FEMS Microbiology Reviews 14 (1994) 339-350
© 1994 Federation of European Microbiological Societies 0168-6445/94/$26.00
Published by Elsevier

FEMSRE 00411

Microbial oxidation and reduction of manganese: Consequences in groundwater and applications

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Abstract: In the natural environment, manganese is found as reduced soluble or adsorbed Mn(II) and insoluble Mn(III) and Mn(IV) oxides. Mn oxidation has been reported in various microorganisms. Several possible pathways, indirect or direct, have been proposed. A wider variety of Mn-reducing microorganisms, from highly aerobic to strictly anaerobic, has been described. The mechanisms of Mn reduction can be either an indirect process resulting from interactions with organic or inorganic compounds, or a direct enzymatic (electron-transfer) reaction. The role of microorganisms in Mn cycle is now well demonstrated by various methods in superficial natural environments, and research has been initiated on subsurface sediments. Observations in vivo (Rhône valley) and under in vitro suggested that bacterial activities are the main processes that promote manganese evolution and migration in shallow aquifers. After the building of hydroelectric dams, the stream of the Rhône was modified, giving rise to mud deposition on the bank. In the mud, bacteria are stimulated by the high organic content and consume oxygen. The redox potential drops. The manganese oxides previously formed under aerobic conditions are reduced and soluble manganese (Mn(II)) migrates into the aquifer. If the subsurface sediments are coarse-grained, the aquifer is well aerated, allowing the re-oxidation of Mn(II) by the oligotrophic attached bacteria in aquifer sediments. If the aquifer is confined, aeration is not sufficient for Mn-reoxidation. Mn(II) remains in a reduced state and migrates to the wells. Furthermore, the presence of organic matter in subsurface sediments results in the reduction of previously formed Mn oxides. Pseudo-amorphous manganese oxides, which were probably recently formed by bacteria, are more readily reduced than old crystalline manganese oxides. Although the concentrations of soluble manganese found in groundwaters are not toxic, it still is a problem since its oxidation results in darkening of water and plugging of pipes in drinking or industrial water systems. Soluble manganese can be removed from water by biological processes involving manganese-oxidizing bacteria, either in situ, or in sand filters after pumping. Various procedures are mentioned.

Key words: Manganese; Oxidation; Reduction; Groundwater

Introduction

Manganese is the fifth most abundant metal on the surface of the earth. It is an essential trace element and is involved in many enzymatic reactions, especially those associated with oxygen (e.g. photosynthesis, oxygen protection via Mn-superoxide dismutase activity) [1,2]. Furthermore, many different microorganisms, including bacteria, algae, yeast, and fungi, can either oxidize Mn(II) or reduce Mn(III) or Mn(IV) oxides [3-8]. It is now well established that microorganisms are, either directly or indirectly, the major catalysts of manganese cycling in the natural environment [2,4,5,7,8]. The purpose of this review is to summarize the present knowledge on the mechanisms of bacterial manganese oxidation or reduction and their occurrence in the natural environment. The

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SSDI 0168-6445(94)00013-O

consequence of these microbial activities are illustrated in the subsurface environment. Present and future biotechnological applications are mentioned.

Mechanisms of microbial oxidation and reduction of manganese

The chemistry of manganese is very complex, particularly in soil and sediments [3,9,10]. Although the oxidation of Mn(II) to either Mn(III) or Mn(IV) is thermodynamically favoured at neutral pH and atmospheric oxygen levels, the activation energy for Mn(II) oxidation is high and the process is normally very slow. The stable oxide phase in water is MnO_2 but Mn(III) and Mn(IV) give a variety of oxides and hydroxides often named MnO_x with $1 < x < 2$. The higher oxides exist in several crystalline or pseudocrystalline states. Mn(II) also readily binds to a variety of different solids, including Mn oxides, resulting in an overestimation of Mn oxides in particulate phase [11]. Furthermore, as Mn(II) is bound to Mn oxide surfaces, the rate of oxidation of the bound Mn(II) is increased relative to Mn(II) in solution. Additionally, Mn(II) can be precipitated without oxidation as carbonate [12], phosphate, or complexed with organic matter [3]. All these difficulties pose major problems in the measurement and understanding of the mechanisms of biological oxidation and reduction.

These mechanisms are studied by several methods: e.g. isolation of active bacteria, microscopic observations, chemical analyses and measurements of oxidation rates, use of a radioactive manganese isotope and various inhibitors of bacterial metabolism. Mn oxidation was the first to be observed. It is now less studied than Mn reduction which recently generated a significant number of studies.

