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Biological manganese removal from potable water using trickling filters

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Abstract

Two pilot-scale trickling filters were constructed and tested for manganese removal from potable water, using different fractions of silicic gravel as support media (mono- and multilayer filter). Manganese oxidation in drinking water was found to be cause by both biological oxidation and heterogeneous catalytic paths. Mixed culture populations were used to inoculate the trickling filters and the feed manganese concentrations and volumetric flow rates (VFRs) were between 0.6–2.0 mg/l and 500–2000 ml/min, respectively. The monolayer filter was flooded for high VFRs, and it was very effective for all conditions tested (100% removal efficiency, up to 2850 mg Mn/day). The multilayer filter was less effective for high manganese concentrations but it could remove up to 3250 mg Mn/day. A new mathematical model was developed assuming heterogeneous autocatalytic and biological as the main oxidation manganese paths. First order kinetics was used to describe the heterogeneous catalytic oxidation, while Monod-type kinetics was used to describe the net biological manganese oxidation. The simplicity of the pilot-scale design, the lack of need for an external mechanical aeration source and the ability to predict operation of the system offers a very attractive solution for manganese removal from potable water.

Keywords: Manganese removal; Biofilm; Modeling; Trickling filter; Potable water; Support media

1. Introduction

Although ingestion of manganese through drinking water of concentrations up to 500 μg/l has no harmful effects upon human health [1], its presence in drinking water at concentrations above 100 μg/l is undesirable to customers due to discoloration of the water and the subsequent staining of laundry and plumbing fixtures. The European Commission recommends an upper limit of 50 μg/l for manganese in water for drinking [2].

Manganese exists in several different oxidation states ranging from 0 to +7, although it is almost always found in nature in its +2, +3, and +4 state. Mn(II) is readily soluble in water while Mn(III) is more unstable and has a tendency to precipitate or dissociate to Mn(II) or Mn(IV) unless chelated to another molecule. Mn(IV) is insoluble and can be detected by the presence of a visible brown or black precipitate in neutral solutions. The oxidation of Mn(II) to Mn(IV) by aeration alone is a slow process unless the pH is raised above neutrality [3–7]. Therefore, manganese cannot be removed by simple aeration and precipitation. Current manganese removal methods generally required the use of strong oxidizing agents such as potassium permanganate, chlorine, hypochlorite, chlorine dioxide or ozone.

The role of microorganisms in the oxidation of Mn in drinking water production plants has attracted considerable attention [8–10]. A wide variety of bacteria are known to catalyze the oxidation of Mn(II). In particular, manganese oxidation can be mediated by species of several genera such as *Leptothrix, Crenotrix, Hyphomicrobium, Siderocapsa, Bacillus* sp. strain SG-1, and *Metallogenium* [11–13]. Mn(II) oxidation rates have been shown to increase by at least 3–5 orders of magnitude in the presence of Mn(II) oxidizing bacteria [14–17], and several researchers have suggested that microbial oxidation is the principal pathway in the marine environment [18,19]. Microbial Mn(II) oxidation proceeds through indirect or direct mechanisms. Indirect mechanisms include the production of O_2 (in photosynthesis) and of alkaline or oxidizing metabolites. Direct Mn(II) oxidation involves the microbial production of specific macromolecules (polysaccharides or proteins) catalyzing the process. The various oxidizing systems differ in many respects. For instance, the process can be catalyzed by metabolically inert spores, by cellular outer membrane components, or by bacterial sheaths. Also, according to the literature, bacterial manganese oxidation appears to be confined to outer surface coverings [20].

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Nomenclature

A_S	specific surface area of the support medium (cm^2/cm^3)
C_{Mn}	manganese concentration (mg/cm^3)
K_1	first order kinetic constant (cm/day)
Q	volumetric flow rate (VFR) (cm^3/day)
S	surface area of the support material (cm^2)
V_T	total volume of the compartment NI (cm^3)
V_L	bulk liquid volume in each compartment (cm^3)
X_{Mn}	biomass density in the suspension (mg/cm^3)
X_{SMn}	surface biofilm density (mg biomass/cm^2)

Greek symbols

ε	porosity
μ_{max}	maximum specific growth (1/day)

Most of the work related to bacterial manganese oxidation has been focused on investigation during batch experiments [21–23] or in natural environments [24–26]. Detailed information about the biological oxidation of manganese and the products produced has been also reported for the case of in situ groundwater treatment plants [27–29]. Recently, several studies have been carried out for the case of continuous groundwater treatment. A filter able to remove Mn from groundwater by biological oxidation and accumulation (bioaccumulation) without the addition of chemicals appears to be the most common method [30–36]. A mature biological filter capable of Mn removal is obtained by passing aerated water vertically through a column of filter sand, and allowing microorganisms to proliferate in biofilms within the void spaces. The success of manganese biofilter maturation may depend on the chemical and biological characteristics of the treatment water and maturation times may vary from weeks to months [10,11].

