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Original Research

The Effects of Sulphate, Nitrate, and Humic Substances on Mn(II) Oxidation with Atmospheric Oxygen in Drinking Water

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Abstract

Manganese removal is an important problem. Mn cannot be removed by membrane filtration without being oxidized to manganese dioxide, and oxidation is one of the conventional methods for removing manganese from water. The aim of this study is to find out the effects of SO_4^{2-} (sulphate), NO_3^- (nitrate), and humic substances on oxidation of Mn(II) with atmospheric oxygen in drinking water when drinking water obtained from ground water and surface water includes many humic substances, SO_4^{2-} and NO_3^-, due to soil. In this paper we studied the oxidation in four-stage batch systems. First, Mn(II) concentrations used different initial concentrations, pH values and filter papers having different pore diameters. Then we investigated the effects of SO_4^{2-}, NO_3^-, and humic acids following determination of optimum initial concentration, pH and filter paper. According to statistical analysis, there are significant effects of additional substances on Mn(II) oxidation with atmospheric oxygen ($p<0.001$).

Keywords: manganese removal, oxidation, humic substances, sulphate, nitrate

Introduction

Manganese is one of the most common contaminants found in both surface and ground waters. Soluble manganese in a distribution system can cause aesthetic problems such as water discoloration and fouling, staining on plumbing fixtures, and consumer complaints [1]. Mn(II) accumulation and release can be a costly and difficult problem for drinking water utilities to resolve [2]. The presence of higher concentrations in source waters means specific treatment processes such as hypolimnetic oxygenation [3].

When manganese is present in a water supply at concentrations exceeding the permitted limits of 0.05 mg/L [4], it is objectionable for the following reasons:

(a) its precipitation gives water a reddish and brown-black color when exposed to air
(b) manganese gives water an unpleasant metallic taste
(c) home softeners become clogged by manganese precipitates and thus their softening efficiency is reduced
(d) deposits of iron and manganese precipitate in the distribution system reduce the pipe diameter and eventually clog the pipe. In addition, manganese has been found to affect the central nervous system [4, 5].

Manganese can be found in natural water both in its most reduced and soluble form, the manganese(II) ion and in the oxided form MnO_2 (pyrolusite), respectively. If not

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oxidized, manganese(II) ions can easily escape through water treatment processes and, once in the distribution system, can gradually be oxidized to insoluble manganese dioxide, causing several problems such as water discoloration, metallic taste, odor, turbidity, biofouling, corrosion and, staining laundry and plumbing fixtures [6].

The reaction of organic matters with Mn(II) in the oxidation of Mn(II) with atmospheric oxygen equations can be written like the reaction of Fe(II) with organic matters.

$$Mn(II) + O_2 \rightarrow Mn(IV)$$
$$Mn(IV) + organic \rightarrow Mn(II) + oxidized\ organic$$
$$Mn(II) + O_2 \rightarrow Mn(IV)$$

The purpose of this investigation is to explain the effect of Mn(II) oxidation with atmospheric oxygen in the presence of dissolved organic and inorganic substances. 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.

Sulphate is a major anion occurring in both natural waters and industrial effluents, such as those of the chemical and metallurgical industries [7, 8], as well as in mine drainage (either neutral or acid) [9].

Nitrate contamination in surface and ground water has become an increasingly important problem all over the world. The most common sources of nitrate are uncontrolled land discharges of municipal and industrial waste water, overflowing septic tanks, processed food, dairy and meat products, and decomposition of decaying organic matters buried in the ground. Nitrates are extremely soluble in water and can move easily through soil into the drinking water supply [10].

Humic substances (HS) present in natural water are high-molecular-weight and heterogeneous macromolecular materials with various molar mass moieties and distinct functional groups [11]. There are plenty of oxygen-containing functional groups in HS molecules, e.g., notably carboxylic and phenolic groups [11, 12], which have a strong capability of complexing metal ions or ionic organic compounds. Thus, HS can modify the chemical speciation of trace metals, stabilize inorganic colloids via adsorption, or facilitate the transport of organic compounds in environments [13]. Pollutants binding to HS may also have a significant effect on the total and free concentrations of pollutants present in surface and ground water. Because HS are crucial to biological availability, mobilization, and transport of many pollutant species, it is essential to elucidate the interactions between HS and pollutants.

