

# Fact Sheet

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## Removal of Manganese from Drinking Water

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### Manganese in Drinking Water

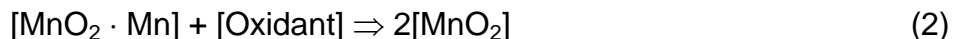
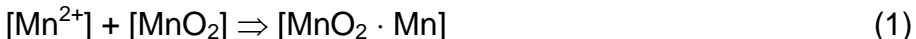
Manganese is commonly found together with iron in groundwater and is normally not considered to be a health concern (MOECC, 2006). However, there are a number of problems which can occur if too much manganese is present in the water, such as generating metallic taste and coloured water, staining of laundry and plumbing fixtures, formation of deposits in the distribution system and plumbing, and interference with the disinfection process (Ellis *et al.*, 2000). The Ontario Drinking Water Quality Standards for manganese indicate an aesthetic objective of 0.05 mg/L (MOECC, 2006); however, due to increased evidence of potential health effects, Health Canada has proposed a maximum acceptable concentration (MAC) of 0.1 mg/L, and an aesthetic objective of 0.02 mg/L for total manganese in drinking water (Health Canada, 2016).

Manganese (Mn) is present in natural waters as different species and valence states, but predominantly in dissolved manganese (II) form. Most literature considers the amount of manganese passing through a 0.45 µm filter as soluble, and the amount that does not pass through the filter as insoluble. Several techniques are available for removing manganese from drinking water sources. Two common methods are the adsorption/oxidation technique and oxidation/filtration approach (Tobiason *et al.*, 2008). The adsorption/oxidation process involves using a filter media (e.g. manganese oxide coated greensand) that has the capacity to adsorb the soluble manganese and then it is oxidized into insoluble manganese by subsequent oxidation. The oxidation/filtration method applies a strong oxidant to oxidize soluble manganese into insoluble manganese, and then the insoluble manganese is removed by physical particle removal process (such as filtration and membrane).

### Adsorption/Oxidation Method

Manganese greensand is made from a glauconitic mineral with chemical treated steps to form a manganese oxide coating on the grain of sand, and manganese oxide (MnO<sub>2</sub>) is capable of adsorbing dissolved Mn (Morgan and Stumm, 1964). Manganese greensand has been used effectively for iron (Fe) and manganese removal for several decades (Knocke *et al.*, 1990). A greensand filter usually consists of three different layers. The top layer usually consists of

anthracite, followed by manganese greensand, with graded gravel on the bottom. The greensand has an effective size of 0.30 – 0.35 mm and a uniformity coefficient of 1.6 or less (Knocke *et al.*, 1988). The removal of soluble Mn is achieved by adsorption followed by oxidation processes. Adsorption of soluble manganese on the oxide surface and its subsequent oxidation by an oxidant are shown below (Van Benschoten, 1992).



When manganese oxide coated greensand filters are used in water treatment, soluble manganese is adsorbed on the sand grain and associated with the manganese oxide coating (Equation 1) but is not yet oxidized. The oxidant then oxidizes the associated soluble manganese to manganese oxide (Equation 2), which is later removed by filter backwashing.

The filter media is regenerated either continuously or intermittently to restore the oxidation capacity (Merkle, 1997a). Continuous regeneration is best suited to water with high iron concentrations (e.g. > 0.3 mg/L) and low manganese concentrations (e.g. < 0.05 mg/L) where iron removal is the main objective. In continuous regeneration, a strong oxidant such as potassium permanganate or free chlorine is fed into the water prior to entering the filter. As a result, iron and some of the manganese are oxidized into insoluble forms before reaching the filter. The remaining soluble manganese is then adsorbed on the surface of the sand grains (Merkle, 1997a). On the other hand, intermittent regeneration is suitable to water with high manganese concentration (e.g. > 0.05 mg/L) and low iron concentration (e.g. < 0.3 mg/L). In intermittent regeneration mode, no oxidant is added pre-filter. Instead, the adsorption and oxidation of manganese occur directly on the greensand grains. After treating a specific volume of water, the adsorption/oxidation capacity of the media will be exhausted and regeneration is required. This process is normally accomplished by soaking the media for several hours in a 2 – 3% solution of potassium permanganate (Sommerfeld, 1999). The excess permanganate from regeneration can be recycled for the next regeneration to minimize the chemical cost (Merkle, 1997b).

