Bacterial and Fungal-Mineral Interactions and Their Application in Bioremediation – A Review

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ABSTRACT

Geomicrobiology is an interdisciplinary field of research that studies the role of microorganisms during the geological process from the inception of the earth and their perspective on the future of the earth. Scientists focused on microbe mineral interactions in various processes such as bioweathering, transformation, and the formation of biominerals to better understand the role of microbes in geological processes. Those processes are part of the geochemical cycles of elements, some of which are essential nutrients for life and others are toxic to life. Microorganisms, especially fungi and bacteria, as well as their exudates, are the major agents of geomicrobiology due to their important geological activities, which have a role in the bioweathering of rocks and minerals. Mobilization and immobilization of metals as well as the formation of new biominerals occur because of these activities and their fast growth. They are well known to be used in different strategies of bioremediation and they are genetically engineered to become more specific in removing and dissolving pollutants in the environment. The goal of the review was to outline the role of bacteria and fungi in bioremediation as well as in important geological processes, such as mineral alteration, bioweathering and biomineralization.

Keywords: biomineral; biomineralization; bioweathering; immobilization; mobilization.

INTRODUCTION

Geomicrobiology is an interdisciplinary study of the role of microbes on earth during a geological time period (from their first appearance on earth about four eons ago on the earth), and their present activities and future events will occur by their actions that are very important to geological processes (Ehrlich, 2006). To understand geomicrobiology, the study of microbial mineral interaction should be the first topic to read (the study of microbial mineral interaction is the heart of geomicrobiology). The microbe-mineral interaction occurs when microbes inhabit a mineral surface and interact with cations and anions in rocks or minerals, dissolving the structure of the rocks or minerals as well as transforming the cations and anions into new minerals (Dong, 2010).

There are differences in composition in the earth's lithosphere (minerals, rocks, and metals) in different areas that contain metal cations and anions as organic and inorganic forms that can be released by the weathering process biotically and abiotically (Gadd, 2010). Silicate minerals are the most common minerals, accounting for 90% of minerals including carbonate oxides, phosphates, and sulfides, as well as the vast majority of mineral metals. They are also dissolved by weathering processes in which they contain metals, some of which are essential to life, while others are toxic to living organisms and anthropogenic activities such as industrial factors and agricultural fields, resulting in contamination of the hydrosphere, lithospheric, and terrestrial environments (Gadd, 2010; Gadd, 2007).

Depending on the metal species, metal structure, metal concentration, and kinds of microbes, microbe-mineral interaction can occur in a variety of ways, at various levels, and in diverse positions through important geoactivities such as bioweathering, biomineralization, and biotransformation through enzymatical and non-enzymatical

reactions by serious redox reactions (Dong, 2010). The biosphere has been inhabited by microbes since its initiation. These are the important geo-microbial agents, which include members of the Prokaryota domains Bacteria (Eubacteria) and Archaea, as well as members of the Eukaryota domains Algae, Protozoa, and Fungi (Barns and Nierzwicki-Bauer, 2018).

Microbe-mineral interaction has a great role in the bioremediation process, which is the best and most efficient strategy to remove contaminants from the soil, water, and even the atmosphere, by using organisms, especially different fungal and bacterial species, due to their capability to survive in various environments contaminated with toxic metals, radioactive materials, and other industrial waste materials. The amount of this waste increases daily and is a large problem for human health because researchers who belong to this sector invent new techniques to clean up or up those pollutants from environment. Remediation processes, through physical and chemical techniques, can be expensive and economically unsuitable, and their performance may be made difficult, so scientists focus on using organisms to remediate contaminants from the environment with different mechanisms depending on the type of organism and contaminants (Jaiswal and Verma, 2018; Brandl, 2002). The goal of the study was to look at how bacteria and fungi are used in bioremediation and important geological processes.

MICROBE MINERAL INTERACTIONS

Microbe mineral interaction is the colonization of mineral surfaces by microbe's subsequent interaction with cations and anions in rocks or in minerals and their dissolution that lead to metal uptake by microbes or their precipitated as new minerals that are called biogenic minerals (biomineral) or secondary minerals (Figs. 2 and 3). Microorganisms can grow under different conditions because they have the capability to survive under extreme conditions and are able to interact with different organic and inorganic surfaces such as rocks, minerals, and organic matter polymers to obtain nutrients and energy. Microbes need the cations that are present in the structure of rocks or minerals in order to grow. They are utilized in different metabolic processes (Gadd, 2010).

Microbe mineral interaction could occur in different ways and at different levels and in different environments, depending on the metal species, metal structure, metal concentration, and type of microorganisms, which has also had a great impact on the solubility, toxicity, and availability of metals for microorganisms. Metal such as Na, K, Cu, Zn, Co, Ca, Mg, Mn, and Fe can be ready to be consumed as nutrients in the compartments of the cell. On the other hand, some metals may be toxic to microbes after the interaction between the microbe and minerals, such as Cs, Ai, cd, and Hg when they accumulate in high concentration in the absence of metabolizing activities for these metals. Thus, the interaction leads to the complete biogeochemical cycles of the elements due to the process of transformations (immobilization and mobilization) (Violante et al., 2008; Abdullah et al., 2022).