The aim of this study is to understand the effects of SO_4^{2-}, NO_3^-, and humic substances on oxidation with atmospheric oxygen of Mn(II) in drinking water. Experimental conditions were kept at alkalinty = 2×10^{-2} eq/L, T= 25ºC, pO_2 =0.21 atm. Experimental studies were carried out in four-stage batch systems. In the first stage, the oxidation with atmospheric oxygen of Mn(II) was studied at 3 mg/L and 5 mg/L initial Mn(II) concentrations at 9.0 and 9.5 pH values, using filter pore diameters having 0.2 μm and 0.45 μm pore diameters and real Mn(II) values were determined. In the second stage, the effects of SO_4^{2-} on the oxidation of Mn(II) were studied at 3 mg/L initial concentration, 9.5 pH and using 0.2 μm filter paper. In the third stage the effects of NO_3^- were investigated at 3 mg/L initial concentration, 9.5 pH and using 0.2 μm filter paper. In the fourth stage, effects of humic substances have been investigated on oxidation at the same pH, initial concentration values, and using 0.2 μm filter paper.

Materials and Method

The oxidation of Mn(II) was studied in a batch reactor of two-liter volume under constant pH, temperature, and O_2 concentration. The experimental setup is shown in Fig. 1.

The reaction vessel was intensely mixed using a Yellow Line OST 20 Basic type of mixer. $NaHCO_3$ was added to the distilled water to obtain a solution with an alkalinity equal to 0.02 M.

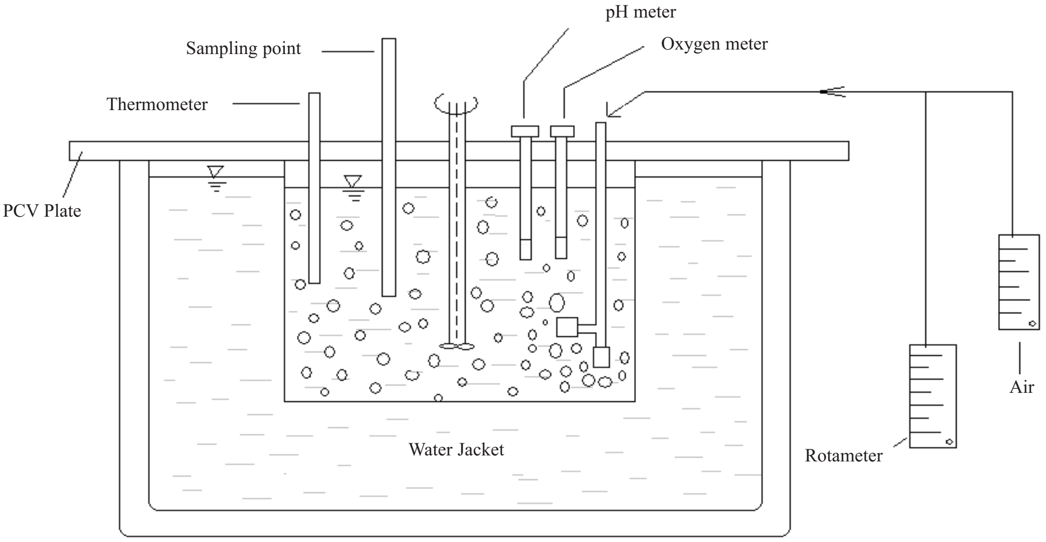

Fig. 1. Experimental setup.

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 JENWAY model 3040 type of ion analyzer with sensitivity of 0.001 pH unit. The dissolved oxygen levels were monitored using a WTW Oxi 538 oxygen meter. Constant temperature (25ºC) was maintained by immersing the reaction vessel into an ORDEL OC770 water bath.

Mn(II) stock solution was prepared by dissolving $MnSO_4 \cdot H_2O$ (manganese sulphate monohydrat) in 1 liter 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. Filtration through 0.2 and 0.45 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 spectrometry [13-15]. 0.5, 1, 3, and 5 mg/L standards were prepared using Merck quality 1000 mg/L Mn AAS stock solution. These standards were determined at UNICAM 929 AAS. Mn (II) values were determined in samples. The detection limit for the AAS manganese measurement was 0.015 mg/L as Mn/L. All experiments were at 25ºC.

