

The Effects of Some Inorganic and Organic Species on Oxidation with Atmospheric Oxygen of Manganese in Natural Water

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Received: 4 February 2010

Accepted: 19 July 2010

Abstract

Manganese (Mn) is an important element in environmental geochemistry. In many natural aquatic systems, high concentrations of manganese are present with organic and inorganic matters. The oxidation of Mn(II) in aqueous systems has been extensively studied. But inorganic and organic matter effects on oxidation have not been fully clarified. It is clear that Mn(II) oxidation in the presence of inorganic and organic matter runs differently.

The aim of this study is to investigate the effects of some inorganic species (Mg(II), Ca(II), Ni(II), Zn(II)) and also some organic species (gallic acid and tartaric acid) on oxidation of manganese Mn(II) with atmospheric oxygen in natural water.

Experimental studies have been carried out in a three-stage batch system. All experiments have been conducted in a condition of alkalinity: $1.2 \cdot 10^{-2}$ eq/L, pH=9.5, T=25°C, $pO_2=0.21$ atm.

According to the results, magnesium and calcium concentrations of 50 mg/L and above slowed down the oxidation of Mn(II), and nickel and zinc did not have any significant effect on oxidation. Similarly, it was found that gallic acid decelerated oxidation when tartaric acid did not have any important effect on oxidation.

Keywords: manganese removal, oxidation, autocatalytic effect, inorganic ions, organic compounds

Introduction

Manganese is an important element in the aquatic environment. It can exist in various oxidation states. But the II and IV oxidation states are of greatest importance in natural waters [1]. Mn(II) is relatively soluble and forms many complexes in aqueous solution. Less than 5% of the dissolved manganese in seawater is associated with carbonate,

bicarbonate, or organic ligands. The sulfato and chloro complexes of Mn(II) are important species in seawater [2]. Manganese is the subject of much interest, because its oxides and hydroxides are highly adsorptive and are thought to scavenge other heavy metals. Of particular interest are the ferromanganese nodules that are abundant in aquatic environments. These deposits contain, in addition to iron and manganese, high concentrations of cobalt, nickel, copper, and other metals [3]. In addition to the above-mentioned species, organic species also are abundant in many natural aquatic environments. In natural waters, oxidated

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Mn(II) can be reduced by naturally occurring organics [4-6]. Appreciable concentrations of dissolved manganese can be maintained in aerobic aquatic systems in the presence of natural organic species [7]. Redox chemistry strongly influences the precipitation and dissolution of Fe and Mn solid phases, and also plays an important role in the early diagenetic behavior of numerous other elements, including phosphorus and trace metals [8]. According to the distinctive conditions such as pH, temperature, and ionic species, etc., interaction between them characterized oxidation-reduction reaction and present species.

Oxidation of Mn(II) in bicarbonate-carbonate solutions was studied by Hem [9] and Morgan and Stumm [10]. A rate law for autocatalytic oxidation of Mn(II) was proposed by Morgan [11]:

$$-d[\text{Mn(II)}]/dt = k_1'[\text{Mn(II)}] + k_2'[\text{Mn(II)}][\text{MnO}_x] \quad (1)$$

...where $k_1' = k_1[\text{O}_2][\text{OH}^-]^2$ and $k_2' = k_2[\text{O}_2][\text{OH}^-]^2$ [12].

Morgan showed that x ranged from 1.24 to 1.43 at pH range 9 to 10 [1].

The first term in Eqn. 1 ($k_1'[\text{Mn(II)}]$) represents homogeneous oxidation and the second term ($k_2'[\text{Mn(II)}][\text{MnO}_x]$) describes a heterogeneous mechanism due to oxidation at manganese oxide surfaces. Mn(II) oxidation may, therefore, be autocatalytic as Mn(II) oxidation increases MnO_x site concentration. Manganic dioxide was known to adsorb the manganese ion, which can be progressively oxidized with time [1, 13-15]. It is found that metal oxides have catalytic effects on Mn(II) oxidation. Catalytic effects of different metal oxides have been studied extensively [1, 3, 11, 14-18].

