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Microbial synthesis of unique nanoscale minerals - challenges and prospects

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Abstract: In this review, we highlight new insights and place the molecular mechanisms of the biogenesis of nanomaterials such as silicified frustules, coccoliths, magnetosomes and bacterial nanowires in the context of the complex biology of a microbial cell. The silicified frustules are formed by diatoms, which are a widespread group of organisms found in the oceans, fresh water, soil and wet surfaces. They are especially important in the oceans, where it is estimated that they contribute to 45% of total primary ocean production. Coccolith is a collective term that designates all of the biomineralized, calcified scales produced by extant and extinct haptophytes (single-celled algae). The orientation of magnetotactic bacteria is based on the presence of unique organelles, magnetosomes, which are intracellular, membrane-enclosed, nanometre-sized crystals of magnetic iron minerals. The discovery of bacterial conductive structures, called nanowires, has fascinated scientists for almost a decade. Nanowires enable bacteria to transfer electrons over micrometer distances to extracellular electron acceptors such as insoluble metal oxides or electrodes. The possible applications of these extremely interesting nanomaterials in different areas of life is also considered.

***Keywords*:** nanostructures, silicified frustules, coccoliths, magnetosomes, bacterial nanowires

1. Introduction

Owing to the wide range of applications offered by nanoscale minerals in different fields of science and technology, various protocols have been designed for their formation (Siegel, 1991; Sakthivel and Venkatesh, 2012). One of the main challenges for the nanominerals market is the reduction or elimination of hazardous substances and the association of these production processes with white biotechnology (Ribeiro et al., 2016). This microbial-mediated synthesis of nanomaterials is a process that provides a "green" alternative approach to commonly used physical and chemical strategies.

In the past 30 years, it has been shown that several types of microbes had a high ability to synthesize various categories of minerals on a nanometric scale. Among them, metallic nanoparticles including gold, silver, palladium, copper, alloy and oxide nanoparticles (zink oxide or titanium oxide), and other miscellaneous nanoparticles have been described (Jamkhande et al., 2019). Generally, it is believed that the biosynthesis of metallic nanoparticles by microorganisms depends on three mechanisms: reductase enzymes and proteins, exo-polysaccharides and electron shuttle quinones (Hulkoti and Taranath, 2014; Grasso et al., 2020; Ruder et al., 2011). Most studies suggest that enzymes and other proteins as the main molecules that are involved in the biomineralization of metal ions (Khan et al., 2018). Although there have been quite a few reports exploring enzymes as reducing as well as stabilizing agents for the synthesis of metallic nanoparticles a clear detailed mechanistic investigation of the reduction of metal salts by enzymes has not been performed.

It should be noticed that microorganisms are able to synthesize the less-discussed but unique nanostructured minerals, such as silicified frustules (Kröger and Poulsen, 2008), calcified coccoliths (Skeffington and Scheffel, 2018), magnetosomes (Yan et al., 2017) and bacterial nanowires (Malvankar

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and Lovley, 2012). In this review article, we focused on two aspects of these nanominerals: type of biosynthesis and biosynthetic pathways and their applications.

2. Silicified frustules

Diatoms are microscopic photosynthetic algae (a few diatoms lost the capacity to photosynthesise, e.g. *Nitzschia alba*) occur in various aquatic environments, both marine and freshwater (Mann and Vanormelingen, 2013). The diameter of their cells ranges from 2 μm to about 1 mm. It is believed that diatoms appeared on the Earth around 200 million years ago (Gross, 2012). Currently, 10,000-20,000 diatom species have been described, but it is estimated that the number of species reaches 200,000 (Mann and Droop, 1996). These microscopic organisms contribute to 40% of the primary productivity of marine ecosystems and 20% of global carbon fixation (Falkowski and Raven, 2007). Diatoms are characterized by the presence of a decorative silicified cell wall that displays intricate patterns and designs unique to each species (Pickett-Heaps et al., 1990). The silicified wall consists of two overlapping halves, an epitheca and a hypotheca. The silica wall elements are closely related to various organic layers and the entire wall assembly is generally named as frustule. It is well established that the inorganic components of the diatom frustule consist of amorphous hydrated silica formed from polymerized silicic acid (Simpson and Volcani, 1981).

