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MANGANESE: ITS SPECIATION, POLLUTION AND MICROBIAL MITIGATION

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Abstract

Manganese is known to be one of the essential trace elements and has plenty of applications. Inspite of its essential nature, concerns have arising due to its toxic nature at higher concentration. Several methods of removing manganese from environment have been proposed during the last few decades. However, the most favourable option based on cost-effectiveness, performance, and simplicity is still under investigation. The current review summarizes updated information on various technical aspects on manganese, including chemical nature, speciation, toxicity and remediation strategies. The review starts with covering the major sources of manganese, its interaction with biological biomolecules causing toxicity. This is followed by its speciation in environment, describing both biotic and abiotic processes. The biotic processes describe the role of microorganisms in the oxidation/ reduction of various oxidation states of manganese. Whereas, abiotic processes mainly describes the role of pH and oxygen taking thermodynamical aspects. The main part of this review focuses on recent developments on using microbial systems for manganese bioremediation. The updated works on different strategies adopted for the remediation of manganese from the environment have also been summarized.

Keywords: Manganese oxide, Manganese speciation, Bioremediation, Bacteria

Introduction

Due to rapid industrialization heavy metals have become worldwide environmental problem. Manganese is known to be one of the plentiful metals on the Earth crust. Manganese is required by living organisms as micro nutrient as well as extensively used by human for their comfort. Manganese is used as fertilizer, food additive, catalysts, act as basic component for welding of manganese containing materials, mining, smelting, pigments or paints and dry cell batteries(Li *et al.,* 2010; Rajic*et al.,* 2009). Not only in bulk form but also its nano compounds are now days extensively used. These have promising applications in catalysis, energy storage, sensors, ion sieves, high density magnetic storage media and drug delivery (Balan *et al.,* 2013; Brock *et al.,* 1998). Along with above anthropogenic sources manganese leaching from manganese bearing rocks, volcanic eruption and forest fires also contributes to its environmental pollution (Schroeder *et al.,* 1987). Manganese mainly occurs in form of minerals like oxides, sulphides, phosphates, pyrophosphates, carbonates and many more (Laznicka, 1992). Natural leaching of manganese from the minerals/bed rocks present is one of the major sources of ground water contamination. Manganese acts as toxicant when it is present in excess range of 0.1-0.5 mg/L (Li *et al.,* 2010). Due to soaring growth in use of manganese and open presence in environment has created concern worldwide. The aim of the current review is to survey the scientific evidences published to date on the strategies applied for the removal of manganese from the environment. The reviews also focus on the various transformations occurring in nature once manganese is exposed and its toxicity towards living system.

Manganese as a pollutant

Manganese is less toxic metal as compared to other heavy metals and also an essential trace metal required for various biological functions. Nevertheless, it has number of detrimental properties such as the obstruction of water distribution grids, staining during laundry and the tainting of drinking water (Hallberg and Johnson, 2005; Mariner *et al*., 2008). Along with above these manganese both in excess and deficiency have harmful effects on health. During early eighteenth century the first occupational exposure of manganese and intoxication was reported (Michalke *et al.,* 2007). Since then, lot of studies has been under taken to investigate and decipher the uptake, transport, metabolism and toxicity of manganese in the living system.

Mostly manganese exposure to living body occurs by inhalation and ingestion of manganese rich compounds and may results in neurological pathology, since brain is thought to be vulnerable target for manganese accumulation (Röllin and Nogueira, 2011). Higher manganese concentrations affect central nervous system, heart, lung, liver and some other organs (Crossgrove and Zheng, 2004). Accumulation of the manganese in brain tissue results in neurotoxicity which leads to progressive disorder of the extra pyramidal system similar to

Parkinson's disease (Crossgrove and Zheng, 2004). High concentration of manganese in the living system also affects DNA replication and cause mutations/ aberrations (Gerber *et al*., 2002).Other effects of manganese toxicity are associated with its role in (i) mucopolysaccharides and (ii) peptidoglycan synthesis (Keen and Leach, 1988).

