Desalination and Water Treatment
www.deswater.com

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doi: 10.1080/19443994.2012.734731

51 (2013) 2225–2230
February

Taylor & Francis
Taylor & Francis Group

An experimental study on manganese(II) removal with manganese dioxide recycling

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Received 13 December 2011; Accepted 23 August 2012

ABSTRACT

Manganese dioxide (MnO_2) particles have a catalytic effect on removing Mn(II) from contaminated water. On the basis of this effect, a manganese removal process was proposed in this paper. For this purpose, the oxidation of Mn(II) was studied first in batch reactor and then in continuous reactor. The experimental conditionals for batch reactor were Mn(II): 3 mg/l, Mn(IV): 0–800 mg/l, pH: 9.6, temperature: 25 ℃ and for continuous system, the conditionals were kept the same except Mn(II) concentration. A quadratic equation was obtained as a function of Mn(IV) concentration to determine the catalytic reaction rate constant. It was experimentally demonstrated that there was no significant effect of Mn(IV) on the Mn(II) oxidation at Mn(IV) concentrations beyond 800 mg/l. Furthermore, reaction kinetics was derived from the data of batch experiments. Based upon the reaction kinetics, it has been theoretically demonstrated that the volume of aeration tank can be significantly reduced by keeping a high concentration of Mn(IV) in the reactor. Lastly, manganese oxidation was studied in a continuous flow lab scale system with and without MnO_2 sludge recirculation. In this system, until Mn(IV) concentration had reached 300 mg/l, Mn(II) removal rate had increased linearly, but beyond this level increase had continued decreasingly. This study shows that, instead of using stronger oxidants in the drinking water treatment systems, recycling of MnO_2 flocks provides important advantages like low investment cost, minimization of treatment area and, because of the lack of using oxidants, low operation cost.

Keywords: Autocatalytic effect; Catalytic effect; Manganese removal; Manganese oxygenation; Reaction kinetics

1. Introduction

Manganese is the second most abundant transition metal after iron in the crust of earth [1]. In drinking water distribution systems, sloughing of manganese oxide deposits results in water of poor aesthetic quality which has a brown-black colour and undesirable taste and which causes staining of fixtures, equipment, swimming pools and laundry [2–9]. To control these manganese-related problems in water distribution systems, water regulatory bodies set recommended levels. Most water authorities adhere to the World Health Organization (WHO) recommended level of 0.05 mg/l [10]. This level is a compromise value set primarily to minimize staining. There is little published experimental evidence available to support the designation of recommended levels, which vary widely (Table 1) [5].

Manganese is generally present in natural water in concentration under 10 mg/l, but it rarely can be present in natural water in concentrations exceeding

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Table 1
Examples of recommended levels for manganese in drinking water [5]

Mn concentration (mg/l)	Reference
0.01–0.02	Griffin [3]
0.05	US EPA [5]
0.1	WHO [6]
0.05	WHO [10]
0.1	NHMRC/AWRC [11]
0.05	WHO [12]
0.05	CCREM [13]
<0.1	This study

Notes: WHO, World health organization; NHMRC, National health and medical research council, Australia; AWRC, Australian water resources council; US EPA, US environmental protection agency; and CCREM, Canadian council of resource and environment ministers.

10 mg/l [14]. The elevated levels of manganese in water are considered undesirable, because when water is exposed to air, Mn(II) is oxidized to Mn(IV) immediately [15]. The oxidation of Mn(II) to Mn(IV), only with aeration, is a slow process unless the pH is raised above neutrality [16]. There are different manganese removal methods in the literature like adsorption [17,18], membrane filtration [19,20], etc., but the most common manganese removal methods generally require the use of strong oxidizing agents such as potassium permanganate, chlorine, hypochlorite, chlorine dioxide or ozone [21]. There are disadvantages in using chemically based oxidation agents for removal of manganese in rural areas of developing countries. The chemicals are costly and require proper handling methods.

In the absence of dissolved oxygen and low pH, Fe(II) and Mn(II) are chemically reduced, soluble forms which exist in a reducing environment. These conditions exist in groundwater and anaerobic reservoir water. When it is pumped from underground or an anaerobic hypolimnion, carbon dioxide and hydrogen sulphide are released, and the pH is raised. In addition, the water is exposed to air creating an oxidizing environment. The reduced iron and manganese start transforming to their stable, oxidized, insoluble forms of Fe(III) and Mn(IV). The rate of oxidation of Fe(II) and Mn(II) depends upon the type and concentration of the oxidizing agent, pH, alkalinity, organic content and presence of catalysts. The natural reaction by oxygen is enhanced in water treatment by using spray nozzles or waterfall-type aerators. The pH for oxidation of manganese should be at pH 9.5 or higher.

