

Review

Microbial Interaction with Clay Minerals and Its Environmental and Biotechnological Implications

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Abstract: Clay minerals are very common in nature and highly reactive minerals which are typical products of the weathering of the most abundant silicate minerals on the planet. Over recent decades there has been growing appreciation that the prime involvement of clay minerals in the geochemical cycling of elements and pedosphere genesis should take into account the biogeochemical activity of microorganisms. Microbial intimate interaction with clay minerals, that has taken place on Earth's surface in a geological time-scale, represents a complex co-evolving system which is challenging to comprehend because of fragmented information and requires coordinated efforts from both clay scientists and microbiologists. This review covers some important aspects of the interactions of clay minerals with microorganisms at the different levels of complexity, starting from organic molecules, individual and aggregated microbial cells, fungal and bacterial symbioses with photosynthetic organisms, pedosphere, up to environmental and biotechnological implications. The review attempts to systematize our current general understanding of the processes of biogeochemical transformation of clay minerals by microorganisms. This paper also highlights some microbiological and biotechnological perspectives of the practical application of clay minerals–microbes interactions not only in microbial bioremediation and biodegradation of pollutants but also in areas related to agronomy and human and animal health.

Keywords: clays; microorganisms; bacteria; fungi; lichens; soil; biogeochemical transformations; biomineralization; biotechnology; bioremediation

1. Introduction

The interactions of clay minerals with microorganisms are ubiquitous on the Earth and have great environmental and economic significance. This phenomenon has attracted increasing interest over recent decades.

Because of the multiple meanings of the source- and context-dependent term “clays” the straightforward definition of the term “clay minerals” is complicated and not generally agreed [1,2]. Clay minerals are primarily referred to as the phyllosilicate family of minerals characterized by the layered structures composed of polymeric sheets of silica tetrahedra and Al-, Mg-, or Fe-containing octahedral, and with small particle size mostly ranging from nanometres to tens of micrometres [1,2].

Clay minerals can also contain variable amounts of alkali metals, alkaline earths, and other cations. The composite tetrahedral-octahedral layers may contain interlayer sites, where the molecules of water, organic molecules or CO₂ can be reversibly intercalated. For some clay minerals the small particle size (<2 μm) puts them in a range overlapping with colloidal material, and this in combination with their large surface area contributes to their immense sorption reactivity. The layered structure of clay minerals has great affinity for water and confined H₂O molecules in clay interlayers are important

elements of their structure [2,3]. A fundamental division in clay mineralogy arises from differences in the occupancy of sites within the octahedral sheet.

The differences in clay minerals structure give them different physical and chemical properties. Clay minerals are generally classified into four layer types based upon the number and arrangement of tetrahedral and octahedral sheets in their basic structure.

The main structural unit of the first layer type 1:1 contain one tetrahedral and one octahedral sheet (e.g., species: kaolinite, halloysite, chrysolite, amesite). Soils dominated by 1:1 minerals exhibit a low capacity for adsorbing cations and have low fertility [4,5].

The structure of clay minerals of the second layer type 2:1 is formed by combining two tetrahedral sheets with one octahedral sheet. This group includes one of the largest and the most important among phyllosilicates the smectite group (e.g., montmorillonite), as well as the mica group (e.g., illite, muscovite, biotite) and talc group [6].

The third group is represented by phyllosilicates of the palygorskite-sepiolite group, with a tape-like structure consisting of a continuous two-dimensional tetrahedral sheet and discontinuous octahedral sheets. Each of the tapes is connected with the next by inversion of SiO_4 tetrahedra along a set of Si–O–Si bonds. Micropores, channels and small particles together with the fibrous structure create a large surface area [7].

The fourth layer type 2:1:1 is represented by chlorite group (e.g., species: baileychlore, ripidolite, chamosite, pennantite) and has a tetrahedral-octahedral-tetrahedral structure, the interlayer of which is provided by additional octahedral hydroxide sheets. These positively charged sheets balance the excess negative charge of the 2:1 layer [8].

The morphological diversity of clay minerals at the micrometre scale: rods (e.g., palygorskite) [9], fibers (e.g., sepiolite) [10], tubes (e.g., halloysite, imogolite) [11] and sheets (e.g., kaolinite, montmorillonite, vermiculite, illite/smectite) [12], also provides them with special physicochemical properties that determine their functions in the environment.

Clay minerals' abundance and their remarkable properties make them especially important minerals in natural history of our planet and of a great potential for various practical applications. Due to their unique physical and chemical characteristics, such as water-retention and cation exchange capacities, surface-to-volume ratio, influence on the configuration of soil fabric, ability to serve as K sink and reservoir of adsorbed organic carbon, the clay minerals became key players in the interaction between microorganisms and the lithosphere [13]. The clay minerals' ability to adsorb, concentrate, and subsequently catalyse the polymerization of important biological monomers might supposedly have played a key role in chemical evolution and the origins of life [14].

Clay minerals are the most stable forms of silicate in the pedosphere, and typical weathering products of other silicate minerals, which are the most abundant on Earth [15,16].

Understanding the changing of near-surface clay mineralogy of the Earth in the past geological times is complicated by the fact that most of the Earth's early clays deposits were erased as a result of tectonic activity and erosion [17,18]. Nevertheless, the evolutionary history of clays can be deduced from the observations of rocks and studies of modern clay-forming processes. Thus, the formation of clay minerals over time is an important part of the Earth's mineralogical history and serves as an example of the principles of mineral evolution and co-evolution with life. The phyllosilicate clay minerals are believed to illustrate the relationship between the geosphere, hydrosphere and biosphere more than any other mineral group [19]. The joint evolution of geo- and biosphere is thought to have begun in the early Archean (at least 3.5 billion years ago) with the emergence of the earliest primitive life-forms represented by anaerobic prokaryotic microorganisms from the domains Archaea and Bacteria [13,20–22]. Despite of that at this anoxic stage the terrestrial microbiota was not numerous and had very primitive effects on clay minerals; the iron-reducing microorganisms might have been able to alter dioctahedral smectite, illite and chlorite [22].

The crucial stage in the mineral-life co-evolution occurred in the Proterozoic (2.5 billion to 541 million years ago), when the level of atmospheric oxygen rose dramatically (the Great Oxygenation

Event) [23]. This oxygen increase triggered an explosive growth in the variety and number of minerals including clay minerals as well as an expansion of a primitive terrestrial microbiota including metabolically diverse prokaryotes (domains Archaea and Bacteria) and first eukaryotic microorganisms (domain Eukaryota), including fungi that emerged at least in the mid-Proterozoic [20,23]. The expansive colonization of primitive terrestrial microbiota is thought to enhance mineral weathering leading to the first volumetric significant formation of pedogenic clay minerals and, as a result, most clay minerals originate in biologically active soils [23].

The majority of biomass on the planet is considered to be microbial, where many microorganisms are actively involved in the processes of biogeochemical transformations of the minerals including their dissolution and weathering as well as precipitation and biomineralization [13,24–26]. The microbial interactions with the clay minerals, as common mineral constituents of soil, are a fundamental part of the processes of soil genesis and functioning. Clay minerals can significantly alter microbial growth and biosynthetic activity by facilitating nutrients and providing protection against unfavourable physico-chemical conditions. The biological effects of clay minerals on microorganisms can be exploited in various biotechnological areas including traditionally considered bioremediation for the cleaning-up of organic and inorganic pollution.

This review is aimed at covering the current views on the broad and very significant phenomenon on a planetary scale of clay minerals' interactions with microorganisms ranging from the effects on organic biomolecules to the interplay with individual and aggregated microbial cells, fungal and bacterial symbioses with photosynthetic organisms, affecting biogeochemical cycling of elements and pedogenesis processes in the lithosphere. It also attempts to cover some important environmental and biotechnological aspects of these interactions which are related to their use in bioremediation and biodegradation as well as in human and animal health, and agronomic biotechnologies.

2. Co-Occurrence of Clays and Microorganisms in Nature

The integral part of the interactions of clay minerals with microorganisms as the most primitive form of life on the planet is inevitably the physical and chemical effects of clays on the biologically important organic molecules. There is a consensus that the interaction of organic molecules with the surfaces of minerals might have played a crucial role in chemical evolution and complexification of organic molecules in a prebiotic era [27]. It was Bernal (1951) who first suggested that clay minerals played a key role in the chemical evolution and origins of life [14]. In solids, the adsorption of organic molecules produces concentration of the adsorbate. Without such a concentration, most scenarios for the origin of life come to a halt, and highly concentrated prebiotic environments may be implausible.

Clay minerals are capable of selectively concentrating and internally binding compounds which made them probably the most geologically relevant and abundant surfaces on the primitive Earth's surface. They might be capable of (1) concentrating the organic molecules present in a diluted ocean by adsorption on clay deposits; (2) catalyzing the polymerization of adsorbed organic compounds; (3) providing protection of these organic molecules from ultraviolet (UV) irradiation and destruction; (4) inducing molecular chirality [28]. The works on the role of clays in prebiotic organic synthesis ranges from elementary adsorbents and catalysts to the controversial claim that clays were the first functional polymerization templates [29].

The adsorption mechanism of organic molecules with clays is a complex phenomenon where different interactions can take place: H-bonding, ion-dipole and interactions of the van der Waals type. The organic compound also may complexate with clay counter-ions or it may undergo ionic exchange [30]. It has been experimentally shown that one ton of montmorillonite incorporated up to 550 kg of protein, 150 kg of fatty acids or 200 kg of carbohydrates [31]. The biomolecules adsorption is generally thought to increase in acidic pH [28]. There are many studies of clay minerals related to the adsorption of the particular types of biological compounds (amino acids, peptides, nucleic acid bases and their derivatives, carboxylic acids and sugars), which is regarded as the initial stage for the variety of reactions occurring within clay [31–33]. The adsorption of amino acids was reported to

increase with decreasing pH and increasing concentration, and their orientation was parallel to the basal surface of the clay, which might affect further polymerization [34]. The mechanisms involved included mainly cation exchange as well as ion-dipole coordination interactions and hydrogen bonds; and these processes were dependent mostly on the isoelectric point, molecular size, shape of the molecule, and pH of the solution [28]. The general observations for the binding of nucleic acid bases, nucleosides, nucleotides and poly-nucleotides in clay minerals demonstrated that adsorption was also more extensive at acidic pH; the adsorption of purines was higher than of pyrimidines, and the extent of nucleotides and nucleosides adsorption was larger than for their corresponding bases [28]. Out of two binding sites of clay minerals, the interlamellar channel and the edges of the clay, nucleic bases are adsorbed mainly in the interlamellar channel. Experimental data on the adsorption of sugars on clay minerals are scarce, showing very low adsorption, as for anionic polymers it is mostly occurring at the edges of the clay platelets [28].

Clay minerals might have provided a protection against high-energy radiation to adsorbed molecules. It was demonstrated that the recovery of the purine nucleobase adenine after a γ -irradiation was higher in the clay-containing system compared to the clay-free control, testifying to the protective role of clays [35]. Clay minerals are also important in catalysis of diverse organic reactions, through several mechanisms: by energy transfer processes, redox reactions, stabilization of intermediates, and as Bronsted or Lewis acids [28]. One hypothesis of the origins of life describes the “RNA world” in which RNA molecules acted as both enzyme-like catalysts and genetic materials [36]. The condensation of activated RNA monomers has been achieved by clay catalysis [37,38]. The activity of the silicate structure in the catalytic process of clays also suggests that other reactions essential for a living cell metabolism might have been feasible, for example transamination (transferring an amino group from an amino acid to a keto acid forming new amino acids) and decarboxylation (removing a carboxyl group from a carboxylic acid and releasing carbon dioxide).

According to the data of Ramos-Bernal and Negrón-Mendoza [28], the ionizing radiation may affect heterogeneous catalysis of a clay mineral and alter the main pathways of transformation of organic molecules adsorbed on clay. They observed that gamma irradiation of the clay-organic acid system led to the enhancing by several orders of magnitude and the predominance of the decarboxylation reaction of carboxylic acids (e.g., malonic acid) catalyzed by a clay mineral (Na-montmorillonite) over the condensation/dimerization pathways of the catalysis. The authors suggested that the phenomenon of radiation-induced catalysis may be connected with ionizing processes in the solid and with the trapped non-equilibrium charge carriers. The authors also discussed the different aspects of the energy and charge transfer in clays as “activated solids” considering, first, that the clays may function as energy-transfer solid moderators thanks to the clays’ ability to provide storage for the energy from environment within and to release this energy in various forms. Secondly, there exist the energy transfer modes across interfaces that are absent in homogeneous phases. Thirdly, both energy and charge transfer may affect the organic molecules absorbed in a clays as an “activated solid”, meaning the possibility of the energy transfer from clays to adsorbate in the case of radiation-induced catalysis [28].

Additionally to the catalytic activity of clay minerals, polymerization thermodynamics is thought to play an important role in the polymerization of organic molecules on a clay surface in the following way [39]. This process is coupled with transformations in which the system passes into a state of low water activity. The reaction of peptide bond formation is a condensation, producing one water molecule for each bond formed, and this water should be removed as the products of any reaction to drive the reaction equilibrium to the right. In the organic compound-clay mineral system, the water molecule is removed in the reaction favouring the condensation.

It was also suggested that porous structures with the sizes ranging from the nanometer to the micrometer probably harboured the first proto-organisms providing protection from dispersion and other damage. Hanczyc et al. (2003) showed that montmorillonite clays facilitated the transformation of fatty acids into encapsulating vesicles, simulating the compartmentalization typical for eukaryotic cells or the efficient functioning of specific organelles in which a lipid layer membrane separates areas

within the cell [40]. In addition, RNA adsorbed to clay can be encapsulated within such vesicles. Enhanced prebiotic encapsulation of mineral particles within membrane vesicles would bring the catalytic potential of the mineral surfaces into the membrane vesicle. For example, oligonucleotides might be synthesized inside vesicles on the surface of encapsulated clay particles. In this way clay minerals might function as a primordial cell prototype [41].

Recent *in silico* studies on the prebiotic processes that possibly occurred on the mineral surfaces of clays and silicates demonstrated that the simulation of these processes through quantum mechanical methods based on the density functional theory can help chemists to address the behaviour of the molecular world through large models mimicking chemical complexity [27].

The clay minerals' ability to adsorb, concentrate, and subsequently catalyse the polymerization of important biological monomers, that supposedly has played a significant role in synthesis of biologically viable molecules on prebiotic Earth and ultimately the origin of life, undoubtedly has been a very important element of the clay interactions with microorganisms in the natural history of our planet.

While elucidating the nature of microbial interactions with clay minerals, the important questions are where and how these interactions occur on the planet, and which characteristics of microorganisms promote their existence and activity in the mineral-rich environment. These interactions are involved in the global geochemical cycles and processes where clay minerals with their unique physicochemical properties are harbouring microbes creating specific microenvironments, providing nutrients and protection, and manifesting various biological effects on microbial growth and biosynthetic activity. On the other hand, through their biogeochemical activity the microorganisms can affect the geochemical processes of the clay minerals' transformations and the whole environment [13,26,42].

The main co-occurrence of clay minerals and microorganisms happens in the pedosphere, which is the intersection of the lithosphere (unconsolidated regolith and consolidated bedrock), atmosphere (air in and above the soil), hydrosphere (water in, on and below the soil), and biosphere (living organisms) [43]. This zone is regarded as a reactor and regulator mediating and controlling chemical and biogeochemical fluxes of energy and substances contributing first to soil formation and development but also to biogeochemical cycles globally.

Microorganisms including bacteria, archaea, cyanobacteria, microalgae, and free-living and symbiotic fungi in association with soil particles represent the soil crust developing at the top of soils and generate a coherent layer which stabilizes the soil [13,44]. In the soil crust, clay and other mineral particles are functioning as the structural materials providing inorganic nutrients as well as protection against radiation and desiccation [45]. As water can be retained in and retrieved from the pores and interlayer space of the expandable clay minerals, the latter are regarded as essential intermediates in the provision of water in soil crust [13,46].

The integral central part of the processes of soil genesis, functioning and fertility is microbial interactions with clay minerals and humic substances, with the latter representing the largest stable organic carbon pool in the terrestrial environments. The humic substances in soils are complex mixtures of microbial and plant biopolymers and their degradation products [47]. In general, the favourable effects of clay minerals and humic matter on microorganisms in soil can be partly explained by the contributions of these colloids to the mineral nutrition of the organisms [48]. Clay and humic matter in soil accumulate pools of reversibly bound nutrient cations (NH_4^+) and anions (such as phosphate species) that can be released to microbes by ion exchange. The essential metals for microbiota released from clay minerals in soils include K, Na, Mg, Ca, Fe, Mn, Co, Zn, Cu, and Mo [13,24,26,42].

Nevertheless, if adsorbed on the clay minerals, the availability of organic matter usually decreases, potentially leading to its protection from microbial attack in soils [13]. The complexes of clay and humic acids were reported to stabilize complex organic compounds such as highly labile biopolymers like proteins and polysaccharides, increasing their resistance to microbial decomposition [48]. It was also observed in a sand/clay microcosm study, that both linear and circular DNA bound to various clay minerals, leading to a retarded enzymatic DNA degradation [49]. The protection of clay-adsorbed

DNA molecules from enzymatic degradation by deoxyribonuclease I (DNase I), which performs DNA cleavage preferentially at phosphodiester linkages adjacent to a pyrimidine nucleotide, was found to be higher in the case of montmorillonite and organo-clay complexes compared to kaolinite and inorganic clays [50]. The authors reported that the adsorption affinity of DNA molecules for the colloids and the conformational change of bound DNA did not obviously control this protection process. The phenomenon of the DNA molecules protection by clay minerals may be of great importance in soils where it can facilitate the efficient gene transfer between microorganisms, including the genes encoding antibiotic resistance in microbes. Little is known about interactions between antibiotics and clay minerals in nature. It was demonstrated that bacteria isolated from montmorillonite-rich/kaolinite-poor soils were more sensitive to streptomycin than those isolated from montmorillonite-poor/kaolinite-rich soils, suggesting that kaolinite, being less effective streptomycin sorbent compared to montmorillonite, caused the changes in bacterial community promoting the survival of the drug-resistant microbes [48].

Microorganisms are ubiquitous on the Earth's surface and by far the most abundant living beings, which have been on the planet much longer than other life forms. They, in great proportion, live in mineral-rich substrata playing key geoactive roles in the biosphere, particularly in the areas of element biotransformations and biogeochemical cycling, metal and mineral transformations, decomposition, bioweathering, and soil and sediment formation [13,26]. Biogeochemically important groups of microorganisms, which are directly involved in the mineral transformations, include iron-oxidizing and -reducing bacteria, manganese-oxidizing and -reducing bacteria, sulfate-reducing bacteria, sulfur-oxidizing and -reducing bacteria, and many other pro- and eukaryotes that can form or degrade silicates, carbonates, phosphates and other minerals [26]. The range of environments colonized by microbes is not limited to the surface but extends deep underground to over 5 km [51] and reaches extreme environments which, until recently, were thought to be inhabitable [52]. Microorganisms are abundant and interact with mineral matter in biofilms and microbial mats associated with ponds, hot springs, marine sediments and sub-seafloor basalts, on the rocks and minerals in cold and hot deserts, dust, as well as in anthropogenic environments including mine drainage areas, mineral-based building materials, constructions and monuments [24,25,53–55]. For example, it is estimated that ~75% of the greatly colonized submarine basaltic glass in the upper 300 m of the ocean crust is being altered through microbially induced weathering which is several orders of magnitude faster than inorganic alteration [13]. Such microbially mediated bioweathering of volcanic glass can be considered as an important path of chemical transfer from the mantle to the oceans. The products of this biogeochemical basalt alteration include clay minerals and are typically enriched in K, serving as a sink of this element helping to equilibrate the unbalanced K budget in the ocean [13].

