some pathogens and heavy metals. However, it is not a standalone method for complete water sterilization. To ensure safe drinking water, it should be used as part of a comprehensive water treatment process that includes coagulation, filtration, disinfection, and, possibly, additional steps based on the specific water source and contaminants present.

8.2. Use of Montmorillonite-Supported Metallic Nanoparticles as a Potential Antimicrobial for Food Packaging

The spoilage and contamination of food with bacteria and fungi can induce serious human infections, especially in the case of resistant bacteria [159]. Metallic nanoparticles have revealed strong antimicrobial activities. Silver, copper, and zinc species nanoparticles have demonstrated powerful antimicrobial effects against foodborne pathogenic bacteria [160–162]. Metallic nanoparticles stabilized on modified montmorillonite clay resulted in a synergistic antimicrobial effect. The fabrication of food packaging based on this modified clay can generate important physical, chemical, mechanical, and antimicrobial properties [160, 163]. It has been shown that the dispersion of montmorillonite in polymers and biopolymers for food packaging leads to interesting thermal and barrier properties. Shiji et al. [164] fabricated packaging films that were reinforced with montmorillonite and silver nanoparticles. The resultant nanocomposite films were revealed to be highly suitable for food packaging. Due to the presence of the montmorillonite and metallic species, the films showed remarkable properties such as mechanical, light transmittance, moisture content, water adsorption capacity, solubility, and great antimicrobial properties. As can be seen from Figure 9i, the prepared film containing silver species and montmorillonite/PVA/rice starch solution (PASM) had a brown color that was due to the formation of the silver nanoparticles. The surface morphology analysis of the hybrid nanocomposite film clearly showed the montmorillonite aggregates, flakes of rice starch, as well as silver nanoparticles in the form of spots. The antimicrobial properties of the PASM film against food-borne pathogens is presented in Figure 9ii. It shows that the PASM film had a remarkable activity against both S. typhimurium and S. aureus, which proved its applicability in protecting food from established pathogens. Promising work was realized by Afsaneh et al. [165] in which they prepared novel active biodegradable food packaging based on the chitosan polymer, glycerol, and montmorillonite-CuO. It was concluded that the incorporation of only 3% of the montmorillonite–CuO nanocomposite increased the antibacterial property of the composite film against both Gram-positive and Gram-negative bacteria. Martucci et al. immobilized Cu (II) cations through complexation with hydroxyl groups in the layered space of montmorillonite to reduce the cations' leaching. The prepared gelatin/Cu(II) montmorillonite films exhibited low leaching in the tested conditions and retained almost 90% of their inhibitory activity against *E. coli* and *L. monocytogenes*. In the conclusion of their study, the addition of the exchanged Cu(II)–montmorillonite material as an inorganic antibacterial material in the film improved the tensile strength and water vapor permeability properties. Another interesting study was realized by Eskandarabadi et al. [166]. The authors synthesized an intelligent active food packaging by incorporating different additives including a modified montmorillonite. The addition of the montmorillonite material decorated with iron nanoparticles improved the thermal stability, mechanical, antioxidant, and antibacterial properties. Consequently, various important aspects for the use of this phyllosilicate material can be adapted as needed to achieve the desired functionality in the composite film [164, 167]. This strategy can prevent food spoilage through the use of its biodegradable food packaging with varying antibacterial properties [168,169].



Figure 9. Digital image of transparency/appearance, SEM image, and antibacterial tests of nanocomposite films based on montmorillonite. Reproduced with permission from [164].