Manganese remediation

There has been an increasing awareness to limit the manganese in the metal contaminated environment. Manganese exists mostly in Mn^{2+} state in aqueous environment (Ellis *et al*., 2000; Hallberg and Johnson, 2005; Li *et al*., 2010). The maximum permissible limit of manganese concentration in drinking water is 0.1 mg L^{-1}, as per Bureau of Indian Standard (BIS) (Rajmohan and Elango, 2005). Oxidation of Mn^{2+} to MnO_2 is most commonly employed approach for its removal from the contaminated environment. Since MnO_2 is insoluble it gets precipitated. The precipitate is easily separated by filtration. The manganese remediation processes are classified into two general categories namely (i) active and (ii) passive processes.

Active processes: In these types of processes, large quantities of oxidant/ chemicals are added to raise the pH of the surrounding medium to enhance the abiotic oxidation (Hallberg and Johnson, 2005). Oxidizing agents like Cl_2, O_3, or H_2O_2 are commonly used. These are frequently used in the case of mine water remediation. During the treatment process, water is first neutralised by using alkaline compounds like limestone ($CaCO_3$), sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH). The use of alkaline compounds causes increase in pH which ultimately causes metal to precipitate. These processes require the installation of agitators, precipitators, clarifiers and thickeners, which increase the operational cost (Gazea *et al*., 1996).Also, in some cases, the reactions lead to formation of undesirable by-products (Dudley, 1998; Han *et al.,* 2007).

Passive processes: Exploit naturally occurring geochemical and biological reactions to remove the manganese from the contaminated water (Gazea*et al*., 1996; Logan *et al*., 2005; Santelli*et al*., 2010). Passive process mainly involves the use biological systems like, photosynthetic algal mat systemin which green algae are integrated with microbial mat with limestone substrate pond (Phillips *et al*., 1995), immobilised cyanobacteria mats in columns packed with glass wool (Bender *et al*., 1994) or wetlands (Sikora *et al*., 2000). Many of the microbial systems are known and reported which can catalyse the oxidation of Mn^{2+} to Mn^{4+} oxide. This microbial system may include bacteria, fungi and algae. These oxides being insoluble are separated from rest of the system.In past decade, various passive processes have been developed, for the removal of manganese, from lab scale to full-scale field applications (Whitehead *et al*., 2005; Whitehead and Prior, 2005). However at times, these are disrupted by changes like variation in pH or metal concentration (Mariner *et al*., 2008).

Manganese cycle/ speciation in the environment

Manganese exists in different oxidation states extending from 0 to +7; though some of the oxidation states like +2, +3, and +4 are found most commonly in nature (Tekerlekopoulou *et al*., 2008). Depending on the local environment, manganese undergoes speciation both abiotically and biotically.

Abiotic speciation

Environmental conditions like pH, temperature, concentration and pE do have influence on metal speciation (Anschutz *et al.,* 2005), it's obvious that the oxidation or reduction of manganese in environment will yield various oxidation states. In anoxic environment Mn^{2+} occurs mostly in solution or adsorbed to minerals, whereas in oxygenic environment it occurs as Mn^{3+}/ Mn^{4+} oxides or hydroxides. In aqueous system, solubility of manganese increases as pH and oxidation-reduction potential decreases. Other anions like nitrates, chlorides and sulphates, if present, in high concentration may also increase the solubility of manganese. Manganese compounds mainly precipitate out in as Mn^{4+} and re-solubilizes in the aqueous system as Mn^{2+} (Moore, 1991). In general, the existence of Mn^{2+} is thermodynamically favourable at lower pH conditions and anoxygenic environment, while, formation of Mn^{3+}or Mn^{4+} are favoured at higher pH and oxygenic environment. Figure 1shows the abiotic speciation of manganese