In this study all experiments were repeated three times at least. In the same conditions, results generally were found to be very close to each other. This shows that experimental conditions have been kept constant and experiments are iterated. In the study, only one experiment was used for each set as a representative.

Results and Discussion

First Stage:
Mn(II) Oxidation with Atmospheric Oxygen Using Different Filter Diameters in Different Initial Mn(II) Concentrations and pH Values

At the first stage of the study, oxidation of Mn(II) with atmospheric oxygen was performed at 3 and 5 mg/L initial concentrations and 9 and 9.5 pH values. During oxidation GF/C filter papers having 0.45 µm pore diameter were used to understand hold efficiency of MnO_2 flocs and determine Mn(II). Therefore filter papers with 0.2 µm pore diameter were additionally used to understand the difference between the filter papers.

As known, AAS measures total manganese. However MnO_2 flocs may mix with the residue. For this reason filter papers with 0.2 µm and 0.45 µm pore diameter are used. Experiments were studied to see the difference between two types of filter pore diameters. As seen from obtained results (Figs. 2-5), oxidation goes ahead slowly at both pH values using 0.45 µm filter paper on the grounds that MnO_2 flocs cannot be held well and pass through filtrate. During the use of AAS, Mn(IV) flocs are determined as if they are Mn(II). Therefore, measured values of Mn(II) in the filtrate are the real values due to holding of MnO_2 flocs efficiently by 0.2 µm filter paper. Actually, there is no difference at the reaction rate and it was seen that what appeared to be different resulted from contamination of MnO_2 flocs to the filtrate.