It is supposed that about 75% of total biological carbon on Earth corresponds to biomass of prokaryotes (~50%) and fungi (25%), of which the majority live in contact with minerals [13]. Both prokaryotic microorganisms (archaea and bacteria) and fungi can be highly resistant to extreme environmental conditions including metal toxicity, desiccation and UV radiation, and they can employ various growth, metabolic and morphological strategies to survive and thrive in the mineral-rich environment. It seems that a considerably smaller number of microalgae is associated with minerals compared to prokaryotes and fungi. Being the most numerous and studied by geomicrobiologists, bacteria and archaea exhibit extensive metabolic versatility growing under both aerobic and anaerobic conditions, and play highly significant geochemical roles in cycling of elements [24,26,56]. Fungi are a very abundant and ubiquitous on the planet and a biogeochemically active group of eukaryotic microorganisms with the ability to perform mineral dissolution more efficiently than bacteria at higher pH values and over a wider redox range [24,26]. The uniqueness of fungi in terms of global geochemical processes on Earth is their ability to form mutualistic symbiotic associations with photosynthetic organisms (plants, algae and cyanobacteria) and to function in these associations as biogeochemical agents [57]. The filamentous growth mode of the majority of fungi contributes to successful colonization of heterogeneous environments by translocation of nutrients and mobile metal species within the interconnected mycelial network with high-surface-area-to-mass ratio, where

individual hyphae in many fungi are surrounded with hydrated mucilaginous sheaths of extracellular polymeric substances (EPS) [24,57–62]. The functions of these EPS sheaths can include protection, attachment and providing encapsulation for the biogeochemical processes including dissolution and precipitation reactions [58,60–62]. This filamentous growth of fungi can contribute to the process of soil aggregation by entrapping and enmeshing the soil mineral and organic matters into stable macroaggregates (50 µm in diameter) by fungal hyphae and fungal polysaccharide EPS, which was experimentally demonstrated for both free-living and symbiotic mycorrhizal fungi (*Rhizoctonia solani* and *Hyalodendron* sp., *Hymenoscyphus ericae* and *Hebeloma* sp.) [63,64]. Fungi can also employ a unicellular mode of growth as yeasts or yeast-like cells, e.g., the rock-dwelling microbial communities of black meristematic or microcolonial fungi [56,65,66].

For both unicellular and filamentous prokaryotic and eukaryotic microorganisms, the growth strategy when microbial cells aggregate together, usually being embedded in the hydrated mucilaginous matrix containing EPS, is a very common phenomenon considerably increasing the microbial chances of survival under unfavourable environmental conditions including metal- and mineral-rich substrata [13,58]. The ultimate result of such an aggregation strategy is a formation of mature microbial biofilms which are widespread in nature three-dimensional structures that can contain diverse communities of bacteria, archaea, fungi, cyanobacteria, and algae [13,67]. Each species in multimicrobial biofilms has metabolic specificity and cells communicate with each other via the signalling system within an EPS matrix consisting predominantly of polysaccharides (50–90%), and also proteins and nucleic acids [13,67]. The soils and subaerial rock surfaces, endolithic environments as well as surfaces submerged in water are all harbouring microbial biofilms facilitating cells attachment to the mineral surfaces [68–70].

The biofilms matrix can enclose either entrapped or microbially precipitated mineral particles, in particular clay particles, as was demonstrated in the comparative study of volcanic glass alteration under exposure to the microbial biofilms and to the abiotic inorganic conditions [69,70]. This phenomenon results in the organo-mineral aggregates and biofilm-mineral structures [3]. Such structures consisting of bacterial microcolonies or individual cells embedded within the EPS matrix with clay particles tangentially attached to the matrix surface were observed in natural marine sediments by Ransom et al. (1999) [71]. It was suggested that due to their great adsorptive capacity and surface area, clays may serve for bacteria in such structures as a sink for the waste products and provide nutrients adsorbed in proximity [71]. The similar “house of cards”-kind densely distributed structures consisting of clay aggregates glued by microbial EPS and surrounding the bacterial cells (so called clay “hutches”) formed on a glass slide in the experiments on the biofilm development in a microcosm with soil dispersed with sterile water [72]. For biofilm formation by microbes on the mineral substrata the factors of great significance are such characteristics of the mineral surfaces as microtopography, surface composition, surface charge and hydrophobicity, which affect the processes of microbial attachment and detachment as well as contact sensing (or thigmotropism for filamentous microorganisms) [26,73].

The process of attachment of microbial cells to the mineral surface is a crucial initial step in biofilm genesis and development on these substrata. The bacterial adhesion is thought to be affected by the surface properties of both microbial cell and mineral as well as the peculiarities of the solution chemistry [42]. Cheng et al. (2019) recently reviewed the mechanisms of bacterial attachment related to the micro- and nano-topography of the surfaces [73]; where the classical DLVO (Derjaguin–Landau–Verwey–Overbeek) theory was compared to the modified extended DLVO version (or XDLVO). The total interaction force between a surface and a bacterium cell is given by the sum of Lifshitz–van der Waals attractive forces and electrostatic interactions in the DLVO theory, whereas in XDLVO the acid–base interaction forces which are dominant in the short range between bacteria and the surface (<1 nm) are also considered. Because of this addition of the acid–base interactions, essentially affecting the total force direction in separation distance of a few nanometers between bacterial cell and a surface, the XDLVO theory is thought to be more accurate in predicting initial colloidal particle attachment [73]. It was also reported that bacterial attachment to the kaolinite surfaces may occur

through cation-bridges, facilitated by the release of interlayer metal cations from smectite particles (e.g., calcium and sodium), as well as through hydrophobic interactions, EPS layer and protein-binding receptors [42,74].

Another geomicrobiologically important microbial strategy of survival and flourishing in the terrestrial environment is formation of mutualistic symbiotic relationships. The extremely biogeochemically-active forms of fungal growth for colonization and exploitation of soil and rock environments are the symbiotic associations of fungi with root cells of land plants (mycorrhizas) and with photosynthetic microorganisms, cyanobacteria and algae (lichens) [75]. In these mutualistic relationships, photosynthetic partners are supplying carbon to fungi whereas fungi are providing the increased access to the mineral nutrients, especially phosphorus, as well as the protection from unfavourable conditions (e.g., metal toxicity and desiccation) [56,57,75–78]. The mycorrhizal fungi, through their biogeochemical activity, cause physico-chemical changes in the root environment leading to the enhanced mobilization of metal cations from soil minerals making them available for host plants [79,80]. Considering that nearly all land plants depend on mycorrhiza, such a form of symbiotic partnership is of tremendous significance for global geochemical processes on the planet [76]. Lichens, regarded as pioneer colonizers of fresh rock outcrops and one of the earliest life forms to occupy the surface terrestrial environments, are also very important biogeochemical agents in global pedogenesis processes contributing to nutrient distribution and retention [75,77,81]. The ability of this form of symbiotic partnership to survive and thrive in extreme sub-aerial environments results in the domination of the lichens on around 6% of the Earth's land surface [56,82].

Rock-dwelling microbial communities in sub-aerial environments deal with extremes such as very scarce nutrients, unfavourable pH, water potential and salinity, metal toxicity, sunlight and UV radiation, and sharp temperature changes. In addition to, already mentioned above, survival strategies such as aggregation of microbial cells within hydrated mucilaginous matrix in biofilms or formation mutual symbiotic partnership in lichens, microorganisms inhabiting rocks also employ specific foraging and protective adaptations [56,57,65,66]. There are microorganisms, called oligotrophic, that are able to scavenge nutrients from the rainwater and air, including organic and inorganic residues such as dust particles, aerosols, waste products of other microorganisms, decaying plants and insects, and animal faeces, which are available in the sub-aerial rock environment [56,57]. The protective strategies of rock-inhabiting microorganisms may include the synthesis of pigments and other biomolecules shielding cells from sunlight and UV radiation such as, for example, melanin pigments and mycosporines accumulated in the fungal cell walls, or also the entrapment of clay particles within mucilaginous polysaccharide sheaths surrounding the cells [65,66]. Exploration of the space within rocks, such as cavities, cracks, grain boundaries and fissures also enables microorganisms to survive in this harsh environment [83–85]. These microorganisms can be classified as (a) epiliths, occurring on the rock and stone surface; (b) hypoliths, dwelling on pebbles; (c) endoliths, inhabiting the rock sub-surface which can occur as (d) the chasmoliths often visible from the rock surface, growing in pre-existing cracks and fissures, (e) cryptoendoliths, growing inside cavities and among crystal grains and (f) euendoliths as a specialized group of cryptoendoliths that are able to penetrate actively into the rock substrate, for example actively burrowing fungi [86,87]. The dark-pigmented microcolonial fungi with thick melanised cell walls often represent the epiliths [88]. Epiliths, endoliths and actively burrowing cryptoendoliths were found among taxonomically diverse filamentous fungi of the phyla Ascomycota, Basidiomycota and Zygomycota (the latter is now divided to two phyla Mucoromycota and Zoopagomycota) [56,89,90].

An interesting example of cryptoendoliths is a recent discovery of both fossilized and active hyphae of anaerobic cryptoendolithic fungi in marine sediments and sub-seafloor basalts (740 m depth at the Laxemar site, Sweden), which may play an important role in the subsurface energy cycle [55]. The deep biosphere is one of the least understood ecosystems on Earth, and anaerobic fungi are so far poorly understood in an environmental context, being probably a neglected geobiological force in the subsurface ecosystem. The anaerobic fungi producing H₂ during their respiration may form

symbiotic relationships with H₂-dependent chemoautotrophic prokaryotic microorganisms (such as methanogenic and acetogenic archaea) in an anoxic environment, including marine sediments [91]. The fossilization process of the cryptoendolithic fungi at the Laxemar site occurred through a transition from maturation of the organic matter to a carbonaceous material, before being finally mineralized by Fe, Mg, Ca-rich clay minerals and Fe-oxides. The mineralization was observed to start from the centre of the hypha where a fully mineralized Fe-oxide dominated the central strand and clay-mineral dominated the margins [55].

It is worth mentioning another example of microbe–minerals co-existence, which is the little studied area of clay minerals interactions with microorganisms in dust, in particular desert dust, where clay minerals may provide protection from harsh environmental conditions, physical support, preservation and transport.

Due to much smaller particle size compared to silt and sand, airborne clay dust is thought to have longer residence time in the atmosphere and to contribute to the microbial ability to survive long-range transport during dust storms by covering microbial cells with mineral particles providing protection from dehydration and UV exposure [92,93]. It has been recently discovered that Saharan dust aerosols can aggregate into large (up to 100 µm) particles termed “iberulites” consisting of quartz, carbonate and feldspar grains embedded within and surrounded with the matrix of clay minerals: illite, smectite and kaolinite [94]. Clays are more abundant in the iberulites than in the total aerosol deposit, suggesting that iberulite formation concentrates clay minerals. Iberulites are formed in the atmosphere by coalescence of aerosol mineral particles captured by precursor water droplets followed by water evaporation. The high clay hygroscopicity probably causes retention of water at the evaporation stage [94]. Perhaps such atmospheric aggregates as iberulites might also interact with microorganisms and play a role in their transport and survival but these interactions have not been studied yet.

Human extensive use of clays can lead to modifications of the natural environment and the changes in the ecological diversity, creating the additional settings for microbe–clay minerals interactions. The illite, kaolinite, chlorite, vermiculite or smectites have been traditionally used in manufacturing ceramic building materials, e.g., bricks, roofing and wall tiles, since antiquity [54]. The porous and rough surfaces of such materials can readily harbour various microorganisms facilitating their attachment and biofilm formation. The microbial colonization of the ceramic surfaces exposed to light is reported to start usually with the establishment of the communities of phototrophic microorganisms (cyanobacteria and microalgae) and their symbiotic associations with fungi (lichens) followed by a successive colonization by bacteria and fungi and, finally, plants [54]. According to the currently available data, the overall biodiversity of ceramic-dwelling microorganisms includes 70 bacterial taxa, 97 cyanobacteria, 65 algae, 49 fungi and 9 lichens. In general, the dominant phyla of bacteria on all studied ceramic materials were *Proteobacteria*, *Firmicutes* and *Actinobacteria*. The common genera of bacteria were reported to be *Bacillus*, *Deinococcus*, *Sphingomonas* and *Streptomyces* [54]. Fungi being widespread airborne microorganisms with a large capacity to survive in different environments were also present in all ceramic substrates with the dominant phylum Ascomycota. *Fusarium* and *Penicillium* were the common fungal genera for bricks, roofing and wall tiles [54]. The extensive microbial colonization of such clay-based materials may cause deterioration of architectural ceramics, an important part worldwide cultural heritage.

Thus, the microbial interactions with clay minerals may occur ubiquitously in the pedosphere and in natural and human-modified environments, where many microorganisms are very fit for survival, thriving, and for biogeochemical activity, employing various strategies of exploration and exploitation of mineral surfaces.

3. Biogeochemical Transformations of Clay Minerals by Microbes

Silicates are the largest class of minerals, comprising 30% of all minerals and making up 90% of the Earth’s crust. Many silicates are unstable in the biosphere and break down readily to form clays [25,83,95]. Microorganisms, including many kinds of prokaryotes (archaea and bacteria), fungi and their symbiotic associations, play an important role in the dissolution of silicates and, therefore, in

the genesis of clay minerals, and in soil and sediment formation [25,69,70,75,96–101]. The processes of biogeochemical transformation of metals and minerals, contributing to the cycling of elements on Earth, are based on two main reactions: dissolution and precipitation [24,26,102–104]. Geoactive microbes are involved in both metal mobilization and immobilization: they can dissolve minerals, including clay minerals, releasing mobile metal species and associated elements into the environment, and immobilize metals by biosorption, transport, intracellular localization and accumulation by living microorganisms, redox immobilization, precipitation and biomineralization, resulting in the formation of secondary biogenic minerals (Figure 1). These processes are of great environmental, economic and social importance. The microbial mobilization processes lead to the release of nutrients (metals and associated elements) in the bioavailable form for plants and other microorganisms in the terrestrial environment, and to soil and sediment formation as a result of weathering and decay of rocks and minerals. Mobilization processes also cause biodeterioration of mineral-based building and barrier materials, and historic and cultural monuments [105]. The environmental and biotechnological significance of metal immobilization by microorganisms relates to the application of the microbial ability for precipitation and biomineralization to remove metals from effluents, and other means of toxicant stabilization/immobilization [24–26,89,102].

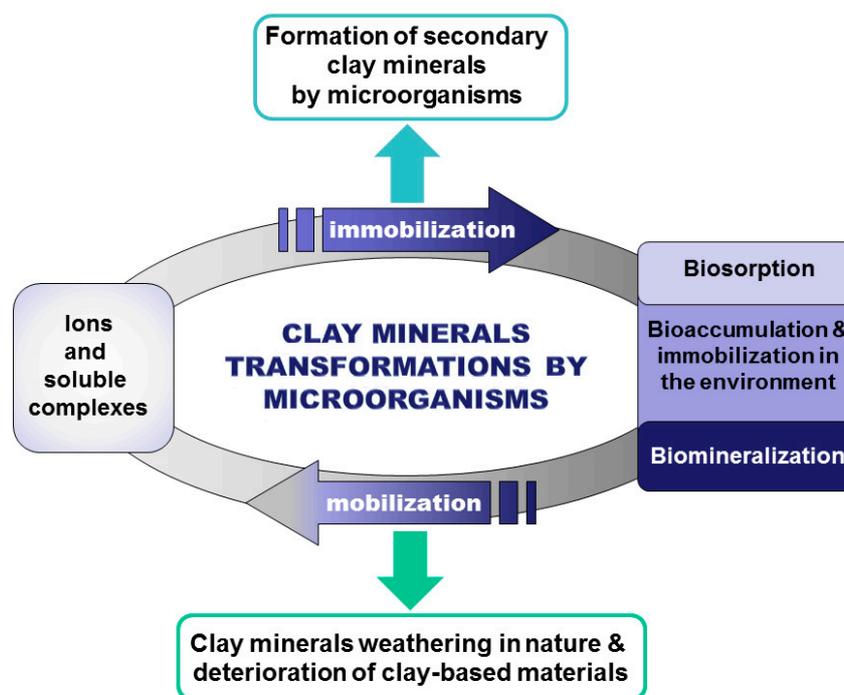


Figure 1. Simplified diagram of the main biogeochemical processes in the transformations of clay minerals by microorganisms.

In nature silicon is involved in a series of biogeochemical cycles of transformations: silica liberated from silicates in these processes may be carried away by surface or groundwater, and then it may either be removed by chemical or biological precipitation, or may be transported into water bodies [96,106]. Silicon environmental distribution is significantly influenced by microbial activity, especially by microorganisms assimilating Si and incorporating it into cell supporting structures, such as diatom microalgae with siliceous cell wall frustules. These microorganisms also include some algae: chrysophytes, silicoflagellates, xanthophytes; and protozoa: radiolaria, and actinopods. Silicon-assimilating microbes are important in the formation of siliceous oozes in oceans and lakes. Such silicon incorporated in cells may later be mobilized by weathering processes. Silicification of natural microbial mats has been shown to be a microbially mediated geochemical process [26,107].

3.1. Microbial Weathering in Clay Minerals and Silicate Transformations

Clay mineral weathering and deterioration of clay-based building materials by microorganisms and their symbiotic associations are affected by the mechanisms common to microbial weathering of other rocks and minerals (Figure 2). There are two synergistic actions by which microorganisms can degrade mineral substrates: biomechanical and biochemical [13,24,53,56,75,77,105,108–111].

The biomechanical actions in microbial weathering of minerals, which are especially pronounced in fungi and lichens, can be a result of a direct interaction of microbial cells with mineral surface or indirect one occurring through the production of the mucilage EPS matrix by microbes and its biomechanical consequences (Figure 2). It should be noted that direct and indirect mechanisms of weathering do not oppose each other, but act in synergy. The biomechanical mineral weathering can occur directly, for example, through fungal hyphae penetration by breaking of intact mineral surfaces at the nm scale and growing along crystal planes, cleavage, cracks and grain boundaries in the decayed rocks [24,56,75,77,89,109,112,113]. Fungal cells can exert considerable mechanical force deriving from the osmotically generated turgor pressure within hyphae [109]. This direct penetration of hyphae into minerals is facilitated by thigmotropic reactions [114] as well as lubrication with extracellular mucilaginous EPS which may contain acidic and metal-chelating metabolites [24]. Thigmotropism or contact guidance is defined as a directed mode of fungal growth towards grooves, ridges and pores in solid material [114,115]. Such tropic reaction may explain how fungal hyphae explore and exploit weakened sites on the mineral surfaces. A very important factor determining microbial colonization of rock and mineral surfaces is moisture which can be retained in the EPS matrix surrounding cells. The shrinking or swelling effects (contractions) of the hydrated mucilage sheath and biofilms, along with organic and inorganic precipitates originated from biogeochemical and general metabolic activity of microbes is another indirect biomechanical action in weathering contributing to the bioerosion and bioabrasion [77,97,116,117].