Fe(III) and Mn(IV) have a catalytic effect on the oxidation of iron and manganese, respectively. Manganese oxides are catalytic in the oxidation of manganese up to 800 mg/l. [22]. The oxygenation of manganese is catalyzed by the reaction product MnO_2. This was evidenced by the improved efficiency of many treatment plants after a coating of oxidized manganese has built up on the contact aerator, or multiple tray aerator, and filter media.

This study was carried out in three stages. In the first stage, the oxidation of Mn(II) is studied in batch reactors in which the concentration of Mn(IV) was in the range of 0–800 mg/l at pH 9.6. In the second stage, reaction kinetics derived from the data of batch experiments in the first stage. In the third stage, manganese oxidation was studied in continuous flow lab scale system with and without MnO_2 sludge recirculation.

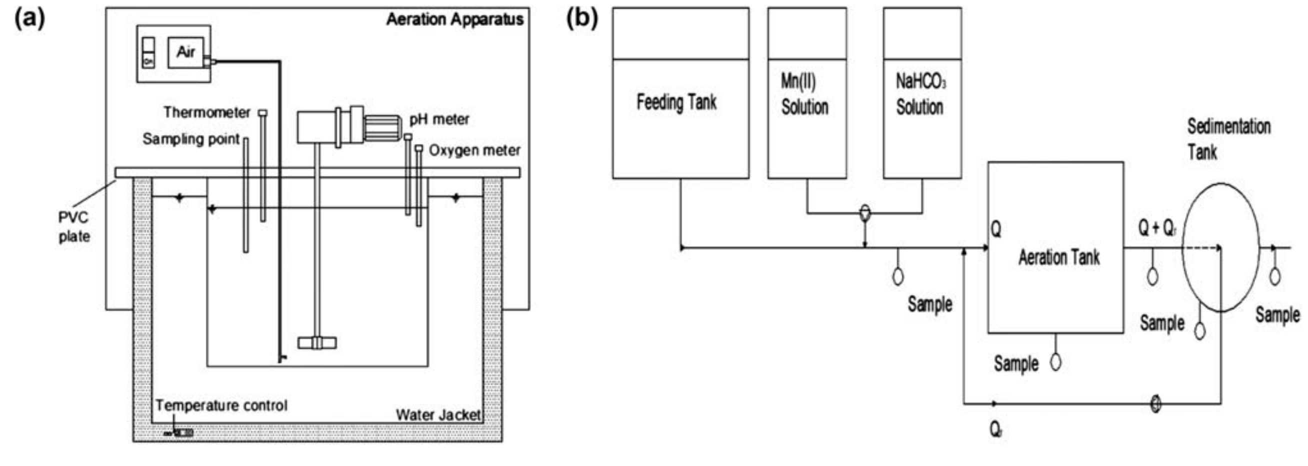

Fig. 1. Experimental set-ups; (a) batch system and (b) continuous system.

2. Experimental and analytical methods

2.1. Batch system

The oxidation of Mn(II) was studied in a batch reactor of a litre volume under the constant pH, temperature and O_2 concentration (Fig. 1(a)). The reaction vessel was intensely mixed using Wisestir HS-50A type of mixer. $NaHCO_3$ was added into the distilled water in order to obtain a solution with an alkalinity equal to 2×10^{-2} eq/l. Air was given into the solution using fine bubble diffusers. The pH of the solution was controlled by adding 0.1 N NaOH and 0.1 N H_2SO_4. The pH of the solution was measured by Schott lab 850 type of ion analyzer with sensitivity of ±0.001 pH unit. The dissolved oxygen levels were monitored using Armfield oxygen meter. Constant temperature (25˚C) was maintained by immersing the reaction vessel into GN 111–200 Gastronorm water bath.

Mn(II) stock solution was prepared by dissolving manganese sulphate monohydrate ($MnSO_4.H_2O$) in 1 l demineralized water. The samples taken at pre-decided times as measured from the start of the experiments were immediately filtered and acidified after filtration with 2 ml HNO_3. The filtration through a 0.22 μm membrane filter is an accepted procedure defined in Standard Methods (3010A) for the determination of dissolved manganese. Residual Mn(II) concentrations were determined by atomic absorption spectrometer (AAS) [23,24]. The detection limit for the AAS manganese measurement was 0.015 mg/l as Mn(II). All experiments were conducted at 25˚C and 9.6 of pH.

