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Effect of drinking water treatment process parameters on biological removal of manganese from surface water

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ABSTRACT

Soluble manganese (Mn) presents a significant treatment challenge to many water utilities, causing aesthetic and operational concerns. While application of free chlorine to oxidize Mn prior to filtration can be effective, this is not feasible for surface water treatment plants using ozonation followed by biofiltration because it inhibits biological removal of organics. Manganese-oxidizing bacteria (MOB) readily oxidize Mn in groundwater treatment applications, which normally involve pH > 7.0. The purpose of this study was to evaluate the potential for biological Mn removal at the lower pH conditions (6.2–6.3) often employed in enhanced coagulation to optimize organics removal. Four laboratory-scale biofilters were operated over a pH range of 6.3–7.3. The biofilters were able to oxidize Mn at a pH as low as pH 6.3 with greater than 98% Mn removal. Removal of simulated organic ozonation by-products was also greater than 90% in all columns. Stress studies indicated that well-acclimated MOB can withstand variations in Mn concentration (e.g., 0.1–0.2 mg/L), hydraulic loading rate (e.g., 2–4 gpm/ft^2; 1.36×10^{-3}–2.72×10^{-3} m/s), and temperature (e.g., 7–22 °C) typically found at surface water treatment plants at least for relatively short (1–2 days) periods of time.

1. Introduction

Manganese (Mn) is often present in drinking water sources in the reduced Mn(II) or oxidized Mn(IV) form. Mn(II) is the more soluble form, and its oxidation results in the formation of a dark brown MnO_2 precipitate, causing unsightly black discoloration of water and scaling of pipes and fixtures (Sly et al. 1990). Mn in drinking water can cause aesthetic and operational concerns at levels below the EPA Secondary Maximum Contaminant Level (SMCL) of 0.05 mg/L (Sly et al. 1990) and has recently been linked to neurotoxic effects in children (Wasserman et al. 2006; Bouchard et al. 2010). One method for soluble Mn removal is to apply free chlorine to the influent directly upstream of a granular filter bed. The result is a natural greensand effect (NGE) where Mn(II) is initially adsorbed onto a MnO_x(s) surface on the media and then subsequently oxidized by free chlorine present in the filter-applied water (Knocke et al. 1988).

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Removal of organic compounds from drinking water sources is also a growing concern, especially for surface water treatment plants. One effective approach is to apply ozonation in order to enhance the biodegradability of the organic compounds prior to biofiltration (Rittmann et al. 1989). Ozonation can also result in soluble Mn oxidation, although its effectiveness for Mn removal is often suboptimal (Wilczak et al. 1993).

Application of chlorine across the filter media to achieve NGE is at odds with biological treatment benefits of the filter. Ideally, an effective biofiltration strategy that removes both Mn and organic contaminants is desirable. This could potentially be achieved by employing manganese-oxidizing bacteria (MOB), which are able to naturally oxidize Mn(II) to Mn(IV). Biological removal of Mn has been studied extensively in the treatment of groundwater and successfully applied at facilities (primarily in Europe) since the 1980s (Mouchet, 1992; Vandenabeele et al. 1992; Hope and Bott, 2004; Katsoyiannis and Zouboulis, 2004; Pacini et al. 2005; Stembal et al. 2005; Li et al. 2006; Burger et al. 2008a; Tekerlekopoulou et al. 2008). Biological Mn removal has traditionally been thought to be restricted to pH > 7.0–7.5 (Mouchet, 1992), although biological Mn removal may be possible at lower pH (6.5) (Burger et al. 2008a, 2008b).

The role of MOB in biofiltration for Mn removal in surface water treatment situations has been far less researched. Granger et al. (2014) reported biological Mn removal to be effective at pH 6.0 with phosphorus enhancement; less effective Mn removal was noted under elevated pH (9–11) conditions. Ozonation was not part of the treatment process stream employed in this study; as such, the organic matter present in the filter-applied water was not readily biodegradable but, instead, was natural organic matter from a lake source.

