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Chapter 3
Manganese Oxidation by Bacteria: Biogeochemical Aspects

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Abstract Manganese is an essential trace metal that is not as readily oxidizable like iron. Several bacterial groups posses the ability to oxidize Mn effectively competing with chemical oxidation. The oxides of Mn are the strongest of the oxidants, next to oxygen in the aquatic environment and therefore control the fate of several elements. Mn oxidizing bacteria have a suit of enzymes that not only help to scavenge Mn but also other associated elements, thus playing a crucial role in biogeochemical cycles. This article reviews the importance of manganese and its interaction with microorganisms in the oxidative Mn cycle in aquatic realms.

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3.1 Introduction

Manganese comprises about 0.1% of the total mass of the Earth (Nealson 1983) and occurs as $MnAl_2O_4$ (Zajic 1969). It is the fifth most abundant transition metal in the Earth's crust (Tebo et al. 2007) and is the second most common trace metal after iron (Tebo et al. 1997). The name manganese is derived from the Greek word mangania, meaning magic (Horsburgh et al. 2002). It occupies the 25th position in the periodic table and belongs to group VII transition elements (Cellier 2002). Mn exist in seven different oxidation states ranging from 0 to +7 and in nature it occurs in +II, +III, and +IV oxidation states (Tebo et al. 1997, 2004). Mn^{2+} has an ionic radius of 0.80 A° and has Gibbs standard energy of −54.5 ΔG° in aqueous solutions (Hem 1978). It occurs at a concentration of 100–1000 ppm in river, 1–10 ppm in ground water (Nealson 1983), and averages 8 μg kg^{-1} in freshwater and 0.2 μg kg^{-1} in seawater (Bowen 1979 and Ehrlich 2002a). The concentration of dissolved Mn (Mn^{2+}) in the open ocean ranges from 0.2–3 nmol kg^{-1} of seawater (Glasby 2006). Further details about its distribution and abundance are shown in Fig. 3.1. As Mn exists at a higher redox potential than iron, following comparisons can be made on Mn–Fe relationships. (1) Mn reduces more easily than iron, (2) Mn is harder to oxidize than iron, and (3) Soluble Mn (Mn^{2+}) occurs at a somewhat higher level in the oxygen gradient than iron (Kirchner and Grabowski 1972). Mn enrichment occurs as a result of both artificial and natural processes. The sources of Mn in the ocean are atmospheric input, intense scavenging at mid-depth, and fluxes from reducing shelf and slope sediments and emanations from submarine hydrothermal vents (Saager et al. 1989). This study focuses on the bacterial groups that participate in Mn oxidation and the recent advancements made in the field of metal–microbe interaction. It also delves into genomic and proteomic aspects covering both freshwater and marine systems. Lastly, the review addresses the bacterial contribution to mineral formation and their potential use in biotechnological applications.

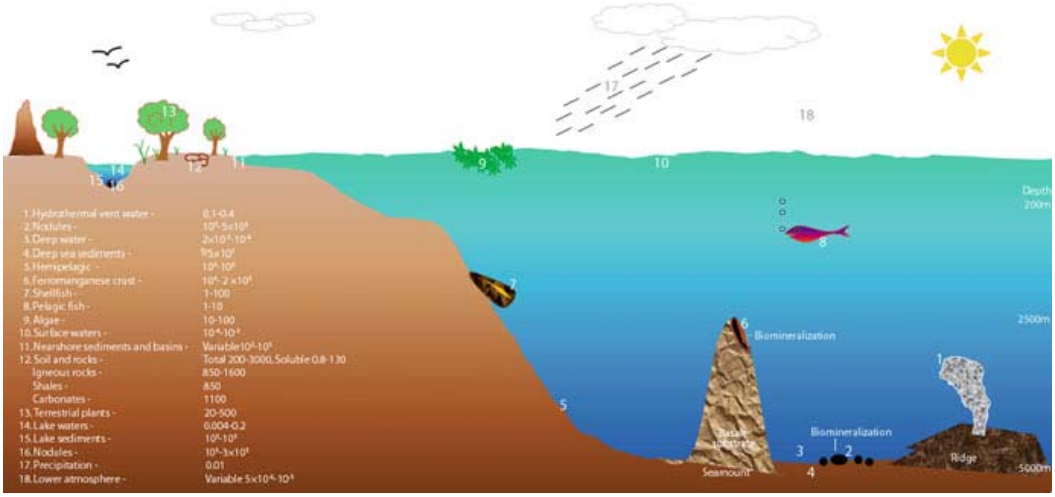

Fig. 3.1 Concentrations of manganese in different environments in ppm (*modified from Nealson 1983*)

3.2 Importance of Manganese

Manganese is a critical trace nutrient required for the growth and survival of many living organisms. It is essential for oxygenic photosynthesis in cyanobacteria (Yocum and Pecoraro 1999; Keren et al. 2002; Ogawa et al. 2002), redox reactions, protection from toxic metals, UV light, predation or, viruses, scavenging of micronutrient trace metals, breakdown of natural organic matter into metabolizable substrates, maintenance of an electron-acceptor reservoir for use in anaerobic respiration, oxygen production, and protection against oxidative stress in bacteria (Christianson 1997; Spiro et al. 2010). It is important for general metabolism, carbohydrate metabolism, and for both anabolic and catabolic functions in anaerobiosis and aerobiosis (Crowley et al. 2000). It is a part of four metalloenzymes manganese superoxide dismutase (MnSOD), mangani-catalase, arginase, and O-phosphatases (Christianson 1997; Shi 2004). Mn^{2+} containing O-phosphatases are involved in controlling spore formation, stress-response, cell density during stationary phase, carbon and nitrogen assimilation, vegetative growth, development of fruiting bodies, and cell segregation (Shi 2004). Additionally, nonenzymatic Mn^{2+} is crucial for the proper functioning of a variety of bacterial products, including secreted antibiotics (Archibald 1986). It also contributes to the stabilization of bacterial cell walls (Doyle 1989) and plays an important role in bacterial signal transduction (Jakubovics and Jenkinson 2001). Mn^{2+} is required for the stimulation of poly-β-hydroxybutyrate oxidation in *Sphaerotilus discophorous* (Stokes and Powers 1967) and exopolysaccharides (EPS) production in *Rhizobium meliloti* JJ-1 (Appanna 1988). Being a part of an enzyme in glycolysis, Mn^{2+} is required for the activity of 3-phosphoglycerate mutase in several endospore-forming gram-positive bacteria (Chander et al. 1998). Indirectly, Mn functions in controlling nutrient availability in freshwater, most significantly by complexing with iron (Kirchner and Grabowski 1972).