2.2. Continuous system

The flow diagram of the experimental set-up designed to test effectiveness of the Mn(IV) in manganese removal by atmospheric oxygen oxidation is given in Fig. 1(b).

The system was constructed using Plexiglas. The volumes of the aeration and sedimentation tanks were 4 and 16 l, respectively, and pH was adjusted by calibrating acid and base. In general, the hydraulic retention time in aeration tank and in the sedimentation tank and detention time were chosen as 20 and 40 min and 20 days, respectively. Throughout the experiment, the pH was kept between 9.5 and 9.7; the temperature was kept at room temperature. The alkalinity was kept constant (equal to 2×10^{-2} eq/l).

3. Results and discussion

As stated before, this study has three stages. These three stages were discussed below.

3.1. First stage: batch system

The results of the experiments with initial Mn(II) concentration of 3 mg/l and with varying initial Mn (IV) concentrations were given in Fig. 2. Catalytic rate constant, k_{cat}, was calculated from the slopes of the lines on semi logarithmic plots of Mn(II) and time. It is evident from these figures that the Mn(II) oxidation is in accordance with the first-order kinetics. Needed time for the completion of the reaction was about 123 min when there was no Mn(IV) in the reactor.

Whereas, the reaction time was reduced to about 35 min when 800 mg/l of Mn(IV) was added initially into the reactor. Thus, the reaction time was fairly shortened with increasing initial Mn(IV) concentrations. The k and k_{cat} rate constants were obtained through the experiments in batch system, respectively (See Fig. 3). As it can be seen from Fig. 3, k_{cat} was linearly increasing as the initial Mn(IV) concentration increases up to 100 mg/l following a second-order polynomial. This means that there was a catalytic effect of Mn(IV) on the Mn(II) of oxidation at Mn(IV) concentrations up to 800 mg/l.

3.2. Second stage: process kinetics

In the presence of Mn(IV), the oxidation of Mn(II) by the atmospheric oxygen occurs by two simultaneous processes. One of these is the homogeneous reaction, taking place in solution, and the other one is the heterogeneous reaction occurring on the surface of the manganese dioxide precipitates.

At constant pH and O_2 concentration, the Mn(II) oxygenation rate has been expressed by Pankow and Morgan [25] as:

$$\frac{-\mathrm{d}[\mathrm{Mn(II)}]}{\mathrm{d}t} = k[\mathrm{Mn(II)}] + k_1\{[\mathrm{Mn(II)}][\mathrm{Mn(IV)}]\} \tag{1}$$

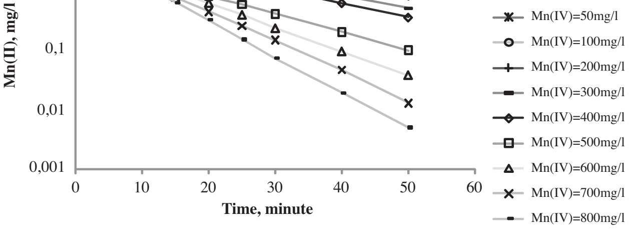

Fig. 2. Variation of log Mn(II) and time with different initial Mn(IV) concentrations (pH = 9.6, temperature = 25˚C, alkalinity = $2x10^{-2}$eq/l and pO_2 = 0.21 atm).

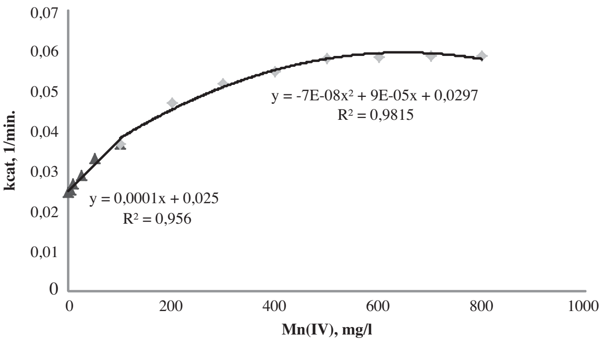

Fig. 3. Changes in k_{cat} with $[\text{Mn(IV)}]_0$.

in which

k: apparent homogeneous rate constant, (s^{-1})

k_1: apparent heterogeneous or catalytic rate constant, $[(\text{mg/l})^{-1}\text{s}^{-1}]$