In equation 1, $[\text{Mn(II)}]$ and $[\text{MnO}_x]$ represent concentrations of dissolved reactant and solid oxidized reaction product, respectively, and k_1' is a pseudo first-order rate constant for Mn(II) disappearance from solution.

The pseudo first-order rate constant k_1' depended on temperature, oxygen concentration, pH, and Mn(II) species in solution. Higher concentrations of $[\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ were observed to lower the rate of Mn(II) oxidation [19].

Stumm and Giovanoli reported the formation of γ -MnOOH when 5-10 μM Mn(II) was oxygenated in simulated lake waters [20]. Sung showed the presence of β -MnOOH when millimolar levels of $[\text{Mn(II)}]$ were oxygenated, both in the presence and absence of HCO_3^- [21].

Davies and Morgan studied Mn(II) oxidation at unit oxygen partial pressure, micromolar level of $\text{Mn(II)}_{\text{total}}$, and low pH in CO_2 - HCO_3^- - CO_3^{2-} solutions [20]. Davies demonstrated that his solutions, while supersaturated with respect to $\text{MnCO}_3(\text{s})$, did not yield any precipitate in the absence of dissolved O_2 . Davies' experiments thus yielded homogeneous first-order oxidation rate constants, k_1 , in the expression:

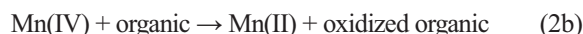
$$-d[\text{Mn(II)}]/dt = k_1[\text{Mn(II)}]$$

...over the pH range 8.95 to 9.25 [19].

Davies also studied the oxidation of Mn(II) by oxygen in the presence of goethite, lepidocrocite, silica, and alumina. It is found that the Mn(II) oxidation rate is inhibited by Mg(II) , Ca(II) , silicate, salicylate, phosphate, chloride, and sulphate in the presence of lepidocrocite. Phthalate had little or no effect on the rate of this reaction. Laboratory studies indicate that in natural waters the important factors that influence Mn(II) on metal oxides are pH, iron oxide concentration, temperature, $[\text{Mg}^{2+}]$, $[\text{Cl}^-]$ and ionic strength [3].

Oxidation of manganese by oxygen depends on those pathways in a particular water environment, e.g. biological, oxide surface catalysis, or homogeneous solution oxidations. Based on a reaction between Mn(II) and oxygen, dissolved Mn(II) species transforms into a sparingly soluble Mn(III) oxyhydroxide phase. The product is subject to removal to the sediments of a water body and/or further oxidation to $\text{MnO}_2(\text{s})$ phase in the water column. Mn(III) and Mn(IV) solid phases are subject to reduction by organic carbon compounds and other reductants with a return to the Mn(II) state [3]. Sunda et al. researched the effect of different organic matter on manganese oxide and determined that marine organic matter caused photoreduction of manganese oxides by a photocatalyzed reaction [5]. The reduction and dissolution of Mn(III) and Mn(IV) by organics was studied by Stone [4].

The reaction of organic matters with Mn(II) in the oxidation of Mn(II) with atmospheric oxygen equations can be written, likewise the reaction of Fe(II) with organic matters. This scheme is given in equations 2a-c.



In the presence of organic matter, manganese complex formation will affect the oxidation rate. Different organic materials show different complexation affinities for metals and it is clear that different inorganic and organic matter types have different effects on oxidation. Diem and Stumm (1984), have shown that Mn^{2+} is not oxidized by O_2 within several years [22]. It is suspected that the persistence of Mn(II) in oxic waters is the evidence of the reduction of Mn(IV) by natural organic matter [5-8]. Investigations help to understand the effects of different matters on oxidation of Mn(II) and have a number of ramifications relative to water quality management [22].