Mn oxidation

Mn oxidation has been reported in a variety of microorganisms: bacteria, fungi, and algae [4]. Most of them are bacteria belonging to group of sheathed bacteria, *Leptothrix*; budding and appendaged bacteria, *Pedomicrobium, Hyphomicrobium, Caulobacter*; or common Gram-positive or Gram-negative bacteria, e.g. *Arthrobacter, Micrococcus, Bacillus, Chromobacterium, Pseudomonas, Vibrio, Oceanospirillum*. The taxonomic validity of *Siderocapsa* is not clear, and *Metallogenium* could be an artefact.

Several possible pathways have been proposed for Mn oxidation (reviewed in [2,4,6,7]). The mechanisms can be operationally described as indirect or direct.

Indirect oxidation may result from the production of hydrogen peroxide [12,13], free radical or oxidant [14]. Mn oxidation via the production of hydrogen peroxide, found among several groups of bacteria (e.g. *Arthrobacter, Leptothrix*), is thought to protect cells from the harmful effect of hydrogen produced by the cells themselves [4,13,14]. Mn oxidation by cyanobacteria was demonstrated by the presence of microgradients of both oxygen and pH around clumps of phytoplankton [2].

Direct oxidation is an enzymatic reaction catalyzed by Mn binding and oxidizing proteins found in crude or purified extracts.

A spore protein of *Bacillus* SG-1 [16] and an intracellular protein of a *Pseudomonas* sp. [17] have been implicated as Mn binding and oxidizing proteins.

An extracellular active protein from *Leptothrix discophora* that has lost its organized sheath has been isolated [18,19]. It is perhaps a component of the sheath in the wild-type parent. Probably two different factors are involved in manganese and iron oxidation [20,21].

It was suggested that other proteins [2], exopolysaccharides [2,4,9], or cell wall components [22], that bind Mn(II), may be significant nucleating sites for Mn oxidation. Attachment of bacteria may favour Mn fixation and oxidation [23]. Both attachment and polymer formation may play a role in budding bacteria with appendages (*Caulobacter, Pedomicrobium, Hyphomicrobium*) [24–27].

Little is known about the mineralogy of Mn oxide precipitates due to bacterial activity. They usually have an amorphous structure [3]. Mn oxide formed in an enrichment culture from lake water resembles vernadite δ-MnO_2 [28]. The morphology of the manganese oxides formed by spores of different *Bacillus* spp. and sheathed *Leptothrix* has features similar to vernadite δ-MnO_2 [2]. An amorphous Mn oxide was observed on the spore coats of a marine *Bacillus* sp., which recrystallizes to hausmannite (Mn_3O_4) [29,30].

A microalga, *Chlamydomonas* forms manganite (γMnOOH) but *Pseudomonas* sp. associated with the alga was found to be primarily responsible for formation of a Mn-disordered precipitate (γMnO_2) [31]. Precipitates of amorphous Mn oxide were formed in sand filters of a rapid filtration treatment plant (where *Leptothrix* were abundant) [32]. However, Mn oxide birnessite was identified in black precipitates formed in a slow sand filtration plant [33].

Very few studies have been reported on the genetics of Mn oxidation. Plasmids associated with Mn depositing activity have been reported [34–36], but no plasmid has been found in *Leptothrix* [4]. In a marine *Pseudomonas* sp., a plasmid involved in enzymatic manganese oxidation encodes heavy metal resistance [36]. Since different mechanisms are possible for Mn oxidation, it is unlikely that a common genetic determinant exists. It was suggested that different types of Mn-oxidizing systems may have independently arisen many times in the course of evolution [6]. Oxidizing activity was frequently lost in liquid subcultures of bacteria ([5]; and personal observations). Whether it is the consequence of the loss of a specific gene (in a plasmid?), or the lack of favourable conditions for induction of synthesis of a specific protein or exopolymer catalyzing Mn oxidation, is not known.

The biological significance of Mn oxidation is not well understood. There is some evidence that oxidation of Mn(II) may be a protective mechanism against Mn toxicity [4] or more likely against oxidant toxicity [4,13–15]. In spite of some observations on marine bacteria [37] there is no unequivocal evidence that Mn is used as an inorganic energy source for autotrophic or mixotrophic growth [4,6].