8.3. Use of Montmorillonite-Supported Metallic Nanoparticles for Water Disinfection

Nanoclays such as montmorillonite are less expensive, less toxic, and more abundant solids with high adsorption capacity for the removal of pathogenic contaminates from wastewater. These solids, with their large surface areas, represent an excellent support for the immobilization of metallic nanoparticles [74,170,171]. The resulting hybrid materials can be used in the disinfection process [83,172–175]. Chao et al. [176] realized a filter paper impregnated with montmorillonite saturated with Fe³⁺ cations, which was produced to filter E. coli bacteria present in water. Figure 10i exhibits the photographs of the filter papers without and with the iron cations. From the SEM images (Figure 10i), it was shown that, after using the paper to filter the contaminated water sample containing E. coli bacteria, some cells remained on the surface of the filter paper. The cells underwent morphological changes, becoming distorted and shrinking. This change was due to the contact with the Fe^{3+} -saturated montmorillonite particles bound to the fibers of the filter paper. The efficiency of water disinfection by the filter paper was evaluated by varying several parameters such as the filter paper/montmorillonite ratio, the amount of bacteria cells in the water, and the presence of Fe-montmorillonite in the filter paper. Figure 10ii presents the water disinfection efficiency results of the filter papers that contained Na-montmorillonite or Fe³⁺-montmorillonite using two different volumes of *E. coli*-bacteria-containing water. After the use of the filter paper without montmorillonite (unmodified), the number of colony-forming units of *E. coli* remained the same, demonstrating that the clay-free paper fibers were not able to trap the cells. During the filtration using the filter paper impregnated with Na⁺-montmorillonite, the cells were trapped, but they remained alive. When the Fe³⁺-montmorillonite-impregnated filter paper was used, the neutralization efficiency of the E. coli bacteria significantly improved up to 99% cell removal. Another form of material was developed to eliminate microorganisms from wastewater. Lovatel et al. [177] prepared montmorillonite-alginate-AgNP hybrid beads for the disinfection of industrial wastewater intended for reuse. The presence of the spherical silver nanoparticles with an average diameter of 13 nm supported by the montmorillonite in the hydride beads indicated a reduction of up to 98.5% of the total coliforms. The authors confirmed that the result was slightly higher when compared to the use of UV radiation. Jiang et al. [174] fabricated a nanomaterial based on montmorillonite decorated with lysozyme-modified silver nanoparticles for bacterial disinfection. The montmorillonite structure prevented the aggregation of the AgNPs and promoted nanomaterial-bacteria interactions.



Figure 10. Photographs of impregnated filter papers that were Fe^{3+} -saturated or contained Na⁺– montmorillonite. Scanning electron micrograph showing *E. coli* cells retained on Fe^{3+} -saturated montmorillonite-impregnated filter paper. Reproduced with permission from [176].

8.4. Use of Montmorillonite-Supported Metallic Species as Antibacterial Materials

Each metal species, whether cations, oxides, or in the zero valent state, exhibits different antimicrobial properties. Their characteristic properties provide desirable contact with the bacterial cell. Several authors have proven that the antibacterial effect of antibacterial metal particles depends on their dimensions, form, distribution, morphology, surface functionalization, and stability. To prevent these species from aggregating, precipitating, and complexing and to retain their antibacterial activity as long as possible, they have been loaded onto various inorganic supports. Due to their well-defined crystal system, montmorillonite along with other layered solid supports are more favorable for metallic species' stabilization. In this sense, several authors have exploited montmorillonite as an inorganic support for antibacterial metallic species. Table 2 summarizes the important recent studies realized from 2015 to date. The collected studies covered the use of montmorillonite as a support for various metallic species and their employment as an antimicrobial agent. We tried to collect the realized studies on a variety of metallic species that mentioned cations, oxides, and nanoparticles to see their behavior on a variety of microorganisms. To prepare antibacterial hybrid materials, most researchers have used montmorillonite as a support for metallic species. It is the most-used inorganic support for the immobilization of metal species with antibacterial and antifungal properties. This solid has been used as an effective carrier for silver, copper, zinc, and other metallic species. The immobilization of silver on montmorillonite as an antibacterial agent is predominant due to the antibacterial effects being very successful against several pathogenic bacteria. Manqing et al. fabricated biocompatible nanomaterials with effective antibacterial activities countering two types of pathogenic bacteria: Gram-positive and Gram-negative [178]. As the result, it was

noted that the bactericidal characteristic of the AgNPs–montmorillonite composite was solely caused by the existence of the silver nanoparticles on the montmorillonite sheets (Figure 11i), and this was caused by the electrostatic forces inhibiting the growth of the bacteria. Despite this highly effective activity against several types of bacteria, the use of silver species alone remains troublesome. Their use alone is always dangerous due of their high toxicity and loss of activity; this type of metal is always in need of a support to be more effective and less toxic.