Previous work on Mn(II) oxidation kinetics has been done at low ionic strengths with low initial Mn(II) concentrations (μM -mM) [1, 3, 23]. Our work was designed to determine the effect of selected inorganic and organic matter on Mn(II) oxidation under controlled conditions of constant as pH=9.5, alkalinity= $1.2 \cdot 10^{-2}$ eq/L, $T=25^\circ\text{C}$, $p\text{O}_2=0.21$ atm. Experimental studies have been performed in three-stage batch systems.

In the first stage, the oxidation with atmospheric oxygen of Mn(II) was studied between $[\text{Mn(II)}]_0=1-25\text{mg/L}$. In the

second stage, the effects of Mg(II), Ca(II), Ni(II), and Zn(II) as inorganic matters were studied for $[\text{Mn(II)}]_0=10$ mg/L. In the third stage the effects of gallic acid and tartaric acid as organic matters on oxidation of Mn(II) were investigated.

Experimental Procedures

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 set up is illustrated 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 $1.2 \cdot 10^{-2}$ eq/L. Air was given into the solution using fine bubble diffusers. The pH of the solution was kept constant using 0.1 N NaOH and 0.1 N H_2SO_4 . The pH of the solution was measured by a JENWAY model 3040 type ion analyzer with sensitivity of 0.001 pH unit. The dissolved oxygen levels were monitored using a WTW Oxi 538 oxygen meter. Constant temperature (25°C) was maintained by immersing the reaction vessel in a water bath (ORDEL OC770).

Mn(II) stock solution was prepared by dissolving a determined amount of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (manganese sulphate monohydrate) 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 with 2 ml HNO_3 after filtration. Samples were filtered through a $0.22 \mu\text{m}$ membrane filter according to Standard Methods (3010A) for the determination of dissolved manganese. Residual Mn(II) concentrations were determined by atomic absorption spectrometer (AAS) [20]. The detection limit for the AAS manganese measurement was 0.015 mg/L as Mn. All experiments were conducted at 25°C and 9.5 of pH.

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

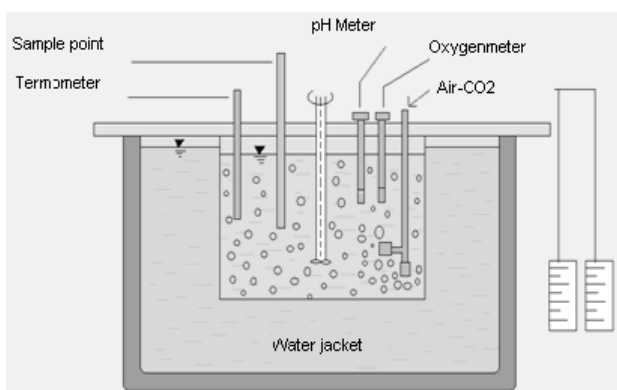


Fig. 1. Experimental Setup.

Results and Discussion

First Stage: Mn(II) Oxidation with Atmospheric Oxygen in Different Initial Mn(II) Concentrations

The results of the experiments performed with different initial Mn(II) concentrations of 1-25 mg/L are given in Fig. 2. Morgan demonstrated the homogeneous rate equation of Mn(II) oxidation reaction with $d[\text{Mn(II)}]/dt = k_1[\text{O}_2][\text{OH}^-]^2[\text{Mn(II)}]$ [1]. At constant pH and P_{O_2} , it yields $d[\text{Mn(II)}]/dt = k_1[\text{Mn(II)}]$ and reaction rate constants (k_1) can be obtained from equations of the lines in linear curves in Fig. 2.

The linear relationship between Mn(II) concentration and time on a semi-logarithmic plot indicated the first order kinetics, in line with the results given in the literature. As can be seen from Fig. 2, reaction rate constant k_1 obtained from the slope of the line for $[\text{Mn(II)}]_0=1.0, 5.0,$ and 25.0 mg/L is 0.0048, 0.009, and 0.0195 min^{-1} , respectively.

