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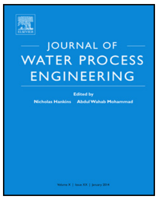

Removal of manganese (II) from drinking water by aeration process using an airlift reactor

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ABSTRACT

The objective of this study is the removal of soluble manganese Mn(II) from drinking water by aeration process in order to oxidize it into insoluble manganese dioxide MnO_2 using a Split-Rectangular Airlift Reactor (SRAR). The description of the global hydrodynamics, liquid mixing and gas-liquid mass transfer properties of the SRAR were presented in previous works and were compared to data and correlations in the literature. The effects of operating conditions were investigated, including initial pH, Mn(II) concentrations and amount of MnO_2 particles. The major findings are that the oxidation of Mn(II) corresponds to a kinetically-slow reaction that is strongly pH-dependent. The kinetic data show an autocatalytic behaviour due to the oxidation of Mn(II) on the MnO_2 surface, which allows the conversion to go to completion. This behaviour is confirmed by the addition of MnO_2 fine particles that increase drastically the reaction rate. At high initial Mn(IV) concentrations, the kinetic law was shown to be pseudo-first order in Mn(II), with an apparent kinetic constant depending on the initial amount of Mn(IV) compounds. This constant was fitted by a linear model as a function of Mn(IV) concentration. This model was shown to be in good agreement with experimental data. Comparing with other techniques, aeration is an efficient process because it gives us a removal efficiency of 90% in less than 40 min at pH 9.5 and initial soluble Mn(II) and insoluble Mn(IV) concentrations between 5 and 20 and 0–500 mg/L, respectively, while avoiding the drawbacks of strong oxidizers and biological oxidation processes. A model able to predict quantitatively Mn removal as a function of pH, initial Mn(II) and initial Mn(IV) concentrations is also developed.

1. Introduction

Manganese is one of the most common contaminants found in both surface and groundwater, but predominantly in the latter. When present even at low concentrations, it can be linked to the following problems: discoloration, turbidity, odor and taste problems, or form slime manganese dioxide accumulations in pipes [1–5]. Thus, high level of manganese in drinking water are considered undesirable, because when water is exposed to air, Mn(II) is oxidized to Mn(IV), this Mn(IV) precipitate can stain household utensils and clothes, also it may impart a metallic, bitter, astringent or medicinal taste to the water [6]. In spite of this, it causes severe economic losses through discoloration of products, specks in finished paper, textile, food and beverage products, and reduction of pipeline carrying capacities [7]. Besides, the metals promote the growth of certain types of chlorine tolerant micro-organisms in water distribution systems. This biota can provide protected sites for noxious organisms and consequently, vastly increase the costs of cleaning and sterilizing systems that contain organisms dangerous to human health [8].

Although there is little evidence that the consumption of water with natural concentrations of this metal has adverse effects on public health and even though it is in fact an essential element for human diet, it does remain problematic from an aesthetic, technical and economic point of view. The guidelines for Moroccan drinking water present a recommended limit of 0.05 mg/L manganese

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Table 1
Advantages and disadvantages of diverse techniques for Mn removal.

Techniques	Advantages	Disadvantages
Hydroxide precipitation	Low capital cost, widely used technique	High pH requirement, sludge generation, high operating cost
Coagulation/flocculation	Sludge settling, dewatering characteristics, bacterial inactivation capability, and sludge stability	High pH requirement, high operating cost
Flotation	High metal selectivity, high removal efficiency, low detention periods.	High maintenance and capital cost
Ion exchange	Environment friendly, energy efficient, no sludge generation, less time consuming, easy to control	Not all ion exchange resins are suitable for metal removal, expensive technique, only used for trace amount of metals in water due to clogging, regeneration of resins causes secondary pollution, cannot be used for large scale
Oxidation/filtration	The majority of iron and manganese treatment system employ this method, low-cost method, no requirement of electricity (suitable for rural areas)	Difficulty in storage and transport of the oxidant, corrosion, formation of solid manganese compounds that may interfere with system operations, formation of by-products
Electrocoagulation	Rapid, required low chemicals, production of less sludge	High capital cost, high energy consumption
Adsorption	Effective and economic method, high-quality of treated effluent, regeneration of the adsorbents is possible	High cost of activated carbon limits the method, so that low cost adsorbents should be used, many natural/low-cost adsorbents show poor adsorption capacity, low efficiency/cost ratio, ineffectiveness at high metal concentration
Membrane filtration	High efficiency, no need for chemicals, no production of solid waste, compact, simple automation	Membrane fouling, high operational cost, low permeate flux

