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. 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. Along with above anthropogenic sources manganese leaching from manganese bearing rocks, volcanic eruption and forest fires also contributes to its environmental pollution. Manganese mainly occurs in forms of minerals like oxides, sulphides, phosphates, pyrophosphates, carbonates and many more. 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. 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. Along with above these manganese both in excess and deficiency have harmful effects on health. 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. Higher manganese concentrations affect central nervous system, heart, lung, liver and some other organs. 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 Mn$^{2+}$ 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$_2$O$_2$ 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$_2$CO$_3$) 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; Santelliet al., 2010). Passive process mainly involves the use biological systems like, photosynthetic algal mat system 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$^{2+}$ 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$^{3+}$ 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$^{4+}$ is thermodynamically favourable at lower pH conditions and anoxic 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 (Lansonet al., 2000; Davison 1993). According to Adams and Ghiorse, (1988), the stoichiometry and the chemical reaction of bacterial Mn$^{3+}$ oxidation (determined by measuring oxygen consumption and hydrogen production) are written as:

$\text{Mn}^{2+} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{H}^+$

(1)

$\text{MnO(OH)/Mn}_2\text{O}_4$

$\frac{1}{2}\text{MnO}_2 + 2\text{H}^+ + e^{-} \rightarrow \text{Mn}^{2+} + \text{H}_2\text{O}$

(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$_2$O$_4$) 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.

![Manganese speciation](image)

**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$_2$O$_2$ 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                     | 1.123 meq 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                     | 232.55 meq kg$^{-1}$ | García-Mendieta et al., 2009 |
| Na$_2$CO$_3$ 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 Gloeothecae 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 (Teboet 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 Schweifurth, 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\(^{3+}\) undergoes further oxidation to Mn\(^{4+}\). Thus, it is believed that Mn\(^{3+}\) solid phase minerals such as feitknechtite (β-MnOOH) or hausmannite (MnO\(_2\)) are the main product of the enzyme catalyzed Mn\(^{2+}\) oxidation reaction. These minerals may further be transformed into Mn\(^{4+}\) 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 case Mn\(^{2+}\) formation proceeds by (i) dissociation of Mn\(^{4+}\) 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.

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           | Gialamoudis et al., 2010       |
| Brazilian verniculite                  | Adsorption                | 0.52 mmol 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/     | Adsorption                | 0.981 mg g⁻¹        | Robinson-Lora and Brennan, 2010|
| deproteinized Crab shell particles     | Adsorption                | 69.9 mg g⁻¹         | Vijayaraghavan et al., 2011    |
| *Firmiana simplex* L. (Thermally      | Adsorption                | 61-66 mg g⁻¹        | Li et al., 2010                |
| decomposed leaf)                       |                           |                     |                                |
| Fungus (*Phoma*) in presence of carbon| Precipitation             | -                   | Sasaki et al., 2004            |
| filter                                  |                           |                     |                                |
| *Gallionella* and *Leptothrix* (Using| Oxidation of Mn and       | 88%                 | Pacini et al., 2005            |
| roughing filtration)                   | filtration               |                     |                                |
| *Leptothrix discophora* SP-6           | Oxidation of Mn and       | 90%                 | Burger et al., 2008            |
|                                        | filtration               |                     |                                |
| Manganese oxidizing bacteria           | Oxidation of Mn           | -                   | Tekerlekopoulos and Vayenas,   |
| immobilized on silica gravel           |                           |                     | 2007                           |
| Manganese oxidizing bacteria           | Oxidation of Mn and       | 63%                 | Tekerlekopoulos et al., 2008   |
| immobilized on silica gravel (Pilot-scale trickling filters) | filtration |                     |                                |
| *Pseudomonas* sp.                     | Adsorption                | 109 mg g⁻¹          | Gialamoudis et al., 2010       |
| *Oscillatoria terebriformis*           | Adsorption and            | 11.78 ± 0.98 and 9.2| Gerasimenko et al., 2013      |
|                                        | chemical precipitation    | ± 0.8 mg.           |                                |
| *Staphylococcus xylosus*               | Adsorption                | 59 mg g⁻¹           | Gialamoudis 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%                          | Tekerlekopoulos 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          |
Acknowledgements

The authors gratefully acknowledge the financial support provided by the Department of Biotechnology (Govt. of India).

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