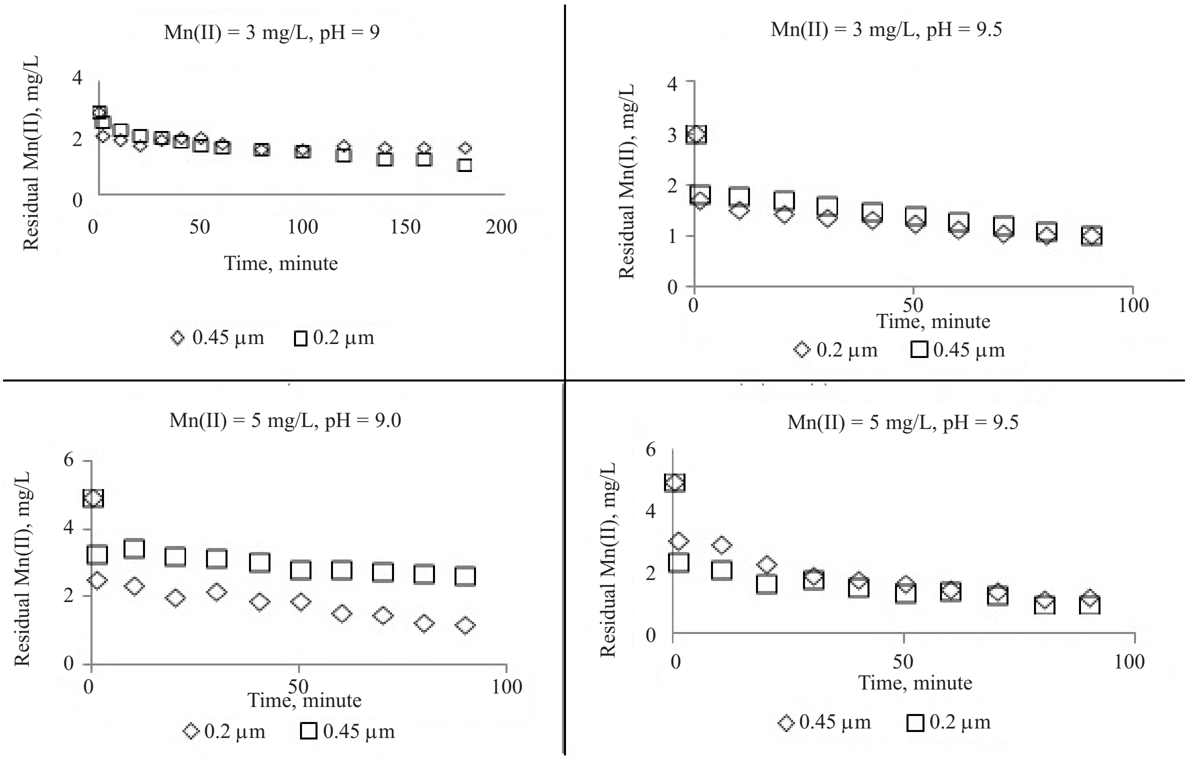

Fig. 2. Effect of different filter diameters at Mn(II) determination ($[Mn(II)]_o$: 3 mg/L and 5 mg/L, pH: 9.0 and 9.5, temperature: 25ºC, alkalinity: 2×10^{-2} eq/L, pore diameter: 0.2 µm, 0.45 µm)

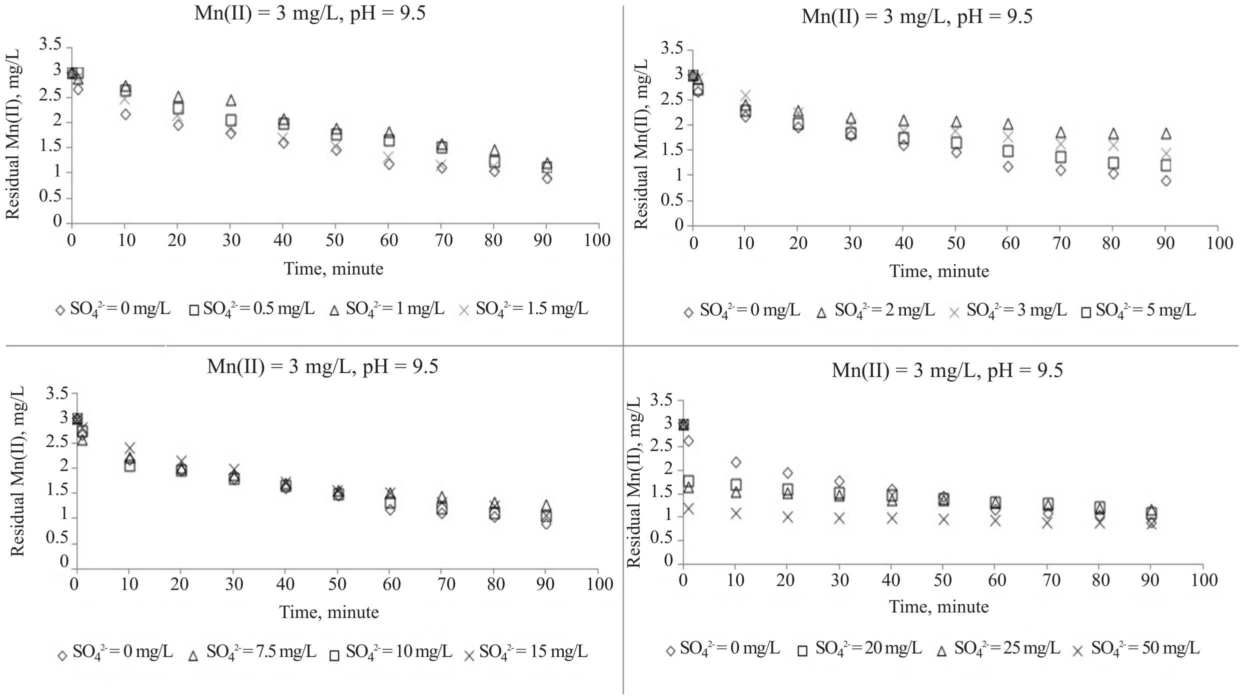

Fig. 3. Effect of SO_4^{2-} on Mn(II) oxidation ($[Mn(II)]_o$: 3 mg/L, pH: 9.5, temperature: 25ºC, alkalinity: 2×10^{-2} eq/L, pore diameter: 0.2 μm).

Effects of SO_4^{2-}, NO_3^-, and humic acids on oxidation experiments were performed in the same conditions including 3 mg/L initial Mn(II) concentrations, 9.5 pH, and using filter paper having 0.2 μm pore diameter. On the grounds that according to preliminary experiments optimum efficiency was obtained at 3 mg/L initial concentrations, 9.5 pH values and using 0.2 μm filter pore diameter. It was indicated that 9.5 pH is an optimum value for Mn(II) oxidation by other authors [16, 17].