Table 2
Solubility of MnO_2 as a function of pH.

pH	Solubility of MnO_2 (ppm)
2.1	1.3
3.0	0.9
5.4	0.5
6.9	0.1
7.0	0.1
8.4	0.3
8.7	0.02
10.2	0.1
10.6	0.2

for aesthetic reasons and the objective is to reach 0.01 mg/L in a near future, while the concentration of Mn(II) species in groundwater may reach up to 20 mg/L in Morocco. This requires changes in process and operating conditions of drinking water treatments.

Indeed, conventional manganese removal plants typically rely on physicochemical treatments by precipitation [9], precipitate flotation [10], ion exchange [11], coagulation/flocculation [12], oxidation/filtration using strong oxidation agents, such as O_3, $KMnO_4$ and ClO_2 [13–21], electrochemical treatments, such as electrocoagulation with aluminium electrodes [22,23], adsorption [24–31], and membrane processes, *i.e.* nanofiltration [32] and microfiltration [33,34].

The processes mentioned above exhibit often operating issues and significant disadvantages, such as high energy consumption, high operating cost and formation of by-products [17–19,35]. In this context, Table 1 summarizes the advantages and disadvantages of each technique.

The aim of the present study is the removal of soluble Mn(II) from potable water by oxidation with atmospheric oxygen in order to oxidize it into highly insoluble manganese dioxide MnO_2 in a 63 L split-rectangular airlift reactor. The hydrodynamic, liquid mixing and gas-liquid mass transfer characteristics of this reactor were described in previous works and compared to data and correlations in the literature obtained for a reactor volume between 4.7 L and 4600 L [36,37]. Airlift reactors constitute a particular class of bubble columns that is highly efficient for carrying out aeration [38]. They combine the advantages of conventional bubble columns (compactness, low operating and maintenance costs due to the absence of internals...) to several additional advantages, such as enhanced mixing and higher mass transfer rates due to the overall liquid circulation [39].

Experiments were carried out using synthetic water under semi-batch flow conditions at room temperature and atmospheric pressure. The effect of operating conditions were investigated, including the influence of pH and initial concentrations of soluble Mn(II) and insoluble Mn(IV) manganese forms.

2. Kinetics of manganese oxidation y dissolved oxygen

Manganese dioxide is slightly soluble; in addition, its solubility varies with pH (Table 2) [40]. At the higher pH levels, the Mn(II) in solution is similar to the Mn(IV) solubility. In parallel, air oxidation of Mn(II) to insoluble MnO_2 is an extremely slow process at pH values typical of natural waters (6–8). Thus, to achieve a higher oxidation rates, an increase in pH is required [13].

The kinetic studies have generally shown that the oxidation of Mn(II) to Mn(IV) includes an autocatalytic mechanism in addition to a term proportional to the reduced metal ion concentration. However, some researchers have concluded that this mechanism of auto-oxidation does not take place between Mn(II) and insoluble MnO_2 particles at pH values below 9 [41–43]. The oxidation of dissolved manganese with dissolved oxygen can be described by the following mechanism [44]:

$$Mn\,(II) + O_2 \xrightarrow{k_1} MnO_2 \quad (1)$$

$$Mn\,(II) + MnO_2 + O_2 \xrightarrow{k_2} 2\ MnO_2 \quad (2)$$

At constant pH and under constant oxygen partial pressure, reaction rate is therefore commonly expressed as a function of Mn(II) and Mn(IV) concentrations [7,44]:

$$r_{Mn^{2+}} = (k_1 + k_2\,[Mn(IV)]) \cdot [Mn(II)] \quad (3)$$

However, as the reaction produces a solid phase and because autocatalysis is a heterogeneous mechanism that competes with homogeneous oxidation, a precise estimation of kinetic constants is difficult. According to Davies et al. [45], the rate of oxidation of