During the vegetative reproduction of diatoms (Round et al., 1990), these organisms must build up a new cell wall of silica. The concentration of silicic acid (the fundamental building block used in the formation of silicas; the dominant form at pH 8.0 of seawater) in surface waters and oceans ranges from 10 to 70 μM (Tréguer et al., 1995) but the solubility of the silicic acid solution is limited to about 2 mM. It is known that above this concentration, silica begins to polymerize into polymers and form an amorphous solid. Several studies (reviewed in Martin-Jézéquel et al., 2000) have established that intracellular concentrations of soluble silicic acid are significantly greater than its saturation limit of 2 mM. The phenomenon is still incomprehensible, but it has been suggested that undescribed organic compounds associate with intracellular silicic acid, preventing polymerization.

It has been believed that silicic acid can diffuse through membranes and the obtained kinetic data indicate that at environmental relevant concentrations, diffusion may be the major mode of absorption (Thamatracoln and Hildebrand, 2008). When the concentration of silicic acid is very low, silicon transporters (SITs) actively facilitate its transport (Hildebrand et al., 1997; Thamatrakoln et al., 2006; Marron et al., 2013). It was found that silicon uptake is dependent upon a sodium gradient. The studies carried out by some authors suggested that SIT proteins are silicic acid/sodium symporters with a 1:1 (Bhattacharya and Volcani, 1980) or 2:1 (Curnow et al., 2012) transport stoichiometry.

Sequence analysis of SIT genes have shown that the SIT proteins contain 10 transmembrane helices and a highly conserved sequence motif, GXQ (X= Gln, Gly, Arg or Met) (Thamatrakoln et al., 2006). Finally, the silica deposition occurs in the special membrane-bounded structures called silica deposition vesicle (SDV). The occurrence of SDV has been shown in various protists and sponges (Simpson and Volcani, 1981). The silicalemma of SDV has membrane potential (Li et al., 1989) and the pH of SDV lumen is acidic (Vrieling et al., 1999). The association of SDV with the cytoskeleton through actin microfilaments and microtubules is necessary for modeling and positioning of SDV and silica formation (Tesson and Hildebrand, 2010).

The analysis of diatom cell walls revealed the presence of organic molecules that are integral components of biosilica and potentially participate in its formation. The coccolith-associated polysaccharides (CAPs) are believed to play an important role in the nucleation and formation of calcite crystals (Borman et al., 1982). CAPs are mainly classified as water-soluble acid polysaccharides composed of neutral monosaccharides, acid sulfate esters and uronic acid residues (De Jong et al., 1976). The uronic acid residues play a key role in modulating calcification because their negatively charged carboxyl groups bind to Ca^{2+} cations and are believed to hinder the precipitation of calcite at key points in cocolithic production. Moreover, the chemical composition of CAPs differs according to species and strain (Lee et al., 2016). Significant differences in the uronic acid content in CAPs influence the shaping of calcite crystals (Marsh and Dickinson, 1997) or to reflect adaptations to different saturation states of the CV calcite (Lee et al., 2016). It should be noted that the polysaccharide material is also extruded with a cocolyte that surrounds the cocolyte and contributes to the organic layer

associated with the coccosphere. The layer of insoluble polysaccharide on the outside of the coccolith is likely to provide some degree of environmental protection (preventing calcite from dissolving under adverse conditions) (Henriksen et al., 2004).