Second Stage:
Effect of SO_4^{2-} on Mn(II) Oxidation with Atmospheric Oxygen

At the second stage of the study, the effect of SO_4^{2-} was investigated on oxidation of Mn(II) with atmospheric oxygen. For these experiments we kept initial concentration at 3 mg/L and initial pH at 9.5. GF/C filter paper having 0.2 μm pore diameter were used for filtration following oxidation due to hold of MnO_2 flocs by 0.2-μm pore diameter efficiently.

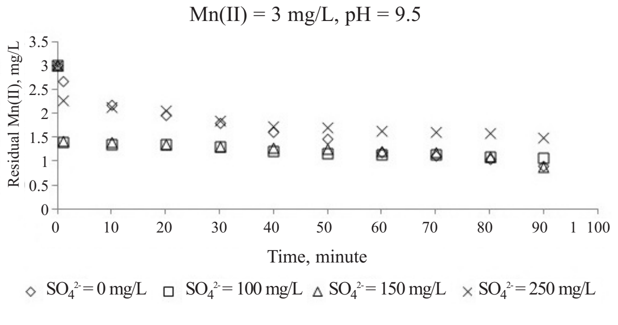

Fig. 4. Effect of SO_4^{2-} on Mn(II) oxidation ($[Mn(II)]_o$: 3 mg/L, pH: 9.5, temperature: 25ºC, alkalinity: 2×10^{-2} eq /L, pore diameter: 0.2 μm).

As shown in Figs. 3 and 4, after the addition of SO_4^{2-} at 0.5-250 mg/L concentration a deceleration was observed in oxidation. However, this case is not a systematic deceleration. According to ionic balance in the medium, the presence of ions such as SO_4^{2-} and NO_3^- redoubles the solubility of $Mn(OH)_2$. Therefore, MnO_2 flocs cannot be formed and the oxidation rate slows down.

Third Stage:
Effect of NO_3^- on Mn(II) Oxidation with Atmospheric Oxygen

The effect of NO_3^- was studied at the third stage of the experiment under the same conditions such as initial conditions, pH and used filter paper having 0.2 μm pore diameter. As nitrate, KNO_3 was used to understand the effects of NO_3^- on the oxidation of Mn(II).

As shown in Figs. 3 and 4, after the addition of NO_3^- at 0.5- 15 mg/L concentration a deceleration was observed in oxidation. However this case is not a systematic deceleration similar to the effect of SO_4^{2-} results. For increasing concentration of NO_3^- from 15 mg/L to 40 mg/L, oxidation rate accelerated a bit and after the 50th minute decelerated. According to ionic balance in the medium, the presence of ions such as SO_4^{2-} and NO_3^- redoubles the solubility of $Mn(OH)_2$. Therefore, MnO_2 flocs cannot be formed and oxidation rate slows down.

Fourth Stage: Effect of Humic Acid on Mn(II) Oxidation with Atmospheric Oxygen

Oxidation of Mn(II) with atmospheric oxygen was examined using various concentrations of humic acids at the fourth stage.

Oxidation rates were investigated with the addition of humic acid at 0.5-15 mg/L concentrations under conditions of Mn(II)= 3 mg/L, pH 9.5, temperature 25ºC, and using 0.2 µm pore diameter filter paper. As can be seen from Fig. 6, after the addition of humic acid at 0.5-15 mg/L concentration, it was observed that oxidation rate accelerated a bit and decelerated beginning from the 50th minute.