Table 2. Various studies on montmorillonite-supported metallic species and their preparation for antibacterial activities.

Samples	Preparation Methods	Antibacterial Activity Assay	Bacteria	Initial Diameter	Final Inhibition Zone Diameter	Antibacterial Properties Comments	References
Montmorillonite	Silver nanoparticles				$6.2\pm0.1~\text{mm}$	 The Ag₂CO₃- montmorillonite nanocomposite exhibited an antibacterial activity higher than the Ag-MMT sample against <i>Escherichia coli</i>. 	[153]
Ag– montmorillonite	were prepared by the reduction of (AgNO ₃) over montmorillonite in	Disk diffusion method	E. coli		$14.5\pm0.3\text{mm}$		
Ag ₂ CO ₃ - montmorillonite	the presence and absence of the Na ₂ CO ₃ compound in ethylene glycol.			$6.0 \pm 00 \text{ mm}$	8.5 ± 0.4 mm		
	The silver-loaded clay (AgNPs– montmorillonite) was		Gram-negative bacteria E. coli (ATCC 25922)	15 mm	$44\pm1.6~\text{mm}$	The nanocomposite of	
Nano-silver-loaded acid-activated (AgNPs- montmorillonite)	synthesized by converting the sodium clay form into an acid-activated clay, form then- it was treated by two concentrations of silver nitrate solution to obtain two types of acid activated Ag-montmorillonite.	Disk diffusion test	Gram-positive bacteria S. aureus (ATCC 29213)	15 mm	54.7 ± 1.2 mm	AgNPs-montmorillonite showed antimicrobial activity marginally lower than silver nanoparticles alone, although the silver content was about 10-times lower than the silver nanoparticles.	[144]
		Diffusion method on Muller-Hinton Agar	S. aureus (MTCC96)	-	13 mm	SnO ₂ nanoparticles supported on montmorillonite showed for antibacterial activity against both Gram + and Gram – bacterial strains.	[34]
Acid-activated montmorillonite- supported SnO ₂ nanoparticles			Proteusvulgaris (MTCC426)	-	10 mm		
	The polycarbonate		S. aureus (ATCC6535)	6.0 mm	9.5 mm	The nanocomposite showed an antibacterial	
Ag- montmorillonite/ polycarbonate	solution was mixed with silver-loaded modified montmorillonite and, then, treated with 1,4-dimethylbenzene to obtain functional Ag-Mt/PC with superhydrophobicity.	Disk susceptibility test	E. coli (ATCC8739)	6.0 mm	10.7 mm	activity against both Staphylococcus aureus ATCC 6535 and Escherichia coli ATCC 8739, and the mean diameter of inhibition zone was almost 50% larger than the polycarbonate alone.	[179]
Zn– montmorillonite- coated AZ31	A Zn-montmorillonite coating was hydrothermally	n-montmorillonite coating was hydrothermally prepared using Disk diffusion ²⁺ -ion-intercalated method -montmorillonite n magnesium alloy AZ31.	E. coli (ATCC 25922) gram (-)	-	22 mm	The good inhibition of the Zn-montmorillonite coatings of bacteria was attributed to the slow and sustainable release of Zn ²⁺ ions (up to 144 h).	[180]
	prepared using Zn ²⁺ -ion-intercalated Na-montmorillonite upon magnesium alloy AZ31.		<i>S. aureus</i> (<i>ATCC</i> 25923) Gram (+)	-	32 mm		
CMC/montmorillonite	Via the casting method,	e <u>E. coli</u> Disk diffusion method <u>S. aureus</u>	E. coli	-	0 mm	The simultaneous incorporation of the	[181]
CMC/montmorillonite 5%/ZnO 4%	novel carboxymethyl-cellulose (CMC)-based nanocomposite films containing m Na-montmorillonite (5% wt) and ZnO nanoparticles at different % were prepared.			-	$1\overline{8.4\pm2.6}\ \mathrm{mm}$		
				-	0 mm	ZnO-montmorillonite material improved the functional characteristics of the film, and it has a wide potential for food packaging applications.	
			S. aureus	-	$20.4\pm3.3~\text{mm}$		