Microorganisms excrete extracellular polymeric substances and also have some types of appendages like hyphae in fungi, cilli in protozoa, a specific type of pill in archaea, and some bacteria have a capsule, slime layer, and s-layer that are used to anchor or to attach the microbes to the surface of minerals (solid surface), and when the microbes can obtain benefits from taking up nutrients, protection from environmental stress and prediction, they produce signal molecules to attract other microbes to colonize the surface and form a structure that is firmly attached to the surface, which is called biofilm. When the biofilms are grown on the surface and start to develop, an important geological process occurs over the rocks and minerals. This process is called weathering, which leads to minerals and rocks dissolving, some of them becoming precipitated, some others mobilized, and some others changing to secondary minerals (Dong, 2010; Harrison et al., 2005).

The term "biofilm" is mostly used for single cellular organisms or bacteria, while fungi can invade the rocks as mycocolonization in the presence of a carbon source, or as lichen with algae or cyanobacteria, or as mycorrhizae with the root of a plant that has a great role in the process of weathering. The weathering process, which is done by organisms and organic matter, is called bioweathering. It is done by a variety of strategies which are categorized into two different mechanisms (biomechanical and biochemical). Fungi are highly active microbes in the biomechanical process by their hyphae, indirectly and directly, and also different microbes involved in the biochemical process by their exudates as organic acids, oxidizing and reducing agents, and ligands

as siderophores. These strategies lead to biotic weathering more quickly than abiotic weathering of minerals and rocks (Kulczycki et al., 2007; Maurice et al., 2009).

BIOWEATHERING PROCESS OF ROCKS AND MINERAL BY FUNGI AND BACTERIA

Weathering is the process in which rocks and minerals are degraded or crumbled into small particles and form secondary minerals, which also immobilize some elements and lead to soil formation under biological, chemical, and physical factors that direct the weathering process. Thus, the weathering process could be a major source of most essential elements such as K, P, Ca, Ma, and many trace elements that can be taken up by microbes for growth and their metabolisms. Algae, fungi, bacteria, and plant roots are major biotic agents that have to play an important role in the process of bioweathering which leads to chemical and physical changes of the structure of rocks and minerals by their structure and exudates. The weathering process, which is done through organisms and organic matters (the abbreviation of "bio"), adds to weathering (bioweathering) that is done by a variety of strategies which are categorized into two different mechanisms (biomechanical and biochemicals) (Uroz et al., 2009; Hoffland et al., 2004; Burford et al., 2003; Ortega-Morales et al., 2016).

Biomechanical mechanism

Biomechanical weathering can occur directly by penetration appendages of organisms, such as hyphae and roots of plants (or both of them as a synergistic relationship between them that is called mycorrhizae) as well as indirectly by extracellular mucilaginous substances produced by some protists, fungi, and also bacteria (as capsules), whereas shrinking and swelling of these organic matters lead to erosion as well as abrasion of rocks and minerals (Kumar and Kumar, 1999; Sterflinger, 2000).

Fungi are the major group that has a great effect on the surface of rocks and minerals, directly and indirectly. Hyphae of fungi can find the pores and fissures through mechanical sensors (thigmotropism) and search for essential nutrients and chemicals by chemical sensors (chemotropism) in order to enable the hyphae to explore, exploit,

and avoid stress (nutrient deficiency and toxic metals) when hyphae penetrate the space, cracks, and pores from the surface of rocks, then expand through the wet and dry as well as freezing and thawing cycles, making a turgor pressure lead to bore the surface of rocks and enhance chemical weathering (Figures 2 and 3) (Watts et al., 1998; Fomina et al., 2000; Money, 2004; Goriely and Tabor, 2006; Gorbushina and Broughton, 2009).

Biochemical mechanism

Biochemical weathering is the chemical weathering of rocks and minerals by microbe able to chemically change the structure of rocks and minerals through pitting, etching, formation of biogenic minerals, and or complete dissolution of minerals which of all these consequences are results of various activities of microbes categorized into two major kinds (proton-based and ligand-based) (Figures 2 and 3) (Hoffland et al., 2004; Gorbushina, 2007; Boswell et al., 2007). The mechanisms used by bacteria and fungi to weather or deteriorate surfaces of rocks include:

Acidolysis and complexolysis

Microbes produce lower weight organic acids with the capability to adhere to the surface, breaking oxygen links, and bind with the metals in minerals and rocks to separate, precipitate, or uptake and accumulate metals inside cells. Fungi produce oxalic acid and citric acid that are strong acids and they are anions with a high capacity to bind to tri-divalent metal cations, such as Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, and Cu^{2+} and then make a complex with these metals as calcium oxalate and iron oxalate, etc. (Figure 1). This enhances the process of dissolution due to weakening of the mineral structure (Gadd and Raven, 2010; Martino et al., 2003).

