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# Effect of organic and inorganic matters on the oxidation of Fe(II) in raw water from Ömerli Dam

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## ABSTRACT

In Turkey, particularly in Istanbul, almost all of the surface and underground water sources contain ferrous iron [Fe(II)] at high concentration levels, which generate serious problems in use of water for industrial processes and at drinking water treatment plants. Ferric iron [Fe(III)] on the other hand precipitates as $Fe(OH)_3$ and blocks the filters installed at water treatment plants, decreasing efficiency. Also, the period for re-wash of filters shortens which increases the cost. In natural waters, high iron concentrations are found together with natural organic and inorganic substances. Humic substances found in underground water sources prevent the oxidation of Fe(II). It was shown in recent studies that oxidation of Fe(II) was decreased dramatically by organic compounds found in humic substances. Although atmospheric oxidation of Fe(II) is a well known method in practice over decades, effects of organic and inorganic substances on the oxidation rate have only recently been investigated. Literature review showed that the research in the area of effect of organic and inorganic substances over the oxidation of Fe(II) was not satisfactory. Since high concentrations of Fe(II) exist in the surface and underground water and it is critically important for the purpose of drinking and industrial use, it will lead to research and development regarding the methods for treatment of Fe(II). An experimental study was carried out by aeration at constant pH, temperature, alkalinity, and mixing conditions in a laboratory scale batch reactor system, which was fed with raw water obtained from entrance of Ömerli Dam Treatment Plant and deionized water. Oxidation was performed for different concentrations of Fe(II). Effects of additional organic and inorganic materials on the oxidation mechanism of Fe(II) were investigated. Potassium hydrogen phthalate (KHP) as organic material and Mn(II), Zn(II), and Ni(II) as inorganic materials were used.

*Keywords:* Ferrous iron; Oxidation; Organic and inorganic materials; Potassium hydrogen phthalate; Catalytic effect.

## 1. Introduction

Iron is the fourth most abundant element by weight in the Earth's crust. Chemistry of aqueous iron involves primarily ferrous [Fe(II)] and ferric [Fe(III)] oxidation states, and is of engineering interest in water supply and wastewater treatment. Iron cycling in nature is also of interest due to its nutrient status and the active surface chemistry of iron oxyhydroxide. Drinking water limit value for iron is 0.3 mg/l, as recommended by American Water Works Association (AWWA), and adopted by United States Public Health Service (USPHS) [1] in 1962. United States Environmental Protection Agency

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(USEPA) secondary maximum contaminant level left the enforcement of 0.3 mg/l iron limit to the discretion of individual states. Also, the World Health Organization (WHO) provided a value of 0.3 mg/l for iron. According to Turkish Standards Institution the Turkish standard specifies the acceptable and maximum limit values for iron in water intended for human consumption (TS 266) as 0.2 and 0.3 mg/l, respectively.

Iron removal from water is commonly conducted by aeration followed by solid/liquid separation. Aeration processes in order to oxidize ferrous iron is generally recommended for water with high concentrations (>5.0 mg/l) of iron to save chemical costs [2]. Sedimentation and/or filtration are applied for solid/liquid separation.

Nayak, R. and Rao, J.R. [3] investigated oxidation of Fe(II) to Fe(III) in the presence of different alkalies, using air as an oxidant. Different alkalies additives were used to see their effects on the rates of oxidation. Out of the three systems studied, $FeSO_4$–NaOH had the highest rates of oxidation while $FeSO_4$–$Na_2CO_3$ had the lowest one. Oxidation rates for $FeSO_4$–$Ca(OH)_2$ were in between those of $FeSO_4$–NaOH and $FeSO_4$–$Na_2CO_3$.

Catalytic activity of layered birnessite type manganese dioxide for liquid phase decomposition of organic substrates was reported by Jha et al. [4]. Oxidation of acetone, methanol and 2-propanol have thus been studied.