Proteins and polyamines have also been identified and it has been shown that they are directly/indirectly related to the formation of biosilica (Volcani, 1978). The presence of amino acids such as 3,4-dihydroxyproline and ε-N, N, N-trimethyl-δ-hydroxylysine (Nakajima and Volcani, 1969; Nakajima and Volcani, 1970) and general analysis of diatom cell walls for amino acid content (Hecky et al., 1979) revealed that proteins are inherent parts of the walls cell diatoms. The first protein isolated from the cell wall of the diatom *Cylindrotheca fusiformis* was α1-frustulin, a glycoprotein of approximately 75 kDa. This molecule was later proved to be general diatom cell wall proteins (Kröger et al., 1994; Kröger et al., 1996). Pleuralins are another group of proteins isolated from the cell wall of *C. fusiformis* diatomaceous silica (Kröger et al., 1997). Chitin may be the main component of organic scaffolding, which resembles the shape of biosilica in the in the girdle band region (Brunner et al., 2009). Furthermore, specific proteins named cirgulins were indentified in a ring-shaped organic matrix called microrings (Scheffel et al., 2011). In addition to cingulins, other biomolecules have been found to be associated with diatom cell walls and are capable of precipitating silica from the silicic acid solution. These structures are silafins and long chain polyamines (LCPA). LCPA are the main components of diatom silica cell walls (Kröger et al., 2000). LCPAs share a common structure of linear oligo-propyleneimine chains attached to an amine-containing basic molecule, but depending on the diatom species, LCPAs differ in their primary molecule and in the number and degree of methylation of propyleneimine units. The basic molecule is putrescine, spermidine or 1,3-diaminopropane, and the number of propyleneimine units is from 6 to 20 (Scheffel et al., 2011; Kröger et al., 2000; Sumper et al., 2006; Sumper et al., 2006). Activity of silica precipitation by LCPA requires the presence of phosphate ions or other polyvalent anions, such as pyrophosphate, sulfate or DNA (Sumper et al., 2003). In addition, the species-specific LCPA structures indicate their participation not only in silica formation, but also in modeling specific silica structures in different diatoms (Kröger et al., 2000; Sumper et al., 2006; Sumper et al., 2006).

The second major class of molecules identified in the diatom cell walls are silafins. Silafins are proteins that combine polycationic (polyamine) and polyanionic (phosphorylation) functions and play an important role in the molecular process of silica formation (Wenzl et al., 2008). Amorphous silica is formed as a result of an inorganic polymerization process with orthosilicic acid as a monomeric building block. The solubility of $Si(OH)_4$ is limited to a concentration of 2 mM in aqueous solutions of neutral pH, and deprotonation at pH values above 9 gives silicates anions of $SiO(OH)^{3-}$ (Iler, 1979). Nucleophilic substitutions between silicate anions and silicic acid molecules lead to reactions of condensation that form siloxane bonds (Si-O-Si). Silicic acid molecules react to form dimeric, trimeric and tetrameric species that further condense with monomers to form branched polysilicic acid forms. These colloidal silica particles are nanometric in size. It was found that at pH values below 7 there is only weak electrostatic repulsion between colloidal silica particles due to their uncharged surfaces and these nanoparticles aggregate into the fibrous, branched chain forming gel. At pH values above 7, negative charges on the surfaces of silica nanoparticles dominate and induce electrostatic repulsion. Therefore, colloidal silica particles form a stable sol, and the particles grow by the Ostwald ripening process (Iler, 1979; Ostwald, 1897).

It was previously found that the biomineralization of silica in diatoms is much faster than the formation of abiotic silica, therefore it is believed that a biological flocculant is necessary for the polycondensation of silica. LCPA and silaffins have been shown to be directly involved in molecular processes of silica frustules biogenesis. Both LCPA and silaffins are highly cationic and therefore it is reasonable to consider them as flocculants for negatively charged silica nanoparticles.