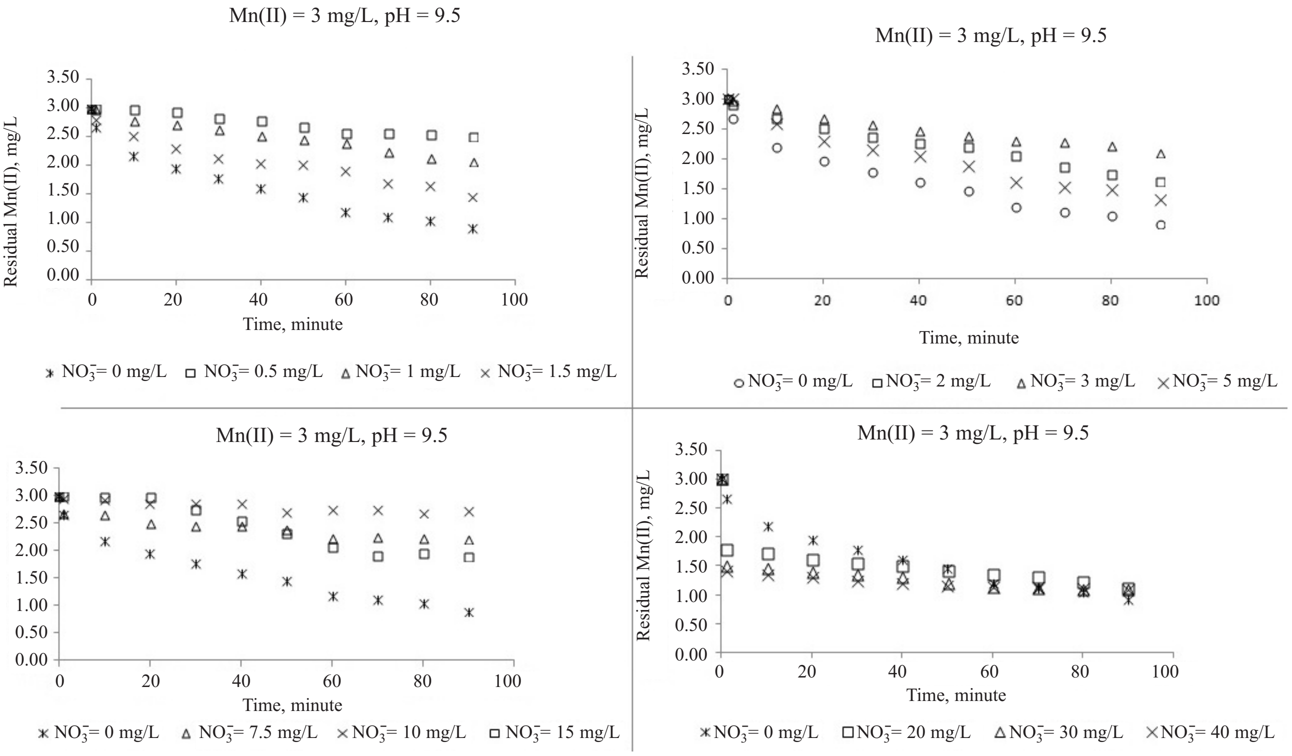

Fig. 5. Effect of NO_3^- on Mn(II) oxidation ($[Mn(II)]_o$: 3 mg/L, pH: 9.5, temperature: 25ºC, alkalinity: 2×10^{-2} eq /L, pore diameter: 0.2 µm).