The biomechanical processes of mineral weathering by microorganisms are strongly connected with biochemical processes which are thought to be much more important than mechanical degradation [24,89,118]. For the majority of eukaryotic and prokaryotic microorganisms called heterotrophs, which are using organic compounds as both carbon and energy sources, the biochemical route for mineral dissolution is dominated by so called heterotrophic leaching (or chemoorganotrophic leaching). Heterotrophic leaching is characterized by two main mechanisms: acidolysis and complexolysis, which may be enhanced by metal accumulation in and/or around the microbial biomass (so called metal sink) [24,90,103,108,118–120]. Proton-promoted dissolution or acidolysis occurs when microorganisms acidify their microenvironment as a result of the excretion of protons, organic acids, and the formation of carbonic acid resulting from respiratory CO₂ [108]. Many fungi and bacteria are able to excrete metal-complexing metabolites which are associated with ligand-promoted dissolution or complexolysis, involving carboxylic acids, amino acids, Fe(III)-binding siderophores and phenolic compounds [24,26,118,121]. Carboxylic acids are providing a source of both protons for solubilization and chelating anions complexing metal cations [122]. Microbial carboxylic acids with strong chelating properties (e.g., oxalic and citric acid) perform an aggressive attack on mineral surfaces [58,118,121]. For example, oxalic acid readily forms soluble oxalate complexes with mobile species of metals, including Al and Fe, which may contribute to the weathering of silicate minerals such as feldspars [123–125]. The microbial attack on rocks is thought to be strongly aggressive if it occurs by biogenic mineral or organic acids and mildly aggressive if it resulted from hydrophilic polysaccharide- and protein-containing slimes in biofilms able to accumulate water and salts [119]. For several bacteria, dissolution of silicates was reported to result from the complexation of cationic components by 2-ketogluconate [111].

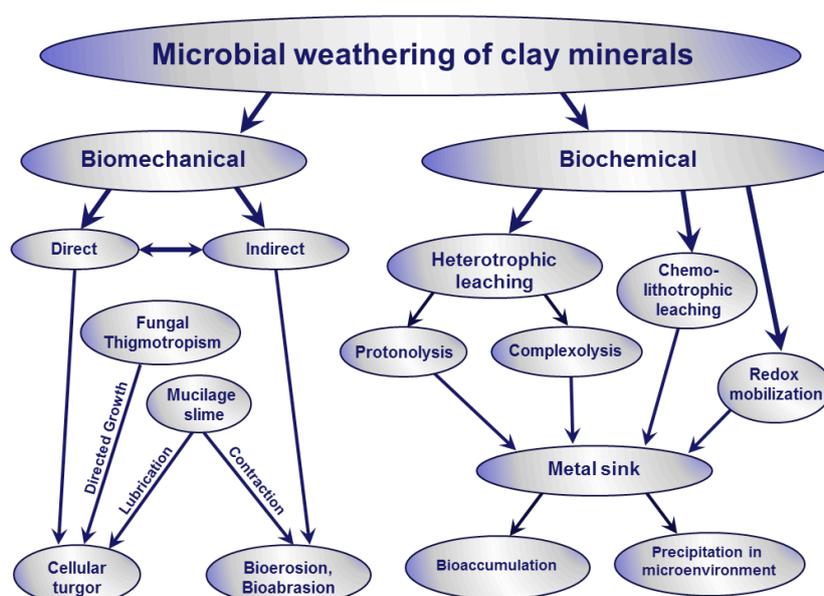


Figure 2. Main mechanisms of microbial weathering of clay minerals (adapted from [57]).

In addition to the majority of heterotrophs, there is a less numerous and very specific group of heterotrophic microorganisms called chemolithotroph, consisting of the representatives of prokaryotes archaea and bacteria, including sulfur, iron and hydrogen oxidizers, as well as nitrifying bacteria. While utilizing organic compounds as a source of carbon as all other heterotrophs, they use inorganic compounds (e.g., reduced iron and sulphur compounds) as the sources of energy and the donors of the electrons for energy production through redox reactions. In contrast to other heterotrophic microbes, the metabolic activity of these microorganisms can result in the formation of the strong mineral acids (e.g., sulphuric acid) [26,119,120]. Chemolithotrophic leaching can be described as the enzymatically catalyzed reactions, often implying a physical contact between the bacterial cells and the leaching material, which leads to the energy gain and mineral destruction, producing the end products (e.g., sulphuric acid, ferric iron) that provide protons contributing to the mineral solubilization process (Figure 2). Despite the similarities in the mechanisms of weathering for all heterotrophic microorganisms (e.g., proton-promoted acidolysis), because of the very distinct metabolism of chemolithotrophs and the different nature of the reactions involved, the chemolithotrophic leaching is shown in the diagram separately from other biochemical mechanisms of mineral weathering (Figure 2).

Mineral surfaces can be also destroyed with the release of metals and associated elements through the processes of microbial redox mobilization (or redoxolysis) [126–128] (Figure 2). For example, the microbial reduction of the fully oxidized species of iron and manganese to Fe(II) and Mn(II) increases their solubility, and also may facilitate mobilization of other metals adsorbed to iron and manganese oxides, especially in the presence of humic substances or related compounds [26,128]. The processes of accumulation and precipitation (including biomineralization) by microorganisms act as a sink for metals mobilized from minerals and rocks which facilitates the dissolution via protonolysis, complexolysis and redoxolysis [108]. It is well known that microbes are capable of efficient bioaccumulation of soluble and particulate forms of metals [26,102,129]. The immobilization of metals, which were leached from minerals, reduces the external free metal activity shifting the equilibrium to the release of more metal into aqueous solution [56,108]. Mobile metal species can be bound, accumulated or precipitated by microbes via (i) biosorption to biomass (e.g., cell walls, cell fragments, pigments, polysaccharides and proteins), (ii) transport and intracellular accumulation, and (iii) extracellular precipitation and formation of secondary biogenic minerals [102,118,129,130].

Additionally to biochemical attack through protonolysis and complexolysis, mechanisms of silicates dissolution by microbes may include alkali (ammonia or amines). The solubilizing metabolites

may be excreted into the bulk phase as well as into the matrix of microbial biofilm attached to the surfaces with the effect of encapsulation [13,131,132]. All these processes together can alter the microtopography of the minerals through pitting and etching of the surfaces enhancing the dissolution of the primary minerals [26,83,89,97,125].

These processes are very important in the mobilization of limiting nutrients such as bound phosphorus and iron, and play a crucial role in the functioning of the mycorrhizal symbiotic associations, where fungi provide mineral nutrition and phosphorus acquisition for a host plant [111,133]. For example, in coniferous forest soils in Europe, it was observed that the weatherable minerals, including silicates such as plagioclase feldspars, contain a network of numerous tubular pores (tunnels). Their origin was explained by the authors by the “rock-eating fungi” hypothesis as a result of ectomycorrhizal fungal dissolution and “burrowing” within the mineral matrix releasing mineral nutrients and translocating them to plant roots [134–137]. An additional “rock-building fungi” hypothesis has also been proposed, explaining how such tubular pores may occur inside weathered minerals through the process of mineral transformation leading to the secondary minerals precipitation around a fungal hypha, death and decomposition of which leave an empty tunnel inside the mineral [110]. According to this hypothesis, the mycogenic secondary minerals in the tubular pores within weathered soil silicates supposedly might be clay minerals; however, this still needs experimental confirmation.

An interesting example of the combined action of heterotrophic bacteria from the natural microbial community in intertidal sediments with silicon-assimilating diatom algae (*Nitzschia* sp., *Navicula* sp., *Cocconeis* sp.) on the silicates surface was presented by Brehm et al. (2005) in laboratory experiments on the microbial weathering of quartz sand and glass [138]. Pronounced etching of the glass and quartz surfaces with imprinting of the distinct shape of the individual microbial cells was observed after 9-month incubation of the mixed cultures of diatoms and bacteria. It was argued that in such mutually beneficial microbial communities the heterotrophic bacteria take part in the silicates dissolution providing bioavailable Si species essential for diatom frustule construction whereas diatoms produce a considerable amount of EPS including polysaccharides necessary for bacterial metabolism and biofilm formation, which, in its turn, creates a microenvironment facilitating silicate weathering [138].

It is suggested that the specificity of microbial attack on minerals can depend on the nature of the minerals and the sites on their surfaces. Some fungal hyphae from lichens overgrew augite and mica but avoided quartz [139]. It was reported that abundant fungal hyphae and algae colonized quartz and kaolin in podzols whereas bacteria were observed mainly on biotite [139]. The bacterium *Bacillus subtilis* was observed to attach to granite, etching mainly plagioclase, and to a lesser extent K-feldspar and quartz, followed by biotite [140]. Another study on bacterial weathering of biotite demonstrated the significance of the mineral surface microtopography and roughness in the microbial interactions with minerals, where the phyllosilicate edges were observed to be associated in greater extent with the predominant attachment of the cells and/or with facilitated mineral dissolution compared to the basal planes [141]. In lichen weathering of silicate minerals, the potassium and iron clay minerals and nanocrystalline aluminous iron oxyhydroxides were found to be mixed with fungal organic polymers [142], while biotite was interpenetrated by fungal hyphae along cleavages, partially converting it to vermiculite [143].

Fungi are thought to take part in the weathering of many silicate-bearing rocks [89]. It has been reported that *Aspergillus niger* is able to weather olivine, dunite, serpentine, muscovite, feldspar, spodumene, kaolin and nepheline, *Penicillium expansum* can degrade basalt, and *Penicillium simplicissimum* and *Scopulariopsis brevicaulis* mobilize aluminium from aluminosilicates [56,57,144,145]. Fungi-producing siderophores were shown to cause pit and etch microfractures in the samples of olivine and glasses under laboratory conditions [146]. The fungus *Penicillium notatum* was shown to be faster in silicate solubilization than the bacterium *Pseudomonas* sp. [147]. It was demonstrated that fungi isolated from weathered rock surfaces (*Botrytis*, *Mucor*, *Penicillium* and *Trichoderma* spp.) were able to solubilize Ca, Mg and Zn silicates [148]. *Aspergillus* sp., *Byssosclamyces* sp. and *Penicillium* sp.

isolated from floodplain sandy-clay-loam sediments were able to produce various organic acids, which may suggest a role in the sediments' weathering [24].

It was shown for *Aspergillus niger* that Si mobilization from clay minerals is a result of oxalic acid excretion by fungus [149]. Oxalic acid is a well-known chelating agent that has been widely studied because of its ability to dissolve different minerals and rocks. In contrast to other low-molecular weight carboxylic acids with low complexing abilities that erode minerals in acid solution by protonolysis (e.g., acetic and lactic acids), oxalic acid is able to mobilize metals very efficiently at neutral pH and even in basic solutions [58,59,118]. A field study on the mineral weathering potential of the ectomycorrhizal fungus *Hysterangium crassum* associated with Douglas-fir trees (*Pseudotsuga menziesii*) in the Pacific Northwest, forming dense hyphal mats in coniferous forest soils, demonstrated that the colonization of soil by hyphal mats was leading to the reduction of the soil pH values compared to non-colonised bulk soil 10–50 cm away from mat edges, with average pH values 4.8 and 6.1, respectively [150]. A striking difference (approximately 22–40 times higher) was found in the concentration of oxalic acid in soil with fungal mats (5.5–9.9 mg·g⁻¹ DW) in contrast to the bulk soil (0.2–0.3 mg·g⁻¹ DW). It was also observed that considerable amounts of crystalline Ca oxalate precipitated in the dense fungal biomass as a symptom of the active mineral transformation in the soil colonized with ecomycorrhiza. The authors argued that abundantly produced oxalate could be in large part responsible for the enhanced weathering of primary minerals and clays as well as for the mobilization of Fe, Al and other cations in soil [150].

It was shown that, when cultivated in a submerged culture (i.e., in liquid medium subjected to continuous agitation), most fungi of the genera *Aspergillus*, *Paecilomyces*, *Penicillium*, *Scopulariopsis* and *Trichoderma* could leach mobile iron species from kaolin from a West Bengal deposit (India) which contains haematite as impurities. *Aspergillus niger* strain reached a 23% release of total Fe from clay being ~1.5 times higher than in the abiotic control where iron was leached with 0.1M oxalic acid, indicating that this strain is probably overproducing oxalic acid [151].

Large amounts of oxalic, citric and gluconic acids were produced by *Penicillium frequentans* in liquid cultures and caused extensive deterioration of clay silicates, as well as micas and feldspars from both sandstone and granite as a result of high cation release and formation of organic salts such as Ca, Mg and ferric-oxalates and calcium citrates [152]. The dissolution of silicates olivine and feldspars by different lichens growing on a basaltic flow in Sanliurfa (Turkey) was accompanied by the formation of whewellite indicating the ligand-promoted mechanism of bioweathering involving excretion of oxalate by fungi [100].

In the experimental study of the nature of fungal weathering of lizardite [(Mg, Fe, Ni)₃Si₂O₅(OH)₄], the dissolution of this silicate mineral and Mg, Si, Fe and Ni release were found to be driven by the over-excretion of oxalic acid and siderophores by the indigenous fungus *Talaromyces flavus* [153]. It was observed that the presence of lizardite in the liquid medium considerably stimulated fungal production of these ligands compared to the mineral-free control, with siderophores concentration becoming ~10 times higher (2 mM and 0.19 mM, respectively) and oxalic acid excretion increasing ~54 times (14.23 mM and 0.26 mM, respectively). As a result of the fungal complexolysis, the mobilization of Fe and Ni was at least 10 times higher than in the abiotic control. Abiotic tests on the chemical dissolution of lizardite confirmed that Fe release was promoted by the siderophores as the specific high-affinity iron-chelating compounds whereas oxalic acid was responsible for liberation of Ni [153].

The different microorganisms may use various mechanisms of weathering in different proportions, employing different strategies of metal mobilization and rock decay [103]. In soils, bacterial dissolution of mica was assumed to occur through two main processes promoting Fe release: acid dissolution (acydolysis) and Fe complexation (complexolysis) [16]. The greater contribution of complexolysis was observed in the biotite weathering whereas FeOOH precipitation was more significant for phlogopite. The weathering of phlogopite was found to be more efficient than biotite presumably due to the differences in the crystal chemistry of these minerals. These processes were successfully modelled with three types of weathering reaction: (1) only protonolysis occurred at pH < 3; (2) iron release

occurred through both complexolysis and protonolysis at pH from 3 to 4–5; (3) Fe release was promoted through metal sink (immobilization as FeOOH) at pH > 4–5 [16]. In the experiments with fungus *Aspergillus fumigatus* weathering of K-bearing silicates K-feldspar and illite, K release was suggested to be promoted by three mechanisms: (1) complexolysis; (2) adsorption to biopolymers (or metal sink); and (3) biomechanical forces [113]. In the case of the ectomycorrhizal association of fungus *Paxillus involutus* with Scots pine, the study of a single fungal hypha interacting with the basal plane of a biotite flake demonstrated that biotite weathering was a combination of local acidification, biomechanical forcing and uptake of leached cations by the fungus cells [112]. For the bacterium *Pseudomonas mendocina* in liquid medium, two mechanisms of Fe-extraction from montmorillonite were observed: (1) the excretion of siderophores into medium (or complexolysis), not requiring cells to contact the montmorillonite particles directly; and (2) the reductive mobilization of iron causing smectite dissolution, which requires microbial contact with montmorillonite [154]. Balogh-Brunstad et al. (2008) [155] showed that fungi accelerated the biotite dissolution by 100–1000 times compared to abiotic control, with mechanisms being mainly acidification of the bulk liquid and cation complexation.

Another study on fungal dissolution of clay minerals demonstrated the medium acidification being a prevailing mechanism of fungal attack on phlogopite by *Alternaria tenuissima*, *Cladosporium cladosporioides* and *Stilbella* sp. [101]. Fungal mycelium generally attached to the phlogopite, formed grooves, and caused deterioration of the mica flakes and the mineral decay. The chemical composition of the weathered flakes strongly depended on the fungal strains. The phlogopite alteration was suggested to be accompanied by rearrangement and loss of cations in situ resulting in the transformation from phlogopite to Al-rich smectite [101].

It should be mentioned that the microbial ability to weather rocks and minerals substantially contributes to the degradation of clay-based ceramic building materials which is governed by the same common main mechanisms of microbial weathering. This includes processes of physical nature (biomechanical action): changes of the volume of microbial cells during the growth, production of extracellular polymeric substances (EPS), penetration ability of the microbial cells and structures (e.g., in lichens), disintegration of the ceramic matrix and spalling; as well as biochemical processes: proton-promoted acydolysis and ligand-promoted dissolution, and the action of strong biogenic mineral acids produced by chemolithotrophs, resulting in the leaching of the structural elements of the ceramic matrix, and also chemical alteration and efflorescences [54,120]. In the degradation of such clay-based materials, the processes associated with their functional biodeterioration by microbes, including extensive microbial growth, production of organic pigments and formation of coloured biofilms on the surfaces, the disfigured visual appearance of the materials as well as the alteration of thermo- and hydro-isolation and solar reflectance, may become of great social, economic and cultural importance.

3.2. The Processes of Immobilization and Secondary Clay Minerals' Formation by Microbes

In the overall biogeochemical transformations of minerals, the microbial processes of metal immobilization occurring by biosorption, bioaccumulation, precipitation, redox immobilization and biomineralization, as mentioned above, contribute to mineral bioweathering processes functioning as a sink for mobilized metals [57,102]. Metal immobilization via biosorption can be defined as metabolism-independent processes of metal uptake by microbial cell walls and other cell components [129,156]. Biosorption occurs via a variety of mechanisms of a chemical and physical nature including ion exchange, complexation, hydrogen bonding, hydrophobic and van der Waals forces, and entrapment in fibrillar capillaries and spaces of the polysaccharide network. Potential binding sites on fungal and bacterial biomass can include acetoamino groups from chitin, amino groups from proteins, sulfhydryl groups from proteins and peptides, hydroxyl groups, phosphate groups, and carboxyl groups from organic acids, polysaccharides, (poly) phenols/quinones, and melanin [121,157,158].

Bioaccumulation of mobile metal species include, in addition to the physico-chemical biosorption, the metabolism-dependent processes of metal transport, intracellular localization and accumulation [26,102]. Generally, metals are likely to be fixed to biomolecules forming compounds of poor-crystallinity or of a non-crystalline nature. Amorphous metal precipitation can also occur in the microenvironment surrounding microbial cells, such as polysaccharide sheaths around fungal hyphae or microbial biofilm matrix. All the major groups of microorganisms have members that are capable of forming minerals or biomineralization [25,26]. Most biominerals are calcium carbonates, silicates and iron oxides or sulphides [26].