In oxygenic environment, Mn^{3+} and Mn^{4+}, occur mainly as insoluble manganese oxyhydroxides (Lanson*et al*., 2000; Davison 1993). According to Adams and Ghiorse, (1988), the stoichiometry and the chemical reaction of bacterial Mn^{2+} oxidation (determined by measuring oxygen consumption and hydrogen production) are written as:

$$Mn^{2+} + \tfrac{1}{2} O_2 + H_2O \longrightarrow MnO_2 + 2H^+ \quad (1)$$

$MnO(OH)/Mn_3O_4$

$$\tfrac{1}{2}MnO_2 + 2H^+ + e^- \tfrac{1}{2} \longrightarrow Mn^{2+} + H_2O \quad (2)$$

Studies on abiotic conversion of Mn^{2+} to Mn^{4+} (equation 1)by different researchers, has shown that it proceed in two steps (i) initial formation of oxyhydroxides (e.g β-MnO(OH) or solid phase Mn^{3+} containing oxides (e.g., Mn_3O_4) the steps are then followed by (ii) very slow disproportionation or protonation of the Mn^{3+} oxyhydroxides or oxides, resulting into Mn^{4+} oxides (e.g. MnO_2) formation (Murray *et al*., 1985; Nesbitt and Banerjee, 1998). Since, in the environment at pH greater than 8 and Mn^{2+} concentrations > ~ 1µM, the Mn (+2,+3) states are thermodynamically stable with respect to disproportionation reaction (Davison 1993; Junta and Hochella, 1994), so the second step i.e. disproportionation

or protonation in equation 1 act as a rate-limiting step (Nesbitt and Banerjee, 1998). The reduction of Mn^{4+} to Mn^{2+} can also take place at low pH and absence of oxygen [equation 2] but may require inorganic or organic reductants (Davison 1993). Taking the advantage of abiotic speciation processes remediation of manganese from the environment has been also been attempted and is summarized in Table 1.

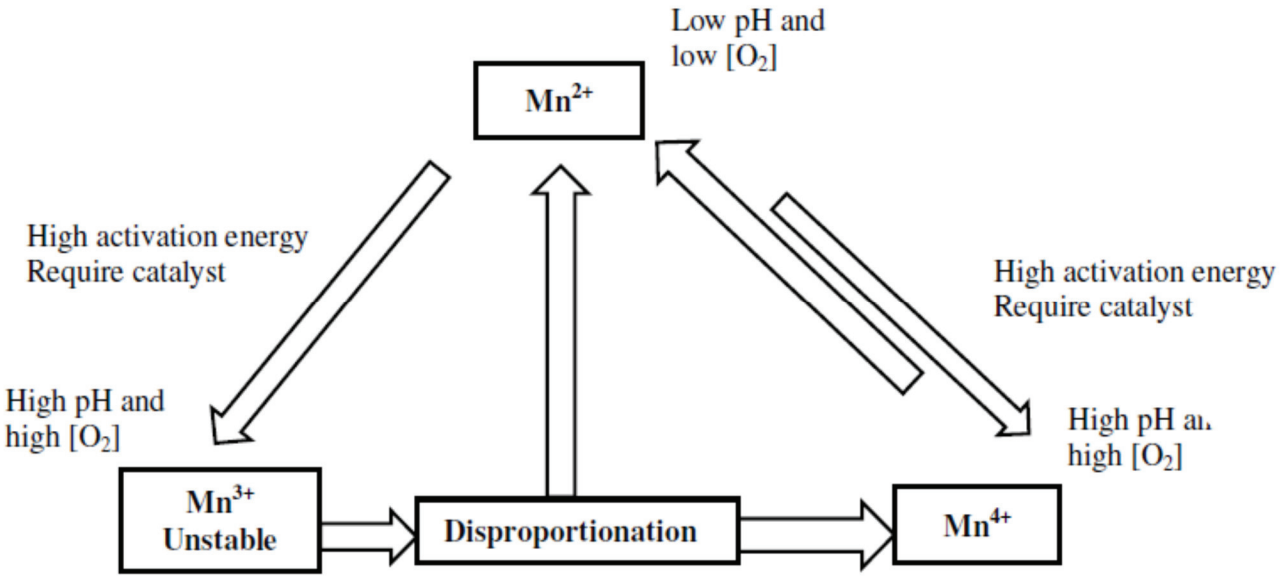

Fig. 1: Abiotic speciation of manganese in environment.