Geological deposits of fossilized diatom skeletons are known as diatomaceous earth. The main component of diatomaceous earth is silicon dioxide and small amounts of aluminum and iron oxide but the exact composition depends on the place of origin (Calvert, 1930). Diatomaceous earth is characterized by specific properties such as low density and conductivity, but a large surface area and adsorption capacity due to the high content of silica frustules. These properties have allowed the wide use diatomaceous earth as an adsorbent (Xiaohua et al., 2007), a natural insecticide (Korunic, 1998),

insulating material (Ivanov and Belyakov, 2008), aid in filtration in wastewater treatment (Osmanlioglu, 2007; Al-Ghouti et al., 2003) or as a catalyst carrier in photocatalytic reactions (Hsien et al., 2009; Zhu et al., 2011). It should be noted that silica is generally recognized as safe (Berthod, 1991; Chaudhry et al., 2008) and therefore is used in cosmetic and the food industry. The highly porous, hierarchically nanostructured architecture and photoluminescent stability of diatom frustules (Hamm et al., 2003; Butcher et al., 2005; Fuhrmann et al., 2004) are properties that allowed their use as templates for the production of metal surfaces with complex patterns that are valuable for surface Raman spectroscopy (SERS) (Payne et al., 2005). Furthermore, silica frustules of diatoms are useful templates for conversion of silica in other materials, such as nanocrystalline silicon or amorphous graphite (Sandhage, 2010; Bao et al., 2011). It was shown that diatom shells exhibit an efficient photoluminescence emission strongly dependent on environmental conditions. This luminescence can be quenched or enhanced with several gaseous substances and diatomaceous biosilica can be used as a material for optical gas detection (De Stefano et al., 2005; Lettieri et al., 2008). Functionalization of the diatom with antibody has been shown to detect complementary antigens by photoluminescence (Gale et al., 2009). Modification of the purified diatomaceous biosilica with biological molecules enables the development of silica microcapsules for targeted drug delivery. Their hollow structures and porosity allow for simple charging and prolonged release of hydrophobic and hydrophilic charge particles (Aw et al., 2011; Aw et al., 2012).

3. Coccoliths

Coccolithophores (Calcihaptophycidae) are abundant, single-celled marine eukaryotic phytoplankton characterized by the production of complex calcite plaques (coccoliths). Coccoliths are porous particles, mainly consisted of calcium carbonate, with further elements such as Mg, Si, Sr, and Fe often embedded in their structure. Due to of their widespread occurrence and ability to form extensive blooms (Westbroek et al., 1993), the coccolithophores are estimated to account for up to 10% of global carbon binding (Poulton et al., 2007) and are the major producers of oceanic biogenic calcium carbonate. It is believed that coccolithophores are a key factor contributing to oceans' biogeochemical cycles. It should be emphasized that most of the research on carbon storage in marine ecosystems focuses on organic carbon. Inorganic carbon processes, such as calcification there are usually not taken into account, despite their key role in the global carbon budget. The findings of Kalokora et al., (2020) indicated that calcification can release a significant amount of CO_2 into the atmosphere and therefore probably counteract carbon sequestration in marine plant ecosystems if this CO_2 is not re-deposited into the system.

The coccolith is a general term that covers all of the biomineralized, calcified scales synthesized by existing and extinct haptophytes (Müller, 2019). The specificity of these structures depends on their micrometric size and unusual symmetry, a homogeneous composition of calcite (also known as aragonite chocolates) and optical properties. It should be noted that the functions of coccoliths are still uncertain (Monteiro et al., 2016). The phenomenon of the ability of several species to grow without coccoliths in laboratory (*Emiliania huxleyi* and *Chrysotila carterae*) was previously described (Paasche, 2001; Marsh, 2003). Many researchers believe that the main function of coccoliths is protection against grazing by zooplankton but other hypotheses are taken into account (Müller, 2019). For example, the coccoliths can increase the rate flow of water with nutrients past the cell surface (the important role of flotation and buoyancy; aspheric forms can reduce the sink rate, loss or addition of cocoliths can be a strategy used to adjust position in the water column to optimize the availability of light or nutrients) or these structures can be a protective barrier against viruses and bacteria. For many years, coccoliths were thought to protect against very high levels of light, which may explain the resistance to photoinhibition observed in *E. huxleyi* (Raven and Crawfurd 2012). There is currently a lack of hard data that can be used to distinguish between various hypotheses regarding coccolith functions, and the variety of coccolith morphology means that they are functionally adapted to perform various functions. Despite their small size, coccoliths are decorative structures that, if the water chemistry is adequate, are produced reliably with minor developmental defects. Calcite is usually transparent to visible light (coccolithophores are photosynthetic), and in cross-polarized light, coccoliths produce characteristic patterns closely related to their structure. The unusual crystallographic structure of