Mn reduction

The existence of microorganisms that can reduce Mn or Fe-oxides has been known for nearly a century. A wide variety of Mn-reducers from highly aerobic bacteria or fungi to strictly anaerobic bacteria have been described [5,7,8]. Nealson and Myers [38] isolated from various environments over 200 strains of manganese reducers consisting of a wide variety of different taxa, including *Pseudomonas* spp., *Bacillus* spp. and many others. They may be more ubiquitous in the biosphere than those capable of Mn oxidation. Most of the reports relate to Fe reduction. Fe-reducers often reduce Mn oxides but the mechanisms may be different.

As with manganese oxidation, mechanisms of manganese reduction are direct or indirect processes (reviewed in [5–8]).

Mn oxide reduction frequently results from a drop of pH and/or redox potential due to bacterial metabolism [39].

Mn(IV) can be reduced by inorganic or organic reductants produced by microorganisms. Mn(IV) reduction by hydrogen peroxide, H_2O_2, was demonstrated by Dubinina [13,14], and by Ghiorse and Ehrlich in a *Bacillus* strain [40] but H_2O_2 production is restricted to environments with molecular oxygen, like soils.

Nitrite-mediated chemical reduction of Mn oxide was demonstrated [8] even at near neutral pH values [41].

Mn oxides are reduced by sulphide [6,8,42]. Any bacterium (e.g. *Desulfovibrio*) that generates free sulphide as an end product of dissimilatory reduction of sulphur compounds is a potential Mn-reducing organism. This mechanism would be confined to anaerobic zones, especially in marine environments containing sulphate. In addition, all bacteria that reductively disproportionate thiosulphate to sulphite and sulphide can reduce MnO_2.

Ferrous iron is a reductant of Mn(IV) oxides [43,44]. Thus, iron-reducing bacteria are potentially Mn reducing, and Fe^{2+} and sulphide do not accumulate if Mn oxides are present in the environment.

Methane oxidation can be coupled with Mn oxide reduction under anaerobic conditions [45].

Nearly all organic acids tested catalyzed Mn reduction at pH values of 5 or less, or even at neutral pH [6,8,46].

It is often difficult to distinguish between indirect or direct Mn reduction. One-hundred strains were isolated from subsurface sediments and tested for their ability to reduce manganese oxides [32,47]. Eighty-one strains reduced manganese. In most cases the bacterial activity decreased the pH and E_h values below 6.75 and 350 mV, respectively, enhancing an indirect reduction of manganese. However, with 12 strains, the reduction occurred at high pH and E_h values which would not permit a spontaneous reduction of manganese. Some of the most active strains were identified as *Pseudomonas, Bacillus, Corynebacterium* and *Acinetobacter*. Two strains were studied in detail. One of the strains, identified as *Acinetobacter johnsonii*, catalyzed manganese reduction by a dialyzable substance (molecular mass cutoff 12000) which was excreted by the bacteria. It was only produced in the presence of manganese oxides. The other strain, identified as *Pseudomonas fluorescens*, required contact between the cells and the manganese oxides for reduction to occur and the reduction was inhibited by 15 mM sodium azide. Further investigations are needed to support the hypothesis that manganese reduction is linked to the electron transport chain.

Direct reduction was postulated by Ehrlich [48], but its demonstration was not clear until recently. It entailed many technical difficulties. Unlike nitrate or sulphate, Mn(IV) oxide is a solid that cannot diffuse through bacterial envelopes. Its direct reduction might require the microorganism to be able to solubilize this solid substrate or to attach tightly to itself for direct transfer of electrons. The presence of the Mn^{2+}/MnO_2 couple results in interference with the redox potential regulation, protein and growth measurements, and disrupts the use of some respiratory inhibitors. The possible excretion of reducing metabolites must always be taken into account.

Enzymatic Mn(IV) reduction was demonstrated in cell extracts of *Acinetobacter calcoaceticus* [49]. It is not clear whether Mn(IV) is reduced by the assimilatory nitrate reductase or a distinct Mn(IV) reductase [8].

Dissimilatory Mn(IV) reduction can be defined as the use of Mn(IV) as an external electron acceptor in metabolism, coupled to organic matter oxidation either in fermentation or in anaerobic respiration.

Electron transport of Mn(IV) has been investigated in *Bacillus* spp. [5] and several other bacteria. Rusin et al. [50] isolated a manganese-reducing *Bacillus polymyxa* strain D1 from a manganiferous silver ore, that uses Mn as an electron acceptor during anaerobic fermentation. Both anaerobic conditions and direct physical contact with MnO_2 particles were necessary for Mn reduction which was three to five times as rapid as with *Shewanella putrefaciens* strains. However, it is was suggested that Mn(IV) reduction is a minor side reaction in the metabolism of these organisms [8].