Samples	Preparation Methods	Antibacterial Activity Assay	Bacteria	Initial Diameter	Final Inhibition Zone Diameter	Antibacterial Properties Comments	References	
CMC- montmorillonite	 Carboxymethyl-cellulose (CMC)-based films incorporating montmorillonite clay nanoparticles modified with silver and copper ions. 	-cellulose <i>E. coli</i> (Gram- negative) 1 films ting Agar diffusion ite clay method ———— nodified topper		-	$\begin{array}{c} 0.00\pm0.00\ \mathrm{mm} \end{array}$	The microbial tests revealed that AgNPs-montmorillonite had significantly higher antibacterial activity than CuNPs-montmorillonite against Gram-negative and Gram-positive bacteria.	[182]	
CMC- montmorillonite- CuNPs			E. coli (Gram- negative)	-	2.19 ± 0.23 mm			
CMC- montmorillonite- AgNPs				-	3.88 ± 0.19 mm			
CMC- montmorillonite			<i>S. aureus</i> (Gram- positive)	-	$\begin{array}{c} 0.87 \pm 0.06 \\ \mathrm{mm} \end{array}$			
CMC- montmorillonite- CuNPs				-	$\begin{array}{c} 2.45\pm0.24\\ mm\end{array}$			
CMC- montmorillonite- AgNPs				-	6.66 ± 0.18 mm			
		Disc diffusion method using Mueller– Hinton agar	E. coli (ATCC 25922)	6.0 mm	$8.74\pm0.23~\text{mm}$	 The silver nanoparticles with a smaller size were found to have significantly higher antibacterial activity, 		
	AgNPs-montmorillonite materials were		E. coli O157:H7 (ATCC 43895)	6.0 mm	$\begin{array}{c} 10.74\pm0.32\\ mm\end{array}$			
AgNPs- montmorillonite	synthesized by the chemical reducing mothed using NaBH4 in		Klebsiellapneumoniae (ATCC 13883)	6.0 mm	$\begin{array}{c} 10.98 \pm 0.17 \\ mm \end{array}$		[00]	
	the external and interlamellar spacing of		S. aureus (ATCC 25923)	6.0 mm	$\begin{array}{c} 10.02\pm0.10\\ \text{mm} \end{array}$	effective growth	[39]	
	montmorillonite at room temperature.		methicillin- resistant S. aureus (ATCC 700689)	6.0 mm	$8.97\pm0.27~\text{mm}$	biological systems, making them applicable to medical applications.		
	The process was to combine the wound healing property of BC with the antimicrobial activity of the Cu-montmorillonite material to design a novel artificial substitute for burns.		S. typhimurium	-	$\begin{array}{c} 34.33 \pm 0.47 \\ mm \end{array}$	The findings demonstrated that	[183]	
Cu-		Agar disc	S. aureus	-	33.16 ± 0.24 mm	 modified montmorillonite- Bacterial cellulose nanocomposites can be used as a novel artificial skin substitute for burn patients and a scaffold for skin tissue engineering. 		
montmorillonite-		diffusion	E. coli	-	$36 \pm 0 \text{ mm}$			
DC		method	C. fruendii	-	$0\pm0\text{mm}$			
			MRSA	-	$0\pm0\text{mm}$			
			P. aeroginosa	-	$0\pm0\text{mm}$			
			S. aureus	-	-	 The antibacterial effects on Staphylococcus aureus, Micrococcus luteus, and Escherichia coli decreased in the order: AgCI-montmorillonite >AgBr-montmorillonite >AgI-montmorillonite. No antibacterial activity was detected for Pseudomonas aeruginosa. 	[14]	
Montmorillonite	_		M. lutes	-	-			
Monunormornic			E. coli	-	-			
			P. aeruginosa	-	-			
			S. aureus	-	$20\pm0.1~\mathrm{mm}$			
AgCl- montmorillonite			M. lutes	-	16.2 ± 0.3 mm			
monunormonne	Silver halides (AgX, X =	Disk diffusion method	E. coli	-	19.3 ± 0.2 mm			
	in the montmorillonite		P. aeruginosa	-	-			
A . P	surface in the dark.		S. aureus	-	$15.4 \pm 0.2 \text{ mm}$			
AgBr– montmorillonite			M. lutes	-	$15.2 \pm 0.2 \text{ mm}$			
			E. coll	-	$14.2 \pm 0.1 \text{ mm}$			
			S aureus	-				
AσI_			M lutes	_	12.0 ± 0.1 mm			
montmorillonite			E. coli	-	-			
			P. aeruginosa	-				
Konjacglucomannan- montmorillonite- AgNPs with 0.1 mol/L of Ag ⁺ concentration	nnan- In the fabrication procedure, hybrid).1 building blocks were assembled with a thin layer of Konjacglucomannan coating on the montmorillonite nanosheets to form Konjacglucomannan- notmorillonite assembled with a thin layer of Konjacglucomannan coating on the montmorillonite the anosheets to form Konjacglucomannan- montmorillonite the silver nanoparticles were incorporated in the composite.	In the fabrication procedure, hybrid building blocks were assembled with a thin layer of		S. aureus	10 mm 9 mm	20 mm 23 mm	The antibacterial test	
Konjacglucomannan- montmorillonite- AgNPs with 0.2 mol/L of Ag ⁺ concentration		Disk diffusion method	E. coli	11 mm 11 mm	21 mm 23 mm	Konjacglucomannan- montmorillonite-AgNPs composite films significantly suppressed bacterial growth, which makes them favorable for the biomedical field.	[184]	