coccolith suggests that coccolithogenesis is a highly organized process that is strictly controlled by biological mechanisms. Protein matrices are believed to be necessary for nucleation of $CaCO_3$ crystals (Schroeder et al., 2005), while polysaccharides control their growth and formation (Marsh et al., 2002).

Moreover, there is a conviction that many other, so far unknown, proteins, enzymes and transcription factors are necessary for the formation, shaping, transport and cellular addressing of various vacuoles surrounding basic components (Ca^{2+}, CO_3^-) (Gal et al., 2016; van der Wal et al., 1983).

Over 60 years ago, the coccoliths were classified into two structural groups, *holococcoliths* and *heterococcoliths* (Braarud and Deflandre, 1955). It is worth noting that holococcoliths and heterococcoliths are produced by individual species at various stages of their life cycle. These processes are based on a common genetic basis, but heterococcololitogenesis and holococcololitogenesis require the participation of different metabolic pathways, at least part of the calcification process. The holoccolliths are formed in the haploid phase of the life cycle and consist of many fine crystallites (~ 0.1 μm) outside the cell wall. It was suggested that calcification of holococcoliths may be localised in a single highly regulated space outside the cell membrane but directly above the Golgi body (Rowson et al., 1986). For this reason, these taxa are called extracellular coccolithophore calcifiers (ECCs). This group also includes ECC braarudosphaerides (the genera and species of *Braarudospaeraceae* are found the Cretaceous and the Cenozoic (Perch-Nielsen et al., 1985); the genera of this family are distinguished by the form of the individual pentagonal nannoliths and by the presence or absence of a hole in each segment) (Bown et al., 2014). The external location of this biomineralization (Cros and Estrada, 2013) clearly suggests that this extracellular calcification may be more sensitive on changes in seawater chemistry than intracellular calcification.

Heterococcoliths are complex structures that are made of modified calcite crystals arranged in meshing cycles. These structures are synthesized in Golgi-derived cytoplasmic vesicles, and the process of their formation is initiated by the nucleation of the proto-coccolith ring of simple crystals ring arranged around the rim of an organic plate in alternating vertical (V) and radial (R) crystallographic orientations (Young and Henriksen, 2003).

Intracellular *coccolithogenesis* requires external supply of Ca^{2+} and inorganic carbon to the intracellular Golgi-derived vesicle in which calcification takes place (Brownlee and Taylor, 2004). It is well known that intracellular concentration and compartmentalization of Ca^{2+} need to be under strict control.

Literature data shows that the use of coccoliths in various industries is still at the stage of collecting ideas. In medical implants, biominerals resemble human bone material and have favorable sound transmission properties (Moheimani et al., 2012). Therefore, it is justified to use coccoliths as artificial tooth roots and artificial bone material (Moheimani et al., 2012). The reducing or increasing the concentration of some metals (iron, copper) can increase the whiteness of coccoliths and make them more suitable for use as pigments in paint. Studies have shown that the coccoliths are porous, so in the future it will be interesting to study their potential as a substrate for varnish or varnish coating or filler in adhesives or materials with increased porosity. Porosity is also an important factor in optical applications (Takano et al., 1993).