Recently the existence of organisms that could couple anaerobic respiration-linked manganese reduction to organic carbon oxidation or growth was demonstrated in two bacterial taxa: an obligate anaerobe GS-15, later named *Geobacter metallireducens* [51] and two organisms identified as *Shewanella* (formerly *Alteromonas*) *putrefaciens*, a facultative anaerobe and obligate respirer [6,8,38,52]. *Shewanella putrefaciens* MR-1 can reduce Mn(IV) but also reduces Fe(III), sulphite and thiosulphate, resulting in an indirect Mn reduction by sulphide or Fe^{2+}. The coupling of metal reduction with oxidation of a non-fermentative carbon source like lactate showed that there is actually an anaerobic respiration. The existence of a specific Mn reductase was demonstrated in mutants lacking nitrate-reductase and Fe(III) reductase. MnO_2 and Fe(III) reduction was inhibited by oxygen and abolished by the presence of a protonophore or an electron transport inhibitor [38].

The reduction rate depends on the mineralogy of Mn oxides [8]. Pseudo-amorphous Mn oxides were preferentially reduced by a strain of *Pseudomonas* sp. whereas the oxides included in a crystalline structure were not or only slightly attacked [53,54]. Di Ruggiero [32] compared the reduction of a commercial Mn oxide (characterized as pyrolusite) and Mn oxides prepared in the laboratory, which were partly amorphous. With an enrichment culture from sediment, she found that amorphous Mn oxide was more rapidly reduced than crystalline MnO_2. *Bacillus polymyxa* strain D1 reduces rapidly pyrolusite (β-MnO_2) [50]. Burdige et al. [55] demonstrated that the strain *Shewanella putrefaciens* MR-1 reduced the highly crystalline β-MnO_2 (pyrolusite) at a slower rate than the amorphous ∂-MnO_2 (vernadite) or Mg-birnessite. They postulated that this result may be due to the difference in the available surface area of the amorphous phases relative to the crystalline pyrolusite. In contrast, identical rates of manganese reduction were observed with an enrichment culture from sediment.

Conclusion

Manganese oxidation by bacteria may be direct or indirect but it is difficult to distinguish between direct or indirect mechanisms and the biological significance of Mn oxidation is not clearly understood. Furthermore, Mn oxidation or reduction may be performed by the same bacteria [56,57]. In natural environments where there are large fluctuations of oxygen availability, Mn oxides accumulated under aerobic conditions could be used for anaerobic respiration when oxygen is missing as suggested for *Bacillus* [2].

Indirect manganese reduction by bacteria is easily explained by spontaneous chemical reactions that are a consequence of bacterial metabolism. Direct electron transport to Mn(IV) can provide energy for growth.

Biogeochemistry of manganese in natural environment

Environmental significance of microbial activity in manganese cycle

The role of microorganisms in the Mn cycle in natural environments has long been suspected. Now it is well demonstrated in marine water and sediment, deep hydrothermal plumes, fjords and estuaries, stratified lakes, streams and swamps as well as in normal or flooded soils [2,4,7,8,58].

Field studies were driven by the microbiological laboratory data as well as geochemical data: high numbers of Mn(II)-oxidizing bacteria, microscopical analyses of natural precipitates, Mn(II) oxidation rates too rapid to be accounted for by chemical oxidation, use of radioactive ^{54}Mn(II) as tracer, and use of poisons, fixatives, inhibitors, antibiotics to separate biological from chemical Mn(II) oxidation [2]. The same approaches were developed for studies on Mn(IV) reduction [8]. Laboratory and field data make a very strong case for the importance of microorganisms in the regulation of Mn chemistry in many environments, especially those with well-developed oxic/anoxic interfaces (fjords, lakes, sediments).

Considering the variety of mechanisms and microorganisms able to act in either oxidation, or reduction, it is difficult to conclude which mechanisms really are used by microorganisms to oxidize or reduce manganese, and under what conditions these mechanisms might be expected to predominate in the natural environment. Besides the factors that have a direct influence on chemical Mn oxidation or Mn reduction, like pH and E_h, Mn evolution may be indirectly influenced by parameters that act on bacterial physiology and activity, like organic matter and other nutrients, texture of sediment, temperature. Seasonal variations of Mn oxidation and the presence of amorphous Mn oxides can be in correlation with biological processes [59–61]. Bacteria involved in Mn oxidation are not the same according to the season. *Leptothrix* were found to be abundant during summer [62] and budding appendaged bacteria during spring and autumn [60].