Table 2. Cont.

Samples	Preparation Methods	Antibacterial Activity Assay	Bacteria	Initial Diameter	Final Inhibition Zone Diameter	Antibacterial Properties Comments	References
Montmorillonite A biofilm DFBF was immersed in the Ag-montmorillonite exchanged material Di montmorillonite solution and oscillated for 24 h and freeze-dried to form the	A biofilm DFBF was immersed in the Ag-montmorillonite exchanged material solution and oscillated	vas e iite ial Disc diffusion ated method	S. aureus	-	-	The montmorillonite, silver cations, and silver nanoparticles resulted in the AgNPs/MMT/DFBF composite films	
			E. coli	-	-		
			P. aeruginosa	-	-		[185]
			S. aureus	-	10.3 ± 0.1		
			E. coli	-	10.8 ± 0.1		
		P. aeruginosa	-	10.2 ± 0.1	effectively inhibiting the		
AgNPs- montmorillonite reduced with 0.01 mol/L NaBH ₄	AgNPs/MMT/DFBF composite.	s/MMT/DFBF	S. aureus	-	8.5 ± 0.1	- growth of G(+) and G(-) bacteria.	
			E. coli	-	8.7 ± 0.1		
			P. aeruginosa	-	7.4 ± 0.2		



Figure 11. (i) Bacteriostatic ring experiment of nanocomposites of AgNPs@LEC-Mt with different silver content against the strains *E. coli* and *S. aureus*. Reproduced with permission from [178].

9. Biocompatibility (Toxicity)

Recently, several authors have evaluated the cytotoxicity characteristics of solid montmorillonite; the usage of this clay mineral as an additive in various medicinal products has been authorized by regulatory agencies [81]. Despite this, the use of montmorillonite in drugs is yet to be approved the reports discussing the biocompatibility and toxicity of nano-clay, organoclays, and pristine clay minerals being important and effective. On the contrary, some nanoparticles are bio-safe materials such as ZnO, which possesses photooxidizing and photocatalysis effects on chemical and biological species [186]. Zinc plays an important role in the human body, since it is one of the most-important trace elements. In this context, we presented various studies that have evaluated the compatibility and toxicity of montmorillonite and its nanocomposites. Jiao et al. [9] evaluated the cytotoxicity of a series of montmorillonite exchanged by metallic cations using zinc and/or copper. In this approach, Cu/Zn-MTT of 0.1 mg/mL exhibited a slight cytotoxicity of 10% to IPEC-J2 cells within 24 h of incubation, while Cu/Zn-Mt-2 with a higher concentration of 0.3 mg/mL led to increased cytotoxicity of about 20% within 24 h. The authors suggested overall that the

Table 2. Cont.