3.3 Biogeochemistry of Manganese

The geochemistry of Mn is a complex pattern of mutually exclusive chemical reactions of oxidation and reduction (Kirchner and Grabowski 1972). The geochemical behavior of Mn differs in environment which shows gradation in oxygen profile (Roitz et al. 2002). Mn occurs as highly soluble Mn^{2+} in oxygen-deficient settings and as insoluble oxyhydroxides under well-oxygenated conditions (Calvert and Pedersen 1996). The concentration of soluble Mn in the environments varies with change in redox condition and the group of microorganisms present. The oxidation of Mn by microorganisms results in decrease in the dissolved Mn^{2+} concentration of metal and increase in the particulate/higher oxidation states (Mn^{3+} and Mn^{4+}) of Mn (Ehrlich 1976, 1978). Redox transitions between soluble Mn^{2+} ions and insoluble Mn^{3+} and Mn^{4+} oxides form the backbone of aquatic

biogeochemistry of Mn (Sunda and Huntsman 1990). Mn^{3+} being a strong oxidant and a reductant, it has been largely ignored due to its property to disproportionate to Mn^{2+} and MnO_2 (Johnson 2006). However, recent improvements in the understanding of Mn chemistry indicate that dissolved Mn exist mostly as Mn^{3+} in sub-oxic regions (Trouwborst et al. 2006). Mn being one of the strongest oxidant in the natural environment, eventually participates in redox reactions and due to its sorptive characteristics controls the distributions and bioavailability of several toxic and essential trace elements (Tebo et al. 2004). Microorganisms like bacteria and fungi are known oxidizers of Mn^{2+} and reducers of Mn oxide-containing minerals. They carry out oxidation/reduction of Mn as a way to conserve energy for growth or oxidation of carbon (Nealson and Myers 1992; Tebo et al. 2005). The oxidation of Mn^{2+} under natural conditions is catalyzed only by microbes under pH range of 5.5–8.0, Eh value above +200 mV and oxygen concentration of 3–5 mg L^{-1} (Schweisfurth et al. 1978).

The three representative stoichiometric relationships that typically follow the oxidation of Mn^{2+} depending on the oxide product formed according to Nealson et al. (1988) are

$$Mn^{2+} + \frac{1}{2}O_2 + H_2O \rightarrow MnO_2 + 2H^+$$
$$Mn^{2+} + \frac{1}{4}O_2 + \frac{3}{2}H_2O \rightarrow MnOOH + 2H^+$$
$$3Mn^{2+} + \frac{1}{2}O_2 + 3H_2O \rightarrow Mn_3O_4 + 6H^+$$

A number of bacteria capable of mixotrophic and autotrophic growth could derive useful energy from Mn^{2+} oxidation. The oxidation of Mn^{2+} by bacteria could yield ΔF_r of +2.79 and $\Delta F'_r$ of −16.31 kcal (Ehrlich 1976, 1978) in the reaction

$$Mn^{2+} + \frac{1}{2}O_2 + H_2O \rightarrow MnO_2 + 2H^+$$

and yield ΔG −18.5 kcal in the reverse reaction

$$MnO_2 + 4H^+ + 2e \rightarrow Mn^{2+} + 2H_2O$$

when allowance for physiological pH of 7.0 is made (Ehrlich 1987).

The key steps in the reduction of Mn^{4+} to Mn^{2+} involve the reactions of strongly bound Mn^{3+} $\{\{Mn^{3+}\}\}$ and weakly bound Mn^{2+} $\{Mn^{2+}\}$ on the surface of MnO_2 (Ehrlich 2002b). The following steps explain the process

$$\{Mn^{2+}\} + MnO_2 + 2H_2O \rightarrow 2\{\{Mn^{3+}\}\} + 4OH^-$$
$$2\{\{Mn^{3+}\}\} + 2e^- \rightarrow \{Mn^{2+}\} + Mn^{2+}$$

The reduction of Mn oxide is predicted based on standard redox potential of +1.29 mV (Rusin and Ehrlich 1995) based on the equation

$$\frac{1}{2}MnO_2 + 2H^+ + e^- \rightarrow \frac{1}{2}Mn^{2+} + H_2O$$

In environment where Mn and iron oxides coexist such as in ferromanganese nodules, bacteria preferentially attack manganese oxides. The possible explanation suggested for the preference of Mn over Fe by bacteria was the lower midpoint potential for the Fe(III)/Fe(II) couple relative to the Mn(IV)/Mn(II) couple (Ehrlich 1987). However, the exact reason is yet to be determined.

3.4 Effect of Salinity on Manganese Oxidation

The solubility of Mn is more in freshwater compared to salt water. However, the oxidation rate of Mn^{2+} decreased sixfold in creek water of an English estuary when the salinity of water increased from 1 to 5 (Vojak et al. 1985). Likewise, Spratt et al. (1994b) also demonstrated a fourfold decrease in the rates of manganese oxide production in high marsh sediments than in creek bank sediments. In another study, Spratt et al. (1994a) showed decrease in rate of Mn oxidation in high marsh sediments experimentally exposed to hypersaline (102) conditions. They demonstrated that Mn oxidation in creek bank sediments exhibit much higher rates of oxidation than high marsh sites (2.31 ± 0.28 and 0.45 ± 0.14 nmol mg dwt^{-1} h^{-1}). In mangrove swamp estuary, highest rates of microbial Mn oxide production was encountered in sediments with salinities between 0 and 8 (50–119 pmol mg dwt^{-1} h^{-1}, respectively) compared with sediments from the mouth of the estuary with salinities of 24 and 34 (3–16 pmol mg dwt^{-1} h^{-1}, respectively). Nevertheless, the overall rates of microbial Mn oxide production in salt-marsh sediments were much higher than in mangrove sediments.

3.5 Toxicity of Manganese in the Presence of Other Metals

In an undisturbed marine environment, metal ions are more likely to occur in combinations than in single (Yang and Ehrlich 1976). The microbial response to individual metals may differ from the response to stress from multiple metals. When interactions of one metal have a protective effect on the toxicity of other metal, the resulting effect is referred as antagonistic and the reverse effect where toxicity of one metal is enhanced in the presence of the other metal is synergistic. Third, interactions where the final toxicity is simply a sum of the individual toxicities of the metal ions is called additive (Babich and Stotzky 1983). The effect of Mn, Ni, Cu, and Co in combinations of 10 μg mL^{-1} in seawater enriched with 1% glucose and 0.05%

peptone at 18°C showed different toxic effects (Yang and Ehrlich 1976). Mn and Co when tested alone had no effect on growth but their combination did. The combination of Co and Ni was more toxic than Co alone but less toxic than Ni alone. Cu was comparatively more toxic than other metals. Its toxicity was slightly relieved by Co or by the combination of Co and Mn, or Co, Mn, and Ni, but by no other metal combinations tried. The mixtures of Mn and Ni and of Mn, Co, and Ni were more toxic than their individual components. Likewise, Appanna et al. (1996) demonstrated the influence of Mn, Co, Cs, and Ni on the ability of *Pseudomonas fluorescens* to adapt to and to decontaminate the multiple-metal environment. There the toxicity of metals was comparatively lower in multiple-metal combinations than when individual metals were tested. Mn was the least toxic followed by Cs, Co, and Ni. Cs and Mn did not alter the cellular yield significantly; however, Ni and Co showed marked inhibitory effect on bacterial growth.