4. Magnetosomes

Bacterial magnetosomes, magnetite (Fe_3O_4) or greigite (Fe_3S_4) nanocrystals covered by phospholipid bilayer membrane, are formed intracellularly by magnetosome-producing microbes including magnetotactic bacteria and some non-magnetotactic bacteria (Yan et al., 2012; Yan et al., 2017). Magnetotoactic bacteria are able to synthesize a wide range of magnetosomes, which are responsible for magnetotaxis. Magnetotaxis is a combination of passive orientation and mobility by flagellates of magnetotactic bacterial cells along the magnetic field lines. Production of bacterial magnetosomes and their properties (size, shape, structure) depends on living conditions of microorganisms, biochemical, chemical and genetic regulation. The well described bacterium producing magnetosomes is *Magnetospirillum magneticum* (Lefevre and Bazylinski, 2013; Dieudonné et al., 2019).

Magnetosomes are bacterial nanomaterials with crystal structure in narrow size in range 35-120 nm (mature), however, some magnetosomes are up to 250 nm formed by uncultured species. Mature

magnetosome is a single-magnetic domain that is very stable, maintains magnetic moment at room temperature and has permanent magnetization (Yan et al., 2012; Yan et al., 2017). Smaller magnetosomes are superparamagnetic at room temperature, that means that they do not have a constant value of magnetization, while bigger magnetosomes do not have a constant value due to the formation of domain walls (Yan et al., 2012; Yan et al., 2017). It is described that magnetosomes synthesized by microorganisms are better stable than chemically synthesized supermagnetic structure (Alphandery, 2014).

Depending on the microroganism that synthesizes these structures, magnetosomes have unique shapes: rectangular, hexagonal or bullet. These nanomaterials are ordered into stable chains in the cell (chain of 20-40 units), arrange parallel to itself without causing mutual magnetism. In general, the distance between the magnetosomes is 3-18 nm, the distance between the magnesium and the membrane is 1.6 nm. The dipole moment of the chain corresponds to the number of magnetosomes. The newly formed magnetosome is placed at the end of the chain (there are smaller magnetosomes). The described properties prevent aggregation of these nanomaterials (Yan et al., 2012; Yan et al., 2017; Alphandery, 2014). The cover of magnetosomes (magnetosome membrane) is created by lipid bilayer with proteins, fatty acids, lipids (glyco-, sulpho- and fosfolipids) and amino, carboxyl, hydroxyl groups. These properties cause magnetosomes to have negative charge and be characterized by good diffusion in water (Yan et al., 2017; Wang et al., 2020).

Bacterial magnetosomes are characterized by good biocompatibility and good surface properties (Yan et al., 2017; Sun et al. 2011). The mechanism of biosynthesis of magnetosomes involves four steps: (1) extracellular ferric ion uptake; (2) formation of magnetosome membrane; (3) crystal forming (biomineralization); (4) chain formation (Yan et. al, 2017).

Microorganisms use proteins (MamM and MamB), and siderophores for the capture of iron ions (Fe^{2+} and Fe^{3}) (Vargas et al., 2018, Yan et. al, 2017). Formation of magnetosome bilayer membrane (second step) depends on certain groups of proteins: MamA, MamL, MamQ, Mps and MamY. MamA protein is responsible for formation of bilayer membrane vesicles, whereas MamB and MamQ proteins transport ion inside the vesicles (Yan et al., 2012). Another groups of proteins- MamN, MamE and MamO- control crystal biomineralization of magnetosomes (third step). MamO and MamE proteins are responsible for nucleation of crystal. The hydrogen ion is transferred to the magnetosome, thus equalizing the potentials after absorption of the iron ion (MamN proteins). The MamK protein is responsible for creating sequence of magnetosomes in the chain. This protein directs the magnetosome to the right place in the chain and stabilizes it. The protein MamJ in interaction with MamK "monitors" chain formation proteins (Yan et. al, 2017).

Magnetosomes due to their magnetic properties can be used in magnetic resonance imaging as contrast media. In addition, magnetosomes can be used to capture antibodies, antigen-detecting elements, and are also useful for the separation of cells and DNA (Alphandery, 2014, Prabhu et al., 2016). One of the breakthrough approaches is to strengthen anti-cancer therapy, using magnetosomes as drug carriers and thermo-agents in the process of hyperthermia (Prabhu et al., 2016, Gandia et al., 2019). Due to good surface properties of these nanostructures, magnetosomes are able to absorb many polymers on their surface, mediating their desired modifications (Alphandery, 2014; Gandia et al., 2019). Magnetoseomes have been used in soil and water bioremediation as particles for the separation of heavy metals and radioactive particles. It has been described that these nanostructures can be used as intermediaries in the generation of energy by induction of electromagnetism (Alphandery, 2014; Gandia et al., 2019).