concentrations of the cell population showed stabilization at concentrations beyond the minimum inhibitory concentration value. They explained this as follows: a lower concentration of Cu or Zn had minimal adverse effects on the cells in vitro. Due to their high absorptive characteristic, this has an importance in reducing several toxin types. Montmorillonite was considered as a dermatological and gastrointestinal protector. It played a strategic role in minimizing the cytotoxicity of the Cu/Zn–montmorillonite composite material. Consequently, the resultant Cu/Zn–montmorillonite was a good antimicrobial material with little cytotoxicity. An interesting approach has been reported by Roy et al. [145] concerning the hemocompatibility and the cytocompatibility of Ag-montmorillonite and Cu–montmorillonite hybrid materials. They found that the hemolysis rate was 18–55% for Ag–montmorillonite hybrids and 15–33% for the Cu-MMT samples, in which the percentage of hemolysis increased with the increasing NP-MMT concentration. The authors revealed that the copper-montmorillonite hybrid materials are healthier than silver-based hybrid materials in terms of blood compatibility within the human body. The authors also evaluated the cytocompatibility of Ag-montmorillonite and Cu-montmorillonite hybrid materials in vitro against human fibroblast cells. It was demonstrated that the smaller dimension of the metallic nanoparticles was the probable reason for the higher cytotoxicity effects of the Ag-montmorillonite and Cu-montmorillonite materials. It was noted that the immobilization of the antibacterial nanoparticles on montmorillonite, which is a non-toxic solid, generated a synergistic effect on its cytotoxicity demeanor, and they developed a novel cyto-compatible material with a high antimicrobial activity. In addition, it was suggested by Krishnan et al. [5] that the Ag/TiO₂/bentonite nanocomposite was an effective non-toxic antibacterial material for public health. They found that the nanocomposite can be used to destroy the bacteria that can cause major diseases by direct infection or producing toxins. More than 25 μ g/mL of Ag/TiO₂/bent nanocomposite can destroy S. aureus and E. coli without any side effects on human health. Mainly, it is an antibacterial material that is non-toxic to human beings. Liliana et al. [187] evaluated the biocompatible properties of montmorillonite and a Ag–montmorillonite biocomposite, which were investigated using cytotoxicity assays with the HeLa cell line. Consequently, the in vitro cytotoxicity assays revealed that the montmorillonite and its nanocomposite did not exhibit any significant toxicity. The montmorillonite and antibacterial silver cations had an excellent synergistic effect on the nanocomposite. These types of materials promise potential future use in biomedical applications. Misuse of these substances always has a negative impact on the environment. Excessive use of nanoparticles in various fields such as biological sciences, medical sciences, and commercial products leads to leaks and accumulations in the ecosystem [188]. Protecting the environment and beneficial bacteria against these nanoparticles is very important [189]. Blind use of these nanomaterials, such as silver or copper, their release into the environment, and their leakage can result in one of the most-serious threats to beneficial microbes and microbial communities in ecosystems and to public health. Many microbes benefit the environment and the ecosystem due to their role in bioremediation, the cycling of elements, and nitrogen fixation for plant growth [188,190]. The particle sizes are also responsible for their toxic characteristic [39]. Several researchers have shown that silver nanoparticles with a size less than 5 nm possess high toxicity against nitrifying bacteria via interaction with the cell membranes [188].

10. The Antibacterial Mechanisms

Several studies have exhibited that montmorillonite, as well as zeolites and layered silicates alone did not present any antibacterial activity [42,101,178], unless some antibacterial agents were absorbed or incorporated onto their surfaces. Usually, these solids serve as a carrier for the dispersion of particles, as well as the adsorption of microorganisms due to their high exchange capacity. Many theories have been proposed regarding the mechanism responsible for the death or growth inhibition of bacteria. The antibacterial mechanisms of various agents vary from cell-wall-/membrane-damaging abrasiveness, the release of metal ions to inhibit certain oxidative enzymes, the denaturation of proteins, or interference with

DNA/RNA replication [191]. Several authors have suggested the interactions between metal species and the bacteria that describe the antibacterial activity [181,192,193]. For this, four main mechanisms are proposed as follows:

- Metallic species are capable of blocking the electron transport system in bacteria.
- Metallic species kill bacteria cells by rupturing the cell membrane and cell wall.
- Metallic species interact with bacterial cell DNA, which results in mutation and causes cell death.
- The destruction of bacterial cells by silver free radicals.