Biochemistry of manganese in groundwater

Groundwater is connected to stream, lake and swamp water filtering through sediments and receives surface water percolating through the vadose zone [63]. It is influenced by anthropogenic activities, particularly through the building of dams, pumping, and irrigation. For understanding manganese evolution in such a system it is necessary to study manganese transformation in all its compartments, especially in surface sediments.

Mn evolution in river and swamp sediments. If stream and swamp water are aerated, aerobic bacteria may precipitate and oxidize soluble manganese Mn(II) at the interface between water and sediment. In addition, Mn(II) can be oxidized by phytoplankton [62,64]. Biological Mn oxidation has been observed even under oligotrophic conditions, for instance in arctic lakes [65,66].

Although Mn(IV) oxides are less abundant than Fe(III) oxides, a higher proportion of Mn(IV) oxides may be available for microbial reduction in sediments. When anaerobic conditions develop, Fe(III) and Mn(IV) reduction has the potential to become a major process for organic matter decomposition by microorganisms [8]. These processes are restricted to narrow zones (few centimeters) near the sediment–water interface in many aquatic sediments. Furthermore, insoluble Mn(II) in the form of Mn_3O_4, $MnCO_3$, and adsorbed Mn(II), may constitute a significant portion of the Mn(II) generated from Mn(IV) reduction [67]. In disturbed sediments there may be rapid recycling between reduced and oxidized iron and manganese. This makes determination of the in situ rates of Fe(III) and Mn(IV) reduction difficult [8].

Mn evolution in subsurface sediments. The microbial ecology of the terrestrial subsurface developed recently. A number of reports relating to the characterization of subsurface microorganisms and their activity is now available [68–71]. Microbial life exists even at great depths provided that enough water, pore space, and nutrients are available [69]. In pristine aquifers, characterized by their low nutrient availability, bacteria are adapted to these oligotrophic conditions by structural adaptation and attachment to surfaces [69,71].

In this stable sedimentary environment, the different processes for decomposition of organic matter are segregated in space or time or both. The reduction sequence is O_2, NO_3^-, Mn(IV), Fe(III), SO_4^{2-}, HCO_3^- and N_2 [69,72]. It depends on the amount of organic matter. In oligotrophic pristine aquifers, this redox gradient decreases slowly with depth. Most pristine drinking-water aquifers contain significant amounts of O_2 [69]. Mn oxidation can occur if aeration is sufficient. Budding and appendaged bacteria, which can oxidize Mn, are frequently observed in subsurface sediments [69,71]. Mn oxidation cannot occur if the aquifer is confined or if there are significant amounts of organic matter. The contamination of groundwater with organic compounds frequently leads to the development of anaerobic conditions. The accumulation of high concentrations of dissolved Fe(II) and Mn(IV) is a common feature of aquifers contaminated with organic compounds [8].

Example of a shallow aquifer in the Rhône valley. After the building of hydroelectric dams on the Rhône, manganese content in well waters increased in many places, often reaching over 1 mg per liter [32,54,73–75]. Soluble manganese in drinking water is not toxic but it is a pollutant since its oxidation results in darkening of water and plugging of pipes in water systems. The aquifer chosen as an example is located in the Rhône valley near Avignon. Wells used for drinking water are located in an island between two branches of the Rhône. They are supplied mainly by the aquifer water coming from the Rhône below the island where there are swamps [75].

The results of chemical and microbiological analyses of groundwater and sediments suggested that bacterial activity is the main process which promotes manganese transformation and migration in the aquifer [32,53,54,57,76]. Many parameters influence the system, especially the level and dynamics of groundwater which depend on the stream flow and its regulation by the dams, canal level, pumping for drinking water and irrigation, and to a much lesser extent rain water. Consequently, analyses were made on stream water and sediments, swamp water and sediments, subsurface water and sediments (boreholes), and laboratory experiments were conducted to know the effect of main parameters on microbial activities. Bacteria were found to be abundant in the Rhône and swamp muds. In subsurface sediments from boreholes bacteria were often as numerous as in surface sediments. In all samples many bacteria were potentially able to oxidize or reduce manganese according to redox conditions.

Stream water is always well aerated. At the interface between water and mud, aerobic bacteria precipitate and oxidize soluble manganese Mn(II). In swamps, in addition to bacterial precipitation, Mn(II) can be ozidized by phytoplankton which is very abundant during summer. In all cases amorphous Mn oxides were found to be predominant in the upper centimeters of the sediments, suggesting a microbial origin [33,53,77,78].