Fungi in relationships with algae and cyanobacteria (lichen) have a better capacity to produce an acid called lichen acid (lobaric acid), and they are pioneer organisms of weathering because their photosynthesis partners act as a good source of carbon for the fungi and also protect the fungi from environmental stresses such as UV light, which enhance the fungi to produce more acids (Bin et al., 2008). In turn, bacteria produce gluconic acid to solubilize phosphate minerals and produce soluble phosphate that can be taken up by bacteria and form energy-rich compounds like
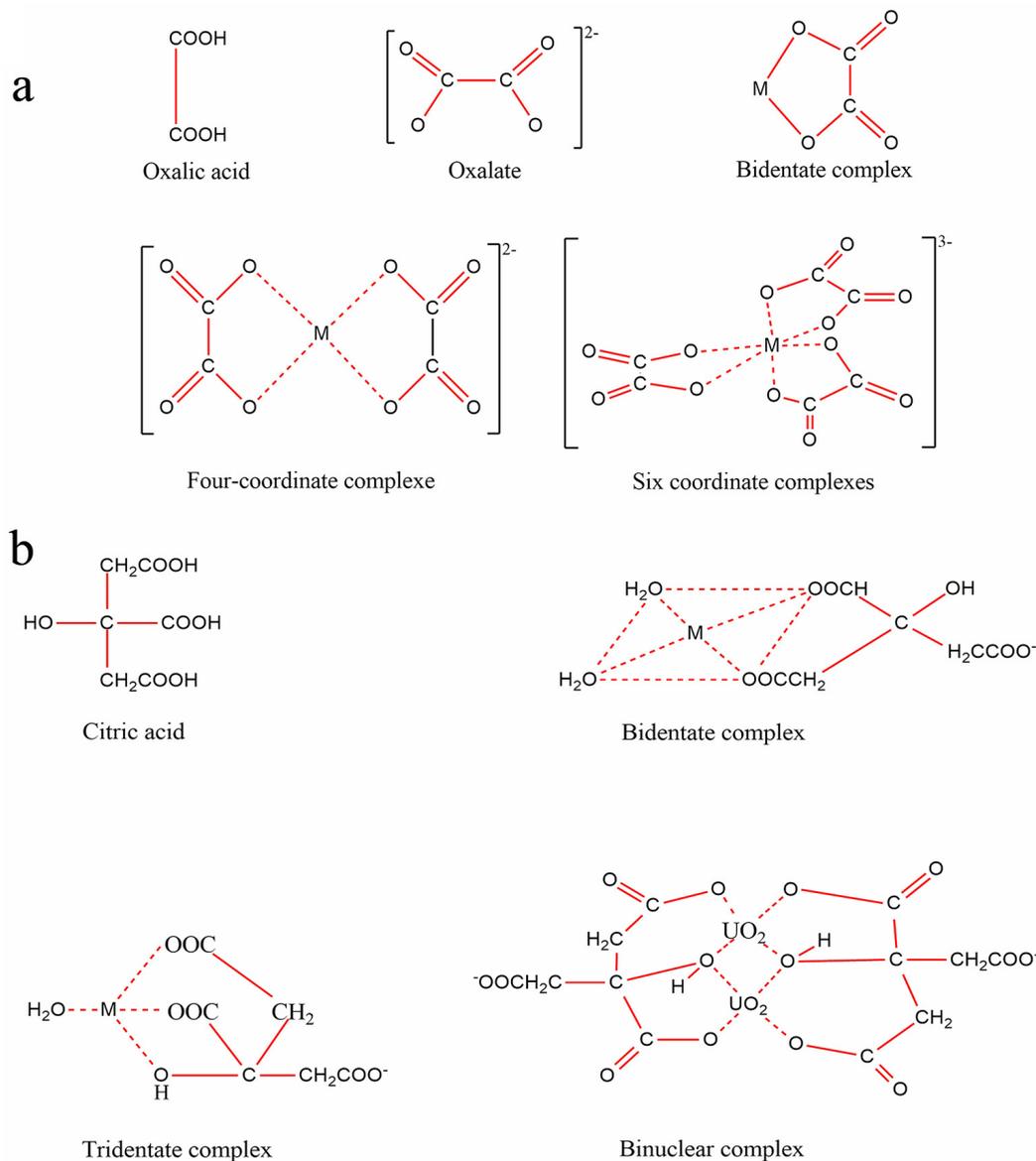
Figure 1. Formation of complexes by organic acids with metals: a, oxalate complexation.
b, citrate complexation (updated from (Gadd, 1999; Francis et al., 1992))

adenosine triphosphate (ATP) as an energy reservoir; these processes are results of the glucose dehydrogenase of phosphate-solubilizing bacteria like *Burkholderia cepacia* (Song et al., 2008).