Biologically induced mineralization, occurring when microorganisms modify their local microenvironment creating conditions for extracellular chemical precipitation of mineral phases, can result from microbial oxidation or reduction of a metal species, metabolite excretion (e.g., sulfide, oxalate) and other metabolism-dependent transformations of metal species. The chemically reactive sites present on the surfaces of microbial cell walls can also lead to the nucleation and formation of mineral precipitates around biomass [26,156,159].

External metal precipitation and biomineralization may also result from indirect effects of bacterial metabolism on microenvironmental geochemistry [159]. Precipitation can also occur due to production of reactive components which either bind metals or catalyse precipitation where the resulting minerals may be affected by the nature of the cell surface, the cellular microenvironment, and the presence of reactive anions [111]. Biomineralization can also be independent of microbial activity occurring on dead biomass. Additionally, with time, mineral phases may undergo further changes in crystallinity and incorporate other metals into their structure [159]. The formation of solid mineral phases by microbial processes may result in mineral deposition over geological timescales [160].

Microorganisms modify the rates and mechanisms of silicate weathering and clay growth, thus playing fundamental roles in the genesis of clay minerals, and soil and sediment formation [24,75,161]. For example, in the weathering of silicate minerals by lichens, the resulting Ca, K, Fe clay minerals and nanocrystalline aluminous Fe oxyhydroxides were found to be mixed with fungal organic polymers [142]. Other examples are the formation Al-rich smectite from phlogopite by fungi [101], and 2:1 phyllosilicates from olivine and feldspars by lichens [100].

In both bacteria and fungi, the formation of secondary minerals can occur through metabolism-independent and -dependent processes [111]. Precipitation, nucleation and deposition of crystalline material on and within cell walls are influenced by factors such as pH and wall composition. Cationic species of Si(IV), Fe(III), Al(III) and Ca(II), may be released through dissolution mechanisms, stimulate precipitation of compounds that may bond soil [26].

In experimentally-controlled systems, it was demonstrated that soil filamentous fungi can modulate cracking properties of soils by realignment of the particulate materials and facilitating the clay minerals nucleation process at the micrometer scale [162]. The fungal hyphae growing through soil can act as the nucleation zones for clay minerals such as kaolinite, and this interaction, which also includes surface charge phenomena, can result in the formation of narrow channels (diameter ~2 μm) lined with clay platelets after the decomposition of hyphae [162]. Various bacteria were shown to accumulate metallic ions from their external aquatic environments, and mediate the crystallization and precipitation of clay minerals [25]. Microbial cell walls and surrounding cells extracellular polymeric substances (e.g., a bacterial capsule, a fungal hypha sheath or biofilms) play a very important role in the precipitation of newly formed clay minerals [13,25]. Tazaki (2005) [163] observed precipitation and maturation on the bacterial cell walls of Si-Fe-rich and Al-poor halloysite spheres in the presence of sediments from the Passo Real Dam (Portalegre, Brazil) containing kaolinite, quartz, cristobalite, and feldspar. These data supported the previous observations of Konhauser et al. (1993) [164] suggesting that Fe is a key element in clay nucleation on the bacterial cells. Other studies also demonstrated Si-Fe-Al composition of the clay minerals precipitated on the bacterial surface, including both bacterial cell walls and surrounding extracellular polymeric substances [165,166]. Nontronite layers, formed within bacterial extracellular polymeric substances in the sediments from the Iheya Basin (Japan), were

oriented within the EPS matrix suggesting its catalysing effect for precipitation similarly to bacterial cell walls [167]. The precipitation of Si-Al-Fe-K dioctahedral smectite on bacterial cell walls was reported to occur by ion uptake and concentration within microbial biofilm after tephra dissolution [168].

The exchange of cations in the interlayer space of the clays is typically involved in their transformation into secondary clay minerals [13,81]. For example, potassium exchange with protons (originated from microbial acidification), or with other cations such as Ca and Na, in mica resulted in transformation of biotite to vermiculite by lichens, forming interstratified biotite-vermiculite [81,169]. Arocena et al. (2012) [170] has also observed a K-depleting reaction in biotite caused by endomycorrhizal association of arbuscular mycorrhizal fungi of the genus *Glomus* with plant roots leading to a formation of illite, smectite, mixed-layered phases and hydroxy-interlayered vermiculite.

The processes of secondary clay minerals formation due to the alterations of the primary ones may also involve redox reactions, for example, the illitization process when microbially induced iron reduction occurs in smectite layers followed by K^+ or NH_4^+ uptake [13]. Thus, in diagenetic settings, underground thermophilic iron-reducing bacteria may contribute to smectite illitization [171]. It was shown that, in a mangrove forests environment, Fe-rich illite is formed in large amounts from detrital kaolinite and goethite via mixed-layer kaolinite-smectite and illite-smectite with cyclically available iron as dissolved Fe^{2+} through reduction processes mediated by microorganisms [13].

The microbially mediated formation of secondary clay minerals from primary clays has an impact on the chemical and mineralogical properties of soils, with the special role of symbiotic fungi of mycorrhizae and lichens in these processes [77,98]. It was demonstrated that the transformation rate of mica and chlorite to 2:1 expandable clays was faster in the ectomycorrhizosphere compared to non-ectomycorrhizosphere soils, likely a result of the high production of organic acids and direct extraction of K^+ and Mg^{2+} by the hyphae of ectomycorrhizal fungi [98]. It was also suggested that in the ectomycorrhizosphere, K^+ and possibly amorphous Al_2O_3 and Fe_2O_3 could reconstitute the degraded mica and chlorite through the formation of hydroxy-interlayered 2:1 clays.

The nature of newly formed clay minerals in a weathered amphibole syenite boulder containing feldspar, ferriannite mica, quartz and ferrohastingsite amphibole was shown to depend on the presence of lichens and the nature of a parental mineral [143]. In the absence of lichens, there was only alteration of the amphibole with Fe-Si smectite formation. If there was lichen growth, the composition of the secondary biogenic clay minerals was homogeneous and determined by the initial weathered minerals: in the case of feldspar and quartz an Al-Si phyllosilicate was formed, and in the case of amphibole a Fe-Si phyllosilicate (possibly nontronite) was formed [143]. It was also demonstrated that organic acids secreted by lichens can produce such secondary clay minerals as tubular halloysite from weathering silicates (e.g., granite and albite) [172].

Poorly ordered alumino-silicate materials and various clay minerals were found to occur as alteration products intimately admixed at the lichen–rock interface in a silicate rock composed mainly of leucite and augite [97]. A variety of newly formed clay minerals associated with lichen-promoted weathering have been identified in many types of silicate rock substrates, including kaolinite, halloysite, vermiculite, goethite, illite, allophane and imogolite. The types of secondary clay minerals formed depend not only on the substrate rocks and minerals, but also on the lichen species. It was reported that, in many cases, halloysite and kaolinite are the most common forms of secondary clay minerals formed in the weathering crusts associated with lichen growth [77]. The formation of hydroxyaluminium vermiculite is believed to be attributable to a pH decrease by organic acids secreted by lichens, with consequent substitution of interlayer potassium ions by aluminium hydroxides [173]. Regarding the effects of lichens on soil-forming processes, as pioneer rock colonizers, they can create a favourable microenvironment by increasing bioavailability of mineral elements and nutrients to successive life-forms that may replace lichens during weathering of rocks and soil development [77]. The positive correlations between lichen communities and vascular plant cover were observed in many cases, because lichen communities concentrate the two essential resources necessary for plant growth, water and nutrients [77].

Due to the abundance of easily extractable mineral nutrients, the volcanic deposits can harbour numerous microorganisms accelerating the processes of weathering and pedogenesis [13]. The study of the rhyolitic glass weathering in natural waters by indigenous microbial communities demonstrated that the resulting clay-mineral products were depending on the water chemistry and the degree of the entrapment of the volcanic glass grains within the microbial biofilms [70]. Abiotic alterations of the rhyolitic glass developed on the surface of glass grains and resulted mainly in a dioctahedral, Al-rich clay mineral presumably beidellite. In hypersaline water, the glass grains entrapment within the biofilm, where solute concentrations were high, was associated with the precipitation of trioctahedral, Mg-rich clay minerals, supposedly saponite. For fresh lake water, in abiotic experiments the high water pH and Mg concentration facilitated formation of the Mg-rich clay mineral, whereas in biological experiments the pH level reduced within the microbial biofilm matrix, favouring formation of the Al-rich clay mineral. In the case of seawater the low magnesium concentration insufficient to produce Mg-rich clay minerals and the absence of the glass grains confinement within biofilms led to the formation of a dioctahedral Al-phyllsilicate [13,70].

4. Biological Effects of Clay Minerals on Microbial Growth and Biosynthetic Activity

Most of the scientific works are devoted to the study of the influence of microorganisms on clay minerals with comparatively less experimental data regarding the opposite phenomena—the clays effects on living organisms. However, considering the important role played by clay minerals in the provision of nutrients, waste sink and habitats for microorganisms, it is clear that the biogeochemical activity of microbes is inextricably linked to the biological effects of clay minerals on microbial growth and metabolic activity.

It is known that the influence of clay minerals on microbial physiological and biochemical properties, which could be both promoting and inhibiting growth, depends on microbial type (e.g., fungi and bacteria) and varies from species to species of microorganisms [174]. Many studies on microbial physiology showed that interactions of microorganisms with clays can lead to an increase of biomass yielding and growth rate, synchronization of microbial development, modification of the duration of growth-delay phase (lag-phase) in the beginning of microbial cultivation, changes of the effectiveness of substrate utilization, of respiration activity and of enzyme and metabolite production [72,175–191].

Providing and retrieving nutrients is obviously one of the most important ways how clay minerals may alter microbial metabolism. Clay minerals were reported to promote growth of taxonomically different bacteria. For example, in experimental studies using the submerged culture technique, it was demonstrated that in case of the bacterium *Escherichia coli* (phylum Proteobacteria) kaolinite addition to the liquid medium in the concentrations $0.1\text{--}0.3\text{ g}\cdot\text{L}^{-1}$ led to a ~ 1.6 times increase of the maximal growth rate values and over ~ 3 times higher yield of viable bacterial cells assessed as colony-forming units (CFU) compared to clay-free control medium [192]. The authors suggested that kaolinite presence enhanced the processes of acetate assimilation while decreasing catabolic activity in the bacterial metabolism. The promotion of bacterial growth by clay minerals was also observed in the experiments with submerged culture of *Bacillus subtilis* (phylum Firmicutes) grown in the presence of saponite [193]. Because of an evident increase in the concentrations of the cations Mg^{2+} , Ca^{2+} , Na^{+} , and K^{+} leached from the mineral (by $63\text{--}191\text{ g}\cdot\text{L}^{-1}$) the positive effect on bacterial growth was thought to be caused by ion exchange processes occurring between the nutrient medium and saponite.

It was also demonstrated that the deficiency of mineral nutrients in the medium may drive up the expression of the specific genes which can facilitate microbial acquisition of these nutrients from clay minerals. Xiao et al. (2012) [194] studied the genetic effects of the deficiency of potassium, the important essential biological metal involved in the transmission of information in microbial communication, in experiments with the fungus *Aspergillus fumigatus* grown under static conditions in liquid medium supplemented with either soluble potassium in nutrient medium or powdered K-bearing silicate minerals, including K-feldspar, hornblende, mica, and montmorillonite [194]. It was

found that the presence of K-bearing silicates under K^+ deficiency increased expression of the genes promoting mineral weathering and potassium leaching by *A. fumigatus*. These upregulated genes were associated with enzymes contributing to heterotrophic leaching: aldehyde dehydrogenase, oxidizing aldehydes to produce organic acids, and carbonic anhydrase, catalyzing the reversible hydration of carbon dioxide turning it into carbonate. K-bearing silicates also induced upregulation of the enzyme cysteine synthase promoting enhanced production of metal-binding sulphur-rich proteins, as well as decreased membrane metal transporter expression leading to the cell membrane modifications allowing the uptake of necessary cations by cells while preventing excessive mineral elements entry into the cell. The molecular biological and biochemical data presented in this study help to illustrate how, in the presence of silicates, microorganisms may adapt to mineral nutrient deficiency through the enhanced biogeochemical activity resulting in mineral weathering and nutrient release [194].

Clay minerals were also reported to be able to enhance enzymatic activity of reductase, the enzyme responsible for the microbial reduction of hazardous Cr(VI) to less toxic Cr(III) [42,195]. In the experimental study on kaolinite and vermiculite effects on the bacterium *Pseudomonas aeruginosa* grown in the submerged culture, the presence of clay minerals increased the rate of hexavalent chromium bioreduction, promoting the efficiency of glucose utilization and the growth of bacteria [195]. The stimulating effects on bacterial growth, substrate utilization and bioreduction were more pronounced in the case of vermiculite compared to kaolinite. Vermiculite addition caused some morphological changes in bacterial cells exposed to Cr(VI), reducing the roughness and hardness of the cells surface. Grown in the presence of vermiculite, *P. aeruginosa* formed clay mineral-cell complexes where vermiculite provided protection from Cr(VI) biotoxicity and acted as growth-supporting material, promoting detoxification of the hazardous pollutant by bacteria through enzymatic bioreduction.

Another example of clay mineral biological effects on microbes that may have global environmental implication is a decrease of methane production by methanogens in the presence of iron-rich smectite such as nontronite [42]. Inhabiting anoxic environments and thought to be the oldest microorganisms on the planet, the methanogens (phylum Archaea) use CO_2 as an electron acceptor in their anaerobic respiration resulting in the formation of methane. If the methanogens use Fe(III) from nontronite as an electron acceptor, its bioreduction to Fe(II) results in the inhibition of methanogenesis because the electrons are transferred from carbon dioxide to ferric iron and as a consequence less methane is released to the atmosphere.

It must be noted that the majority of studies on the biological effects of clay minerals on microbial growth and biosynthetic activity employed a simplified experimental design to be carried out under laboratory conditions with a single or a few model microbial strains selected by researchers for various reasons. Such a simplistic approach has its biases and limitations and results in systems very far from the true complexity and multiplicity of factors of microbe–clay mineral interactions in the natural systems. Nevertheless, even at the simplified level, such information derived from this analytical approach is helping us to elucidate many aspects of mineral impact on microbes and this insight is used for developing biotechnologies associated with environmental protection, agronomy, and human and animal health.

In the following subsections we will be focusing on the biological effects of clay minerals on some specific groups of microorganisms common in soils: melanin-producing fungi and bacteria promoting plant growth; as well as on the interactions between clay minerals, viruses and microorganisms.

4.1. Clay Mineral Effects on Melanin-Producing Fungi

The biological effects of clay minerals on the melanin-producing microscopic fungi are of particular interest because this group of dark pigmented microorganisms is well adapted to mineral substrata and harsh environments, commonly occurring in soils and on the rock surfaces, and might play a significant role in pedogenesis because the melanin pigment, in terms of its chemical nature, is one of the most important precursors of the humic substances in soil [65,85,105,111,175,196–198]. It is well known that fungal melanins and other phenolic polymers possess many potential metal-binding sites with

oxygen-containing groups including carboxyl, phenolic and alcoholic hydroxyl, carbonyl and methoxyl groups [129,156]. The structure of melanins, including the presence of unpaired electrons, makes these pigments highly reactive biopolymers and effective scavengers of the free radicals [199]. Due to these properties melanins provide microorganisms with protection from irradiation and oxidative stress.

For example, the ubiquitous soil melanin-producing fungi of genus *Cladosporium*, which are also commonly associated with mineral surfaces, such as dust, man-made constructions and building materials, have a remarkable resistance to extreme environments, surviving low levels of nutrients and water activity, as well as severe radiation [24,54,197,198,200–202]. *Cladosporium* spp. are thought to be able to withstand various physical and chemical stresses thanks to the melanin in the cell wall comprising about 20–30% of biomass [196]. Because of their ability for melanin synthesis this group of fungi has attracted attention of the researchers, and the strain *Cladosporium cladosporioides* 396 has been studied as a potential producer of melanin preparation with radioprotective, antioxidant and detoxifying properties for medical use and also as a biosorbent of toxic metals and radionuclides [157,203–205].

Regarding the microbial interactions with clay minerals, there are a few experimental studies on the biological effects of clay minerals on the growth of melanin-producing microfungi, including *Cladosporium cladosporioides* 396, carried out using a submerged culture technique [157,175,185,205,206].

It was observed that clay minerals, especially montmorillonite at concentrations up to 1.0% (w/v) in liquid medium, accelerated biomass yield and glucose consumption, and enhanced the efficiency of glucose utilization for cell synthesis of the microscopic fungus *Epicoccum nigrum*, which produces and stores melanin in the cell walls, especially in spores [185].

In the series of our experimental studies on the clay mineral effects on melanin-producing fungi, we focused mainly on the biotechnologically relevant strain *C. cladosporioides* 396, investigating the impact of montmorillonite on the physiological parameters of fungal growth in submerged culture, the morphological changes of fungal growth, the melaninogenesis and also the metal sorption properties of the fungal–clay composites [157,175,205,206].

We found that the presence of 0.5% (w/v) montmorillonite in the medium changed some key growth parameters of *C. cladosporioides* 396 grown on the glucose-containing liquid medium [206]. Traditionally used in the studies of microbial growth kinetics in an aqueous environment, the empirical Monod model relates the growth rate to the concentration of a single growth-controlling (or limiting) substrate via two main parameters, the maximum specific growth rate (μ_{\max}) which is a rate at which the substrate concentration is not limiting, and the substrate affinity constant (K_s) or half-saturation constant, equal to the growth limiting substrate concentration when the growth rate is half of μ_{\max} [207–209]. In the cases when the active transport of a substrate into a cell controls the cell growth, K_s may become similar to the enzyme kinetics Michaelis–Menten constant (K_m) for the permease carrier or extracellular enzymes involved in this substrate acquisition [208,210]. Further increase in the substrate concentration above certain values leads to the inhibition of the key enzyme activity resulting in the inhibition of microbial growth by the substrate. This process is reflected in the inhibitor constant K_i or the highest substrate concentration at which a specific growth rate is half of μ_{\max} . It was shown that the maximum specific growth rate (μ_{\max}) of *C. cladosporioides* 396 was twice higher in the presence of 0.5% montmorillonite (0.0615 h^{-1}) compared to the clay-free control medium (0.0275 h^{-1}), whereas the clay addition to the medium did not change the values of K_s (0.011% glucose) and K_i (65% glucose) [206]. This might indicate that an increase of the maximum growth rate by montmorillonite is not related to alterations of the key enzyme–substrate interaction, which is reflected in the unchanged parameters of glucose saturation and inhibition constants. The values of the yield coefficient, which is the ratio of mass of grown microorganisms to mass of utilized substrate, were higher for *C. cladosporioides* 396 grown in the presence of montmorillonite compared to the clay-free control ($Y_{\text{clay}} = 35 \pm 4.0\%$ and $Y_{\text{control}} = 24 \pm 3.5\%$). Thus both maximum specific growth rate and yield coefficient indicated the increased efficiency of glucose consumption observed for growth of *C. cladosporioides* 396 biomass in the presence of montmorillonite. The mechanisms that might be involved in the stimulation of fungal growth by clay minerals can include mitigation of various limiting or inhibiting factors and modification of the

microbial microenvironment resulting in microzones with altered conditions beneficial for microbial growth [177,180–183,211]. For example, clays were reported to have an affinity for enzymes secreted by microbial cells in the microenvironment or liberated at their autolysis [212].