A study on redox transformation of Mn in Antarctic lakes (Krishnan et al. 2009) showed maximum stimulation of Mn oxidation (81 ± 57 ppb d^{-1}) in Lister Hooded (LH) strains with Mn–Co combination rather than combinations of Fe (37 ± 16 ppb d^{-1}) and Ni (40 ± 47 ppb d^{-1}), suggesting the role of Co in Mn oxidation. Conversely, maximum stimulation of Mn reduction occurred in combinations of the metals containing Ni. The rates were >50 ppb d^{-1} with strain LH-11 and >125 ppb d^{-1} with strain LH-8 in combinations of Mn–Ni and Mn–Fe–Ni which suggest the critical role of Ni in Mn reduction.

3.6 Manganese Oxidation by Marine Bacteria

The oxidation of Mn^{2+} by marine bacteria is more versatile. Dick et al. (2008a) have shown that *Aurantimonas* sp. Strain SI85-9A1, a marine α-proteobacterium, contain genes for organoheterotrophy, methylotrophy, oxidation of sulfur and carbon monoxide, the ability to grow over a wide range of oxygen concentrations, and the complete Calvin cycle for carbon fixation. In an early study, Ehrlich (1963) observed that bacteria in Mn nodules can enhance the adsorption of Mn^{2+} from seawater in the presence of peptone. He proposed that bacteria play a crucial role in nodule development. Besides, Mn^{2+} oxidation by cell-free extract from a Mn nodule bacterium *Arthrobacter* 37 was found to be mediated by enzyme activity (Ehrlich 1968). The rate of oxidation of free Mn^{2+} by the enzyme depended on the concentration of cell-free extract used. In another study on the effect of temperature and pressure on *Arthrobacter* 37, Ehrlich (1971) demonstrated that at 5°C, temperature optimum for Mn^{2+} oxidation increases with pressure and the effect of pressure on cells can be counteracted by an appropriate increase in temperature. Further, Arcuri and Ehrlich (1979) stated the involvement of cytochrome in Mn^{2+} oxidation by two marine bacteria. With the use of conventional electron transport chain, the bacterium could derive useful energy from Mn^{2+} oxidation by oxidative phosphorylation. By a detailed observation of bacteria that catalyze Mn^{2+} oxidation, Ehrlich (1980) postulated that two groups of Mn^{2+}-oxidizing bacteria exist, one that acts on

free Mn (Mn^{2+}) and the other that acts only on Mn^{2+} bound to Mn(IV) oxide and derive energy from the reaction. At the same time, Arcuri and Ehrlich (1980) proposed that cytochromes were involved in Mn^{2+} oxidation by *Oceanospirillum* BIII 45. They could observe that addition of periplasmic/intracellular fraction to membrane fraction was essential for Mn oxidation. Yet in another study on the removal efficiency of Mn^{2+} from seawater by marine sediments and clay minerals with the same organism, Ehrlich (1982) observed that ferric chloride pretreatment of clays is essential when intact cells are used and not when cell-free extracts are used. He remarked that ferric chloride pretreatment was necessary for activating the sediment for bacterial oxidation of sorbed Mn^{2+}.

Another interesting observation on Mn^{2+} oxidation by bacterial isolates from hydrothermal area (Ehrlich 1983) showed that Mn^{2+} oxidation could occur through an inducible enzyme system and an initial fixation of Mn(II) to Mn(IV) oxide was not essential for oxidation to proceed. Our earlier observation on the bacteriology of Fe–Mn nodules from the Indian Ocean region showed that psychrotrophic heterotrophic bacteria were capable of mobilizing and immobilizing Mn. The maximum percentage of Mn oxidizers (32.2%) was restricted to nodule surface and possessed various hydrolytic enzymes (Chandramohan et al. 1987). Later on, Ehrlich and Salerno (1990) demonstrated the coupling of ATP synthesis with that of Mn^{2+} oxidation by a marine bacterial strain SSW22. They proposed chemiosmosis (diffusion of ions across a selectively permeable membrane) as the probable mechanism for energy coupling by intact cells, membrane vesicles, or cell extracts.

In a different study, Rosson and Nealson (1982) observed that live/killed mature spores of *Bacillus* Strain SG-1 could oxidize Mn^{2+} once bound but not when free in solution. They hypothesized that Mn^{2+} may form complex with exosporium or a spore coat protein. In another observation, Kepkay and Nealson (1982) identified that spores rather than vegetative cells are responsible for Mn^{2+} oxidation by SG-1. The adherence of bacterial cells to solid surfaces was found to be essential for proper sporulation and Mn^{2+} oxidation. Using radiotracers, Emerson et al. (1982) explained that Mn^{2+} oxidation in Saanich Inlet is bacterially mediated and the removal of Mn^{2+} is very fast and would occur in a matter of few days on solid surfaces. The study on the role of plasmids in Mn^{2+} oxidation (Lidstrom et al. 1983; Schuett et al. 1986) showed that in marine *Pseudomonads*, increased levels of both binding and oxidation of Mn^{2+} could occur in the presence of plasmids. Using radiotracers, Tebo et al. (1984) provided evidence for Mn^{2+} oxidation with oxygen as the terminal electron acceptor in Saanich Inlet and Framvaren Fjord. The Mn^{2+} oxidation was found to occur faster under air-saturated condition than under conditions of oxygen limitation. Interestingly, Rosson et al. (1984) using poisoned control could differentiate biological from abiotic Mn^{2+} oxidation and demonstrated that bacteria could significantly enhance the rate of Mn^{2+} removal from manganese-rich particulate layer in the water column. Further, by in situ experimental evidence on Mn^{2+} oxidation in Saanich Inlet, Tebo and Emerson (1985) showed that the rate of Mn^{2+} oxidation was limited by both oxygen and the concentration of microbial binding sites in the environment. In a study on Mn^{2+} removal from porewater, Edenborn et al. (1985) observed that Mn^{2+} removal rate is

faster in the oxidized surface sediment where the Mn-oxidizing bacteria are abundant.

In an attempt to describe the general mechanism of Mn^{2+} oxidation, Tebo and Emerson (1986) describe a model where they conclude that Mn oxidation rate is not dependent on Mn concentration in the water column but is rather a function of the total number of surface-binding sites available. Similarly, de Vrind et al. (1986b) showed with experimental evidence that mature spores of marine *Bacillus* SG-1 could oxidize Mn^{2+}. On the other hand, de Vrind et al. (1986a) demonstrated that vegetative cells of the same organism could reduce manganese. The reduction of Mn by the vegetative cells was thought to make Mn^{2+} available for sporulation in a manganese-limited environment. Accumulation of MnO_2 by the spore coat prevented further oxidation of bound Mn^{2+} as the active sites get masked when oxygen gets consumed and protons get liberated. In another approach, the marine *Pseudomonas* sp. Strain S-36 when grown in continuous culture was found to obtain energy for CO_2 fixation from Mn^{2+} oxidation (Kepkay and Nealson 1987).