Respiratory carbon dioxide

Microbes respire to produce energy, and one of the products of respiration is CO_2 that is excreted by microbes, leading to a decrease in pH through the formation of carbonic acid in order to promote mineral dissolution. In mycorrhizae, 50% of the respiration occurs at the mycelia, while some bacteria are aerobic and produce CO_2, and others, known as nitrifying bacteria, use nitrogen and produce nitrous acid and nitric acid,

which leads to further dissolution (Bhupinderpal-Singh et al., 2003; Daghino et al., 2010).

Oxidation and reduction reactions

Redox reactions are series of chemical reactions that occur on the surface of microbes and their products with minerals surface due to transfer electron between both surfaces through enzymatical and non-enzymatical reaction, for instance, all fungi can oxidize rhodochrosite which is a manganese carbonate mineral by fungal-derived superoxide produced at hyphae tips and also bacteria surface has a variety of ligands, such as hydroxyl, carboxyl, phosphoryl which react with cations of minerals lead to oxidize or reduce

them, for example *Acidithiobacillus ferroxidans* oxidize sulfide minerals like pyrite and make an acid environment named acid mine drainage that dissolve the pyrite to ferrous iron and sulfate that is an environmental problem (Włodarczyk et al., 2016; Tang et al., 2013; Hao et al., 2010).

Siderophore

A siderophore is an organic ligand molecule with a high affinity to metals like aluminum and iron due to their hydroxyl and carboxyl groups, which are produced by many fungal and bacterial species to extract metals from the environment, especially in low concentrations. Siderophores are produced by fungi such as the ectomycorrhizal fungus *Suillus granulatus*, which dissolves geothite mineral (ferric oxyhydroxide) and by bacteria such as *Azotobacteria sp.*, which weathers iron minerals, such as olivine $\{(Mg,Fe)_2SiO_4\}$ and glauconite $\{(K,Na)(Fe,Al,Mg)_2(Si,Al)_4O_{10}(OH)_2\}$ (Liermann et al., 2000, Haselwandter and Winkelmann, 2002).

MINERAL FORMATION

Biominerals or biogenic minerals, are the two terms refer to the minerals formed by living organisms and nonliving organic matter with various sizes, shapes, crystallinity, isotopic and different elements. About 50% of the total biominerals contain calcium as calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4$) due to widespread calcium in the environment and involvement in many metabolisms of cells (Berridge et al., 1998). Biominerals may be amorphous, meaning that those minerals do not have an ordered structure with a low melting point and have covalently bonded networks. In contrast, some biominerals are crystalline with an ordered structure, separated by a layer of organic matter, have a sharp melting point, and covalent bonds, ionic bonds, Van der Waals forces, and metallic bonds (Addadi et al., 2003). Approximately, 60% of biominerals are hydrate minerals such as monohydrocalcite ($CaCO_3.H_2O$), vivianite ($Fe^{2+}(PO_4)2.8H_2O$) and gypsum ($CaSO_4.2H_2O$) that contain water molecules or hydroxyl groups because of lowering energetic barriers for starting nucleation and growth precipitation is more favorable in aqueous solution (Weiss et al., 2002).

The process of the formation of biominerals is called biomineralization, which started with nucleation on or within the cell because the structure of the cell had ligands like hydroxyl, carboxyl, phosphoryl, and sulfuryl…etc. Most of the ligands are negatively charged and can react with cations in the minerals or rocks. Then, the unite grows inside or outside the cell and after it develops to mature minerals, the final location for precipitation may be inside the cell or on the surface of the cell or in the environment surrounding the microorganism (Weiner and Dove, 2003; Borrok et al., 2005; Konhauser, 2007).

The process of biomineralization is divided into two types: biologically induced mineralization (BIM), and biologically controlled mineralization (BCM); organisms such as as protista, fungi, archaea, and eukaryotic multicellular with shell and skeleton are involved in one of these mechanisms. For instance, the latter one is most common in algae, protista, and eukaryotic multicellular organisms with shell or skeleton (Addadi and Weiner, 2014), and also in the case of magnetotactic bacteria. It is only the microbial case in the BCM process, while BIM is the most common in microbes, especially in fungi and bacteria. The next section shows some important examples of biominerals formed by fungal and bacterial species (Weiner and Dove, 2003; Mann, 2001; Bazylinski and Frankel, 2003; Braissant et al., 2004; Dong, 2010).

Biological induced mineralization (BIM)

BIM is the most common methods of mineral formation by microbes as the result of the biological activities of a microbe to induce physiochemical changes in the environment that result in nucleation, growth, and influence of mineral morphology (De Muynck et al., 2010). In this mechanism, the surface of the cell is a causative agent of nucleation, and the cell has less control on the size, shape, and final location of mineral deposition. Although the organism mediated the environment (pH and PCO_2) and composition of the secretion product, biominerals may remain firmly attached to the cell surface while in the open water column, gravitational overcome of buoyancy may result in encrustation (Benning and Waychunas, 2008; Cubillas and Anderson, 2010).