5. Bacterial nanowires

Bacterial nanowires are proteinaceous pilus-like stuctures with nanometer diameter involved in long-range electron transport processes (Reguera et al., 2005). It has been reported that nanowires can be generated by dissimilation metal reducing bacteria (DMRB) such as anaerobic *Geobacter* (Gorby et al., 2006; Lovley and Walker, 2019) and *Shewanella* (Gorby et al., 2006) genera, aerobic bacteria such as *Pseudomonas aeruginosa* (Liu et al., 2019) and photosynthetic cyanobacteria such as *Microcystis* genera (Sure et al., 2015).

Microbial dissimilatory reduction of metals is a globally important biogeochemical process that drives the cycle of Fe, Mn, associated trace metals and organic matter in soils and sediments, as well as in marine and freshwater environments (Lovley et al., 2004; Nealson et al., 2002).

Similar to respiration with most electron acceptors commonly used by prokaryotes (oxygen, nitrate, sulfate and carbon dioxide), electrons generated during the metabolism of organic carbon are utilized to reduce minerals containing oxidized forms of Fe or Mg (Lovley et al., 2004). Microbial dissimilatory reduction of Fe(III) is a process in which microorganisms transfer electrons to external Fe(III), reducing it to Fe(II) without iron assimilation. Most microorganisms that reduce Fe(III) also can transfer electrons to Mn(IV), reducing it to Mn(II). However, due to the fact that the oxidized forms of these minerals are insoluble, they cannot easily diffuse into the cell (Lovley edt al. 2004; Rosenberg et al., 2013). In anaerobic environments, dissimilation metal reducing bacteria must overcome the fundamental problem of transferring electrons to insoluble electron acceptors. Several species of anaerobic metal-reducing proteobacteria use different extracellular electron transfer (EET) strategies to deliver electrons produced during respiration to the final acceptors in the external environment (Kracke et al., 2015).

Geobacteraceae family is one of the best studied groups of microorganisms performing extracellular electron transport reactions (Reguera et al., 2005; Lovley and Walker, 2019). They form specialized piluses (thin cytoplasmic bridges) which transfer electrons from the inside of the cell to the ferric iron minerals located outside the cell (Reguera et al., 2005). Piluses described as bacterial nanowires or e-pili were initially found in *G. metallireducens* biofilms grown on insoluble iron oxides, but not when grown with soluble or chelated Fe(III) as electron acceptor (Childers et al., 2002).

Similar flagella and pili structures were also observed in *G. sulfurreducens* biofilm during growth on Fe(III) oxide, but not with soluble Fe(III) (Reguera et al., 2005). The mechanism of electrical conductivity through *G. sulfurreducens* nanowires is the subject of intensive research. To explain this phenomenon, several electron transport models have been proposed. One model suggests that electrical conductivity involves electron exchange between redox active sites, such as OmcS cytochromes, which are associated with nanowires fibers (Agapova et al., 2010; Qian et al., 2011; Wang et al., 2019).

Filman et al. have discovered that *G. sulfrogucene* nanowires are composed of monomers of the six-heme C-type cytochrome OmcS assembled into filaments (Filman et al., 2019). Research carried out by Wang et al. show that nanowires previously thought to be type IV piles actually consist of polymerized OmcS fibers with unique structural features, which also explains the molecular basis of long-range electronic transport in proteins (Wang et al., 2019).