Table 1: Manganese remediation by abiotic systems or active processes.

Abiotic system	Nature of process	Efficiency	Reference
Activated carbon	Adsorption	-	Okoniewska *et al*., 2007
Air mediated precipitation	Hydrometallurgical processes	10%	Zhang *et al*., 2010
Air and O_2 mediated precipitation	Hydrometallurgical processes	99.5%	Zhang *et al*., 2010
Electrokinetic cell	Electrokinetic removal	18%	Genc *et al*., 2009
Granular activated carbon	Adsorption	2.54 mg g^{-1}	Jusoh *et al*., 2005
H_2O_2 and hollow fiber micro-filter	Oxidation and filtration	95%	Teng *et al*., 2001
Kaolinite	Adsorption	0.446 mg g^{-1}	Yavuz et al., 2003
$KMnO_4$ mediated precipitation	Oxidation and microfiltration	-	Ellis *et al*., 2000
Manganese oxide coated zeolite	Adsorption	1.123meq Mn^{2+} g^{-1}	Taffarel and Rubio, 2010
Mexican clinoptilolite-rich tuff (natural)	Adsorption	138.88 meq kg^{-1}	García-Mendieta *et al*., 2009
Mexican clinoptilolite-rich tuff (Sodium modified)	Adsorption	232.55meq kg^{-1}	García-Mendieta *et al*., 2009
Na_2CO_3 mediated precipitation	Hydrometallurgical processes	90%	Zhang *et al*., 2010
NaOH mediated precipitation	Hydrometallurgical processes	71%	Zhang *et al*., 2010
Natural zeolite	Adsorption	0.259 meq Mn^{2+} g^{-1}	Taffarel and Rubio, 2010
Natural zeolite tuff	Adsorption	10.0 mg g^{-1}	Rajic *et al*., 2009
Oxidation by ozone	Oxidation of manganese	83%	El Araby *et al*., 2009
Polyacrylic acid (chelating polymers) in combination with ultrafiltration	Chelation of Mn	-	Han *et al*., 2007
SO_2/ air mediated precipitation	Hydrometallurgical processes	99.5%	Zhang *et al*., 2010
SO_2-O_2 gas mixtures mediated precipitation	Precipitation of Mn as oxide	-	Schulze-Messing, 2007
Ultrafiltration in conjunction with an in-line prechlorination	Oxidation of Mn	86%	Choo *et al*., 2005

Biotic speciation

Although, the oxidation of Mn^{2+} to higher oxidation states is thermodynamically more favourable, but because of higher activation energy requirement the process necessitates involvement of reductants or microbial enzymes (Davison, 1993; Miyata *et al*., 2004). Some of the microorganisms grow well in presence of high metal concentration and play important roles in biogeochemistry (Gadd, 2010). These microbes can be isolated from the source sample directly or by enrichment methods to study their interaction behaviour in respective environment and bioremediation potential (Sinha and Khare 2011; Sinha *et al.,* 2013).

In late nineties the environmental data and the redox characteristics of oxidized manganese intrigued many investigators to speculate that there might be some role of microbes wherein they may be undergoing coupled anaerobic respiration linked reduction of metal to oxidation of organic carbon for growth (Nealson *et al.,* 1992). Then after many microbial systems like bacteria, fungi and algae have been isolated to study their interaction with manganese and found to be playing vital role in manganese biogeochemistry. Many of these microbes accelerate the catalysis rate of Mn^{2+} oxidation much higher than natural abiotic oxidation (Nealson, 1983). Microbial communities like *Bacillus* sp. SG-1, *Leptothrix discophora*strain SS-1 and SP6, *Pseudomonas putida* strains MnB1 and GB-1, and *Pedomicrobium* sp. ACM 3067 (Brouwers *et al.,* 2000; Geszvain *et al.,* 2013; Webb *et al*., 2005; Ridge *et al*., 2007; *Saratovsky et al.,* 2006; Villalobos *et al*., 2003), fungi *Acremonium*, *Paraconiothyrium*, *Phanerochaete*, *Cephalosporium*sp., *Coniothyrium*, *Periconia* sp., *Sporothrix* sp., *Phoma* (Santucci *et al*., 2000, Sasaki *et al*., 2006;*Saratovsky et al.,* 2009; Timonin *et al.,* 1972) and algae like *Gloeothece Magna* and *Cladophora* (Duggan *et al.,* 1992; Mohamed, 2001) play an important role in the transformation and speciation of manganese in the environment along with the abiotic processes.