## Oxidation/Filtration Method

The oxidation of manganese is commonly accomplished by free chlorine, chlorine dioxide, ozone and potassium permanganate. Free chlorine is often used because it is economical and easy to feed. Sufficient chlorine dosage and contact time must be available for effective oxidation of soluble Mn. In addition, this oxidation process is not efficient at pH < 9 (Knocke *et al.*, 1988). Other chlorine demand such as the presence of natural organic matter and ammonia will require a much higher chlorine dose to completely oxidize the soluble manganese. Formation of disinfection by-products is a concern when chlorine is used in waters with high levels of natural organic matter.

Potassium permanganate ( $\text{KMnO}_4$ ) is widely used in water treatment plants for the oxidation of soluble iron and manganese. The theoretical stoichiometric dose for soluble iron ( $\text{Fe}^{2+}$ ) and manganese ( $\text{Mn}^{2+}$ ) oxidation is 0.94 and 1.92, respectively (Knocke *et al.*, 1991a). Therefore, the

calculation for determining the required dose of permanganate to oxidize iron and manganese ahead of the filter is given by Equation 3 (Sommerfeld, 1999). It is important to optimize the permanganate dose as excessive permanganate in water produces a pink solution which will lead to customer complaints, and insufficient permanganate will not be able to oxidize the soluble Mn to a suitable level (e.g. <0.01 mg/L). However, low temperature and the presence of natural organic matter can increase the amount of time it takes for effective oxidation to occur (Gregory and Carlson, 2003), therefore making the process difficult to optimize.

$$\text{KMnO}_4 \text{ Dose (mg/L)} = 1 \times [\text{Fe Concentration}] + 2 \times [\text{Mn Concentration}] \quad (3)$$

Media filtration is commonly used to remove insoluble Mn after the oxidation process. Therefore it is important to monitor whether all the soluble Mn in the water has been converted to the insoluble state. When not all the soluble Mn is converted into insoluble state, some Mn will be left out in a colloidal size range. It has been found that colloidal Mn present in filter influent may not be removed efficiently by media filtration (Knocke *et al.*, 1991b, Carlson *et al.*, 1997). Membrane filtration can also be applied to remove manganese, and soluble manganese cannot be effectively removed by membrane without being oxidized to the insoluble form. For example, microfiltration with pre-oxidation by permanganate as well as advanced oxidation process (Teng *et al.*, 2001; Ellis *et al.*, 2000), and ultrafiltration with in-line pre-chlorination have been successfully applied to remove manganese and/or iron from groundwater (Choo *et al.*, 2005).

## Biological Method

Biological methods have been tested to treat Mn containing groundwater in recent years, and particularly by bio-filtration processes utilizing manganese-oxidizing bacteria (Burger *et al.*, 2008). This technology is a low-cost alternative treatment method and has shown much promise in removing dissolved Mn as well as other contaminants (Han *et al.*, 2013). Tekerlekopoulou *et al.* (2013) reviewed a variety of full and pilot-scale biological filters that have been used for combined or simultaneous removal of manganese, iron, and ammonia, as well as factors and conditions that were found to affect the process. The bio-filtration can achieve manganese removal without using chemical oxidants and under natural pH conditions (Pacini *et al.*, 2005), in which over 95% manganese removals were achieved. The advantages of biological treatments compared to physical and chemical treatment methods are: no use of chemicals, higher filtration rates, and lower operation and maintenance costs.

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