An alternative hypothesis suggests metallic-like conductivity along the nanowire due to the richness of aromatic amino acids in PilA protein, the type IV pilin assembled into e-pili (Malvankar et al., 2011, Malvankar et al., 2015). The deletion of pilA gene leads to the inhibition of iron oxide reduction and production of conductive biofilms by *G. sulfurreducens* and *G. metalreducens* (Cologgi et al., 2011; Lampa-Pastirk et al., 2016). The N-terminus of PilA sequence in *G. sulfurreducens* and various eubacteria is well preserved, while the C-terminus of PilA protein differs from the end of other species. That suggests a general method for the synthesis of highly conductive microbial nanowires (Holmes et al., 2016; Liu et al., 2019). It was noted that the pilus monomer of *Geobacter metallireducens* and *Geobacter sulfurreducens* is significantly shorter and consists of only 60-90 amino acids, compared to more than 120 amino acids typically found in PilA sequence in most other bacteria (Reguera et al., 2005; Holmes et al., 2016). It is believed that the shorter PilA monomer results in closer packing and positioning of aromatic amino acids in pilin forming a conductive path, and thus enables efficient electron transfer along the pilin (Malvankar et al., 2015).

G. sulfulfurense generate nanowires with a diameter of 3 nm and can grow tens of micrometres long forming nanostructures which transport electrons along their length for centimeters long distances, which is thousands times longer than the size of the bacterium (Reguera et al., 2005; Gorby et al., 2006; Bjerg et al., 2018). Such electron transport over long distances in a biological protein is unique. Typically, electron transport is around 10 nm is considered a large distance for protein complexes (Bjerg et al., 2018; Bostick et al., 2018).

Bacteria from the *Shewanella* genus may also serve as model organisms for the study of bacterial extracellular electron transfer (EET). The best studied organism of the genus is *S. oneidensis* MR-1, which exhibits a wide versatility of terminal electron acceptors (TEA). *S. oneidensis* may use oxygen for efficient respiration, but under anaerobic conditions it can also utilize different electron acceptors such as organic compounds (fumarate, humic acids, trimethylamine N-oxide, dimethyl sulfoxide and others), as well as oxidized metals [Mn(III) Mn(VI), Fe(III), Cr(VI), U(VI), S, NO_3, NO_2] during respiration (Heidelberg et al., 2002; Beliaev et al., 2005).

Culture of *S. oneidensis* biofilms with limited electron-acceptor conditions revealed the formation of a dense network of fibers. These long, flexible pilus-like structures protruding from the cell had diameters from 50 to> 150 nm and extended to tens of microns or longer. This nanowires showed the ability to transfer electrons to extracellular iron oxides at positions distant from the cell surface (Gorby et al., 2006).

The production of nanowires by the aerobic bacteria such as *Pseudomonas aeruginosa* (Liu et al., 2019) and photosynthetic cyanobacteria such as *Microcystis genera* (Sure et al., 2015) show that electrically conductive processes may actually be a common strategy for effective electron transfer and energy distribution in bacteria.

Nanowires are interesting not only for microbial electron transfer reactions, but also as "green," sustainable electronic materials which have numerous advantages compared to electronic materials synthesized using complex chemical processes which may contain toxic components (Lovley, 2017).

In addition, nanowires have many advantages, such as durability, biodegradability and lack of toxic components, which eliminates waste generation. Nanowires can be mass produced with high homogeneity from inexpensive, renewable raw materials such as acetate, with energy inputs estimated at 100 times less than when processing traditional electronic materials (Lovley, 2017) and their conductivity is comparable to that of organic polymer wires of similar diameter (Malvankar et al., 2011). Bacterial nanowires are very promising nanostructures in the bioelectronic field for the development of a new biomaterial for microbial fuel cells and electrochemical (bio) sensor devices (Grasso et al., 2020).

6. Conclusions

Based on literature data published in recent years, microbial nanotechnology is a fascinating and dynamically developing areas of the future breakthrough synthesis of nanomaterials. Microbial nanotechnology, thanks to its environmentally friendly and sustainable approach, can spur innovation in nano-production with a strong impact in several areas, including sensor science and biomedicine.

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