Dolomite $\{CaMg(CO_3)_2\}$ is a biomineral that is formed by microbes and is the most common sedimentary material. The formation of

dolomite in a laboratory by chemical means is not successful due to the kinetic energy barriers in its formation. Sulfur-reducing bacteria can induce the formation of dolomite by overcoming the kinetic energy barriers and mediated pH and carbonate alkalinity, and also removing sulfate, which is an inhibitor for nucleation of the dolomite biomineral in solution (Wei and Sun, 2021; Pasquale et al., 2019).

Mycogenic minerals are referred to the minerals that are formed by fungi that can mediate the environment to lead to the nucleation and growth of minerals, for instance, the formation of calcium oxalate as dihydrate wedelite ($CaC_2O_4.2H_2O$) as a more stable form of monohydrate whewellite ($CaC_2O_4.H_2O$) through decreasing the pH of the environment by releasing acids (oxalic acid that has a high capacity to bind with metals)(Pinzari et al., 2013).

Biological controlled mineralization (BCM)

BCM is another type of biomineralization and is performed by various organisms, from microscopic as bacteria to macroscopic as mollusks and insects, which depends on the types of organisms and final location of minerals (De Muynck et al., 2010). BCM is subdivided into extracellular, intracellular, and intercellular.

In this mechanism, the genetic material of organisms highly controls the shape, size, morphology, and the final location of mineral precipitation that may be within space between the cells (intercellular) or may be precipitated away from the cell by a macromolecular matrix that has a key role in the formation of minerals (extracellular: as formation of amorphous calcium carbonate by urchin larvae into spicule forming vesicles)(Cubillas and Anderson, 2010) or may be within the cell as in vacuoles may remain or release to the outside after formation of the unit and/or growth mineral (intracellular) (Yoshida et al., 2010). The typical example of biologically extracellular controlled mineralization is the formation of magnetite (Fe_3O_4) and gregite ($Fe^{2+}Fe^{3+}_2S_4$) with a structure called magnetosome by magnetotactic bacteria when extracting iron from the environment. A series of redox reactions occurs to form nucleation, which may remain inside the magnetosome, or may be released to the outside as higher order growth or as an individual unit, and the formation of magnetite in a magnetosome is highly controlled by the cell, because it is important to direct the bacteria to the magnetic field of the earth to find favorable micro environment (Monteil et al., 2021).

FUNGAL AND BACTERIAL ROLE IN METAL TRANSFORMATION IN ROCKS AND MINERAL SURFACES

Rocks and minerals are important reservoirs of essential nutrients for organisms. While they are unavailable for most organisms, the activity of microorganisms in weathering of these metal-bearing rocks and minerals plays a key role in the dissolution of those metals into soil and water bodies that could be biologically available. However, the mechanisms that change the speciation and mobility of metals are the most important parts of the biogeochemical cycles of metals and other elements, such as carbon, nitrogen, phosphorous, and sulfur (Mao et al., 2013). When microbes interact with metals in minerals and rocks, the metals, while immobilized or mobilized, result in these metals becoming a good source of nutrients for organisms or becoming toxic metals for microbes, mostly in high concentrations (Ezeonyejiaku et al., 2011).

Metal mobilization

Metals from rocks and minerals can be mobilized through a variety of mechanisms, such as protonolysis, complexation, via excreted metabolites as organic acids and chelating molecules, chemical redox reaction, methylation, and volatilization. Fungi and bacteria use the above-mentioned mechanism to mobilize metals from rocks and minerals and lead to the further dissolution of minerals and metals solubilized in solution (Hsu-Kim et al., 2013). Fungi produce organic acid as oxalic acid (Figure 1a) that excretes metals like aluminum and iron from aluminum and iron-bearing minerals like bauxite (Ghorbani et al., 2007). In turn, bacteria produce gluconic acid to solubilize phosphate minerals and produce soluble phosphate that can be taken up by bacteria and form energy-rich compounds like ATP as an energy reservoir, these processes are the result of phosphate-solubilizing bacteria, like *Burkholderia cepacia* producing glucose dehydrogenase. Bacteria and fungi can also methylate metals and metalloids by adding one methyl group (CH_3) to their structures which leads to their volatilization,

for instance methylation of arsenic compounds as arsenate (AsO_4^{3-}), arsenite ($AsO_2^{-})_n$, and methyl-malonic acid ($C_4H_6O_4$) to volatile di and trimethy-larsine (C_2H_7As) or (C_3H_9As) (Song et al., 2008; Bentley and Chasteen, 2002).