There have been slight changes in the reaction rate up to 10 mg/L of initial concentrations of Mn(II), but the reaction rate increases significantly for concentrations greater than 10 mg/L. This shows that the autocatalytic effect was introduced obviously for Mn(II) concentrations greater than 10 mg/L. This autocatalytic effect has also been observed in recent studies [17, 25, 26].

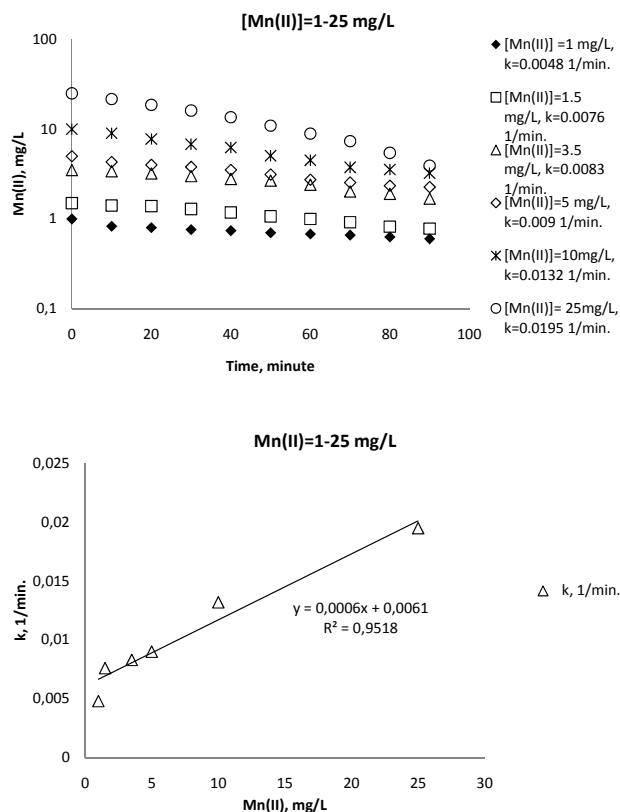


Fig. 2. Variation of Mn(II) with time under varying initial Mn(II) concentrations ($[\text{Mn(II)}]_0=1-25$ mg/L, $\text{pH}=9.5$, $T=25^\circ\text{C}$, alkalinity= $1.2 \cdot 10^{-2}$ eq/L, $p_{\text{O}_2}=0.21$ atm).

Second Stage:
The Effect of Inorganic Species (Mg(II), Ca(II),
Ni(II), Zn(II)) on Mn(II) Oxidation with
Atmospheric Oxygen

In this stage, 10 mg/L, which was found to be the maximum concentration in natural waters, was chosen as the initial concentration of Mn(II) and the effects of some dissolved inorganic species on oxidation were investigated. Like ferrous iron, pseudo-first-order kinetics with respect to Mn(II) were observed in treatment plants or seawater. Therefore, like the first stage, reaction rate constant k_1 is obtained from equations of the lines in linear curves, in the second and third stages of the study.