The modification of the microenvironment may include various morphological strategies of mycelial growth of microscopic fungi. We observed the morphological changes in fungal pellets of *C. cladosporioides* growing on medium with 0.5% bentonite (containing 97% montmorillonite) compared to the clay-free control [175]. The size of fungal pellets decreased 3 times whereas there was a 3 times increase of the porosity of the pellets (the ratio of surface hyphae length to pellet radius). Bentonite was involved in pellet formation as a structural element at all stages of fungal growth (Figure 3).

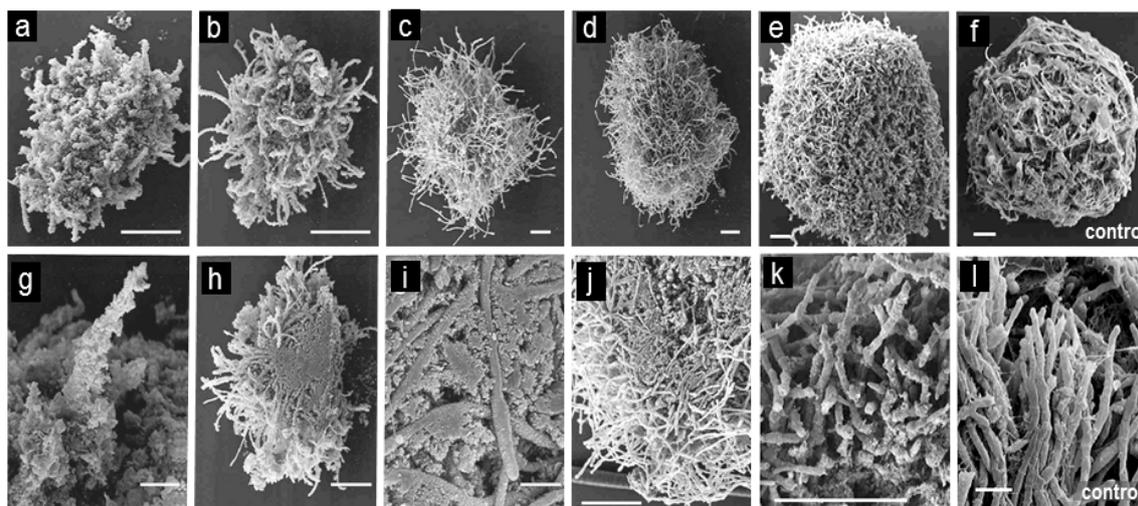


Figure 3. Scanning electron micrographs (SEM) showing the morphology of *Cladosporium cladosporioides* 396 pellets grown in submerged culture in a medium containing 0.5% (w/v) bentonite which were cultivated for different time periods after spore inoculation: (a,g) 17 h; (b,h) 24 h; (c,i) 38 h, (d,j) 45 h and (e,k) 140 h. It is also shown the morphology of 140 h-old pellets grown in the clay-free control medium (f,l). SEM images present the whole pellets (a–f) and internal structure of fractured pellets (g–l). Scale bars = 100 μm (a–f,h,j,k), 10 μm (g,i,l) (adapted from [175]).

Such clay mineral effects on fungal morphology may positively influence the diffusion of oxygen and nutrients within a pellet or/and the removal of toxic metabolites. Similar to *Cladosporium cladosporioides* 396, in the same experimental settings, it was shown that the size, shape and structure of the mycelial pellets of other melanin-producing fungi (*Humicola grisea* and *Cladosporium herbarum*) were also affected by the bentonite, palygorskite and kaolinite presence in the medium [175]. The common tendency for all tested clay minerals was also a reduction of polysaccharide-like exopolymer production in *C. cladosporioides*, *H. grisea* and *C. herbarum* with increasing clay concentration. Such an effect may be a result of clay protection of the fungal mycelium from a decline in the stationary growth phase so that less stress-induced protective EPS is required [175].

It is known that clay minerals can both reduce and increase the length of the lag-phase, which is the phase of microbial growth delay occurring immediately after inoculation of the microorganisms and required for microbial adaptation to the new growth conditions before proceeding to the active exponential growth [182]. The more microorganisms are adapted to the new environment the shorter the lag-phase is thought to be [207]. If the microbial inoculum was pre-grown under precisely the same conditions as for the main experiment, the microorganisms may start the exponential growth phase missing the lag-phase. Such an absence of the lag-phase was observed for *C. cladosporioides* 396 in the control clay-free liquid medium [206]. However, the addition of montmorillonite to the liquid medium 0.5% (w/v) caused a substantial growth delay (lag phase = 15 h) for *C. cladosporioides* 396 [206]. This additional time was obviously required by fungi to adjust to the presence of montmorillonite

e.g., through expressing specific genes and synthesizing necessary enzymes leading to the adaptation of fungal spores to the new clay-rich environment prior to the start of the active germination and hyphal growth. As a result of this adaptation *C. cladosporioides* 396 was able to exploit the presence of montmorillonite, interacting with clay particles as the structural components of pellet formation, and manifesting accelerated growth and more efficient production of biomass compared to clay-free control.

For *C. cladosporioides* 396 grown in submerged culture, it was also observed that the addition of montmorillonite (0.5% w/v) to the liquid medium seemed to create more favourable conditions for greater biomass yield under the deficiency of mineral nutrients, including the most important for active growth sources, nitrogen and phosphorus, as well as the essential metal potassium [24,196,206]. It was found that, if no KH_2PO_4 (1 g/L) and NH_4NO_3 (2 g/L) were added to the modified Czapek medium, biomass yield was 4 times higher on the clay-containing medium (1 g/L) compared to the clay-free control medium (0.25 g/L) [206]. If only NH_4NO_3 was added, montmorillonite presence also increased fungal biomass yield by 4 times (3.25 g/L) compared to control biomass grown on clay-free medium (0.8 g/L).

While growing *C. cladosporioides* 396 at a wide range of glucose concentrations in liquid medium (0.01–60%), the presence of 0.5% (w/v) montmorillonite caused a biomass increase approximately 1.5–3 times that of the clay-free control, depending on the initial concentration of glucose in the medium (Figure 4) [206]. The beneficial effect of the montmorillonite presence on the fungal growth was observed even at the very low concentrations of glucose in the medium, starting from 0.01%, which was within the limiting microbial growth range, as the conventional medium contains 2% glucose. Such a growth-promoting effect of montmorillonite under the scarce nutrient conditions might reflect the ability of montmorillonite to facilitate microbial nutrition, providing the sorptive surfaces on the solid-liquid interface that could concentrate deficient nutrients in the microenvironment of the microbial cells.

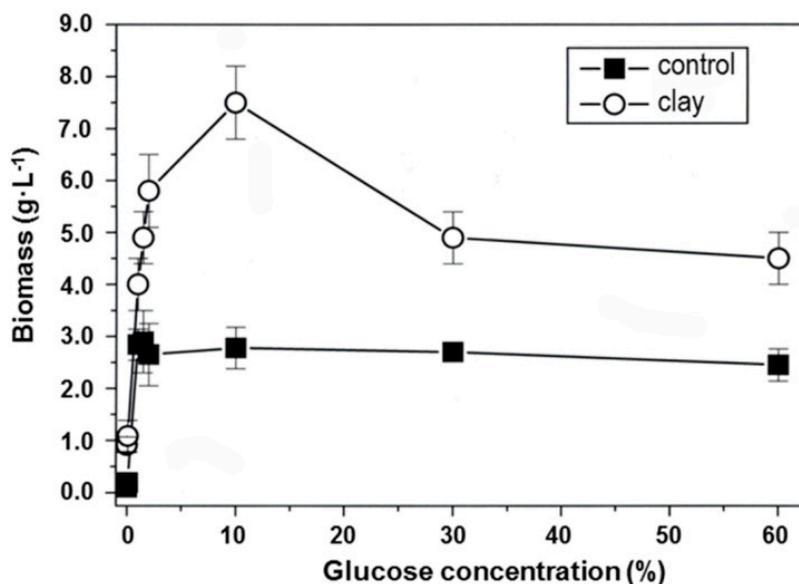


Figure 4. Montmorillonite effect on *Cladosporium cladosporioides* 396 biomass yield at the different initial glucose concentrations in the medium (montmorillonite concentration 0.5% w/v) [206].

The maximum value of *Cladosporium cladosporioides* 396 biomass yield was reached at 10% glucose (Figure 4). At higher glucose concentrations (30–60%), montmorillonite presence maintained a 1.8× increase of biomass yield compared to clay-free control. Glucose concentrations around 60% and over substantially reduce water activity of the medium and are regarded as significantly inhibiting growth of the majority of microbes, except the group of xerotolerant microorganisms. The fact that *Cladosporium cladosporioides* 396 was able to sustain growth at such high glucose concentrations in

the clay-free control medium obviously indicates the xerotolerance of this fungus. Thus, at high glucose concentrations, the clay mineral seemed to protect the fungus from substrate inhibition and the consequences of the increased oxidative and osmotic stresses. This is consistent with the reports that, in contact with microbes, clay minerals, for example, montmorillonite may protect the organisms from various physical and chemical stresses [48]. It can be concluded that, at a very wide range of glucose concentrations, the presence of montmorillonite in the medium provided *C. cladosporioides* 396 not only with proximity of the carbon source but also with a waste sink and protection.

In the studies of the effects of various concentrations of montmorillonite on *C. cladosporioides* 396 growth and melaninogenesis, we observed the significant increase of fungal biomass yield values, up to 3 times, at montmorillonite concentrations ranging from 0.01 to 10% (w/v) (Figure 5) [206]. Observed for *C. cladosporioides* 396, the remarkable growth-promoting ability of montmorillonite at rather high concentrations (up to 10%) might be related to the ecological characteristics of this species. The melaninogenesis of *C. cladosporioides* 396 in the presence of montmorillonite was assessed by using two parameters: (i) the concentration of melanin pigment in the fungal biomass and (ii) the intensity of electron paramagnetic resonance (EPR) signals as an indicator of unpaired electrons, which are related to the high reactivity and scavenging ability of free radicals of melanin. In general, the melanin content in *C. cladosporioides* 396 biomass decreased (1.2–2.0 times) in the presence of montmorillonite, except at the lowest concentrations 0.01 and 0.05% (w/v), when the pigment concentration values did not differ significantly from the clay-free control variant [206] (Figure 5). However, EPR spectrometry data demonstrated the significant effect of montmorillonite on the paramagnetic properties of *C. cladosporioides* 396 melanin. It was revealed that the EPR signal intensity registered in both melanin within the intact biomass (calculated from melanin content in dried fungal biomass) and melanin powder obtained by using an acid-extraction method [203] had the similar tendency of a significant increase when 0.1% (w/v) of montmorillonite was added to the medium [206] (Figure 5). Further increase of clay mineral concentration above 0.1% (w/v) resulted in a decrease of EPR signal intensity. Obviously, the procedure of acid-extraction of melanin from biomass might have altered the paramagnetic properties of the obtained powder and decreased EPR intensity compared to the melanin in the intact biomass. For melanin in the intact biomass, the addition of 0.1% (w/v) montmorillonite doubled EPR signal intensity compared to that of the clay-free control medium. Thus, the melanin synthesis by *C. cladosporioides* 396 was not increased by the presence of montmorillonite but decreased in biomass at some montmorillonite concentrations. This might be explained by the protective effects of montmorillonite on fungal growth so that fungal cells needed less amount of shielding melanin pigments. Claus and Filip (1990) also reported that bentonite addition to the medium did not enhance the enzymatic activity of the phenoloxidases involved in the microbial melanin synthesis (laccases and tyrosinases) in their experiments with the fungi *Polyporus versicolor* and *Pleurotus osreatus*, and some streptomycetes [184]. However, as it was revealed in our study on *C. cladosporioides* 396, while reducing the amount of melanin in the cells, montmorillonite (0.1% w/v) can increase its chemical reactivity and ability to scavenge free radicals. This finding is also important from the biotechnological point of view as the strain of *C. cladosporioides* used in these experiments has been considered as a perspective producer of melanin [157,203–205].

It is known that the presence of melanin in pigmented cell walls is responsible for higher levels of biosorption in comparison with albino mycelium [156,213]. Due to their high ability to sorb toxic metals, clays and fungal biomass have been investigated mainly separately [214–222], with the exception of a few studies on mixtures of clay minerals and microbial biomass [157,223–225].

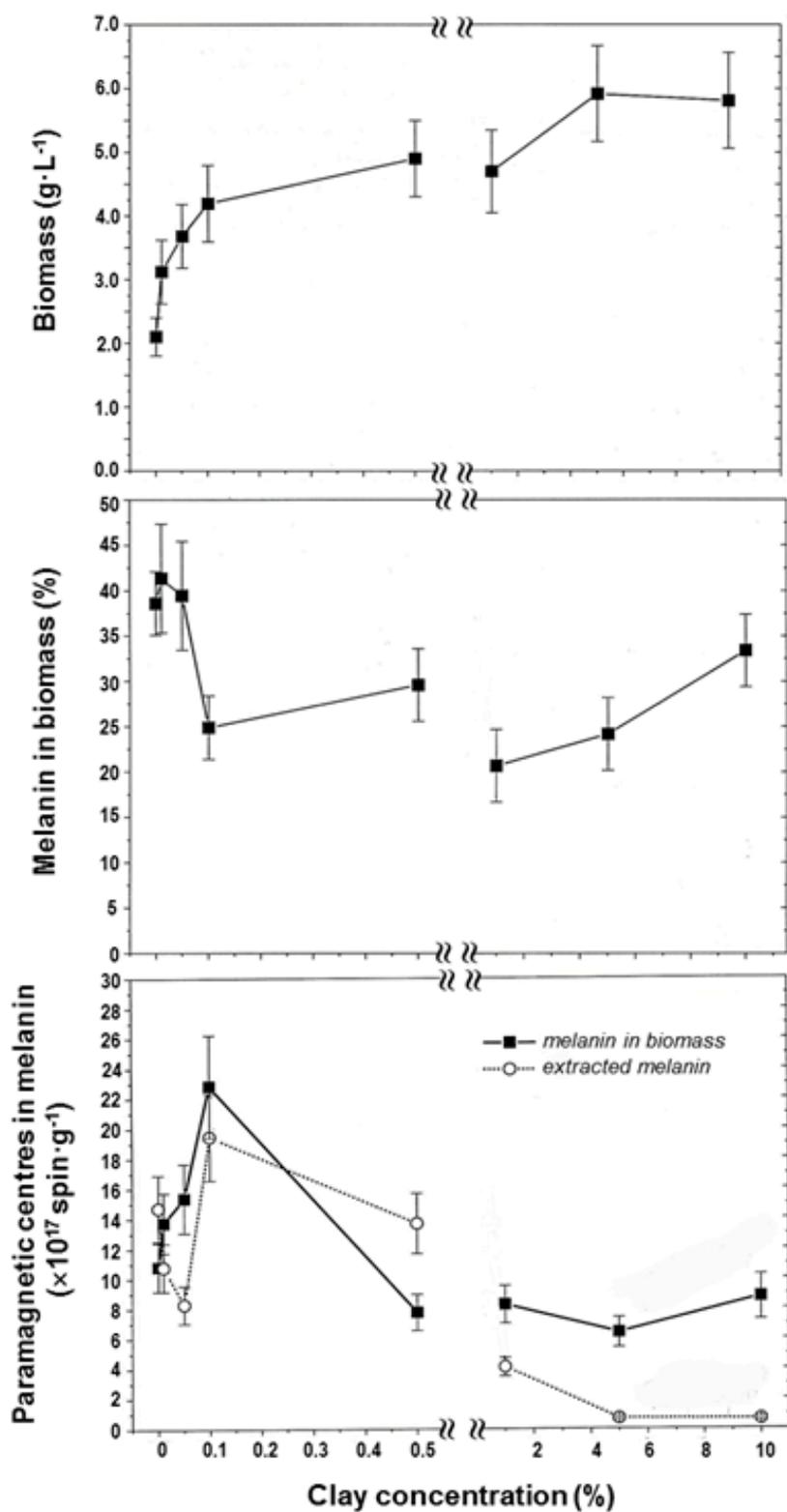


Figure 5. Effects of montmorillonite concentration on the biomass yield, melanin concentration in biomass and the electron paramagnetic resonance intensity in both melanin in biomass and extracted melanin of *Cladosporium cladosporioides* 396 [206].

In studies of the sorptive properties of clay–organic matter complexes, increasing organic molecules adsorbed on the clay surface, in general, led to a decrease in metal sorption [226,227] due to the partial

or complete blocking of adsorption/catalytic centres. However, it was also reported that sorption of the metals (Cd, Cu, and Zn) can be significantly enhanced by the siderophore desferrioxamine B in montmorillonite suspensions, which has implications for the soil environment [228]. This increased metal sorption is thought not to necessarily lead to reduced bioavailability as the chelates are bound electrostatically, making these elements exchangeable [228]. In our studies, metal (Cu, Cd) sorption capacity of fungal-clays composites, formed by melanin-producing fungi (e.g., *C. cladosporioides* 396 and *Aureobasidium pullulans*) grown in submerged culture in clay-containing media, was determined by a batch equilibrium method [157]. The presence of kaolinite and palygorskite in the medium generally reduced both Cu and Cd sorption capacity and the metal-binding ability of the fungal-clay mixtures [157]. In contrast, the addition of 5% (w/v) bentonite (containing 97% montmorillonite) to the liquid medium did not considerably alter the Cd sorption ability but increased the sorption of Cu by the composites with *Aureobasidium pullulans* and *C. cladosporioides* [129,157]. A common feature for tested fungi grown in the bentonite presence was an increase in Cu sorption capacity of the biomineral sorbents and a reduction of their affinity compared to the control clay-free biomass [157]. In addition, it was found that *C. cladosporioides* 396 grown in the form of small pellets in a medium containing 5% (w/v) kaolinite demonstrated an enhanced ability to sorb ^{90}Sr (2670 Bq/g) compared to pure kaolinite (1951 Bq/g) and pure biomass (1551 Bq/g) [205]. Copper and radionuclides sorption by *C. cladosporioides* 396 generally increased with a decrease of fungal pellet size [157,175,205]. This effect of pellet size on sorption ability of fungal/clay composites can be explained by an increase of the ratio of surface area to volume with decreasing pellet size, which leads to an increase of the sorbing surface area and thus to more efficient sorption.

In conclusion, the use of the submerged culture technique for the cultivation of microscopic fungi provides a classic tool for the detailed studies on microbial growth physiology, giving insights into biological effects of clay minerals on the growth and biosynthetic activity of microorganisms. Using the biotechnologically important strain of melanin-forming fungi *C. cladosporioides* 396 as a model, it was demonstrated that clay minerals such as montmorillonite may significantly accelerate fungal growth and biomass yield, alter the growth morphology of fungal mycelium, facilitate microbial nutrition and mass transfer, and provide mechanical support and protection, as well as influence metal/radionuclides sorption properties of the resulting clay–fungal composites. They also are able to affect the production of melanin pigments and their reactivity, which may have impact on the functioning of the antioxidant system of fungal cells.