[Mn(II)]: manganese ion concentration, mg/l

[Mn(IV)]: manganese ion concentration, mg/l

$$\frac{-\text{d}[\text{Mn(II)}]}{\text{d}t} = \{k + k_1[\text{Mn(IV)}]_0\}[\text{Mn(II)}] \tag{2}$$

$$k_{\text{cat}} = \{k + k_1[\text{Mn(IV)}]_0\} \tag{3}$$

in which $[\text{Mn(IV)}]_0$ is the initial Mn(IV) concentration, or:

$$\frac{\text{d}[\text{Mn(II)}]}{\text{d}t} = -k_{\text{cat}}[\text{Mn(II)}] \tag{4}$$

where k_{cat} is a constant for a constant pH and O_2 concentrations. Integration of Eq. (4) yields:

$$[\text{Mn(II)}] = [\text{Mn(II)}]_0 e^{-k_{\text{cat}} \cdot t} \tag{5}$$

Applying the curve fitting techniques to the data of Fig. 4, the following equations are obtained between the k_{cat} and Mn(IV) concentration.

$$k_{\text{cat}} = 0.0001[\text{Mn(IV)}]_0 + 0.025 \text{ for } \leq 100\text{mg/lMn(IV)} \tag{6}$$

$$k_{\text{cat}} = -7 \times 10^{-8}[\text{Mn(IV)}]_0^2 + 9 \times 10^{-5}[\text{Mn(IV)}]_0 + 0.0297 \text{ for } 100 < \text{Mn(IV)} \leq 800\text{mg/l} \tag{7}$$

Batch experiments were carried out to determine the dependence of k_{cat} on $[\text{Mn(IV)}]_0$. The following equations were given by substituting the k_{cat} equations into Eq. (5) for pH = 9.6, temperature = 25℃, alkalinity = 2×10^{-2} eq/l and $\text{pO}_2 = 0.21$ atm.

$$[\text{Mn(II)}] = [\text{Mn(II)}]_0 \cdot \text{e}^{-\{0.0001[\text{Mn(IV)}]0+0.025\}\cdot t} \text{ for } \leq 100\text{mg/lMn(IV)} \tag{8}$$

$$[\text{Mn(II)}] = [\text{Mn(II)}]_0 \cdot \text{e}^{-\{0.0297+9\times10^{-5}[\text{Mn(IV)}]_0-7\times10^{-8}[\text{Mn(IV)}_0^2]\}t} \text{ for } 100<\text{Mn(IV)} \leq 800\text{mg/l} \tag{9}$$

By applying the process kinetics which was obtained in batch system, to the continuous flow systems, the following equation was given for the required volume of the aeration tank [26].

$$V = \frac{Q([\text{Mn(II)}]_0 - [\text{Mn(II)}])}{k_{\text{cat}}[\text{Mn(II)}]} \tag{10}$$

If the required volume of the aeration tank with the catalytic effect of the Mn(IV) is V, and the required volume without the catalytic effect of Mn (IV) is V_{o}, then the following equation can be written [25].

$$\frac{V}{V_{\text{o}}} = \frac{k}{k_{\text{cat}}} \tag{11}$$

or by substituting the values of k_{cat} as appears in Eqs. (12) and (13).

$$\frac{V}{V_{\text{o}}} = \frac{0.025}{0.025 + 1 \times 10^{-4}[\text{Mn(IV)}]_0} \leq 100 \text{ mg/l} \tag{12}$$

$$\frac{V}{V_{\text{o}}} = \frac{0.0297}{0.0297 + 9 \times 10^{-5}[\text{Mn(IV)}]_0 - 7 \times 10^{-8}[\text{Mn(IV)}_0^2]} \text{ for } 100<[\text{Mn(IV)}]_0 \leq 800\text{mg/l} \tag{13}$$

High Mn(IV) concentrations were used in this study, because Mn(II) concentrations in natural waters are low to produce the required Mn(IV) concentrations in the aeration tank. Therefore, recirculation of the Mn(IV) sludge from the sedimentation tank to the aeration tank was suggested similar to the activated sludge process of the wastewater treatment.

The change of V/V_0 ratios with the $[\text{Mn(IV)}]_0$ and $[\text{Fe(III)}]_0$ were illustrated in Fig. 4. For the purpose of the comparison, the V/V_0 ratios—as given by Sarikaya [26] and Tufekci [27]—up to initial Fe(III) concentrations of 200 and 600 mg/l, respectively, were also shown in Fig. 4.