Several approaches have been used to express the rates of biological manganese oxidation. Studies on manganese oxidation reported in the literature use first-order [25,36] or Michaelis–Menten-type rate expressions [16,22,24,26] to describe the rate of Mn(II) removal, while there are only limited references concerning modeling of biological filters [34,36].

During Mn(II) oxidation the oxidized manganese is deposited as MnO_2 in the form of a black precipitate coating ον the sand surface. It is well known that the MnO_2 layer has a catalytic effect on Mn(II) oxidation by dissolved oxygen, accelerating the process of manganese removal [37]. Thus, in spite of the great importance of biological processes, the chemical ones cannot be neglected.

In the present study, two pilot-scale trickling filters with fractions of various sizes of silicic gravel (mono- and multilayer filters) were constructed and tested for the biological oxidation of manganese in potable water. A series of experiments were carried out in order to study the effect of the operating parameters, namely of the manganese feed concentration and of the volumetric flow rate, as well as, the effect of the support media (mono- and multilayer) on filter efficiency. A novel mathematical model was developed to describe the biological and autocatalytic manganese oxidation in the trickling filter. The proposed model is based on three assumptions: (a) the bacterial manganese oxidation is confined to outer surface coverings [20], (b) the bacterial cells attach on the frame of the biofilm forming a monolayer (this assumption has been also applied to the case of iron oxidation [38–40]) and, (c) the biofilm surface density varies at the different gravel layers due to the aggregated biomass which is deposited on the monolayer surface (this assumption was verified experimentally). Finally, mixed-culture experiments were conducted in flasks to determine the net rate of biological Mn(II) oxidation and to estimate the kinetic parameters.

2. Materials and methods

The pilot-scale trickling filters (Fig. 1) consisted of a Plexiglas tube, 160 cm high and with 9 cm internal diameter. This pilot-filter height is typical of a full-scale industrial filter. Since it is the loadings (hydraulic load and manganese concentration) per unit cross-sectional area that matter, no scale-up is necessary. For the monolayer filter, the support material was silicic gravel with a mean diameter of 1.9 mm, and specific surface area (As) of 31.05 cm^2/cm^3. The depth of the support media was 143 cm and the filter porosity (p) 0.39. The support material was not flooded for flow rates up to 1000 ml/min or hydraulic loadings up to 226 m^3/m^2 day. All flow rates used in this filter were within this limit.

In order to study the resistance of the filter at higher volumetric flow rates or hydraulic loadings, a filter with three different gravel sizes (multilayer) was also constructed. The upper part of the filter (26 cm) was filled with silicic gravel of mean diameter 3.9 mm (As = 13.85 cm^2/cm^3, $p = 0.39$). The next 39 cm were filled with silicic gravel of mean diameter 2.4 mm (As = 22.74 cm^2/cm^3, $p = 0.39$), while the lower part (78 cm) was loaded with silicic gravel of mean diameter 1.9 mm (As = 31.05 cm^2/cm^3, $p = 0.39$). The support media in this filter was not flooded for flow rates up to 2000 ml/min or hydraulic loadings up to 452 m^3/m^2 day. All flow rates used in this filter were within this range.

The filter media was loaded in the filters and was washed with water from the supply network for 48 h. The silicic gravel originated from a quarry near the city of Larissa, Greece. At the top of the filter, there was a fixed nozzle, which distributed the incoming water evenly to the whole filter surface. An underdrain system collected the treated water and any biological solids that would detach from the media. Along the filter depth, there were 10 sampling ports for manganese concentration measurements in the bulk liquid. Thus, it was possible to have an experimental assessment of the manganese concentration profiles along the filter depth.

The pH and dissolved oxygen measurements were carried out using the Hanna pH211 pH meter, and the Hanna HI9143 dissolved oxygen meter, respectively. During all experiments, pH, temperature and total manganese concentration were measured on a daily basis. The liquid samples after filtration through a 0.2 μm membrane filter were analyzed for total dissolved man-