In a different approach, Sunda and Huntsman (1987) used radiotracers to determine the kinetics of particulate Mn formation in seawater. According to them, Mn^{2+} oxidation is microbially catalyzed and the rates depend upon the increase in temperature with respect to the ratio of particulate to dissolved Mn in estuarine water. The indirect process of Mn^{2+} oxidation by *Chlorella* sp at high pH (>9.0) resulting from photosynthesis was reported by Richardson et al. (1988). They demonstrated that growth of photosynthetic organisms as aggregates or as concentrated cell suspension in pelagic waters could generate microenvironments with steep gradients of oxygen and pH conducive for Mn^{2+} oxidation. Radiotracer studies on hydrothermal vent locations showed the scavenging of Mn^{2+} at higher rates under in situ incubations compared to onboard studies (Mandernack and Tebo 1993). Their results could suggest that bacteria not only enhance the scavenging of Mn within vent waters, but also facilitated Mn deposition to the sediments. In another interesting observation by Hansel and Francis (2006), the unrecognized role of *Roseobacter* like planktonic bacteria in Mn^{2+} oxidation and cycling in coastal waters was identified suggesting an alternative means of Mn^{2+} oxidation in the photic zone. The bacterium showed the ability to oxidize Mn^{2+} in the presence of light through photooxidation pathway and by direct enzymatic action in the dark. Based on a kinetic model of the oxidative pathway, Webb et al. (2005) stated that Mn^{3+} is a transient intermediate and the rate-limiting step in the oxidation of Mn^{2+}. They suggested that oxidation of Mn^{2+} could involve a unique multicopper oxidases (MCOs) system capable of two-electron oxidation of its substrate. MCOs are a class of enzymes that have metallocentre assembly containing four Cu atoms (Brouwers et al. 2000b). They couple the four-electron reduction of dioxygen to water with the oxidation of substrate. The well-defined MCOs are laccase, ascorbate oxidase, and ceruloplasmin. The others include phenoxazinone synthase, bilirubin oxidase, dihydrogeodin oxidase, sulochrin oxidase, and FET3 (Solomon et al. 1996).

Our observation on microbially mediated Mn^{2+} oxidation in bacterial isolates belonging to *Halomonas* sp from Carlsberg Ridge (Fernandes et al. 2005) showed that Mn is precipitated extracellularly. Same isolates when grown in the presence of Ni and Co in the absence of Mn^{2+} showed the ability to accumulate these metals both intra- and extracellularly (Sujith et al. 2010; Antony et al. 2010). Further, study from the mangrove sediments Krishnan et al. (2007) offered experimental evidence to demonstrate that both autochthonous autotrophs and heterotrophs work in tandem in reducing Mn^{2+} and other related metal ions in sediments. These processes may indirectly promote more metal oxidation by removing end product inhibition.

3.7 Manganese Oxidation by Freshwater Bacteria

The Mn and Fe oxidizing/depositing bacteria in freshwater habitats belong to *Sphaerotilus*, *Gallionella*, *Leptothrix*, *Pedomicrobium*, *Metallogenium*, *Hyphomicrobium*, *Crenothrix*, *Clonothrix*, and *Cladothrix* groups (Gregory and Staley 1982; Ghiorse 1984). Based on their abundance, Pringsheim (1949) stated that their significance in biochemical processes in rivers must be great but require further investigations to know about their nutritional needs, metabolism, and enzymatic systems. Knowing the importance of Mn^{2+} oxidation by bacteria, Johnson and Stokes (1966) readily stated with experimental evidence that *Sphaerotilus discophorus* belonging to β_1 subdivision of proteobacteria could oxidize Mn^{2+} to dark-brown manganic oxide. They pointed out that cells can lose the Mn^{2+}-oxidizing activity on heating and not poisoned by treatment with $HgCl_2$ suggestive of endogenous Mn^{2+} oxidation catalyzed by an inducible enzyme(s). In continuation of the earlier study with *Sphaerotilus discophorus*, Stokes and Powers (1967) ruled out that endogenous oxidation of Mn^{2+} could be stimulated by the oxidation of poly-β-hydroxybutyrate, a storage product within the cell. Further study by Ali and Stokes (1971) could observe autotrophic growth promotion in *Sphaerotilus discophorus* with Mn^{2+} as the sole source of energy. The results were later on evaluated with evidence that in the late phase of growth, *S. discophorus* do oxidize and accumulate MnO_2 but do not serve as energy source in this organism (Hajj and Makemson 1976). Conversely, Mills and Randles (1979) using electron transport chain inhibitors in their study suggested that Mn^{2+} oxidation in *Sphaerotilus discophorus* could be cytochrome mediated.

In an another study with different Mn-oxidizing filamentous budding bacteria *Pedomicrobium* belonging to α-proteobacteria, Ghiorse and Hirsch (1978) noted that very active Mn-depositing bacterial strains are also very active iron depositors. The presence of budding bacteria in freshwater distribution systems leads to the formation of biofilms heavily encrusted with Mn oxides (Tyler and Marshall 1967; Sly et al. 1988). The depositions of Mn oxides occur in close association with an extracellular matrix of acidic polysaccharides or polymer in these bacterial strains

(Ghiorse and Hirsch 1979; Sly et al. 1990). The mechanism of Mn^{2+} oxidation was found to involve a two-step process composed of rapid binding of Mn^{2+} to EPS followed by the oxidation of Mn^{2+} by an unknown factor (Ghiorse and Hirsch 1979). Incidentally, they could identify the unusual factor, perhaps a protein responsible for Mn^{2+} oxidation associated with the polymer that could not be completely inhibited by glutaraldehyde, $HgCl_2$, or heat. Further findings using inhibitors and cellular fractionation methods (Larsen et al. 1999) showed that heat treatment of cells could enhance Mn^{2+} binding but abolish Mn-oxidizing activity. They could restore the activity of the enzyme upon the addition of Cu in the medium and suggested that Cu-dependent enzyme MCOs catalyze the Mn^{2+} oxidation in *Pedomicrobium* ACM 3067.

Jaquet et al. (1982) indicated that *Metallogenium* plays a key role in Mn cycling in Lake Leman. In contrast, Maki et al. (1987) using ^{54}Mn tracer could not find any significant difference between poisoned and non-oxygen controls in the biological Mn^{2+} oxidation and the number of *Metallogenium* morphotypes in Lake Washington. They suggested that *Metallogenium* plays only a weak role in Mn^{2+} oxidation in Lake Washington. In a discussion on the retention of Mn in the Wahnbach reservoir by bacteria, Herschel and Clasen (1998) state that *Metallogenium personatum* could be a propelling force behind microbially catalyzed transformation of Mn in the reservoir. They explained that increase in dissolved oxygen level in deep water is conducive for Mn^{2+} oxidation. In some earlier observations, Tyler and Marshall (1967) and Tyler (1970) addressed the widespread occurrence of stalked, budding bacteria *Hyphomicrobium* belonging to α-proteobacteria in Mn deposits and suggested that some *Hyphomicrobia* could preferentially oxidize Mn over Fe in hydroelectric pipelines.