Recent quantitative studies have been carried out to investigate the kinetics of Fe(II) oxidation in natural waters. King et al. [5] investigated the production of superoxide ($O_2^-$) and hydrogen peroxide ($H_2O_2$) by Fe(II) oxidation with dissolved oxygen in bicarbonate solution at nanomolar level total iron concentrations and their effects on Fe(II) oxidation. Oxidation of ferrous sulfate with molecular oxygen at high temperatures (60–130 °C) and under high pressures (4–10 bar) was studied by Rönnholm et al. [6]. They proposed a reaction mechanism and developed a rate equation based on the experimental results. Emmenegger et al. [7] determined the oxidation rate of Fe(II) as the key kinetic parameter to evaluate the cycling of Fe(II) and Fe(III) at epilimnion layers of lakes. Wolthoorn et al. [8] investigated the effect of $PO_4^{3-}$, Mn, silicates, and dissolved organic carbon on the heterogeneous oxidation of Fe(II). Tamura et al. [9] observed that oxygenation of Fe(II) ions in neutral solution was accelerated by ferric hydroxide [$Fe(OH)_3$], which was in fact the product of oxygenation reaction. Sung and Morgan [10] determined the effect of ionic media, alkalinity, and temperature on the oxidation of Fe(II). They observed autocatalysis of Fe(II) oxidation at pH values around 7 and above. Catalytic effect of $Fe(OH)_3$ became noticeable at Fe(III) concentrations exceeding 5–10 mg/l [11]. Tufekci and Sarikaya [12] investigated catalytic effects of high Fe(III) concentrations on the oxidation of Fe(II). They obtained significant catalytic effect of Fe(III) of about 600 mg/l concentrations on the oxidation of Fe(II) by atmospheric oxygen. Tüfekci et al. [13] determined the effects of the organic matters as tannic acid, acetic acid, and glucose effect on the oxidation of Fe(II). Catalytic effects of Fe(III) decreased by addition of tannic acid. Any noticeable effect of acetic acid and glucose on the ferrous oxidation was not observed. Liang et al. [14] determined the effect of natural organic matter, fulvic acid and polyglutamate on the oxidation of Fe(II) at neutral pH and under partial pressure of oxygen. They concluded that natural organic matters had a little effect on the Fe(II) oxidation rate at the high partial pressures of oxygen (0.2 atm.), and that natural organic matter or fulvic acid increased the Fe(II) oxidation at low partial oxygen pressure (0.005 atm.) and also affected the stability of iron oxide colloids. Theis and Singer [15] investigated the effects of organic materials on the Fe(II) oxygenation. Their findings have shown that organic matter might generate complexes with ferrous iron, and despite the presence of sufficient dissolved oxygen, these complexes might be resistant to oxidation. As an example they showed that tannic acid significantly retarded the oxidation of Fe(II).

The aim of this study was to determine the effects of organic and inorganic substances, chosen as potassium hydrogen phthalate (KHP), and Ni, Zn and Mn ions for this study, on the oxidation of low concentration of Fe(II) by atmospheric oxygen using raw water from Ömerli Dam, and to present the behavior of Fe(II) ions under oxidizing conditions in natural waters.

## 2. Materials and methods

### 2.1. Experimantal

Oxidation of Fe(II) was carried out by aeration in a 2 l tank. Water temperature was kept constant by Clifton mark water jacket. Temperature of reaction solution was kept at 25 °C. Air was introduced into the tank by means of diffusers (Armfield Aeration Apparatus). Solution was stirred by stirring equipment at a rate of 110 cycle/min (Armfield Aeration Apparatus). Orion model 720 A pH meter with a sensitivity of ±0.001, was used to measure pH values. Solution pH was kept at pH 7.0 and controlled by regulating $CO_2$ and air streams. $Na_2CO_3$ was added into solution to obtain an alkalinity of $2 \times 10^{-2}$ eq/l. Experimental setup was shown in Fig. 1.

### 2.2. Reagents

Fe(II) was obtained through dissolving $FeSO_4(NH_4)_2 \cdot 6H_2O$ in 1 l of double distilled water containing 2 ml concentrated $H_2SO_4$. Zinc, Manganese, Nickel (Merck) and KHP were avaliable in solution, (1 + 4)

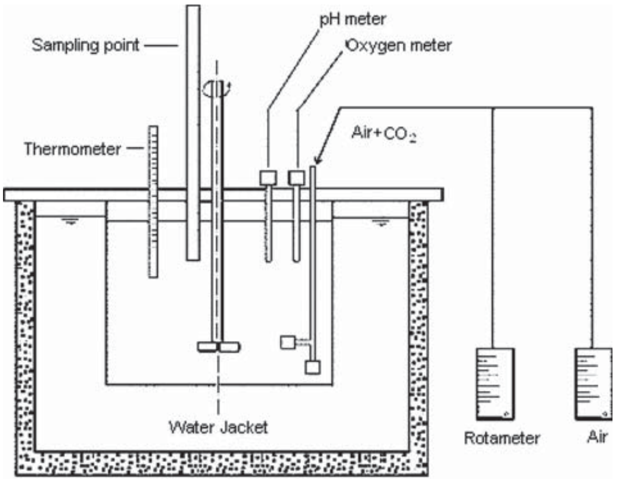

Fig. 1. The experimental setup.