Metal immobilization

Metal immobilization is the process of removing metals from solution and accumulating the by organisms through different mechanisms as adsorption and binding to organic matters. Bacteria cell wall contains different ligand groups as in peptidoglycan have carboxyl (Gram-positive bacteria) and phosphate group (Gram-negative bacteria) are a major site to bind to cation and fungi also have ligand group in their chitin layers of the cell wall as amine group of nitrogen, while the fungal phenolic polymers and melanin contain other ligand groups as carboxyl, phenolic, and alcoholic hydroxyl, etc. which act as a site for adsorption of metals on the surface of fungi and their precipitation on the surface or in the surrounding environment or accumulation inside the cells (Abbas et al., 2014; Olaniran et al., 2013; Gadd, 2007). For instance, the proteins, amino acids, and polysaccharides produced by algae, bacteria, fungi, and plants also act as metal binding agents to immobilized metals. For example, *E.coli* has methionine in the structure of the
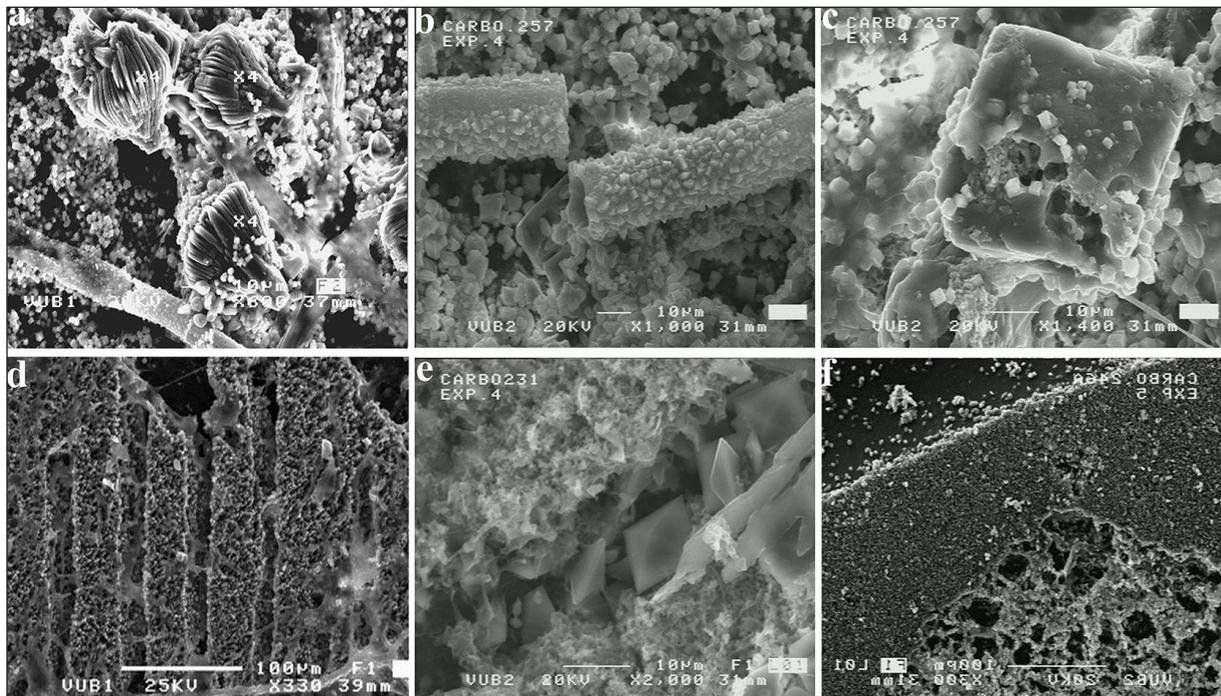
Figure 2. Scanning electron microscope (SEM) images showing fungal interaction with carbonate substrates, formation of biominerals through metal complexation with Ca and Mg of substrates and the alteration of substrates through bioweathering. a. Formation of Glushinskite biominerals by Mg complexation and adhering to hyphae as single large crystals (40 µm). Much finer Ca-oxalates are observable in the background. b. Fungal hyphae entirely encrusted with biominerals (Mainly Ca-oxalates) while the substrate background is shows a newly formed biomineralized substrate. c. A dolomite crystal showing fugally produced intragranular