In an interesting observation, Uren and Leeper (1978) stated that microbial oxidation of Mn^{2+} in soil could occur at low oxygen pressures provided CO_2 supplied is adequate. With *Arthrobacter* sp from soil, Bromfield and David (1976) had also showed that oxides of Mn could rapidly adsorb manganous ions from aqueous solutions but not in the case of abiotic control. In a kinetic study with cell free extracts of two bacterial isolates *Pseudomonas* III and *Citrobacter freundii* belonging to γ-proteobacteria, Douka (1980) identified that the rate of Mn^{2+} oxidation increased with its concentration, suggesting a strong affinity between the oxidizing system and Mn. Conversely, Chapnick et al. (1982) could show that Mn^{2+} removal from water column and oxidation in Lake Oneida during summer months are mediated by metabolically active Mn-oxidizing bacteria. They also showed that particles in lake water when removed by filtration or killed by ethanol treatment inhibit the activity. Besides, Gregory and Staley (1982) suggested that plasmids may be directly involved in Mn oxidation by providing essential gene products or may act indirectly by altering the microenvironment in a way as to make the chemical oxidation of Mn^{2+} favorable. Using in situ dialysis technique, Kepkay (1985) showed that Mn precipitation in soil could be a microbially mediated process causing a fivefold enhancement of abiotic process such as adsorption. Likewise, Vojak et al. (1985) stated that biological process could be responsible for the change in oxidation state of Mn^{2+} to Mn^{4+}. The rates of Mn^{2+}

oxidation in their study differed with increase in salinity and were depressed in the presence of inhibitors. Similarly, Johnson and Kipphut (1988) showed by in situ incubation technique, the rate of Mn^{2+} oxidation is largely microbially mediated in Toolik lake and is regulated by Mn^{2+} concentration rather than temperature or oxygen concentration. With more detailed experiment on mutants that lack the ability to oxidize Mn^{2+}, Caspi et al. (1998) stated that the Mn-oxidizing ability of *Pseudomonas putida* MnB1 can be recovered by complementation of the mutation in a c-type cytochrome biogenesis-defective mutant. In the kinetic studies on Mn uptake and oxidation by Moy et al. (2003), the uptake of Mn^{2+} by *Rhizobium* sp was greater than the conversion of Mn^{2+} to Mn oxides with significant production of polysaccharides. They suggested that polysaccharides might be involved in the uptake of Mn and in minimizing Mn oxide production. The study on redox transformation of Mn in Antarctic lakes (Krishnan et al. 2009) showed that Co could have a more profound role in Mn^{2+} oxidation and Ni on Mn oxide reduction. Although several studies report the oxidation of Mn^{2+} by bacteria, the identity of Mn-oxidizing bacteria remained undisclosed. Recently, Falamin and Pinevich (2006) determined the phylogenetic position and phenotypic properties of *Pseudomonas siderocapsa* sp.nov. They suggested a mixotrophic mode of nutrition in the strain and deposition of Mn oxides in their capsules rather than in outer membrane as observed in other *Pseudomonas* species.

As an attempt to understand the Mn-oxidizing ability of *Leptothrix discophora* SS-1 Adams and Ghiorse (1986) examined the ultrastructure of the strain by electron microscopy. They could observe extracellular blebs in cells and proposed it as vehicles for Mn-oxidizing protein. Manganese oxidation by sheathless strain of *Leptothrix discophora* SS-1 belonging to β_1 subdivision of proteobacteria (Boogerd and de Vrind 1987) in buffered medium at pH 7.5 showed the release of Mn^{2+}-oxidizing factors in the spent culture medium and was found associated with MnO_2 aggregates. Meanwhile, Adams and Ghiorse (1987) isolated the Mn^{2+}-oxidizing protein from *Leptothrix discophora* SS-1 and characterized the extracellular Mn^{2+}-oxidizing activity. The same authors in 1988 identified the oxidation states of Mn in the Mn oxide produced by *Leptothrix discophora* SS-1. They could identify that the oxidation state of Mn in fresh samples exist as Mn^{3+} and on aging give rise to a mixture of Mn (III,IV) oxides in older samples. Later, study by Corstjens et al. (1997) could identify that gene *mofA* is linked to Mn oxidation. In addition, Nelson et al. (1999) showed that Mn oxides produced by SS-1 can adsorb toxic metal lead. Moreover, Brouwers et al. (2000b) stated that being the core element in putative MCOs, Cu^{2+} could stimulate the oxidation of Mn^{2+}. Investigation on kinetics of Mn^{2+} oxidation by Zhang et al. (2002) explained that at circumneutral pH, at a relatively low numbers of Mn-oxidizing bacteria (*Leptothrix discophora* SS-1), biologically mediated Mn^{2+} oxidation exceeded abiotic oxidation. Interestingly, a recent study by El Gheriany et al. (2009) remarked that Fe is essential for efficient Mn^{2+} oxidation in *Leptothrix discophora* SS-1.

3.8 Manganese Oxidation: A Genomic Perspective

In the recent years, several studies were attempted by researchers to understand the genetics involved in bacterial Mn^{2+} oxidation. Marine bacteria are efficient Mn oxidizers; however, only few studies report the genetic mechanism(s) involved in Mn oxidation. The well-studied Mn-oxidizing bacteria is *Bacillus* sp. Strain SG-1, a marine gram-positive bacterium isolated from shallow marine sediment that produces Mn-oxidizing spores (van Wassbergen et al. 1993, 1996; Francis et al. 2002; Francis and Tebo 2002). This is the only organism for which the direct involvement of MCOs in Mn oxidation is established. They proposed MnxG as one of the first gene products ever shown to be associated with the exosporium possessing oxidase activity. Francis et al. (2002) demonstrated that MnxG is localized to the exosporium of wild-type spores and is absent in the nonoxidizing spores of transposon mutants within the *mnx* gene cluster. Dick et al. (2006) based on phylogenetic analysis of 16S rRNA and *mnxG* genes explained that Mn-oxidizing *Bacillus* sp isolated from Guaymas Basin resembled deep-sea isolates reported earlier from coastal sediments, with few representing novel strains and clusters. Recently, Mayhew et al. (2008) proposed that vertical inheritance and gene loss influenced the distribution of the gene *mnxG* among the *Bacillus* sp.