MOB are phylogenetically diverse and include various species (Tebo et al. 2004) that appear to have evolved the ability to oxidize Mn independently. Several MOB have been studied in pure culture, including: *Pseudomonas putida* strain GB-1 (Okazaki et al. 1997), *Leptothrix discophora* strain SS1 (Boogerd and Devrind, 1987; Katsoyiannis and Zouboulis, 2004) and *L. discophora* strain SP-6 (Hope and Bott, 2004; Burger et al. 2008b), and *Bacillus* sp. strain SG-1 (Devrind et al. 1986; Bargar et al. 2000). In particular, *Bacillus* sp. strain SG-1 (Devrind et al. 1986; Bargar et al. 2000) and other Mn-oxidizing *Bacillus* (Francis and Tebo, 2002; Cerrato et al. 2010) are able to oxidize Mn in the dormant spore form. Bacteria in spore form are known to be resistant to a host of environmental threats, including heat and oxidants (Nicholson et al. 2000).

The overall goal of this study was to evaluate the potential for simultaneous Mn and organics removal via biofiltration over a range of pH and loading conditions relevant to surface water treatment facilities, especially those employing upstream coagulation and ozonation. Removal of Mn and organics was evaluated in four lab-scale anthracite coal biofiltration columns over a pH range of 6.3–7.3. The resilience of the columns to shifts in Mn concentration, hydraulic loading rate, and temperature was evaluated. The results of this study provide insight into the range of conditions conducive to biological Mn removal in surface water treatment plants and the corresponding role of microbial communities in accomplishing Mn removal.

2. Materials and methods

2.1. *Laboratory-scale biofilters*

Lab-scale glass columns were used to simulate the anthracite coal layer of a biologically active filter at a surface water treatment plant. Glass columns with 5 ft (1.52 m) length and 1.5 inch (3.81 cm) inner diameter were constructed with sampling ports at 4–6 inch (10–15 cm) intervals along the column length. Anthracite coal media (effective size 0.95–1.05 mm; uniformity coefficient <1.4) were obtained from a full-scale biofilter at the Newport News Waterworks Lee Hall Treatment Plant (Newport News, VA). The columns were inoculated with a mixture of six MOB isolated from four water treatment facilities and distribution systems (Cerrato et al. 2010). MnO_2(s) deposition capability over a range of pH (6.0–7.4), rapid growth rate, and representation of available genera were the primary criteria for isolate selection. The species classifications of the six MOB isolates were *Bacillus pumilus* (MB-2 and MB-3), *Lysinbacillus sphaericus* (MB-17), *Lysinbacillus fusiformis* (MB-22), *Pseudomonas aeruginosa* (MB-33), and *Brevundimonas nasdae* (MB-38). The media were inoculated with the MOB mixture and distributed into the four columns to a depth of two feet (0.61 m). A six-inch gravel layer (nominal size of 0.25–0.5 in, 0.64–1.3 cm) supported the anthracite coal media bed, and the columns were shielded from light with aluminum foil.

Isolates MB-2, MB-3, MB-17, MB-22, and MB-38 were reinoculated after 30 days of operation by recirculating feed water for four days with 2.5 mg/L Mn(II), as recommended by Hope and Bott (2004), because only the *Pseudomonas* isolate MB-33 remained detectable on MOB selective media during start-up.

2.1.1. *Feed water system*

The initial feed water system before reinoculation consisted of tap water from Blacksburg, Christiansburg, VPI Water Authority, dechloraminated using granular activated carbon (Calgon Centaur 12x40) with an empty bed contact time of 10 min. The average water quality characteristics of the tap water were as follows: pH – 7.7, alkalinity – 49 mg/L as $CaCO_3$, hardness – 46 mg/L as $CaCO_3$, dissolved organic carbon (DOC) – 1.2 mg/L, ammonia – 0.73 mg/L, Mn – <0.5 mg/L, nitrate – 0.45 mg/L as N, phosphate – 0.24 mg/L as P, with N and P levels sufficient to ensure carbon was the limiting nutrient. The water temperature was maintained above 20 °C and aerated to achieve 7.5–8.0 ppm dissolved oxygen. The water was pumped into the columns at 2 gpm/ft^2 (1.36×10^{-3} m/s) and supplemented with soluble Mn, pH adjustment, and biodegradable organic matter (BOM). Concentrated sulfuric acid diluted in distilled water was used for pH adjustment. Manganous sulfate monohydrate ($MnSO_4 \cdot H_2O$) was added to distilled water to achieve a 0.1 mg/L soluble Mn feed to the columns. The Mn concentration was increased 16 days after startup to 0.5 mg/L Mn in an attempt to stimulate MOB acclimation and was returned to 0.1 mg/L once Mn removal was established across the filters.