4.2. Influence of Clay Minerals on Plant Growth-Promoting Rhizobacteria (PGPR)

In the recent decades great interest has been generated by such significant representatives of soil microbiota as plant growth-promoting Rhizobacteria (PGPR), playing an important role in the rhizosphere in maintaining the stability and productivity of agroecosystems [229]. Both free-living non-symbiotic bacteria (genera *Bacillus*, *Azotobacter*, *Azomonas*, *Pseudomonas*, *Azospirillum*) and bacteria symbiotic with roots of legume plants (genera *Rhizobium*, *Mesorhizobium*, *Bradyrhizobium*) belong to the PGPR group. PGPR are in the intimate contact with clay minerals in soil, which can significantly affect their growth and biosynthetic activity [230].

Bacteria of the family Rhizobiaceae, forming specific symbiotic nodules on legume roots, take a crucial part in the process of symbiotic nitrogen-fixation, converting atmospheric N_2 to NH_3 , which can be efficiently assimilated by the host legume plants. This symbiotic nitrogen fixation is an important link in the global nitrogen cycle [231].

In experiments using the submerged culture technique, the cells growth of bacterial strain *Agrobacterium radiobacter* 10 (synonym *Rhizobium radiobacter*) was increased by 71.5% or 78.6% in the presence of 1% (w/v) montmorillonite or palygorskite in the liquid nutrient medium, respectively, compared to the number of viable bacterial cells in clay-free control. However, the cultivation of these bacteria with kaolinite resulted in a 28.6% decrease in the number of viable bacterial cells [232]. The authors suggested that the negative effect of kaolinite on *A. radiobacter* growth might be due

to the high aluminium content in the mineral. A number of authors found that clay minerals (e.g., kaolinite) and clay-rich rock (e.g., bentonite) with high aluminium content inhibited growth of many bacteria: *Escherichia coli* [233], *Pseudomonas* [234], *Desulfovibrio vulgaris* [235] and other representatives of different genera.

For the nitrogen-fixing bacterial strain *Bradyrhizobium japonicum* 634b grown in submerged culture, the biomass yield on clay-free medium was 5.0×10^{10} cells/ml while the addition of palygorskite or montmorillonite (1 g/L) increased the number of cells by an order of magnitude [236]. Moreover, montmorillonite and palygorskite were found to increase the viability of this strain at superoptimal temperatures. For example, the 15 min incubation of *B. japonicum* 634b at 45 °C in the presence of 1 and 10 g/L montmorillonite showed that the number of viable cells comprised 69% and 83% of the unheated control, respectively. For a clay-free medium, the survival of bacterial cells after heating was significantly reduced with only 32–41% of viable cells left [237].

It was reported that clay minerals significantly increased the adhesion of microorganisms to plant seeds, which facilitates growth of bacteria on plants [232]. For example, after addition of 1% of the clay minerals montmorillonite and palygorskite to an *Agrobacterium radiobacter* 204 suspension, the number of bacteria attached to wheat seeds increased by 12.5–150%. The number of *Bradyrhizobium japonicum* 634b attached to the soybean seeds increased by 48% in the presence of clay minerals [232].

It was shown that clay minerals (saponite, glauconite, palygorskite) can significantly affect the growth of biotechnologically important strains of free-living bacteria *Azotobacter vinelandii* IMV B-7076 and *Bacillus subtilis* IMV B-7023 actively used in crop production [238–240]. The species *Azotobacter vinelandii* is a common nitrogen-fixing soil bacterium and *Bacillus subtilis* IMV B-7023 is an efficient phosphate-mobilizing strain with antagonistic activity towards phytopathogenic microorganisms as well as a producer of the metabolites with insect pest control potential (particularly with action against the Colorado beetle eggs). The cultivation of these bacteria in medium containing 1 g/L saponite led to a 2- and 3-fold increase of the number of *B. subtilis* IMV B-7023 and *A. vinelandii* IMV B-7076 cells, respectively, compared to the mineral-free control. The most pronounced increase of viable cells assessed as CFUs for both bacteria was observed at 10 g/L of saponite in the medium. It was assumed that a saponite-induced increase in bacterial growth activity can be due to the intensification of the substrate intake by microbial cells. This bacterial growth stimulation could be explained by saponite accumulating nutrients on its surface which resulted in their improved availability for microorganisms as well as by the buffering capacity of saponite which maintained the pH of the nutrient medium at an optimal level for sustainable bacterial growth through cation exchange processes [241,242]. However, further increase of saponite concentration in the nutrient medium suppressed bacterial growth [238–240,243]. It is known that a layer of adsorbed mineral particles can be formed at the surface of bacterial cells as a result of microbial interaction with dispersed materials at certain concentrations [244]. It might be suggested that at increasing concentrations of saponite the presence of such a layer might become a mineral barrier which inhibits penetration of the substrate into cells reducing the growth activity of microorganisms [243]. Glauconite's effect on growth activity of *A. vinelandii* IMV B-7076 was similar to saponite: the number of viable cells increased with glauconite presence at 5.0 and 10.0 g/L into the nutrient medium. However, the bacterial growth also decreased with increasing glauconite concentration similarly to saponite [243]. Palygorskite had a more pronounced stimulating effect on the growth of *B. subtilis* IMV B-7023: the number of bacteria increased by 263% in the medium with 10.0 g/L palygorskite, compared to mineral-free control. A further increase in palygorskite concentration was also accompanied by a decrease of stimulating effect on bacterial growth [245].

In the experiments on biological effect of montmorillonite on the phosphate-solubilizing *B. subtilis* IMV B-7023, 2–10 g/L of montmorillonite significantly stimulated *B. subtilis* IMV B-7023 growth on a medium containing sparingly soluble $\text{Ca}_3(\text{PO}_4)_2$ as the sole source of phosphorus nutrition compared to clay-free variant. However an increase in the montmorillonite concentration up to 20 g/L in the medium led to the inhibition of growth. The authors suggested that this might be associated with a

significant amount of the main energy sources being adsorbed on this clay mineral (about 22% glucose and 11.3% phosphate) [245].

Exfoliated vermiculite at concentrations 5–10 g/L was found to cause a significant stimulating effect on *A. vinelandii* IMV V-7076 growth in different liquid nutrient media: there was a ~20% increase of cell numbers for both Berk and Ashby media. The addition of vermiculite (5 g/L) also stimulated *B. subtilis* IMV B-7023 growth, increasing cell numbers by almost 50%. Kameneva (2009) showed that vermiculite with a particle size up to 1 mm in diameter and concentration of 2% (w/v) is an important component for the biotechnological production of heterophase microbial preparation of nitrogen-fixing nodular bacteria *Mesorhizobium ciceri* H-12. Bacterial titer was 6.9–8.0 billion/mL, and cell viability and nodular activity were maintained for three months. The microbial interactions with clay minerals with beneficial biological effects can successfully help the paramount task of improving the quality of microbial preparations of agriculturally valuable bacteria in order to ensure a high number of viable microbial cells in the preparation and the long-term preservation of their viability [246].

The clay minerals as well as other various environmental factors, such as ionizing and UV radiation, extreme changes of temperature and osmolality, toxic substances and mechanical damage may have considerable impact on the stability of the antioxidant complex of the living cells within microbial populations. Such factors might trigger in the cells the formation of elevated levels of reactive oxygen species (ROS), which are highly reactive oxidizing products of incomplete oxygen reduction. ROS can be very damaging for the biomolecules, posing a threat for the whole cell. A powerful complex of enzymes and low molecular weight antioxidants is employed by microbial cells to mitigate the damaging effects of ROS and to counterbalance the oxidation process to the optimal level [247,248].

In modern scientific literature, there are very scarce data about clay minerals' effect on the synthesis and activity of the components of the antioxidant system of bacteria [249,250]. Our study demonstrated that the levels of extracellular peroxidase activity of *B. subtilis* IMV B-7023 increased by 155% and 178% when bacilli were grown in the presence of 1.5 and 2.5 g/L vermiculite, respectively [251]. However, when the mineral concentration in the nutrient medium was 5 g/L, this enzyme activity decreased. Since the proportion of SiO₂ in vermiculite is quite high (37–42%), it could be assumed that it can initiate biomolecular peroxidation [252], thereby activating the extracellular peroxidase of bacilli at certain doses of mineral particles in the nutrient medium. However, increasing vermiculite concentration up to a certain level led to the suppression of peroxidase activity in the culture medium. It is well known that the clay mineral effect on the biochemical processes under the oxidative stress is dose-dependent for various micro- and macroorganisms, specifically affecting the activity of antioxidant defense enzymes [253].

At the same time our study revealed that cultivation of bacilli with vermiculite did not directly cause significant changes in the intracellular peroxidase activity since the mineral did not penetrate the cells. The mineral did not affect the extracellular and intracellular catalase activity. [251]. A catalase is an antioxidant enzyme that only activates the decomposition of H₂O₂ but does not affect other peroxides [254]. Perhaps, that is why the changes in catalase activity were not significantly increased in the vermiculite presence in our study [251].

Low molecular weight antioxidants that function in both aqueous and lipid phases have a number of advantages over enzymes [255]. These protectors prevent and minimize damage caused by aggressive ROS. Some L-amino acids (e.g., phenylalanine, proline, tryptophan, arginine, and histidine) are considered to play a role as antioxidants due to their structure and physicochemical properties. The total amounts of free amino acids accumulated in the culture media of *B. subtilis* IMV B-7023 when grown with glauconite or saponite (5 g/L) were found to be 1.7 or 3.4 times lower, respectively, than the total amino acids amount in the clay-free control [256]. However the addition of glauconite and saponite demonstrated an evident stimulating effect on the synthesis of amino acids by *A. vinelandii* IMV B-7076 [256]. During submerged cultivation of this strain in a medium with glauconite particles, eight amino acids were found with the total amount ~14.4 µg/mL, where the concentrations of the amino acids with antioxidant properties (arginine, phenylalanine and histidine) were the highest. The

total accumulation of amino acids in the culture medium of *A. vinelandii* IMV B-7076, grown in the presence of 5 g/L saponite, exceeded 16 µg/mL, which was 6 times higher than the clay-free control. In this case, the highest concentrations of accumulated amino acids were noted for proline (9.55 µg/mL) and phenylalanine (3.16 µg/mL) [256].

Soil microorganisms can produce different hormonal compounds that regulate physiological and biochemical processes in plants, including the stress responses, and play an essential role in the development of plants at different stages [257,258]. Cultivation of *A. vinelandii* IMV B-7076 and *B. subtilis* IMV B-7023 in a nutrient medium with vermiculite promoted accumulation of phytohormones. The addition of 5 g/L of vermiculite increased by 2.3 and 6 times biosynthesis of the total abscisic acid (ABA) and free ABA by *A. vinelandii* IMV B-7076, respectively. Vermiculite increased *B. subtilis* IMV B-7023 synthesis of free ABA up to 65.0 ng/mL, which was 1.4 times higher than the levels observed for the clay-free control [259]. The apparent stimulating effect of vermiculite was also observed for the synthesis of cytokinins by both *A. vinelandii* IMV B-7076 and *B. subtilis* IMV B-7023. It was found that for cultivation of these bacilli, in the presence of 5 g/L of vermiculite the concentration of zeatin in the culture medium increased by 17%, zeatin riboside by ~20 % and zeatin glucoside by 144%. Vermiculite addition to the nutrient medium increased *A. vinelandii* IMV B-7076 synthesis of zeatin riboside by 2.3 times compared to control, however it did not change the production of zeatin and actually reduced the concentration of zeatin glucoside by 20% [260].

It was found that clay minerals, in particular palygorskite, significantly stimulated the synthesis of vitamins with antioxidant and prooxidant activities by bacteria. *Azotobacter chroococcum* 20 grown in Ashby medium containing 2 g/L palygorskite increased the synthesis of thiamine (vitamin B1) by 116.6%; whereas, under such conditions *A. vinelandii* 56 produced 7 times more pyridoxine (vitamin B6) compared to clay-free control [261].

The clay effect on the bacterial synthesis of phenolic compounds, which are the most powerful components of the antioxidant system, is of particular interest. In our studies three compounds of phenolic nature were found to be synthesized by nitrogen-fixing bacteria *A. vinelandii* IMV B-7076: 1.2-benzenediol (catechol), hydroquinone, and 2.3-dihydroxy-benzoic acid [262]. After bacterium cultivation in the presence of 0.05–0.5 g/L of palygorskite for 48 hours, only 1.2-benzenediol was identified among the phenolic metabolites [262]. The absence of two other phenolic compounds in the medium can be explained, based on their chemical structure, by their adsorption on palygorskite particles. It is known that the symmetric hydroquinone molecule can easily interact with the surface of clay mineral due to the presence of 2-nd hydroxyl groups [263]. The high adsorption capacity of 2.3-dihydroxybenzoic acid is due to the location of the OH group in the meta-position. The hydroxyl groups of 1.2-benzenediol in the ortho-position most likely form a chelate structure with one of the active centers of palygorskite through two free hydroxyls on its surface. However, these surface groups of palygorskite are not always available, which affects the reduction of the sorption efficiency of the catechol [264,265].

It was also found that bentonite significantly influenced the amount of phenolcarboxylic acids synthesized by *B. subtilis* IMV B-7023. At the cultivation of this strain with 0.05 g/L montmorillonite-containing bentonite, the concentration of gallic acid in the methanol extract of the bacterial culture medium increased by 12.9%, that of trans-cinnamic acid by 54.4% and that of 4-hydroxyphenylacetic acid (4-HPA) did not change considerably compared to clay-free control. In the case of bentonite concentration increased up to 0.5 g/L, the amount of gallic acid increased by 31.9%, that of 4-HPA by 54.8%, and that of trans-cinnamic acid decreased by 35.1% [266,267]. Therefore, the bentonite effect on the synthesis of phenolic acids by bacteria is directly related to mineral concentration in the nutrient medium and to the chemical structure of the studied bacterial metabolites [268].

Because clay minerals influence important components of the antioxidant system of bacteria, including enzymes and low-molecular compounds, they determine the microbial antioxidant potential as a whole. In conclusion, our results demonstrated that such clay minerals as montmorillonite, palygorskite and vermiculite at certain concentrations may have significant effects on the different

parameters of antioxidant potential of plant growth-promoting Rhizobacteria which might also have an impact on the associated plants [251,256,259,260,266,267]. However, the insights of the clay minerals impact on the complex pro- and antioxidant processes occurring in the microbial cells are still insufficient and require further detailed interdisciplinary research.

4.3. Interactions between Clay Minerals, Viruses and Microorganisms

Another important issue of the effects of clays on microorganisms is the interaction of clay minerals with viruses and microorganisms. Viruses are submicroscopic infectious agents which can replicate only inside the living cells of the host organisms. Every known microorganism has specific viruses infecting it, and microbial viruses are the most abundant viruses on the planet [269]. Whether viruses of microorganisms kill or do not kill their microbial hosts, their interactions play an important ecological role in the modifying microbial communities, nutrient cycling and evolution of their hosts through virus-mediated horizontal gene transfer [269–272]. The viruses of prokaryotic microorganisms, bacteriophages (or phages) infecting bacteria and archaeoviruses infecting archaea, are the most studied [271]. Bacteriophages are thought to be very abundant in the terrestrial environment, reaching up to 10^{10} virions (virus particles) per g of soil and exceeding the number of soil bacteria by nearly six orders of magnitude, which suggests that the majority of bacteria in soil can be infected by phages at any time [271]. However the functional significance of the interaction of the clay minerals with viruses and microorganisms in soils and the real scale of its ecological consequences are still very little understood and largely disregarded. It is required to develop the adequate methodological approaches for the in situ studies of these interactions. For example, Starr et al. (2019) has recently used for the first time metatranscriptomic analysis to assess the diversity and ecology of soil RNA viruses, previously unexplored in such complex environments as soil [272]. This study revealed the dominance of fungal viruses (or mycoviruses) of the family Narnavirida which are persisting in fungal cells and may have significant impacts on physiology, reproduction, and biogeochemical activity of fungal hosts in soils. It was also found that the phages Leviviridae are abundant, suggesting that Proteobacteria represent, in addition of fungi, another main host for RNA viruses in the studied soils [272]. Such RNA phages can lead to the lysis of host bacterial cells, releasing low molecular weight carbon compounds, biopolymers, and the fragments of cellular and viral debris to soil. Some part of the microbial necromass may be stabilized in soil, for example, lipids and polysaccharides can attach to mineral surfaces including clay minerals or become trapped within soil aggregates contributing to pedogenesis processes [272].

This view is in agreement with modern hypothetical concepts on the role of microbial viruses in biogeochemical turnover of the elements in soils, which were introduced by Kuzyakov and Mason-Jones (2018) and integrated the previously proposed theories [271]. These concepts include the importance of phages as the determinants of bacterial death rates, leading to the accelerated release of easily available C and nutrients (e.g., P and N) for soil biota. Two pathways of distribution of carbon and other nutrients were also suggested to be possible after viral lysis of bacterial cells, both involving clay minerals: (1) the sequestration of empty viral capsids and microbial necromass (“entombment”) within soil nano-pores ($<0.1 \mu\text{m}$) mainly within clay minerals and colloids, until the pores are disrupted or removed with water flow making this debris bioavailable for microorganisms and other soil biota, and (2) the stabilization on clay minerals of microbial endoenzymes, released after cell lysis, which retain the ability to decompose low molecular weight organic substances [271].

As clay minerals are responsible for a large portion of sorption and ion exchange processes that occur in soils, it is important to understand the role that clays play in the adsorption of viruses. The ionizable surface groups on the virion’s protein capsid generates a negative charge at the typical soil pH values, which may lead to electrostatic repulsion with common soil organic matter and minerals facilitating viral dissemination. However, soils have both negatively and positively charged sites as well as hydrophobic sites which can play an important role in the immobilization of virions [271,273–275]. There are also epidemiological concerns in relation to virus ecology in soils, which are first of all, to trace the fate of pathogenic viruses discharged from wastewater treatment facilities and those present

in aquifers and groundwater [273]. Here the knowledge of viability and transport of viruses from their point of origin, which could be significantly affected by adsorption on clay minerals, is necessary to determine their potential effects on the neighbouring groundwater systems [276]. A variety of soil and environmental factors affect viral inactivation and infectivity to host organisms, among which are temperature, pH, clay type and its content, organic matter content (nutrient status), toxic metals and acid pollutants, available oxygen, ionic strength (salinity), and moisture content [273,277].

Experimental studies demonstrated that the adsorption of viruses to various clay minerals is highly dependent on the viral strain [275,278]. For example the adsorption of bacteriophage MS2, infecting Enterobacteriaceae including *Escherichia coli*, was far more effective in kaolinite than montmorillonite [275], whereas *E. coli* phages T1 and T7 demonstrated higher adsorption affinity in montmorillonite than kaolinite [278]. The phages of order Caudovirales such as T1, T2 and T7 have tails, multiprotein structures responsible for the penetration into a host cell, which may also be involved in the attachment to clay minerals. In a transmission electron microscopy study, Bystricky et al. (1975) observed that phages T1 were adsorbed to clay mineral particles (kaolinite and montmorillonite) by their tails [279].