For the first time, van Waasbergen et al. (1993) identified the genes involved in Mn^{2+} oxidation. They demonstrated that *mnx* region encodes factors that are required for oxidation of Mn^{2+} by SG-1 spores by protoplast transformation and mutagenesis. Later, van Waasbergen et al. (1996) suggested that among the several genes (*mnxA* to *mnxG*) that were earlier proposed to be involved in Mn^{2+} oxidation, the *mnxG* gene product may function like a copper oxidase and would be directly responsible for the oxidation of Mn^{2+} by the bacterial spores. The first direct evidence for the presence of RubisCo genes in a gram-negative Mn-oxidizing bacterium strain S185-9A1 was given by Caspi et al. (1996). The genes were more related to those from non-chlorophyte algal chloroplasts than from bacteria. Dick et al. (2008b) suggested that MnxG catalyzes two sequential one-electron oxidations from Mn^{2+} to Mn^{3+} and from Mn^{3+} to Mn^{4+}, a novel type of reaction for a multicopper oxidase.

Aurantimonas manganoxydans Strain. SI85-9A1 (Dick et al. 2008a, Anderson et al. 2009a, b) and *Erythrobacter* sp Strain. SD-21 (Anderson et al. 2009b) are the two other marine Mn-oxidizing α-proteobacteria known to oxidize Mn^{2+} that have been recently studied in detail. Anderson et al. (2009b) identified five annotated MCOs in the genome sequence of the above strains but none of the MCOs were reported to have any role in Mn^{2+} oxidation. In contrast, they could illustrate the role of heme peroxidase in Mn^{2+} oxidation and tentatively suggested MopA for the putative Ca^{2+} binding heme peroxidase.

Leptothrix discophora SS-1 a freshwater bacterial species that deposits Mn oxides on its extracellular sheath was studied in detail by Corstjens et al. (1997) and Brouwers et al. (2000a) using sophisticated molecular tools. Based on the results, they proposed that MCOs like gene *mofA* (manganese-oxidizing factor) to be involved in Mn^{2+} oxidation and genes *mofB* and *mofC* to be a part of the same

mofA operon. At the same time, Siering and Ghiorse (1997b) by variable stringency hybridization analysis using digoxigenin-labelled mofA probe of *Leptothrix discophorora* SS-1 showed that Mn-oxidation genes of other *Leptothrix* spp were closely related to one another but were not homologous to the unidentified presumptive Mn oxidation genes from other genera. In the meanwhile, Siering and Ghiorse (1997a) could detect sheathed bacteria (*Leptothrix* spp) in environmental samples based on their designed 16S rRNA-targeted specific probes and proposed its applications in further research.

The other common bacterial genera known for Mn^{2+} oxidation are *Pseudomonas putida* Strains MnB1 and GB-1. There are several reports (Caspi et al. 1996; Caspi et al. 1998; Brouwers et al. 1999; de Vrind et al. 2003) that describe the Mn-oxidizing ability of these strains. But only few (Brouwers et al. 1999, 2000a) attempts have been made to understand the genetic mechanisms involved in Mn^{2+} oxidation. They could identify by molecular analysis that gene *cumA* (copper protein involved in Mn oxidation) participates with MCOs in Mn^{2+} oxidation and *cumB* for optimal growth. Later, Francis and Tebo (2001) surprisingly observed highly conserved *cumA* gene sequences in non-Mn-oxidizing *Pseudomonas* strains. Based on the results, they suggested that *cumA* gene may not be expressed or that it may not be the only gene to confer the ability to oxidize Mn^{2+}. Conversely, they could exert an alternative function in these organisms and the gene could occur in phylogenetically diverse *Pseudomonas* strains.

Pedomicrobium sp. ACM3067 another aquatic bacteria could oxidize Mn^{2+} in close association with an extracellular matrix of acidic polysaccharides or polymer (Ghiorse and Hirsch 1979). Further, understanding about the mechanism involved in Mn^{2+} oxidation (Larsen et al. 1999) showed that Mn^{2+} oxidation is catalyzed by a copper-dependent enzyme in *Pedomicrobium* sp. ACM3067. Recent study by Ridge et al. (2007) provided evidence that *moxA* gene encoding a MCO homolog is essential for both Mn^{2+} oxidation and laccase-like activity in *Pedomicrobium* sp. ACM3067.

Mn-oxidizing genus *Hypomicrobium* is less probed at genetic level. Only one study by Layton et al. (2000) recorded the abundance of *Hypomicrobium* populations in activated sludge based on 16S rRNA analysis. About 5% of 16S rRNA in activated sludge corresponded to *Hypomicrobium* sp. Gregory and Staley (1982) showed experimental evidence that Mn^{2+}-oxidizing ability in the bacterial isolates was lost when maintained in the absence of the metal in the laboratory. They hypothesized that Mn oxidation may be directly related to the presence of plasmids.

3.9 Manganese Oxidation: A Proteomic Perspective

Metal ion efflux systems are central to cellular physiology. The uptake of Mn in bacteria occurs through (1) P-type ATPase (MntA) (Hao et al. 1999), (2) metal binding protein-dependent ABC transport system: Group PsaA, (3) pH-dependent

metal ion transporter: MntH Groups A, B, C, and (4) natural resistance-associated macrophage protein (NRAMP) family (Jakubovics and Jenkinson 2001; Cellier 2002; Papp-Wallace and Maguire 2006). Metallochaperones are responsible for the incorporation of correct metal into some of the proteins; however, most metalloproteins acquire their metals directly from cellular pools. In an attempt to understand the cellular mechanisms that govern metal acquisition by most nascent proteins, Tottey et al. (2008) identified the most abundant Cu^{2+}-protein, CucA and the most abundant Mn^{2+}-protein, MncA in the periplasm of cyanobacteria *Synechocystis* PCC 6803. They showed that compartmentalization kept competitive metals out of the wrong nascent proteins during protein folding.

The only Mn-oxidizing proteins identified and characterized so far in bacteria were the MCOs (Brouwers et al. 2000b; Francis and Tebo 2000). Another class of proteins in bacteria rarely known to oxidize Mn is the heme-containing manganese peroxidases (MNPs) (Palma et al. 2000; Anderson et al. 2009b). The known Mn-oxidizing proteins include the MnxG (~138 kDa) of *Bacillus* SG-1 (van Wassbergen et al. 1996; Francis et al. 2002) and MopA of *Aurantimonas manganoxidans* Strain. SI85-9A1 and *Erythrobacter* sp Strain. SD-21[Anderson et al. (2009b)]. In marine α-Proteobacterium SD-21, manganese-oxidizing factors of ≈250 and 150 kDa was observed in the logarithmic phase of growth. However, the expression of Mn(II) oxidase was not completely dependent on Mn^{2+} rather it was required for higher growth yield (Francis et al. 2001). They claimed it as the first group of Mn-containing metalloenzyme in gram-negative marine bacteria. Francis and Tebo (2002) could identify the first active Mn-oxidizing enzymes in spores or gram-positive bacteria. Their study came across proteins of different molecular weights in Mn-oxidizing marine *Bacillus* sp isolated from coastal marine sediment. Based on the inhibition of Mn-oxidizing activity by azide a multicopper oxidase inhibitor suggested that the unidentified proteins belong to the MCO group of enzymes. The role of metalloregulatory protein MntR, a transcriptional regulator of Mn homeostasis, was determined by Lieser et al. (2003). They demonstrated that differences in metal-activated DNA binding could play a role in the mechanism of Mn(II)-selective transcription of factors and the oligomerization of MntR that was metal independent. Further, Huang and Wu (2004) revealed the identity of the genes under control of manganese response regulator ManR in the cyanobacterium, *Anabaena* sp. PCC 7120.