Manganese biogenesis has been extensively characterized in bacterial systems. Bacteria catalyse the oxidation of Mn^{2+} either directly or indirectly. Indirect Mn^{2+} oxidation is carried out by microbes by modifying the pH of the surrounding medium along with the redox environment (Tebo*et al.,* 2004). They may also release metabolites of organic or inorganic nature that act as chemical oxidant for Mn^{2+} (Gounot *et al*., 1994). In direct oxidation process, the oxidation is carried out by the cellular polysaccharides (Beveridge, 1989; Ghiorse and Hirsch, 1979) or proteins or enzymes (Adams and Ghiorse 1987; Jung and Schweisfurth, 1979; Miyata *et al.,*2007; Okazaki *et al*., 1997; Tebo *et al.,* 2005). Molecular and biochemical studies in bacterial system like *Leptothrix discophora* SS-1 (Brouwers *et al*., 2000; Corstjens *et al*., 1997) *Pseudomonas putida* strains MnB1 and GB-1 (Caspi *et al*., 1998; Geszvain *et al.,* 2013), and *Bacillus* sp. strain SG-1 (Francis *et al*., 2002; Francis and Tebo, 2002; van Waasbergen *et al*., 1996), *Pedomicrobium* species (Ridge *et al.,* 2007) and the *Erythrobacter* (Francis *et al*., 2001) have revealed that the Mn^{2+} oxidation is mainly carried out by the enzymes similar to multicopper oxidases. Multicopper oxidases are multi-domain family of enzymes. These enzymes utilize multiple types of copper ions as cofactors to oxidize different organic and inorganic substrates (Solomon *et al*., 1996).

Initially the Mn^{2+} is oxidized to Mn^{3+} through one electron transfer, later on Mn^{3+}further undergoes oxidation to Mn^{4+}. Thus, it is believed that Mn^{3+}solid phase minerals such as feitknechtite (β-MnOOH) or hausmannite (Mn_3O_4) are the main product of the enzyme catalyzed Mn^{2+} oxidation reaction. These minerals may further be transformed into Mn^{4+} oxides abiotically via disproportionation and protonation reactions. The oxidation of Mn^{3+} to Mn^{4+} might also proceed without undergoing through solid phase intermediate**,** in this caseMn^{4+} formation proceeds by (i) dissociation of Mn^{3+} from the enzyme (ii) enzyme mediated one electron transfer oxidation of Mn^{3+} to Mn^{4+} or (iii) two electron transfer reaction. Study on marine *Bacillus* sp. strain SG-1 spores (Webb *et al.,* 2005) has also shown that oxidation of Mn^{2+} to Mn^{4+} is the outcome of two consecutive one-step electron transfer processes. Both consecutive steps are mediated by putative multicopper oxidase, MnxG, resulting Mn^{3+} as transient intermediate. With above manganese oxidizing property of microorganisms exploring them for the removal of soluble manganese from the environment seems promising. Many remediation processes attempted based on manganese oxidizing abilities of different biological systems and are summarized in Table 2.

Use of immobilized microbial cells for manganese bioremediation

Immobilized of microbial cells and enzymes provide viability and cost effectiveness to the process. Hence, for the removal of heavy metals from environment, application of immobilization of microbial cells and enzymes has been used in many bioremediation methods (Li *et al*., 2008, Moreno-Garrido, 2008, Sinha *et al.,* 2012; Sinha and Khare, 2012). There are very few reports on microbial bioremediation by immobilized cells. Some of these are summarized in Table 3.