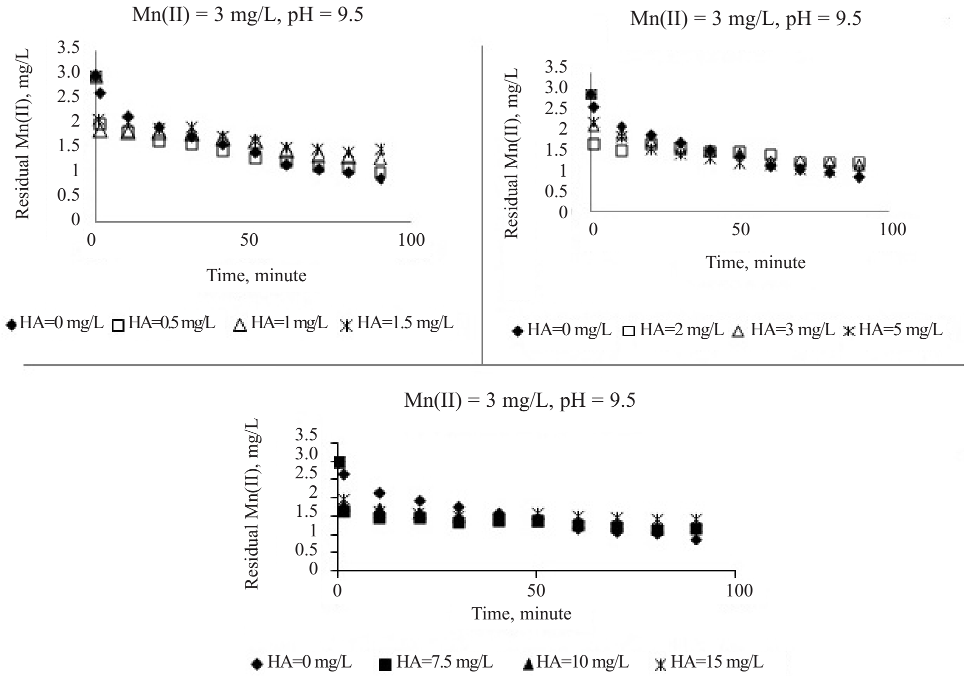

Fig. 6. The effect of humic acids on Mn(II) oxidation ($[Mn(II)]_o$: 3 mg/L, pH: 9.5, temperature: 25ºC, alkalinity: 2×10^{-2} eq/L, filter diameter: 0.2 µm).

Table 1. One-way ANOVA table.

	ANOVA				
Mn (mg/L)	Sum of squares	df	Mean square	F	Sig.
Between groups	66.703	36	1.853	6.973	0.000
Within groups	98.316	370	0.266		
Total	165.019	406			

Reason for this case, oxidation at 9.5 pH value and solubility of humic acid in alkali medium cause an acceleration in oxidation at the beginning. $Mn(OH)_2$ decreases the pH value of the medium and complex aptitude of humic acid and Mn(II) increases. For this aptitude [Mn(II)]/(humic acid), proportion is effective.

Although humic acids accelerate the oxidation, Mn(II) can be kept without exposure to oxidation for a while due to organic matter concentration and pH value. Humic acids prevent the formation of MnO_2 flocs.

Statistical Analysis (ANOVA)

For the analysis of our results, the SPSS 11 statistical package was employed. As it is seen in Table 1, a one-way ANOVA was carried out to assess the effects of additional substances on Mn(II) oxidation with atmospheric oxygen and, according to the results, there are significant differences in their oxidation rate among those additional substances (one way ANOVA, F (36, 370) = 6,973, $p<0.001$). Once we found out that there is a difference, Tukey test was conducted. According to our multiple comparisons, the Mn(II) oxiditation rate is significantly different when we add NO_3^- (0.5 mg/L) and NO_3^- (10 mg/L).

Conclusion

SO_4^{2-}, NO_3^-, and humic acids are found in natural water. In this study effects of these matters were investigated on Mn(II) oxidation with atmospheric oxygen. Firstly, oxidations were performed at 3 mg/L and 5 mg/L initial Mn(II) concentrations, and at 9.0 and 9.5 pH values then 0.2 μm and 0.45 μm diameter pore filter papers were used. Diameter pores of 0.2 μm filter pore diameter are smaller than 0.45 μm filter pore diameter and can hold Mn(IV) better on the paper.

The addition of SO_4^{2-} and NO_3^- at various concentrations has considerable slowing down effects on the oxidation of Mn(II) with atmospheric oxygen. During the oxidation of Mn(II) the solubility of $Mn(OH)_2$ increases and in this case prevents the formation of MnO_2 flocs in the presence of SO_4^{2-} and NO_3^- ions. Depending on this, oxidation rate decelerates.

Various concentrations of humic acids in the medium at first considerably accelerated and later on decelerated the oxidation of Mn(II) with atmospheric oxygen. Oxidation is speedy for a definite period by reason of high solubility of humic acid. Mn(II) can be kept without exposure to oxidation for a while due to organic matter concentration and pH value. Oxidation decelerated after a specified time by reason of humic acids prevents the formation of MnO_2 flocs. Formed $Mn(OH)_2$ decreases the pH value of medium and complex aptitude with humic acid increases. Oxidation rate declined with complexing of Mn(II) and humic acid.

In conclusion, whereas sulfate and nitrate have a slowing down effect on Mn(II) oxidation with atmospheric oxygen, humic asit accelerated until the 50th minute and then decelerated the oxidation rate of Mn(II).

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