The river mud contains organic matter brought by the stream. In swamps, organic matter is produced by phytoplankton and surrounding vegetation and accumulates in the sediment. Inside the Rhône and swamp muds, oxygen is rapidly consumed by active heterotrophic microflora, organic matter disappears and anaerobic conditions prevail. Nitrates are then reduced by facultative anaerobic bacteria and Mn oxides are reduced, especially those that are not included in crystalline structures. Sulphate reducers may develop when redox conditions are sufficiently low. Soluble Mn(II) can migrate into the aquifer with the underflow. This migration is slow since Mn(II) is adsorbed on colloids and fine particules of sediments.

If the sediments are coarse-grained, and the superficial vegetation sparse, then the aquifer is aerated. In the saturated zone, oligotrophic aerobic bacteria can re-oxidize Mn(II) that was reduced in the mud river. Mn is precipitated as Mn oxide and does not migrate into the aquifer. This process occurs on the Eastern riverside.

Inside the island the aquifer is often confined. The profile of subsurface sediments is heterogeneous, some layers have a fine texture and more organic matter. Bacteria cannot re-oxidize manganese, which remains in reduced soluble state. Furthermore, Mn oxides present in subsurface sediments (formed during a previous aerated period before the building of the dams) can be reduced where organic matter is abundant. In confined subsurface sediment, amorphous Mn oxides, which are easily reduced by bacteria [53–55], are much less abundant than in the river or swamp muds [32,79].

Near the wells, the less abundant vegetation and the coarse-grained layer above the ground watertable allow more aerated conditions. Soluble reduced manganese can be oxidized by aerobic bacteria but their activity is restricted by the limited oxygen supply. Part of the manganese remains in a reduced soluble state in well water. However, if water is aerated during pumping, bacterial oxidation of manganese starts and causes Mn oxide deposits on pipes and darkening of the water. This hypothesis, backed up by experimental data on the Ile de la Motte site [53,54], was further confirmed by observations on several other sites in the Rhône valley (A.M. Gounot, unpublished data).

Biotechnological applications

Biological manganese oxidation is exploited in water treatment for Fe(II) and Mn(II) removal. Various procedures are used, either in situ or on filters [80–82]. All of them are based on an increase in aeration.

In the Vyredox procedure, Fe- and Mn- oxidizing bacteria are stimulated in situ by injection of aerated water [83–85]. A typical Vyredox plant unit comprises several injection wells, through which degassed aerated water is injected into the aquifer and a pumping well through which water, partly free of iron or manganese, is removed. This procedure is widely used in Northern Europe [81] and less commonly in France [79,86].

Three procedures, exploited for instance and in Finland and Austria, use slow filtration: overland flow method, slow sand filtration and re-infiltration [33,88–91].

In the floating filter procedure [92,93], before sand filter, water flows recurrently through a floating coarse-grained filter and through the boundary surface between air and water. This promotes chemical oxidation, creates favourable conditions for biological activity and accelerates the sedimentation of the precipitate on the bottom of the basins.

Rapid filtration occurs in biological reactors [82,94]. After pumping, Mn-containing water is aerated and injected through rapid sand filters where native water bacteria (e.g. *Leptothrix*) develop and precipitate manganese. If water contains iron, *Gallionella* are stimulated and iron is removed before manganese. This procedure proved to be very efficient for Mn removal in the case of the 'Ile de la Motte' described above [95]. The dominant bacteria on sand filters were found to be *Leptothrix* [96]. Rapid filtration reactors are used in France [82], Germany [97], Belgium [98].

However, physico-chemical treatments remain the rule in the United States [99], despite the fact that biological manganese removal is under investigation [100].

Furthermore, Fe(III) and Mn(IV) oxides strongly adsorb a wide variety of toxic trace metals [101,102]. This results in the filter effect of sediments towards heavy metals [103,104]. This ability is used in a variety of waste treatments. It may be possible to exploit these properties for metal recovery processes [105].

In contrast, the remobilization of heavy metals is a potential hazard to aquatic ecosystems and drinking-water supplies when Fe(III) and Mn(IV) are reduced [8,106,107]. The bioleaching of manganese and other metals from ore could be envisaged in reactors [8,108,109].

On the other hand, the contamination of ground water with organic compounds frequently leads to the development of anaerobic conditions. Lovley [8] postulated that microbial Fe(II) and Mn(IV) reduction may be an important natural mechanism for contaminant removal in subsurface environments.

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