$H_2SO_4$, 2 M of ammonium fluoride, 1.10 phenanthroline, and 3 M of hexamethylenetetramine solutions were prepared according to 1.10 phenanthroline method [1].

### 2.3. *Ferrous iron analysis*

Ferrous iron [Fe(II)] concentration was determined using spectrophotometer by following the 1.10 phenanthroline method. 15 ml samples were taken into 25 ml flasks containing 1 ml (1 + 4) $H_2SO_4$ in every 2 min. Then, 2 ml of 2 M ammonium fluoride, 2 ml of 1.10 phenanthroline solution, and 3 ml of 3 M Hexamethylenetetramine were added. Solutions were diluted with double distilled water to 25 ml. Then, absorbances were measured at 510 nm with the Pharmacia model spectrophotometer device [9].

### 2.4. *Raw water*

In this study, prepared Fe(II) solutions, organic matters, and inorganic matters were injected into raw water samples from Ömerli Dam. Ömerli Dam supplied raw water to Ömerli Water Treatment Plant, which supplies approximately 50% of total water demand for city of Istanbul. Dam is 16 m deep with a maximum storage volume of 235,700,000 m$^3$, and maximum treatment capacity of the plant is 1,100,000 m$^3$/d. Small increases at iron and manganese concentrations could be expected at the period of seasonal changes. Characterization of Ömerli Dam Surface Water was shown in Table 1.

## 3. Results and discussion

### 3.1. *Fe(II) oxidation with atmospheric oxygen at different initial Fe(II) concentration*

Results from experiments with different initial Fe(II) concentrations, which were chosen to be between 0.5 and 10 mg/l, were given in Fig. 2. Slight changes in the reaction rate up to 5 mg/l of initial concentrations of Fe(II) were observed, whereas the reaction rate increased significantly for more than 7.5 mg/l of Fe(II) concentrations. This showed that autocatalytic effect was introduced for Fe(II) concentrations higher than 7.5 mg/l. In other words, $Fe(OH)_3$ flocs accelerated the oxidation. Low concentrations of Fe(II) (0–10.0 mg/l) might be found in surface waters. For this reason, low Fe(II) concentrations of 0.5 mg/l, 1.0 mg/l and 3.0 mg/l were used in this study.

### 3.2. *Fe(II) oxidation in a medium containing organic material (KHP)*

In natural aquatic systems, high iron concentrations and organic substances could co-occur. In this part of the study, potassium hydrogen phthalate was used as the organic substance. Effect of KHP concentrations, 3 mg/l, 5 mg/l, and 10 mg/l, on Fe(II) oxidation was shown in Fig. 3.

Effects of KHP on the oxidation of Fe(II) were investigated. Presence of KHP reduced the oxidation of Fe(II) at the beginning of the oxidation for ferrous iron concentrations of 0.5 mg/l and 1.0 mg/l. In the course of reaction time it was observed that the presence of KHP had no significant effect on the oxidation rate of Fe(II). However, KHP slowed down the oxidation for the case that had an initial Fe(II) concentration of 3 mg/l. It was observed that effects of KHP on the Fe(II) oxidation depended on the ratio [KHP]/[Fe(II)]. It was

Table 1
Characterization of Ömerli Water Treatment Plant Inlet water

| Sample Date | pH | Total Hardness (mg $CaCO_3$/l) | Total Alkalinity (mg $CaCO_3$/l) | Total Iron (mg/l) | Total Manganese (mg/l) | TOC (mg/l) |
|---|---|---|---|---|---|---|
| February, 2008 | 7.40 | 100 | 70 | <0.2 | <0.05 | 2.58 |
| March, 2008 | 7.54 | 104 | 59 | <0.2 | <0.05 | 4.79 |
| May, 2008 | 8.00 | 90 | 61 | <0.2 | 0.056 | 3.58 |
| December, 2008 | 7.04 | 97 | 58 | 0.36 | 0.49 | 4.52 |

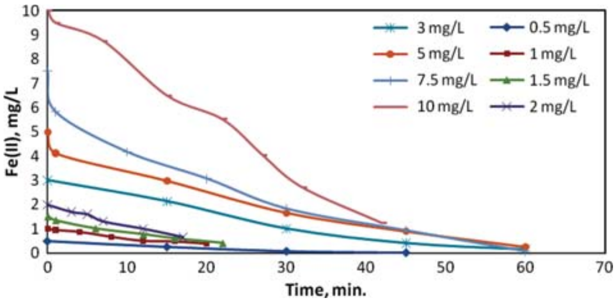

Fig. 2. Variation of Fe(II) with time under varying initial Fe(II) concentrations ($[\text{Fe(II)}]_0 = 0.5–10$ mg/l, pH = 7, $T = 25$ °C, alkalinity = $2 \times 10^{-2}$ eq/l, $pO_2 = 0.21$ atm.).

assumed that oxidation of Fe(II) in the presence of KHP formed a resistant structure. It was observed that KHP diminished the oxidation rate of Fe(II) with increasing of Fe(III). The reason for this was considered to be that KHP reduced Fe(III) and thus catalytic effects of Fe(III) were diminished.