It is evident from Fig. 4 that substantial saving is possible in the volume of aeration tank of the continuous flow manganese removal systems by maintaining

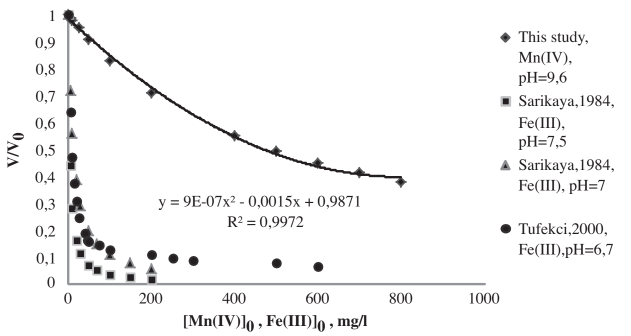

Fig. 4. The change of V/V_0 rations with the $[Mn(IV)]_0$ in the aeration tank.

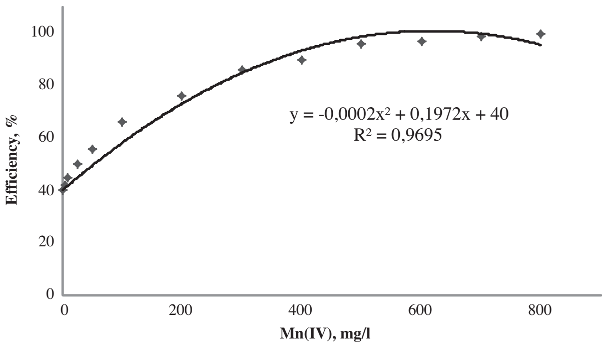

Fig. 5. The change of efficiency of Mn(II) with the Mn(IV) concentration.

high concentrations of the Mn(IV) in the aeration tank.

The oxygenation rate increased linearly with the increasing Mn(IV) concentrations up to 100 mg/l and a second-order polynomial relationship was found between the reaction rate and the Mn(IV) concentrations in the range of 100–800 mg/l. The required volume (V) of the aeration tank and the effluent Mn(II) concentrations were determined as a function of the Mn(IV) concentration. The volume of the aeration tank, required for the same Mn(II) conversional, was reduced by a factor of 38 when the Mn(IV) concentration was raised from 0 to 800 mg/l. The 15-fold reduction in the volume of aeration tank was experimented by Tufekci before [27]. Because of the long period of manganese oxidation, there was more reduction of aeration tank from the study which made with Fe(II) [27].

3.3. Third stage: continuous system

In this stage, the experiments were repeated with Mn(II) concentration of 3 mg/l in the continuous system, but the oxidation phase did not observed clearly. Instead of such low Mn(II) concentrations like this, 7.5–10 mg/l Mn(II) concentrations were used in the continuous system.

The efficiency of conversion was plotted against Mn(IV) concentration in the aeration tank in Fig. 5.

When there was no Mn(IV) concentration in the aeration tank, oxidation rate was 40%, but when the addition of Mn(IV) concentrations—which were between 5–800 mg/l—started, increase in the oxidation rate started too (Fig. 5). For instance, the oxidation efficiency was 40% at the start of the experiment, but it increased up to 99.8% towards to the end of the run.

On third stage, the temperature was changed between 23 and 27°C and influent Mn(II) concentration varied within the range of 7.5–10 mg/l. Although there was random variation of the parameters which affect the rate of Mn(II) oxidation, such as pH and temperature, there has been systematically an increase of the oxidation rate with the increase of Mn(IV) concentration.

However, the increase of oxidation efficiency rate was decreased with increase of Mn(IV) concentrations, no significant effect of Mn(IV) was observed at Mn (IV) concentrations between 400 and 800 mg/l.

4. Conclusions

This study had demonstrated the catalytic effect of Mn(IV) on the Mn(II) oxidation by atmospheric oxygen up to the Mn(IV) levels of about 800 mg/l.

On the first stage, a quadratic equation had been obtained to determine the catalytic reaction rate constant, k_{cat} as a function of Mn(IV). For low Mn(IV) concentrations, the oxidation rate was dominated by homogeneous reaction whose rate constant, k, had been determined as $k = 0.025$ for values equal and lower than 100 mg/l Mn(IV) concentrations and $k = 0.0297$ for the values between 100 and 800 mg/l Mn(IV) concentrations.

On the second stage, the data which experimented on the first stage was adapted successfully to reaction kinetics for continuous system. Thus, 38-fold reduction in the aeration tank volume was experimented.

On the third stage, the experimental result had been proved that Mn(IV) improves the efficiency of Mn(II) oxidation by atmospheric oxygen significantly. The oxidation efficiency was increased from 40% when Mn(IV) concentration was negligible at the start of experimental run to a value of 99.8% at the end of the experiment.

Acknowledgement

This work was supported by the Research Fund of the University of Istanbul (Project number BAP-UDP-18042).

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