The mechanisms involved in phage adsorption to clay minerals may include van der Waals forces, hydrophobic interactions as well as electrostatic adsorption via cation bridges [271,280–283]. It was reported that divalent cations such as Ca^{2+} can bridge two negatively charged surfaces (a virion and a clay surface) with the relatively labile force resulting from electrostatic adsorption [282,283]. It was also observed that the *E. coli* phage T2 adsorbed on kaolinite, montmorillonite and illite by cation bridging more efficiently through divalent Ca^{2+} than monovalent Na^+ [281].

According to Kuzyakov and Mason-Jones (2018), phage virions are passively distributed within the soil system more easily than bacteria, since (i) they are much smaller and fitting the smallest nano-pores; (ii) their interactions with soil surfaces are likely to be mainly reversible; and (iii) unlike bacteria, virions are not attached by exopolysaccharides to mineral and organic surfaces [271].

Clay minerals are reported to protect viruses against both biological and abiotic inactivation, enabling them to persist in soils for longer periods of time in the absence of their hosts [273]. For example, it was shown that montmorillonite was effectively protecting the phages T1 and T7 from abiotic inactivation by temperature and chemicals, enabling viruses bound to clay particles to infect cells [284]. In studies of adsorption of *Bacillus subtilis* phage PBS1 on montmorillonite or kaolinite, the phage exposure to UV irradiation (254 nm) for 10 min in the clay-free control variant decreased the titre of infective viral particles by ~2 orders of magnitude and the frequency of genetic material transduction among bacterial cells by ~3 times, compared to the variant with phages adsorbed on clay minerals [285].

Clay protective effects in the threesome interactions between clay minerals, microbial viruses and microorganisms may depend on the particle size of clay minerals. Roper and Marshall (1978) demonstrated that the fine particle-size fraction of montmorillonite (0.08–0.6 μm) provided almost complete protection of *E. coli* cells from the bacteriophage attack, whereas clay particles with an effective spherical diameter above 0.6 μm did not protect bacteria from the lysis [286]. It was suggested that, unlike for the fine particles' fraction, the larger size particles failed to form a continuous protective barrier around the bacterial cells, allowing phages to attach to unprotected sites and infect bacteria.

Thus, the various still poorly understood aspects of clay minerals effects on viruses and microbes may have important underappreciated implications for soil ecology and biogeochemical processes.

5. Applied and Biotechnological Aspects of Microbial Interactions with Clay Minerals

5.1. Clay–Microbial Interactions in Human and Animal Health

One of the topical areas of the application of the clay–microbial interactions is their use in human and animal health. Macroorganisms such as humans and animals evolved along with millions of microorganisms dwelling in their bodies and collectively composing the microbiome of such

macroorganisms or their organs e.g., gut or skin microbiome. A microbiome plays a very important role in various aspects of the host organism functioning and health [287]. As clay minerals can have biological effects on microbial community and nutrient distribution dynamics, as well as on microbial growth and metabolism, they potentially could modify the diversity and functioning of the microbiomes of the host macroorganisms and as a result the fitness and health of the latter.

Clay minerals have had a medicinal use since the earliest recorded history. This included the ancient practice of geophagy using earth materials containing clays for physical soothing an infected and inflamed gastrointestinal lining, as well as topical use of clays to treat skin infections or rheumatism [288]. Clay applications benefiting digestion as well as cleansing and protection of the skin, mainly based on the clay minerals' sorptive properties, have been traditionally promoted all over the world. However, the literature on the nature of the mineral antimicrobial impact on human and animal pathogens is limited and this phenomenon is still poorly understood. There are a few studies related to the treatment of skin diseases by clays [288–290]. It was reported that the so-called French green clay which is rich in Fe-smectite can be successfully used for healing a Buruli ulcer, a necrotizing fasciitis ("flesh-eating" infection) caused by *Mycobacterium ulcerans* [288]. It was demonstrated that the antimicrobial component of the clay can be removed through cation exchange and the clay aqueous leachates effectively killed the bacteria [288]. It has been suggested that incorporated metal ions, such as adsorbed silver, copper and zinc may have strong inhibitory and bactericidal effects on a broad spectrum of bacteria [289]. In addition to the possible chemical cause of the antibacterial action of clays there could be also biotic factors contributing to healing properties. For example, it was reported that a consortium of bacteria found in clays from Jordan, containing predominantly montmorillonite, kaolinite, illite, vermiculite and palygorskite, manifested antimicrobial action [290]. These bacteria belonged to the phyla Actinobacteria, Firmicutes (e.g., *Bacillus* spp.) and Proteobacteria (e.g., *Lysobacter* spp.) and were able to produce antibiotics, which is a common microbial adaptation facilitating their competition fighting against other microbes for resources and survival [290]. The bacteria of the phyla Proteobacteria, Actinobacteria and Firmicutes were also found in the natural healing Chamliyal clay from India which is traditionally used for different skin disorders (e.g., psoriasis). This microbial diversity profile was similar for other medicinal clays, particularly illite/smectite- and smectite/kaolinite-rich Dead Sea clays [289]. However sulphur- and iron-reducing bacteria like *Deferribacterales*, found in both Dead Sea clays and Chamliyal clay, are particular to clays used for skin healing and it could be suggested that metabolic activities of these microbes could generate sulphur compounds which may play a role in skin disease management [289].

The beneficial effect of clay minerals related primarily to their high sorption ability and high cation exchange capacity is used in medicine and veterinary medicine and to provide a waste sink for various toxins which may be the products of microbial metabolism as well as of the macroorganism itself [291,292]. In livestock, for example, bentonite and other clay-rich materials are used as feed supplements for the prevention of mycotoxicosis caused by such deadly toxins as aflatoxin produced by microscopic fungi [293–297]. However, despite these abilities, studies have been rarely conducted for the effects of clay minerals on gut microbiome and the abundance of beneficial intestinal microorganisms. It has been shown that the addition of clay supplements may affect the composition of the gut microbiota of domestic animals, for example, in the case of copper-bearing montmorillonite, significantly reducing the total viable counts of *E. coli* and *Clostridium* spp. in the gut of piglets which was accompanied by a 70% decrease of diarrhea incidence [298,299]. In studies on anti-obesity effects of clay mineral preparations, the use of Chinese montmorillonite DLA-M and Korean bentonite Bgp35b-p demonstrated beneficial remodelling of gut microbiome in rats and mice models under conditions of high fat diet [300,301]. The high-fat diet caused microbial dysbiosis with reduced relative abundance of *Bacteroidetes* and an increase in the abundance of *Firmicutes* and *Proteobacteria*, whereas the addition of bentonite Bgp35b-p led to the significant increase of the relative abundance of *Ruminococcaceae*, the family of beneficial bacteria producing short-chain fatty acids, with the reduction of *Clostridiaceae* and *Lachnospiraceae*. This means that Bgp35b-p induced compositional changes in intestinal microbiota

close to that in mice fed with a normal diet, thus suggesting that bentonite may be a potential functional supplement with prebiotic properties, i.e., promoting the growth of beneficial intestinal microorganisms, which are also known as probiotics [300]. The beneficial effect of palygorskite to pullet growth and health as a result of modulation of the gut microbiota was also demonstrated in another metagenomic study of clay effects on animal gut microbiome [302]. Palygorskite supplements led to a more favourable and homogeneous gut microbial profiles, comprised largely of beneficial bacteria with probiotic properties, able to produce short-chain fatty-acid (butyrate) and degrade resistant polysaccharides [302].

At the same time, data on the effects of clay minerals on representatives of the normal microbiota and common bacterial probiotics—lactic acid bacteria (LAB)—are limited and somewhat contradictory. When different clay minerals were used as feed supplements for piglets, there were reports about an increase in number of beneficial bifidobacteria and lactobacilli by montmorillonite supplements [303], a decrease of lactobacilli by supplementing sericite [304], and no effect of biotite on the number of the beneficial lactobacilli and potentially pathogenic bacteria of the *Enterobacteriaceae* family including *Salmonella* spp. [305].

Very little information is available on the interactions of clay minerals with commercially important probiotic strains of lactic acid bacteria. According to the submerged culture experiments by Garmasheva et al. (2016) [306], kaolinite and montmorillonite significantly promoted growth of the probiotic strain *Lactobacillus plantarum* 337D UKM B-2627. *Lactobacillus plantarum* species represents lactic acid bacteria commonly found in fermented food (especially in fermented vegetables such as sauerkraut) and the gastro intestinal tract of humans and animals, and used in the food industry as a potential probiotic starter culture for the fermentation process [306]. Compared to the clay-free control medium, the bacterial growth rate increased 5.2× and 6× in the presence of kaolinite (4% w/v) and montmorillonite (1% w/v), respectively. Clay minerals, especially montmorillonite, delayed the process of reducing pH during *L. plantarum* 337D UKM B-2627 growth and production of lactic acid, which is very important as lactic acid overproduction by lactic acid bacteria is very undesirable for the fermentation process, spoiling the quality of the product and reducing its shelf-life. A transmission electron microscopy study of aggregates of *L. plantarum* 337D UKM B-2627 cells and nanoparticles of clay materials formed in aqueous suspensions showed that the interaction between bacteria and mineral particles occurred directly at the surface of the bacterial cell walls or on the polysaccharide capsule surrounding bacterial cells extracellularly [306]. Kaolinite plates and nanotubes of halloysite within the kaolinite material were sorbed on the polysaccharide capsule of *L. plantarum* 337D UKM B-2627 cells. The clay interaction with *L. plantarum* 337D UKM B-2627 cells did not change completely the pore space characteristics of the clay; however, the pore size distribution became wider due to the formation of large diameter pores. In the presence of lactic acid bacteria, the surface area was reduced but the adsorption capacity and the layered structure of clay minerals was preserved [306].

Since both probiotic bacteria and clay minerals are used in the treatments of the various gastrointestinal tract disorders, the exploration and exploitation of their interactions is of current interest and may become of great significance in human and animal health, including the correction of their microbiomes. Understanding the fundamental mechanisms involved in these interactions might help to develop complex preparations combining beneficial and therapeutic effects of microbial probiotics and clay minerals with prebiotic potential of the latter and the ability to function as a sorbent, preserver, protector and carrier for microbial cells.

5.2. Applications of Clay Minerals in Microbial Bioremediation and Biodegradation

Anthropogenic activities, industrialization, and intensive agriculture have resulted in the contamination of soils and water with potentially harmful inorganic and organic compounds including toxic metals, radionuclides and persistent xenobiotic organic pollutants. Bioremediation refers to the application of biological systems to the clean-up of organic and inorganic pollution, with bacteria and free-living and mycorrhizal fungi being the most important organisms in this context [26]. There are

also several plant-based biotechnologies for remediation of metal-polluted soil, sediment or water (aka phytoremediation), which involve (i) extraction and accumulation of contaminants in harvestable plant tissues; (ii) volatilization of selenium, mercury and arsenic; and (iii) immobilization of pollutants by adsorption and precipitation by plant biomass [102]. However phytoremediation can be a very slow process (sometimes taking years), also possessing a risk of further transfer of toxic metals accumulated by plants to the food chain, and pollution of air by volatile metal species [102]. Microorganisms grow much faster than plants, have greater metabolic diversity, powerful biogeochemical and enzymatic activity, and are able to facilitate plant growth and to protect them from pollution.

The use of prokaryotic (bacteria and archaea) and eukaryotic (fungi) microorganisms combined with clay minerals for bioremediation purposes might become a promising cost-effective and environmentally friendly area of biotechnology representing a sustainable solution. The sorption properties of clay minerals and their functioning as a waste sink and the ability to protect microbial cells from various stresses could enhance the bioremediation and biodegradation abilities of microorganisms, and of mycorrhizal symbiotic associations of fungi with plants, which is enormously important for terrestrial environments in the course of phytoremediation [26,57,102,123].

Fungal biomass, as any other microbial biomass, can be a very efficient accumulator of toxic metals immobilizing soluble metal species and particulate metal forms, and was biotechnologically considered as a prospective biosorbent material for metal-contaminated aqueous solutions, because of the ease with which they are grown and the availability of fungal biomass as an industrial waste product, e.g., microfungi *Aspergillus niger* (citric acid production) and yeasts *Saccharomyces cerevisiae* (brewing) [156]. One of the aspects that attracted the attention of researchers was the possibility to improve biosorptive properties of microbial (fungal) biomass if combined with clay minerals. As clay minerals and biomass have some differences in sorption mechanisms and are more efficient in different ranges of metal concentrations, fungal/clay complex sorbents could combine the sorptive advantages of the individual counterparts. Fungal biomass has a high density of metal binding sites per area unit and sorption affinity, whereas clay minerals are characterized by high specific area, mechanical strength and the efficient sorption at high metal concentrations. For example, as mentioned earlier in this review, the biomass of melanin-forming fungi grown in a bentonite-containing medium generally showed increased metal sorption capacity compared to individual biomass and highly efficient metal sorption at higher concentrations of toxic metals [157].

According to Tazaki (2013), the immobilization of toxic metals by clay minerals, surrounding exopolymeric capsules of microbial cells, might be one of the detoxification mechanisms for the indigenous microorganisms inhabiting environments heavily contaminated by metals (e.g., mining ponds), helping microbes to tolerate inorganic pollutants and stimulating microbial growth and biofilm formation [130]. For example, as was observed in a transmission electron study of environmental samples from a gold mine in Tanzania, the particles of clay minerals (smectite, halloysite and kaolinite) can be attached around the thick EPS bacterial capsules forming a protective barrier able to adsorb Au, Hg, Ag and Fe [130].

Electron microscopy study of samples of paddy soils in the Fukushima area, severely contaminated by radionuclides ^{131}I , ^{134}Cs and ^{137}Cs after the emission from the Fukushima Daiichi Nuclear Power Plant (NPP), showed abundant indigenous filamentous bacteria and bacilli which were covered by clay particles [130]. The particles of clay minerals (predominantly smectite) were encrusting extracellular polymers around the cells suggesting that they may have contributed to the microbial tolerance to radionuclides. Bioremediation using local natural microbial communities and minerals such as clay minerals was regarded by the authors as safe, inexpensive, simple, and sustainable, and worth to explore for application in Fukushima [130].

There is increasing public concern about the wide variety of toxic organic chemicals such as petroleum hydrocarbons and phenols that are being introduced into the environment [307,308]. The application of the biotechnological processes that involves microorganisms with the objective of solving organic pollution problems is rapidly growing [307]. The use of natural and cost-effective

materials as supportive matrices appears to make bioremediation by microbial degradation more efficient [309]. The survival, retention and performance of bioremediation microbial agents, degrading organic pollutants in the various contaminated sites (e.g., reactors, soils and waters), can be significantly improved by the immobilization of microbial cells in a carrier. The immobilization process, defined by Willaert (2011) as “the physical confinement or localization of intact cells to a certain region of space; without loss of desired biological activity”, has been a very important aspect in biotechnology since the 1970s–1980s and found numerous practical applications in the areas of environmental bioremediation and pollution control [307,310]. The reported advantages of the immobilized cell systems included providing: favourable microenvironmental conditions, high biomass yield, cells reuse (recovery and recycle), high flow rates with high volumetric productivities and minimized cell washout, improved genetic stability, and high resistance to toxic chemicals, extreme pH or temperature, solvents and heavy metals [307].

Clay minerals are a traditional inorganic carrier. For example, microfungi *Candida parapsilosis* and *Penicillium frequetans* immobilized on granular clay in column vessels effectively degraded n-alkanes [311]. Aromatic hydrocarbon removal was reported by immobilized bacteria of genera *Pseudomonas* and *Staphylococcus* in a fluidized bed bioreactor [312]. The biodegradation rate of benzo[a]pyrene was remarkably higher when the mixed consortium of microfungi *Mucor* sp. SF06 and bacteria *Bacillus* sp. SB02 was co-immobilised on vermiculite compared to the vermiculite-free variant with freely suspended cells [313].

Cell immobilization on clay was often used to achieve a higher efficiency of phenol degradation and to reduce inhibitory effects of this toxic compound and the products of its chemical decomposition [308,314,315]. In our experimental study, a prospective phenol-biodegrading bacterial strain *Rhodococcus aetherivorans* UCM Ac-602 immobilized on vermiculite was able to grow and completely degrade 2000 mg L⁻¹ phenol over 96 h, whereas freely suspended cells were not able to grow at phenol concentrations above 1750 mg L⁻¹ [308]. It was also demonstrated that the decrease of phenol concentration in the culture broth occurred due to the bacterial biodegradation and not because of sorption by vermiculite. These results were in agreement with other data reporting negligible interactions of natural non-modified clays (vermiculite and bentonite) with phenol (the amount of sorbed phenol was 0.05 mmol·g⁻¹ of vermiculite) as well as the absence of phenol adsorption on kaolinite [315,316]. As the process of phenol biodegradation produces acidic intermediate products and decreased pH, one of the possible reasons for the enhanced phenol-degrading ability of vermiculite-immobilized *R. aetherivorans* UCM Ac-602 could be the pH buffering effect of vermiculite [308]. pH stabilization in a phenol-degradation medium in the presence of kaolinite was also observed by Gong et al. (2016) [315]. The buffering effects of clay minerals are attributable to the adsorption of protons derived from the acidic intermediate products of phenol oxidation. The effectiveness of the process of cell sorptive immobilization on vermiculite in our study on *R. aetherivorans* UCM Ac-602 was assessed using the CFU parameter that reflects the number of viable bacterial cells [308]. Initially, prior to immobilization, the culture broth contained 6.1 × 10⁹ CFU·mL⁻¹ whereas the amount of freely suspended cells in the supernatant after immobilization was 2.2 × 10⁹ CFU·mL⁻¹, indicating that 63.9% of bacterial cells were associated with the vermiculite [308]. The number of cells attached to the clay after the triplicate sediment washing and ultrasonic treatment was 1.8 × 10⁸ CFU·per gram of vermiculite. Scanning electron microscopy of the bacterial-clay sediments resulting from the sorptive immobilization process demonstrated that *R. aetherivorans* UCM Ac-602 cells were not only adsorbed on the surfaces of large vermiculite particles but also seemed to be enveloped by small vermiculite particles (Figure 6). This result is similar to that previously reported by Gong et al. (2016) of sorptive immobilization of the phenol-degrading bacterium *Sphingomonas* sp. GY2B on kaolinite [315].

Bioremediation and biodegradation cell-immobilization biotechnologies also include a technique of cell encapsulation within alginate-containing beads. Clay minerals were also tested as a part of such complex alginate-based organo-mineral matrices for bacterial biodegradation. It was reported that immobilization of the phenol-degrading bacterium *Sphingomonas* sp. GY2B in polyvinyl alcohol-sodium

alginate-kaolin beads significantly improved the biodegradation performance while protecting microorganisms from the substrate toxicity [317]. Therefore, the application of such combined PVA-alginate-kaolin beads in microbial bioremediation may contribute to a practical and economical treatment of phenolic wastewater.