The known Mn-oxidizing proteins include the CumA (50.5 kDa) of *Pseudomonas putida* GB-1 (Brouwers et al. 1999), MofA (~180 kD) of *Leptothrix discophora* SS-1 (Corstjens et al. 1997; Brouwers et al. 2000a), and MoxA (52.47 kDa) of *Pedomicrobium* sp. ACM3067 (Ridge et al. 2007). Several regulatory pathways for Mn in bacteria were investigated by different authors. Que and Helmann (2000), Guedon et al. (2003), and Moore and Helmann (2005) found that MntR, Fur, TnrA, and σ^B regulons regulated Mn uptake in *Bacillus subtilis*. Platero et al. (2004) stated that Fur was involved in manganese-dependent regulation of *mntA*. Patzer and Hantke (2001) and Hohle and O'Brian (2009) provided evidence to show that *mntH* gene encoding NRAMP like Mn^{2+} transporter was repressed by Fur and MntR of the *mntH* gene. Conversely, Kehres et al. (2000) inferred that NRAMP

proteins are selective Mn transporters involved in response to reactive oxygen. Diaz-Mireles et al. (2004) affirmed that Fur-like protein Mur (manganese uptake regulator), a Mn^{2+}-responsive transcriptional regulator of *Rhizobium leguminosarum*, differs from Fur that binds Fe^{2+} in γ-proteobacteria and engage in Mn uptake. Groot et al. (2005) identified the expression of three putative Mn transport systems (*mtsCBA*, *mntH1*, *and mntH2*) besides *mntA* in *Lactobacillus plantarum*. They observed the specific derepression or induction of transport systems upon Mn^{2+} limitation, suggesting their role in Mn^{2+} homeostasis. Subsequently, Jakubovics and Valentine (2009) identified the novel Mn^{2+} efflux system MntE in *Streptococcus pneumoniae*. They stated that disruption of the *mntE* gene could lead to widespread transcriptional changes that are distinct from responses to extracellular Mn^{2+}.

The expression of 25 kDa cytoplasmic protein was identified as superoxide dismutase isoenzyme (Mn-SOD) in *Arthrobacter* sp (Ercole et al. 1999). The functioning of the protein under both aerobic and anaerobic conditions in the presence of Mn oxide was found to have additional physiological function. The higher-molecular-weight surface protein (30 kDa) showed no homology with any of the identified proteins and its function is yet to be identified. Jung and Schweisfurth (1979) observed that *Pseudomonas* sp. Strain MnB1 produced a heat labile intracellular Mn-oxidizing protein during stationary phase of growth. Mn-oxidizing protein was not induced by the presence of Mn^{2+}, rather it was particularly dependent on the age of the culture. Likewise, in a comparative study on Mn oxidation using growing and resting cells of a freshwater bacterial isolate strain FMn 1, Zapkin and Ehrlich (1983) observed enzymatic nature of Mn-oxidizing activity in the strain. The activity of the enzyme was inducible. In a review, Shi (2004) stated that protein phosphatases are metalloenzymes with active centers containing two metal ions functioning as cofactors. The Mn-dependent prokaryotic protein O-phosphatases and their function were stated to add new insight into Mn^{2+} homeostasis and protein O-phosphorylation in prokaryotic cells.

3.10 Molecular Biomineralization

Organisms are capable of forming a diverse array of minerals, some of which cannot be formed inorganically in the biosphere. Biogenic minerals may be amorphous, paracrystalline, or crystalline (Lowenstam 1981). The mineralization processes driven by biological activity involving microorganisms constitute biomineralization (Wang and Müller 2009). The microorganisms and their interaction with geologic materials result in geochemical transformations switching between soluble and insoluble phases (White et al. 1997). As a result of close interaction between mineral and bacteria, biomineralization co-occur (Fig. 3.1). It can lead to precipitation of the metal leachate and formation of metal oxide coatings on bacterial wall and other inert surfaces contributing directly as

nucleation sites for further mineral formation (Fortin et al. 1995). Microorganisms interact with minerals for creating a more hospitable surrounding by extraction of nutrients and sequestration of toxic substances. Microbes use minerals as sources and sinks of electrons, for coupled oxidation–reduction reactions. Many of these reactions enable the release and capture of energy from unstable or metastable minerals (Shock 2009). Deep-sea minerals in polymetallic nodules, Fe–Mn crusts, and hydrothermal vents are not only formed by abiogenic mineralization but also by free-living and biofilm-forming bacteria which form matrix for Mn deposition. Here the mineralization processes proceed in close association with organic molecules or matrices. It can be an either induced (biological–chemical) or a controlled (enzymatic) process and the details of the processes and the references have been described by Wang and Müller (2009). Besides, in order to understand the biogeochemical phenomena occurring in the Mn-rich marine environments, several microbiological studies have focused on hydrothermal vents and Fe–Mn encrusted seamounts in the recent years (Davis et al. 2009; Emerson 2009; Glazer and Rouxel 2009; Rassa et al. 2009; Sudek et al. 2009). Few extended their research on biologically induced mineralization (Douglas and Beveridge 1998; Wang et al. 2009a, b; Dong 2010). Wang et al. (2009b) examined the biogenic components of the crust and He et al. (2008) examined the microbial community composition of Iron–Manganese nodules using sophisticated analytical tools. They found acidobacteria and proteobacteria in nodules and associated sediments. The firmicutes were restricted to nodules and the soils had more acidobacteria and Verrucomicrobia compared to nodules. Advancement in element-specific mapping of rock surfaces revealed hot spots of Mn accumulation in microbial biofilms (Templeton and Knowles 2009).

The mineral phases produced by bacteria are mostly amorphous and sometimes poorly crystalline. The crystallization process occurs with prolonged incubation time (Tazaki 2005) and the characteristic oxides thus produced are not identical to known synthetic solids possibly, because of solid-phase incorporation of biomolecular constituents (Parikh and Chorover 2005). It is observed that surficial proteins associate with Mn oxidation during the production of a poorly crystalline Mn(IV) phase. The formation of mixed phase minerals like hausmannite (Mn_3O_4), feiknechtite (β-MnOOH), manganite (γ-MnOOH), and Na-buserite following Mn (II) oxidation by *Bacillus* SG-1 was reported by Mann et al. (1988) and Mandernack et al. (1995). Whereas, a todorokite-like mineral was found to be produced by *Leptothrix discophora* Strain SP-6 (Kim et al. 2003) and MnOx produced by *Pseudomonas putida* Strain MnB1 was most similar to "acid" birnessite (Villalobos et al. 2003). Recent understanding about the genes and proteins involved in Mn oxidation help to spread its application in biotechnology. The gene *mnxG* responsible for Mn oxidation in Bacillus SG-1 (van Wassbergen et al. 1996), *cumA* in *Pseudomonas putida* GB-1 (Brouwers et al. 1999), *mofA* in *Leptothrix discophora* SS-1 (Corstjens et al. 1997; Brouwers et al. 2000a), *moxA* in *Pedomicrobium* sp. ACM3067 (Ridge et al. 2007), and *mopA* in *Aurantimonas manganoxidans* Strain. SI85-9A1 and *Erythrobacter* sp Strain. SD-21 (Anderson et al. 2009b) could be cloned and the products expressed under laboratory condition.