Although the antibacterial effects of metal species against various bacterial systems are well established, several studies were based on TEM and SEM analysis in order to reach the real mechanism of these species. Matai et al. [193] tried to establish a plausible mechanism at the molecular level and the mode of action of these metallic species. Four possible actions of these species against bacteria have been shown, as presented in Figure 12i. As can be seen, the principal actions are summarized as follows [193–199]:

- 1. The direct interaction with the bacterial cell membrane via electrostatic interactions between the ions released and the negatively charged bacterial cell wall.
- 2. The second action is the disruption of the bacterial cell membrane, by paving a way into the bacterial cells, leading to membrane protein and lipid bilayer damage.
- 3. The third action is at the cellular level by the disruption of the bacterial cell membrane, by either altering the membrane proteins or enzyme activity in an ROSmediated manner. At the molecular level, it inhibits DNA/plasmid replication and proteins/enzymes in cells either via ROS formation or by metal ions directly.
- 4. The fourth action is the leakage of intracellular material owing to membrane disruption, which may cause the shrinkage of the cell membrane, ultimately leading to cellular lysis.



Figure 12. Schematic representation of the four plausible antibacterial mechanisms of the Ag–ZnO nanocomposite. Reproduced with permission from [193].

11. Conclusions, Future Research Proposition, and Deficits

Montmorillonite alone has been utilized as a good living microorganism adsorbent owing to the existence of differing types of active sites located on the sheets, such as high ion exchange sites and Lewis and Brønsted acid sites. The direct modification of montmorillonite by antibacterial metallic species was obtained by a variety of rapid, simple, and inexpensive processes. Additionally, its indirect modifications using organic surfactants provide a higher specific area for metallic species' immobilization.

This review unveiled the antimicrobial materials based on the supported antibacterial metallic elements on montmorillonite for the elimination of a variety of pathogenic bacteria. A comparison of the antibacterial activity of each nanomaterial alone, namely montmorillonite, montmorillonite-supported metal, and metal revealed that the activity of the montmorillonite-supported metal is the most-effective among them. The good dispersion of the metallic species on the surface of the montmorillonite was the parameter responsible for the exposure of the antibacterial activity. The results demonstrated that the order of the antibacterial activities of the nanomaterials were in order of metal species-montmorillonite > metal species > montmorillonite. Metallic species impregnated on montmorillonite as additives can be used not only for water disinfection, but also for the removal of organic contaminants from water. Several benefits might be generated through the use of metallic species supported on montmorillonite in the elaboration of hybrid composites such as compatibility, biodegradability, and reducing the toxicity and the cost. Another challenge that can be awaiting these antibacterial materials is their competition with conducting polymers for bio-applications. These types of polymers resemble metals due to their electrical and optical properties. These materials are versatile because their properties can be easily modulated by surface functionalization and/or doping. Their structure allows the possibilities of interaction and incorporation/immobilization, as well as the even dispersion of the material, and their design and easy synthesis result in the inheritance of more advantages that offer new functionalities due to the synergistic effects between the components. Therefore, it is possible to combine these two classes of materials to arrive at nanocomposite structures with unusual physicochemical properties, biocompatibility, and multifunctionality, facilitating their bio-applications. The synergistic effects between these two classes can also make these materials particularly attractive in biomedicine.

From the perspective of low cost, antibacterial materials such as natural clays modified with metallic species hold great promise. Future efforts will involve large-scale application of modified montmorillonite, which will require significant financial and technological resources. Montmorillonite modified with these antibacterial metallic species would be the subject of several future studies in which work has been initiated. To minimize human contamination of public surfaces, it is important to use them as additives in paints, cements, and general building materials.

Certain challenges remain to be assessed for this type of composite, namely:

- The need to establish the antimicrobial activity of these materials with different bacterial populations.
- The evaluation of antibacterial activity efficiency after several cycles of regeneration.
- Studies should be carried out to quantify and detect the chemical nature of the metallic substances released.
- Ensuring that the antibacterial property of these materials is preserved over time.

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