porosity being refilled with biominerals. The fill is composed of micron-size crystals "laid" in the "nest". The size of the biomineral crystals outside the nest is larger, suggesting a different process or controls of formation. d. Differential dissolution induced by fungi along lines of substrate weakness. The cleavage planes on calcite crystals show straight and deep dissolution compared to the rest of the thin section. The pitting dissolution marks the entire thin section and produced columnar structures. It indicates removal of finer material. The fungal hyphae network crisscrossing the surface should be noticed. e. Differential dissolution induced by fungi along lines of substrate weakness and neoformation of biominerals which it shown that the cleavage was filled with Ca-oxalates. f. Formation of alveolar-honeycomb structures by fungal interaction with dolomitic substrates. The chambers are deep and empty while the separating walls are topped by biominerals (white crystals). Here, the biomineral deposition on the grain boundaries is sharper and a clear layer of Ca-oxalate substrate has formed. The chambers form moldic porosity after the dissolved dolomite grains (Kolo and Claeys, 2005; Kolo et al., 2007)
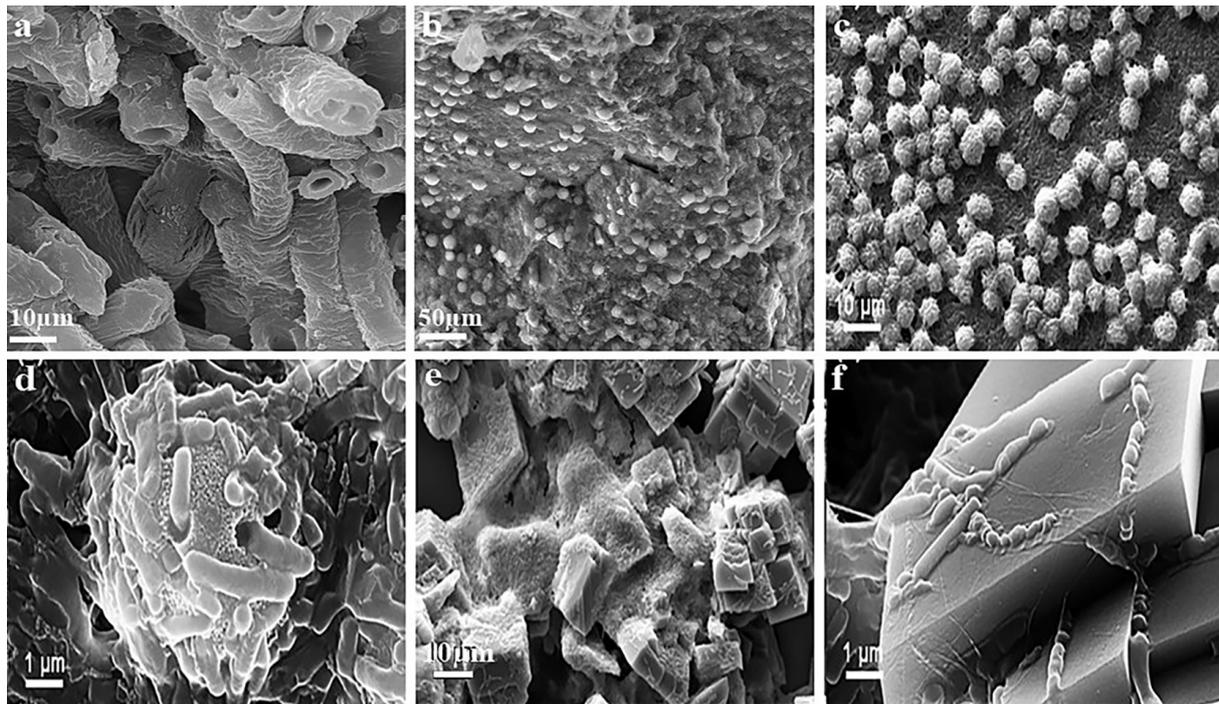
Figure 3. Scanning electron microscope (SEM) images showing bacterial interaction with carbonate substrates, formation of biominerals; a and b. show fossilized bacteria that were highly encrusted with iron elements; c and d. show living bacteria bound to crystalline microspheres (d zoom section of c); e. typical calcite precipitation with dead bacterial cells; f. zoom section of image (e) showing orthorhombic crystal structure of precipitates (Ghosh et al., 2019)