3.11 Biotechnological Applications of Manganese Oxidation

Manganese, a comparatively less toxic element, can become toxic to domestic and aquatic lives when its concentration exceeds beyond the EPA permissible levels (0.05 mg L^{-1}). During summer, it is observed that Mn oxides undergo reduction when the oxygen level drops in public and private wells, municipal water supplies, etc. The solubilized Mn is quite stable in the presence of oxygen and therefore can become a health risk for public who consumes the drinking water. The Mn-oxidizing bacterial residents of the Mn^{2+}-rich environments can oxidize Mn^{2+} and reduce its solubility and thereby provide protective mechanism against toxic levels of soluble Mn (Bromfield 1978). An application of Mn oxidizers or their products to such habitats offer chemical/biological solution to the problem on a seasonal/permanent basis (Czekalla et al. 1985). Mn oxides are also excellent electron acceptors for anaerobic respiration (Nealson et al. 1989). The application of Mn-oxidizing bacteria and Mn in sedimentary environments can stimulate respiratory carbon mineralization and could offer a natural system of "Pumping" (via precipitation and sedimentation of Mn oxides) electron-acceptor equivalents into an anaerobic environment (Nealson et al. 1989). It is observed that Mn oxides are potent chelators of several other trace metals, their application has proved to be efficient in the removal of radium from water supplies (Moore and Reid 1973), in retaining heavy metals like Co, Ni, Zn, and others in soil, polymerization of organic compounds, participation in humus formation by oxidation of phenols and quinines (Vodyanitskii 2009).

The removal of Mn^{2+} is conventionally achieved by inorganic oxidation such as chlorination or permanganate oxidation, followed by sand filtration (Miyata et al. 2007). In 1986, Ghiorse proposed the exploitation of Mn-precipitating microorganisms for industrial metal recovery processes. The use of Mn-oxidizing bacteria in treating effluents can minimize the addition of chemical reagents and unwanted by-product formation. The increase in filtration rate and longer runs due to less clogging, savings on wash water, and rapid return to equilibrium following a backwash sequence reduce the operational cost in treatment and maintenance of sludge in biological effluent treatment (Mouchet 1992; Katsoyiannis and Zouboulis 2004; Stembal et al. 2005). The biological processes take advantage of active and passive process in treatment by a variety of mechanisms like adsorption, accumulation, precipitation, and oxidation. The drawback of using bacteria for treating effluent biotechnologically is the slow rate of Mn oxidation. As an early solution to the problem, Stuetz et al. (1996) proposed the usage of combined algal–bacterial Mn oxidation and optimization of bioreactor parameters for treating metal effluents effectively. When using Mn oxide (scavengers of the environment) for treatment of any effluents with unknown composition, precaution needs to be taken as it is known that sometimes interaction of Mn oxide with other elements can result in phase transformations [Se(IV) to Se(VI), Cr(III) to Cr(VI), and As(III) to As(V)], contributing to increase/decrease in metal toxicity (Vodyanitskii 2009; He et al. 2010).

Recent advancement in the understanding of microbial Mn oxidation provides insight into the mechanisms of metal oxidation and the processes involved. This oxidation proceeds at rates up to five orders of magnitude greater than abiotic oxidation (Tebo et al. 1997). The Mn oxides produced by microorganisms are abundant environmental nanoparticles, they have great importance in biotechnology for the removal of heavy metals from aqueous matrices and oxidation of organic micropollutants in wastewater treatment plants (Villalobos et al. 2005b). The higher specific surface area of negatively charged biogenic Mn oxides than synthetic d-MnO_2 and commercially available pyrolusite allow greater sorption of positively charged heavy metals in solution (Hennebel et al. 2009). The bacterial spores from a potent Mn-oxidizing bacteria *Bacillus* sp. SG-1 have found extensive capacity for actively binding and oxidizing Mn and passively binding other metals. Likewise, Mn-oxidizing protein from *Pseudomonas putida* Strains MnB1 and GB-1 as well as sheath of *Leptothrix discophora* is found to have similar function (Francis and Tebo 1999). It was observed by Nelson et al. (2002); Villalobos et al. (2005a) that Mn oxides produced by Leptothrix *discophora* SS-1 and *Pseudomonas putida* MnB1 can adsorb five times more Pb per mole of Mn than abiotic Mn(IV) (hydr) oxide and 500–5,000 times more than pyrolusite oxides, thus stimulating interest in the development of Mn oxides for use in bioremediation. Likewise, Toner et al. (2006) observed a tenfold higher capacity for biogenic Mn oxides in adsorbing Zn than chemically synthesized Mn oxides, and Murray and Tebo (2007) detected seven times higher adsorption of Cr in biogenic Mn oxides produced by *Bacillus* sp. SG-1 than synthetic d-MnO_2. The utilization of these microorganisms in concentrating metal ions from effluents will have intense application in biotechnology for treatment of wastewaters and metal-containing effluents.

It has also been observed recently that biogenic Mn oxides can oxidize 17a-Ethinylestradiol, a potent endocrine-disrupting recalcitrant, and reduce its estrogenic activity to 81.7% (de Rudder et al. 2004). In another recent observation, Forrez et al. (2010) have shown that biogenic Mn oxides can oxidize diclofenac, a nonsteroidal anti-inflammatory drug and can reduce its lethal concentration and toxicity. Similar observations made for triclosan (Zhang and Huang 2003) and ciprofloxacin (Zhang and Huang 2005) with biogenic Mn oxides suggest that biogenic manganese oxide can be a promising polishing technique for sewage treatment plant effluents.

3.12 Conclusion

The current understanding about bacterial Mn oxidation comprises the participation of MCOs, but their direct link to oxidation is emphasized only in *Bacillus* SG-1 and not in other organisms like *Pseudomonas putida* MnB1, GB1, *Leptothrix discophora* SS1, or *Pedomicrobium* sp. ACM3067. The various regulatory mechanisms and transport systems for Mn uptake in bacterial cells are studied but the role of metalloproteins in Mn oxidation or how the proteins select the right

metal when competitive metal ions are in excess is still not fully understood. What is known at present is that the compartmentalization of protein during folding regulates the binding of correct metal. Therefore, the production and utilization of biogenic Mn oxide nanoparticle in biotechnology requires further understanding about the molecular mechanism of Mn oxidation.

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