In the reaction time, Fe(II) oxidation rate was increased, but the oxidation rate for 3 mg/l KHP was higher than the 10 mg/l KHP. Ferrous iron oxidation was retarded a bit less by KHP concentration of 3.0 mg/l at the beginning. It was apparent that retarding of Fe(II) oxidation was increased by elevated KHP concentration in initial. This situation could be explained by oxygen consumption of KHP. In this low ferrous concentration the complexes of organic matter, in the presence of raw water, with ferrous iron may occur, the complexes might be resistant to oxidation [15]. KHP addition into raw water might decrease the occurring of the complexes. Retarding of the Fe(II) oxidation was obviously seen at the Fe(II) concentration of 3.0 mg/l. Morgan and Stumm [16] proposed a scheme (Eq. [1] to [3]) to define the inhibition of ferrous oxidation by organic matters.

As shown in Fig. 3, retarding of the Fe(II) oxidation at 3.0 mg/l was in accordance with these equations. Fe(II) oxidation rate was decreased between 8 min and 16 min. After this period, the oxidation rate of ferrous nearly approached the rate of ferrous in the raw water.

$$\text{Fe(II)} + O_2 \rightarrow \text{Fe(III)} \tag{1}$$

$$\text{Fe(III)} + \text{organic} \rightarrow \text{Fe(II)} + \text{oxidized organic} \tag{2}$$

$$\text{Fe(II)} + O_2 \rightarrow \text{Fe(III)} \tag{3}$$

### 3.3. Fe(II) oxidation in a medium containing inorganic material effects of Nickel (Ni)

Nickel was used as an inorganic matter in this study. Oxidations of Fe(II) were performed at 0.5–3 mg/l initial Fe(II) concentration at the presence of different Ni(II) concentrations (0.5, 1.0 and 1.5 mg/l). The effect of Ni(II) on ferrous oxidation is shown in Fig. 4.

Iron and Nickel, both belonging to VIIIth group of periodic table, have approximately same physical and chemical characteristics. However, Fe(II) in water is more active than Ni(II), thus Fe(II) is oxidized easier than Ni(II), whereas Ni(II) is rarely oxidized as $Ni_2O_3 \times H_2O$. Effects of Ni(II) on the oxidation of Fe(II) were investigated. Up to 1.5 mg/l of Ni(II), effects of Ni(II) on the oxidation of Fe(II) were not observed. Therefore, it was considered that there was no effects of Ni(II) on the oxidation of Fe(II). The results of this study were fitting well with data reported in the relevant literature.