protein from the outer membrane, which leads to the formation of metallothioneins (Chen and Lin, 2007) and the melanin-containing chlamydospores of *Aureobosidium pullauans* can absorb copper metals and have a great role in the accumulation of metals (Gadd and de Rome, 1988; Abbas et al., 2014).

MICROBIAL GEOACTIVITIES IN BIOREMEDIATION PROCESSES

The bioremediation process is the most effective and best strategy to remove contaminants from the soil, water, and even the atmosphere by using organisms, especially different fungal and bacterial species, due to their capability to survive in various environments contaminated with toxic metals, radioactive materials, and other industrial waste materials. The amount of these wastes increases daily and is a great problem for human health because researchers who belong to this sector invent new techniques to clean up or up those pollutants from environments. The remediation processes through physical and chemical techniques can be expensive and economically unsuitable, and their performance may be made difficult, so scientists focus on using organisms to remediate contaminants from an environment with different mechanisms depending on the type of organism and contaminants (Lloyd, 2002; Gadd, 2002; Rahman and Singh, 2020).

Fungi and bacteria have a great role in the processes of bioremediation due to their surveillance and diversity of mechanisms in interaction with different surfaces under different conditions; the sections above explain the great importance of these mechanisms, and new terms in the bioremediation field are used to describe these mechanisms as bio extraction, biosorption, bioleaching, and bioaccumulation (Figure 2 and Figure 3) (Kushwaha et al., 2018; Tabak et al., 2005). Both of them, fungi and bacteria, play a key role in the formation of nanoparticles due to their interaction with minerals and their metals to form oxide species of metals to increase the surface area of the element to be more active in interaction with a pollutant. These nanoparticles are produced by bacterial and fungal interaction with metals used in the remediation of different contaminants and also in the process of bio-recovery to recover some important economic element like gold (Lloyd, 2003; Ruta et al., 2010).
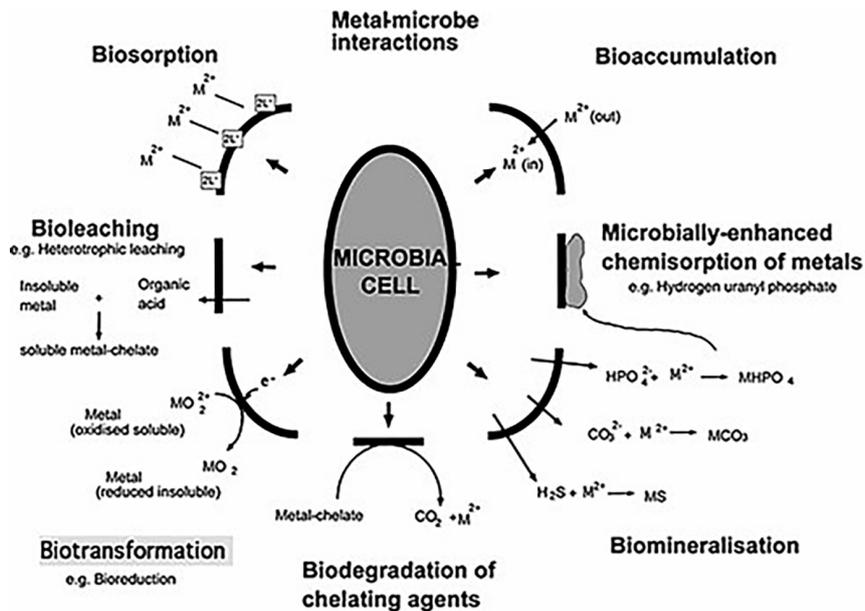
Figure 4. Metal–microbe interactions impacting bioremediation (Tabak et al., 2005)

Role of bacteria in bioremediation strategies

Bacteria are single-cellular microorganisms that grow fast under different conditions and can survive under extreme conditions such as high salinity, high temperature with different PH, and the environment with toxic metals because of bacteria have a great role in bioremediation processes.

The cell walls of bacteria and their exudation (organic acid) solubilize and precipitate different metals in various insoluble complexes. For example, fly ash, copper-containing ores, and cyanide compounds pollute the environment. For example, HCN-forming bacteria as pseudomonas fluorescence can mobilize Ni, Au, and Cu from these compounds and lead to being soluble in the solution, while other species of bacteria precipitate different metals, as cyanobacteria produce polysaccharide to precipitate and remove sulfide and oxides from water. Another example is sulfate-reducing bacteria can precipitate toxic metals, such as chromium (VI) and uranium (VI) through a reduction process mediated by multiheme cytochrome proteins. Another group of bacteria can adsorb metals to the surface and accumulate them at a sorbate-biosorbent interface. For instance, metalloregulatory protein (MerR) on the surface of *E.coli* has a high affinity and selectivity for mercury lead to remove and accumulate. Bacteria also take into account in nano-biotechnology by formation nanoparticles through series redox reaction which are active in remediation process. For example, some species of bacteria, such as magnetotactic bacteria, oxidize iron to oxides formed as nanoscale magnetite (Fe_3O_4), and are also highly reactive in the remediation of halogen compounds through the process of dehalogenation, which is faster than enzymatic reaction.

Role of fungi in bioremediation strategies

Fungal cell walls contain many ligands, such as carboxyl, hydroxyl, and amino groups in the chitin layer that are an agent of fungi to interact with the environment and perform many important mechanisms for mobilization, immobilization, and adsorption and accumulation of metals and other pollutants in the environment (Figure 4). Fungi also secrete many different metabolites, such as organic acid and chelating molecules that can solubilize many insoluble compounds in the environment (Göhre and Paszkowski, 2006; Rosén et al., 2005).

Phosphate and the carboxyl group of hyphae of *Penicillium chysogenum* are major agents on the surface of hyphae to adsorb lead and zinc, respectively, and while phosphate-solubilizing fungi produce oxalic acid to solubilize pyromorphite, which causes contamination of soil and is produced industrially (Fomina et al., 2004) and some produce hydrocyanic acid to solubilize metals like gold and gold cyanide in the case of *Chromobacterium violaceum*. Mycorrhizae also promotes phytoremediation directly or indirectly by increasing the plant biomass and also

immobilizing many metals in the rhizosphere layer, such as nickel and uranium, and some produce glycoprotein glomalin, which sequesters and stabilizes toxic metals like copper, lead, and chromium (Gonzalez-Chavez et al., 2004).

CONCLUSIONS

In conclusion, it is well known that fungi and bacteria grow and survive under different conditions due to their structures, which have a great role in interactions with the environment because they perform different processes in the biosphere such as bioweathering, biotransformation, and biomineralization, because they interact with different surfaces and produce various metabolites for dissolution mobilization, immobilization of metals in rocks and minerals, and the formation of secondary minerals, so that they would be an important agent of bioremediation to remove contaminants from the environment, such as toxic metals and to recover important economic elements like gold. Genetic engineering techniques modify the bacterial and fungal genes to make them more powerful and specific in the processes of bioremediation and nanotechnology.

Acknowledgments

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