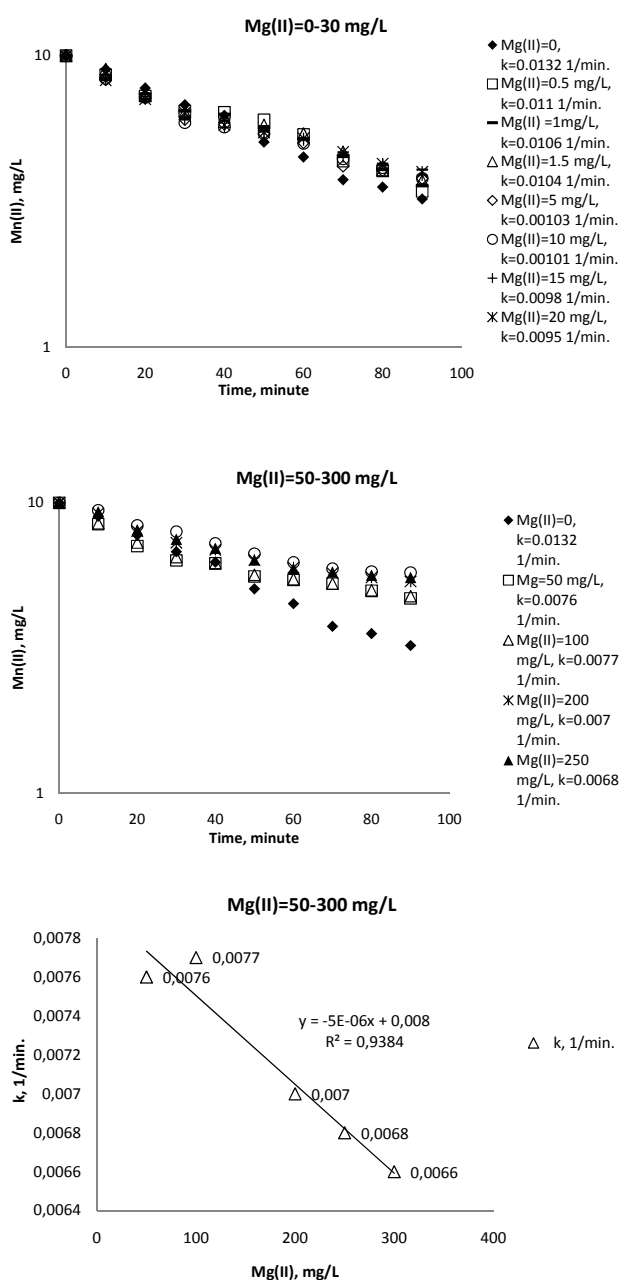


Fig. 3. Variation of Mn(II) with time under different initial magnesium concentrations ($[Mg(II)]_0=0-300$ mg/L, $pH=9.5$, $T=25^\circ C$, alkalinity= $1.2 \cdot 10^{-2}$ eq/L, $pO_2=0.21$ atm).

Effect of Magnesium on Mn(II) Oxidation

Oxidations of Mn(II) were performed at 10 mg/L initial Mn(II) concentration in the presence of different Mg(II) concentrations (0.5-300 mg/L). Experimental conditions were kept at a constant $25^\circ C$, $1.2 \cdot 10^{-2}$ eq/L alkalinity, and 9.5 pH. Results are given in Fig. 3.

As can be seen from Fig. 3, at 10 mg/L initial Mn(II) concentration, 0.5-20 mg/L Mg(II) additions were a little decelerated in oxidation when compared with oxidations without Mg(II) addition. This effect is conspicuous when Mg(II) concentrations go up to 50 mg/L and more. According to the figure, reaction rate constant was 0.0132 min^{-1} without the addition of Mg(II). This rate was 0.0095 min^{-1} , 0.0077 min^{-1} , and 0.0066 min^{-1} for 30, 100, and 300 mg/L Mg(II) additions, respectively. After adding 50 mg/L and more Mg(II) to the reactor, it was observed that water turned white. This color change can be explained by the formation of magnesium hydroxides and carbonates due to suitable pH value, and it is considered that these formations can decelerate oxidation. As we know, increasing dissolved salt concentration in water decreases the saturation concentration of oxygen. Furthermore, diffusion of oxygen decelerates by reason of turbidity.

Davies researched various ion effects, including Mg on Mn(II) oxidation and explained in terms of the effects Mg has binding of Mn(II) to the surface [3].

Effect of Calcium on Mn(II) Oxidation

As can be seen from Fig. 4, oxidation slowed down insignificantly with the addition of 0-15 mg/L Ca(II) concentrations when compared with no Ca(II) addition. According to the figure, at the initial Mn(II) concentration of 10 mg/L, reaction rate constant was 0.0132 min^{-1} without calcium addition. Moreover, rate constants were 0.0094 min^{-1} , 0.0064 min^{-1} , and 0.0061 min^{-1} with the addition of 50, 100, and 300 mg/L Ca(II), respectively.