Conclusions

Need for the removal of manganese from the environment seeks development of reliable and eco-friendly processes. To accomplish this, the use of natural sources like microbes seems promising. Of the various biological systems, the use of manganese oxidising microbial strains are relatively easy in way that they form insoluble manganese oxides which can be separated out easily,

whereas immobilized microbes have an advantage of easy handling and large-scale applications. However, we need more to understand the biochemical and molecular mechanisms operation in microbes during interaction of manganese, so that they can be more efficiently and with maximum potential can exploited to remove the excess manganese from the environment.. Also, manganese containing minerals like oxides and hydroxides play vital role in the bioavailability and movement of other heavy metals. It is therefore becomes more important to understand more about its geo-microbiology and biogeochemical cycles.

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Table 2: Manganese remediation by using biological systems

Biological system	Nature of process	Efficiency	Reference
Bacillus sp.cells	Accumulation	Complete removal	Sinha *et al*., 2011
Bean pod waste	Adsorption	23.4 mg g-1	Budinova *et al.,* 2009
Blakesleatrispora	Adsorption	40 mg g^{-1}	Gialamouidis *et al*.,2010
Brazilian vermiculite	Adsorption	0.52mmol g^{-1}	da Fonseca *et al*., 2006
Chitin (crab-shell) demineralized	Adsorption	5.437 mg g^{-1}	Robinson-Lora and Brennan, 2010
Chitin (crab-shell) demineralized/ deproteinized	Adsorption	0.981 mg g^{-1}	Robinson-Lora and Brennan, 2010
Crab shell particles (*Portunussanguinolentus*)	Adsorption	69.9 mg g^{-1}	Vijayaraghavan *et al*., 2011
Firmiana simplex L. (Thermally decomposed leaf)	Adsorption	61-66 mg g^{-1}	Li *et al*., 2010
Fungus (*Phoma*) in presence of carbon filter	Precipitation	-	Sasaki *et al*., 2004
Gallionella and *Leptothrix* (Using roughing filtration)	Oxidation of Mn and filtration	88%	Pacini *et al*., 2005
Leptothrix discophora SP-6	Oxidation of Mn and filtration	90%	Burger *et al*., 2008
Manganese oxidizing bacteria immobilized on silica gravel	Oxidation of Mn	-	Tekerlekopoulou and Vayenas, 2007
Manganese oxidizing bacteria immobilized on silica gravel (Pilot-scale trickling filters)	Oxidation of Mn and filtration	63%	Tekerlekopoulou *et al*., 2008
Pseudomonas sp.	Adsorption	109 mg g^{-1}	Gialamouidis *et al*.,2010
Oscillatoria terebriformis	Adsorption and chemical precipitation	11.78 ± 0.98 and 9.2 ± 0.8 mg,	Gerasimenko *et al.,* 2013
Staphylococcus xylosus	Adsorption	59 mg g^{-1}	Gialamouidis *et al*.,2010

Table 3: Manganese bioremediation by immobilized microbial cells

Microorganism	Support matrix	Manganese removal efficiency	Reference
Agrobacterium tumefaciens	Amberlite XAD-4	22 μ mol g^{-1}	Baytak and Turker, 2005
Aspergillus niger	Alginate	52.3%	Tsekova *et al*., 2010
A. niger	Polyvinyl alcohol hydrogel	44.6%	Tsekova *et al*., 2010
Chlorella salina	Alginate	40%	Garnham *et al*.,1992
Cyanobacteria	Glass wool mixed withensiled grass	40%	Bender *et al*., 1994
Leptothrix discophora	Ferromanganese nodules	90%	Hallberg and Johnson 2005
Manganese oxidizing bacteria	Silicic gravel	100%	Tekerlekopoulou *et al*., 2008
Pseudomonas aeruginosa	Multi-walled carbon nanotubes	5.83 mg g^{-1}	Tuzen *et al*., 2008
Saccharomyces carlsbergensis	Amberlite XAD-4	-	Baytak and Turker, 2004

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