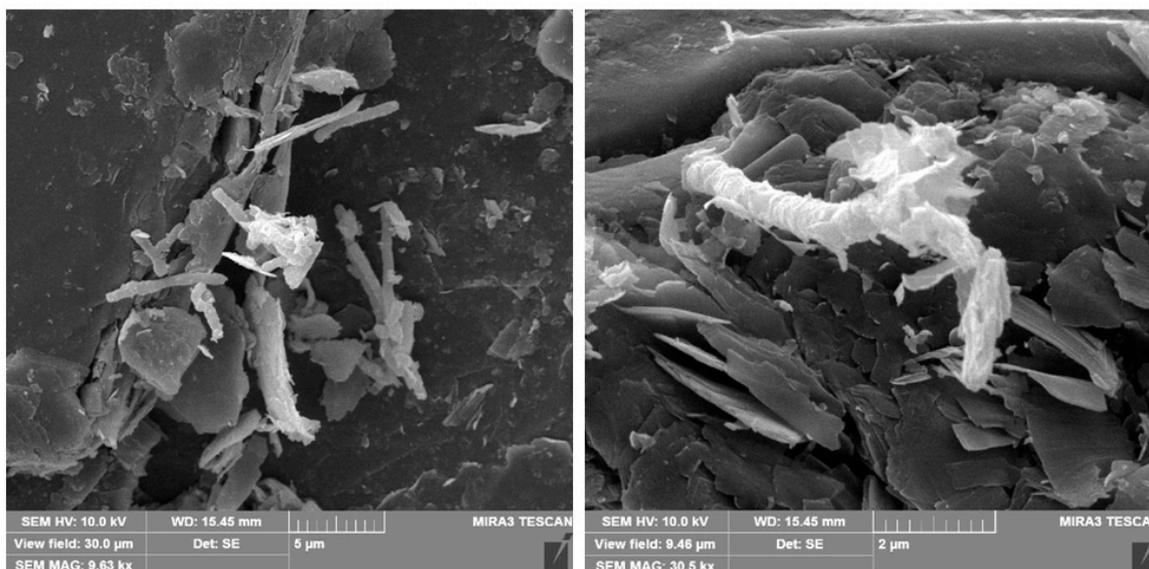


Figure 6. SEM images of critical point dried samples illustrating the sorptive immobilization of the phenol-degrading bacterium *Rhodococcus aetherivorans* UCM Ac-602 on vermiculite: the rod-shaped bacterial cells were not only attached to the surfaces of large vermiculite particles but also appeared to be enveloped by the small mineral particles. These are representative images from the study by Nogina et al. (2020) [308].

During the few last decades, the microbial ability of hydrocarbons biodegradation has attracted great attention and made bioremediation of oils spills one of the major remediation methods all over the world [130,309,318–321]. For example, long-term studies, both in situ and in the laboratory, were carried out by Japanese researchers on the microbial bioremediation of heavy oil spill into the Sea of Japan after the accident of the tanker “Nakhodka” in 1997 [130,319,320]. After 5 years of spill bioremediation by indigenous microbial communities, the resulting microbiota in contaminated marine and coastal environments was dominated by bacteria of the genus *Pseudomonas* and hydrocarbons(alkanes)-utilizing microbes comprised around 1% of total microbial isolates [319]. However, out of all isolates only one bacterial strain (*Pseudomonas aeruginosa* A5), isolated from the contaminated Atake seashore, was able to utilize both aliphatic and aromatic compounds [319]. As the most capable of hydrocarbon biodegradation, this strain was used along with other indigenous microbes in the subsequent experimental studies of the clay minerals’ impact on the oil spill bioremediation process [130,320]. At an extremely high concentration of heavy oil, both montmorillonite and kaolinite were able to promote microbial growth and biofilms formation, where microbial cells were embedded in the EPS matrix and firmly attached to the clay particles, which resulted in significantly accelerated rates of bioremediation. The authors suggested that clay minerals were protecting microbes from the toxic effects of high hydrocarbons concentrations, and acted as natural buffers maintaining favourable pH values and supporting materials for microbial growth and biodegradation [320]. As was also proposed by Tazaki and Chaerun (2008), the formation of C-O-Na-Si complexes on the surfaces of bacterial cell walls may stimulate growth of oil-degrading bacteria in seawater contaminated with the “Nakhodka” oil spill [322].

Warr et al. (2016) tested ex situ the effect of the addition of industrial clays (Ca-bentonite, Fuller’s Earth and kaolin), both unfertilized and fertilized (e.g., with sources of N and P), on the process of

microbial biodegradation of oil samples from water contaminated in the Deepwater Horizon accident in 2010 at the Gulf of Mexico [321]. Both treatments, with unfertilized and fertilized clays, showed selective reduction of polycyclic aromatic hydrocarbons (PAHs) predominantly of molecular weight 200–300, but without considerable change in their toxicity. However the addition of fertilized clays demonstrated a 6–10 times increase of alkanes biodegradation by indigenous bacteria as well as 8 times higher rate of O₂ consumption indicating enhanced bacterial metabolic activity compared to other treatments [321]. Therefore, in oil-polluted environments, the fertilizing of clays may significantly boost the growth and the ability to degrade hydrocarbons of indigenous microbial communities.

There are various ways clay mineral modifications are aimed at improving their properties to eliminate particular pollutants [309,323]. The area of clay mineral modifications has attracted increasing attention of researchers especially in the view of organic pollution, including oil spills, considering that clay flakes can be engineered to float on seawater, attach to the oil, as well as slowly release contained nutrients for local microbiota [321]. The modifications of physico-chemical properties of clay minerals include techniques like acid activation, thermal modification, cationic substitution (homoionisation), pillaring, integration with other compounds (e.g., clay-polymer composites), organic modification (generation of organo-clay complexes), etc. [309,323]. As the surface of natural clay minerals is negatively charged and hydrophilic, to be able to remediate organic hydrophobic contaminants (e.g., PAHs) clay minerals should be modified with a surfactant providing hydrophobicity. Another strategy for hydrophobic organic pollutants attraction is clay intercalation with organic cationic substances with long chains of hydrophobic character [309]. For example, while natural vermiculite was not absorbing phenol [308], its hydrophobic modification through the insertion of hexadecyltrimethylammonium in the interlayer resulted in a high phenol sorption capacity (0.45 mmol·g⁻¹) [316]. However in order to achieve a complete removal of organic contaminants, the modified clay-based materials have to be integrated with hydrocarbon-degrading microorganisms [309]. Research on this topic is still mainly limited by laboratory studies. Biswas et al. (2016) observed that, in a simulated soil slurry system, phenanthrene biomineralization by bacterium *Burkholderia sartisoli* was enhanced by thermally activated (400 °C) palygorskite, which led to aggregation of the clay mineral particles, facilitating bacterial survival and activity [324]. However, the studies of Ugochukwu et al. (2014a and b) demonstrated that modified by different techniques clay minerals may have ambivalent effects on the process of microbial degradation of crude oil hydrocarbons depending on the nature of these modifications [325,326]. An organo-montmorillonite complex manifested an inhibitory effect on the biodegradation of crude oil hydrocarbons by a microbial community [325]. However the untreated Na-montmorillonite promoted hydrocarbons biodegradation in these experiments due to its high surface area and cation exchange capacity (CEC), providing better access of microorganisms to the hydrocarbons accumulated on the clay surfaces. The authors suggested that inhibition of biodegradation by the organo-montmorillonite is a result of the hydrophobic interaction between the hydrocarbons and the organo-clay which reduces the availability of hydrocarbons for microbes. In the similar experimental setting, the study of the effect of “homoionic” montmorillonites (containing Na, K, Mg, Ca, Zn, Al, Cr, or Fe) on hydrocarbons biodegradation by microbial community revealed that the biodegradation process is affected by the metal cations in the interlayer space [326]. K- and Zn-montmorillonites appeared to inhibit the biodegradation of crude oil, whereas Na-, Ca- and Fe-montmorillonites stimulated biodegradation. The authors pointed out that, despite the stimulatory role of the high surface area and the “local bridging effect” (effective delivery of nutrients to the cells thanks to zeta potential reduction or repulsion of electrical double layer), the clay modification with trivalent cations results in the hydrolysis of the interlayer water, generating protons and increasing acidity, leading to the inhibition of hydrocarbon biodegradation [326]. Considering the contradictory effects of the modified clays on microbial biodegradation and the lack of field testing and ecotoxicity data, it seems important to assess the possible consequences of the introduction of such clay-based materials to the environment polluted with hydrocarbons, including the impact on the local microbiota. Biswas et al. (2019) compared the impact of bentonite, cationic surfactant-modified bentonite and

palmitic acid-grafted surfactant-modified bentonite added to PAHs/cadmium-contaminated soil on the diversity and respiration activity of soil bacteria and archaea [327]. It was revealed that, after 70 days of treatment, the number of metabolically active microbial cells decreased in the soil amended with modified organoclays compared to the soil amended with natural non-modified bentonite. The addition of bentonite and its modified forms also altered the structure of the microbial community among the dominant groups Actinobacteria, Proteobacteria, Firmicutes and Chloroflexi. For the variant with the highest clay addition to soil (5%), palmitic acid-grafted surfactant-modified bentonite manifested less reduction of the microbial diversity than cationic surfactant-modified bentonite [327]. Such studies are of great importance in the exploration of modified clay-based materials for environmental remediation to ensure their biocompatibility and safety for microbial diversity and metabolic activity.

Regarding redox immobilization of toxic metals [26,102], a recent approach considered redox manipulation of clays through microbial action [123]. It is assumed that oxidized forms of toxic and radioactive metals such as technetium [328,329], uranium [330], and chromium [331] can be reduced to less soluble species and immobilized in the course of ferrous Fe oxidation within previously reduced clay minerals such as smectites [123]. The structural Fe(II) was initially generated through the biogeochemical activity of Fe(III)-reducing bacteria. For Tc(VII) reduction to Tc(IV), it was reported that structural Fe(II) is most reactive in smectite and least in illite [328], and that for nontronite reduced Tc(IV) is firmly immobilized within the mineral matrix, minimizing the potential for remobilization and suggesting long-term bioremediation [329].

Also, such reduced smectites have been found to be effective in degrading organic compounds, including pesticides, 2,4,6-trinitrotoluene, nitroaromatics, carbon tetrachloride, chlorinated and nitroaliphatic compounds [123,332,333].

Thus, the clay properties resulting from microbial redox activities could be explored for waste disposal. Iron-bearing clay minerals can buffer the redox conditions and minimize any chance of re-oxidizing reduced toxic metals and radionuclides [123]. There have been approaches to the in situ reduction of Fe(III) within soil or sediments by stimulating indigenous Fe-reducing bacteria through the addition of a carbon source and an electron donor, such as ethanol or glucose [332]. Fe(III) produced from the reduction of the toxic metals or the degradation of organic compounds can be microbially reduced back to Fe(II), generating a renewable source of electrons. Clay minerals are ideal matrices for toxic metal and radionuclide immobilization for long-term disposal due to their low permeability and rapid particle aggregation [329].

There are more possible practical applications for clay minerals in relation to microorganisms and their enzymes in various areas, which may also include environmental protection. For example, clay minerals can be used as immobilization support for enzymes with protective antimicrobial properties because layered clay minerals can prevent the enzymes from microbial contaminations [334]. Enzymes immobilized onto clay minerals could be applied as biosensors for detection of certain pollutants as well as for chemical and clinical purposes [334]. Also some clay minerals precipitated by microbes may have catalytic and other properties in nanoparticle, crystalline or colloidal forms, and these are relevant to the development of novel biomaterials for structural, technological, environmental and antimicrobial purposes [26].

5.3. Microbial–Clay Interactions in Agronomic Biotechnology

The positive influence of clay minerals on PGPR has been one of the remarkable examples of biotechnological use of clay-microbial interactions in agriculture. Such microbial preparations are helping to reduce the use of chemical fertilizers and pesticides in crop production, limit environmental pollution and generate agricultural products commercially labelled as “organic” [231].

Clay minerals have a multilateral positive effect on the functioning of microorganisms, their viability, and their attachment to plant seeds, which is enhancing positive interactions of PGPR with plants. Seed germination and seedling development greatly benefit from production of biologically active substances such as vitamins, phytohormones, enzymes, and protective antioxidant molecules

as well as from the inhibition of pathogenic microbiota by PGPR [335]. Given the natural origin of clay minerals, their environmental friendliness, and excellent physico-chemical properties [6], these minerals have been a promising basis for creating microbial preparations for crop production.

Field studies of the influence of granular bacterial preparation which was based on bentonite and PGPR (bacilli and azotobacter) on the growth and yield of the different varieties of spring barley have shown that pre-sowing inoculation of seeds with this clay-microbial preparation increased the height of plant stems by 19.8–22.6% and barley yield by 11.4–18.9% [336]. The stimulating effect of the bacterial preparation on plant yield was variety-dependent, for example, for barley varieties Nezabudka, Oberig and Scif the yield increased by 11.4%, 13.7% and 18.9%, respectively. It was also established that, in the rhizosphere of the plants treated with a bacterial preparation, there were certain changes in the number of ecological-trophic groups of microorganisms and of the enzymatic activity, indicating the positive influence of the preparation on soil microbiota [337]. Along with bacteria introduced with the preparation, the microbes of the studied ecological-trophic groups can also contribute to the soil fertility in the rhizosphere [336,337].

Montmorillonite and palygorskite were successfully used to obtain compact and mechanically strong granular preparations of the nitrogen fixing bacterium *Bradyrhizobium japonicum* with a viable cell yield of 80% and 60%, respectively, following 6 months storage, if compared to the initial concentration of viable cells [338]. The observed difference is apparently due to the structural features of these minerals: palygorskite has needle-like particles whereas montmorillonite consists of flake-like particles. When in contact with bacterial cells, the needle-shaped palygorskite particles can cause the puncture of the cells during the process of mixing and extruding the granulated mass, leading to the death of some bacterial cells in the preparation [232]. The study of clay minerals' effect on the quality of granular preparations of nitrogen-fixing bacteria *Azotobacter chroococcum* 20 showed that the viable cell yield in the preparations with montmorillonite was almost 100% of the initial number of viable cells in suspension, twice higher than with palygorskite [339]. Therefore, the use of montmorillonite as the mineral matrix for the production of granular bacterial preparations is preferred.

A montmorillonite-based granular bacterial preparation with a high number of viable cells was also obtained for bacterium *Pseudomonas aureofaciens*, which is capable of synthesizing antifungal compounds and inducing systemic resistance in plants [237]. This granular preparation demonstrated stability of the number of viable bacterial cells during prolonged storage and high antifungal activity against phytopathogenic fungi during 12 months.

Commercially successful in Ukraine for the last decade, the complex bacterial preparation "Azogran" with long-term stability was developed based on the interaction of the previously mentioned bacteria *Bacillus subtilis* IMV B-7023 and *Azotobacter vinelandii* IMV B-7076 with montmorillonite-containing bentonite [238,340]. "Azogran" significantly improves the nitrogen and phosphorus nutrition of plants (e.g., cereals, including winter wheat and spring barley). Strain *A. vinelandii* IMV B-7076 has nitrogen-fixing capacity converting atmospheric nitrogen into ammonium compounds available for plants' assimilation. Phosphate-mobilizing strain *B. subtilis* IMV B-7023 provides the transition of poorly soluble soil phosphorus compounds into the more soluble forms readily bioavailable for plants [240,341]. This bacterial preparation stimulates the growth and development of different plants considerably through synthesis of biologically active substances by both bacteria and their ability to inhibit phytopathogens (both fungal and bacterial) and phytophages (e.g., such insects as Colorado potato beetle *Leptinotarsa decemlineata* and whiteflies of the family Aleyrodidae) [342–346].

It was also demonstrated that the introduction of "Azogran" into agroecosystems significantly affected the growth and development of a wide range of plants, including lawn grass, many species of decorative plants (e.g., *Chlorophytum*, *Dracaena*, *Buxus* and *Thuja*), flowering plants (*Begonia*, roses, etc.), and seedlings and young plants of Scots pine (*Pinus silvestris* L.) and Norway spruce (*Picea abies*). This preparation also increased yields of technical crops and vegetables (sugar beet, tomatoes, cucumber and cultivated cabbage) by 16–37% [347–349].

Field tests of a multimicrobial preparation based on vermiculite, combining nitrogen-fixing symbiotic legume-root nodulating bacteria (4 strains of *Rhizobium* spp. and 5 strains of *Bradyrhizobium japonicum*) along with bacilli (2 strains of *Bacillus* spp.) and pseudomonads (3 strains of *Pseudomonas* spp.) manifested a high yield of viable bacterial cells and their stability, and considerably increased legume yields [350].

In conclusion, the research area related to the agricultural use of microbial–clay mineral interactions is a very promising exploration of environmentally friendly agronomic technologies that can ensure efficient and sustainable crop production.

6. Concluding Remarks

The growing interest in the microbial interactions with clay minerals is related to the enormous significance of this vast and ubiquitous phenomenon, which has greatly influenced the shaping of the evolution of the biosphere, and has important environmental and biotechnological implications (Figure 7).

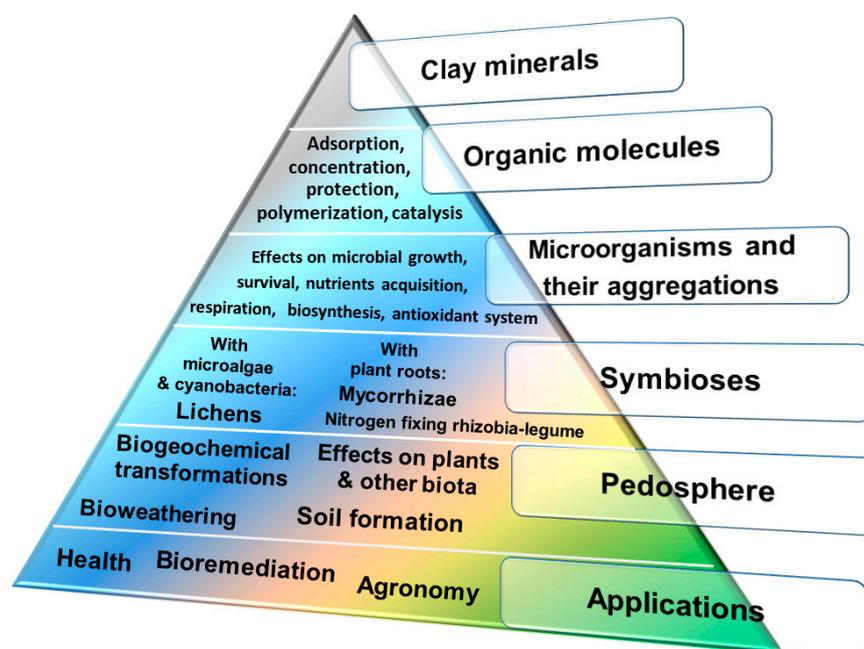


Figure 7. Some important aspects of the interactions of clay minerals with microorganisms at different levels of complexity: organic molecules, individual microbial cells and their aggregates (e.g., biofilms), fungal and bacterial symbioses with photosynthetic organisms, pedosphere; and their environmental and biotechnological implications.

Despite numerous geological and microbiological studies, and available information, this complex phenomenon is still imperfectly understood. In many cases, our knowledge of microbe–clay interactions is derived from laboratory experiments which are greatly simplified compared to what is happening in nature. The progress in this field requires a multidisciplinary and coordinated investigation with united efforts from geologists, biologists, physicists, chemists, biotechnologists and environmental engineers.

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