With the addition of Ca(II) concentrations of 50 mg/L and more, a deceleration was observed in oxidation of Mn(II). Likewise, Mg(II), when Ca(II) was added to the media at concentrations of 50 mg/L and more, caused the formation of a white colour in the water. This case could be explained in the same manner as Mg(II), which at suitable pH and in the presence of calcium hydroxides forms carbonates due to the addition of calcium. Possibly, the formation of these dissolved salts decelerate diffusion of oxygen and decreases saturation and slows down the oxidation in the same way.

Effect of Nickel and Zinc on Mn(II) Oxidation

In this stage of the study, the effect of Ni(II) and Zn(II) on oxidation of Mn(II) was investigated and initial Mn(II) concentration was kept constant at 10 mg/L. According to Figs. 5a and b, it can be seen that an insignificant change occurs in k_1 values. Therefore, it can be concluded that Ni(II) and Zn(II) shows the same behaviour and does not have any important effect on Mn(II) oxidation.

Third Stage: The Effect of Organic Substances (Tartaric Acid, Gallic Acid) on Mn(II) Oxidation

The initial concentration of Mn(II) was 10 mg/L and tartaric and gallic acid was added at concentrations of 0.5-1.5 mg/L to the media, separately. Although in the literature it is stated that the addition of tartaric acid will decrease the oxidation rate, according to Fig. 6, it can be seen that the addition of tartaric acid increased the oxidation rate at the beginning and then it decreased after 50 minutes.

Gallic acid also increased the oxidation rate in the early age of the reaction, but this effect was not persistent. The common point obtained from all concentrations is that tartaric and gallic acid slowed the oxidation down after 30-40 minutes. Rate deceleration effect of gallic acid is conspicu-

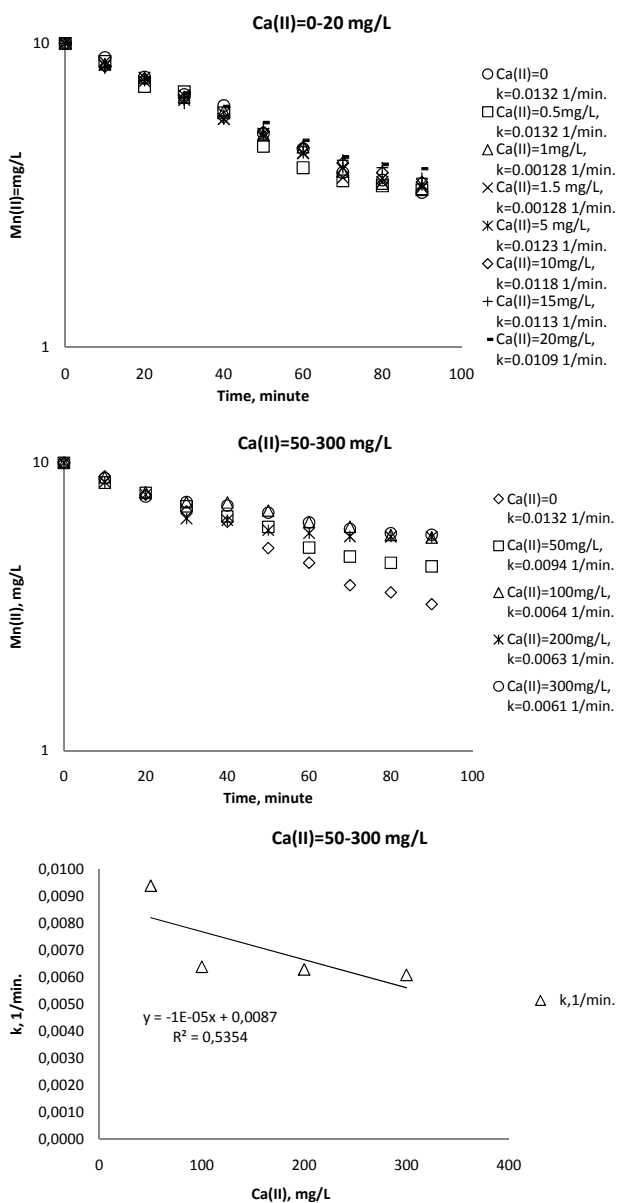


Fig. 4. Variation of Mn(II) with time under varying initial calcium concentrations ($[Ca(II)]_0 = 0-300$ mg/L, pH=9.5, T=25°, alkalinity= $1.2 \cdot 10^{-2}$ eq/L, $pO_2 = 0.21$ atm).

ous. This can be explained that it blocks Mn(II) after Mn(II) forms complexes with tartaric acid and the oxidation slowed down [21, 22, 25, 26].

Conclusions

In this study investigating that the effects of inorganic substances (Mg(II), Ca(II), Zn(II), Ni(II), and organic substances (gallic acid, tartaric acid) on the oxidation with atmospheric oxygen of Mn(II), results are given below.

- There have been slight changes in the reaction rate up to 10 mg/l of initial concentrations of Mn(II), but the reaction rate increases significantly for concentrations more than 10 mg/l. This shows that the autocatalytic effect was introduced obviously for values greater than 10 mg/L.
- It was seen that the addition of different Mg(II) concentrations slightly decelerated Mn(II) oxidation. This effect is insignificant (even though negligible) in the concentration range of 0-30 mg/L, while the addition of 50 mg/L and more magnesium to the reactor resulted in white coloration. This case can be explained with the formation of magnesium hydroxides and carbonates that decelerated oxidation. A known increase in dissolved salt concentration decreases the saturation concentration of oxygen. This condition effects oxygen diffusion to the water and slows down oxidation.

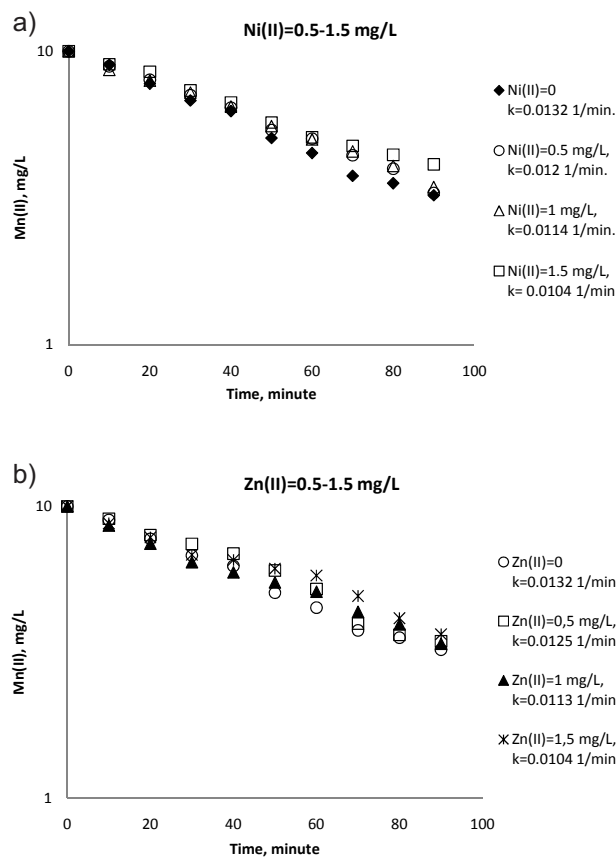


Fig. 5. a) Mn(II) oxidation for $[Ni(II)]_0 = 0.5-1.5$ mg/L, b) Mn(II) oxidation for $[Zn(II)]_0 = 0.5-1.5$ mg/L ($[Mn(II)]_0 = 10$ mg/L, pH=9.5, T= 25°C, alkalinity= $1.2 \cdot 10^{-2}$ eq/L, $pO_2 = 0.21$ atm).

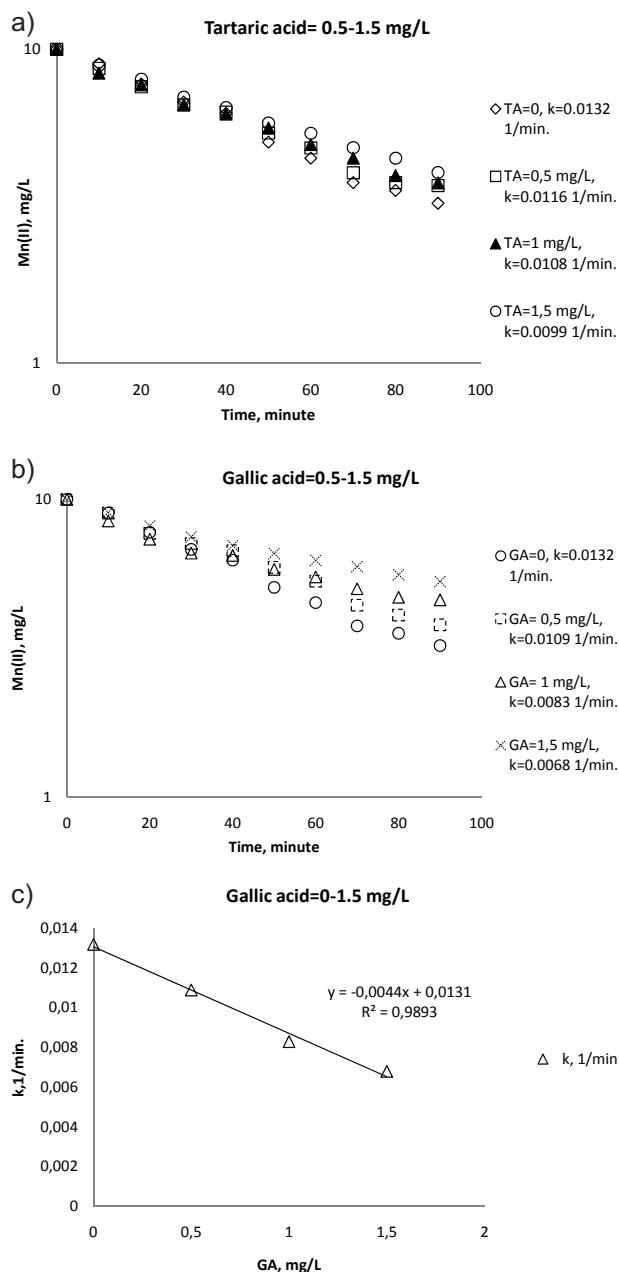


Fig. 6. a) Mn(II) oxidation for 0.5-1.5 mg/L tartaric acid b) Mn(II) oxidation for 0.5-1.5 mg/L gallic acid (pH=9.5, T= 25°C, alkalinity=1.2·10⁻² eq/L, pO₂=0.21 atm).

- In the early stages of the reaction it was observed that small concentrations of Ca(II) and Mg(II) accelerated Mn(II) oxidation. But these effects were not permanent. With the addition of Ca(II) and Mg(II) concentrations of 50 mg/L and more, a deceleration was observed in oxidation of Mn(II). As emphasized before, water turned white after the addition of calcium at 50 mg/L, and more than 50 mg/L concentrations due to the formation of calcium hydroxides and carbonates in water. Moreover, an increase in dissolved salt in water gives rise to a decrease of concentration of oxygen and this situation causes a slowdown in oxidation.
- It was seen that Ni (II) and Zn(II) did not affect Mn(II) oxidation considerably.

- Tartaric acid and gallic acid increased the oxidation rate in the beginning and then the oxidation rate decreased. The rate deceleration effect of gallic acid was more important than tartaric acid. This could be explained with the fact that it blocked Mn(II) after Mn(II) formed complexes with tartaric acid and oxidation slowed down.

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