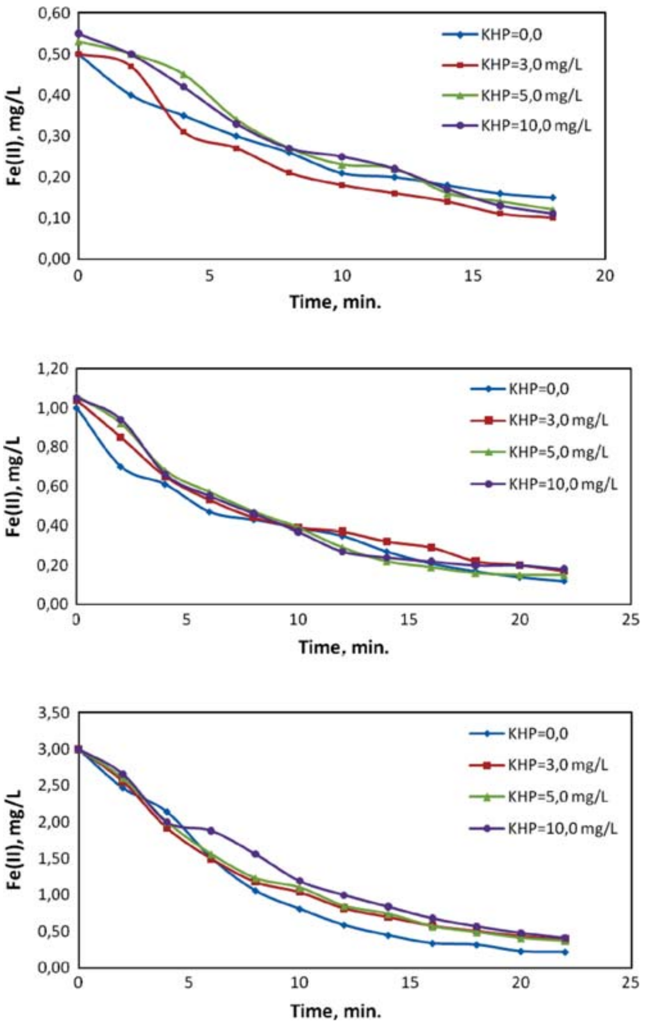

Fig. 3. Effect of KHP on the oxidation of ferrous iron ($[\text{Fe(II)}]_0 = 0.5–3$ mg/l, pH = 7, $T = 25$ °C, alkalinity = $2 \times 10^{-2}$ eq/l, $pO_2 = 0.21$ atm.).

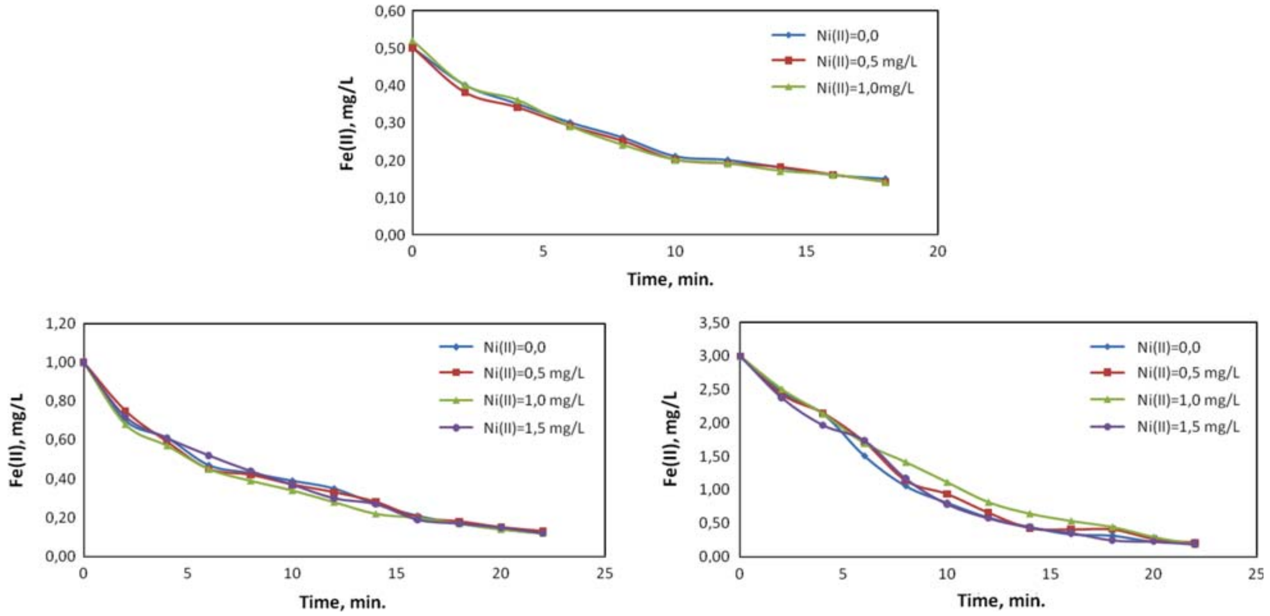

Fig. 4. Effect of Ni(II) on the oxidation of ferrous iron ($[Fe(II)]_0$ = 0.5–3 mg/l, pH = 7, $T$ = 25 °C, alkalinity = 2 × $10^{-2}$ eq/l, $pO_2$ = 0.21 atm.).

### 3.4. *Effects of Zinc (Zn)*

Oxidations of Fe(II) were performed at 0.5–5 mg/l initial Fe(II) concentrations at the presence of different Zn(II) concentrations of 0.5–10 mg/l. The effect of Zn(II) on ferrous oxidation was shown in Fig. 5.

As seen from the Fig. 5, it was observed that there was no significant increase or decrease in the oxidation rate in regard with Zn(II) concentrations. Like Ni, Zn belongs to VIIIth group of the periodic table. Any effect of Zn(II) on the oxidation of Fe(II) was not determined.

### 3.5. *Effects of Manganese (Mn)*

Oxidations of Fe(II) were performed at 0.5–5 mg/l initial Fe(II) concentration at the presence of different

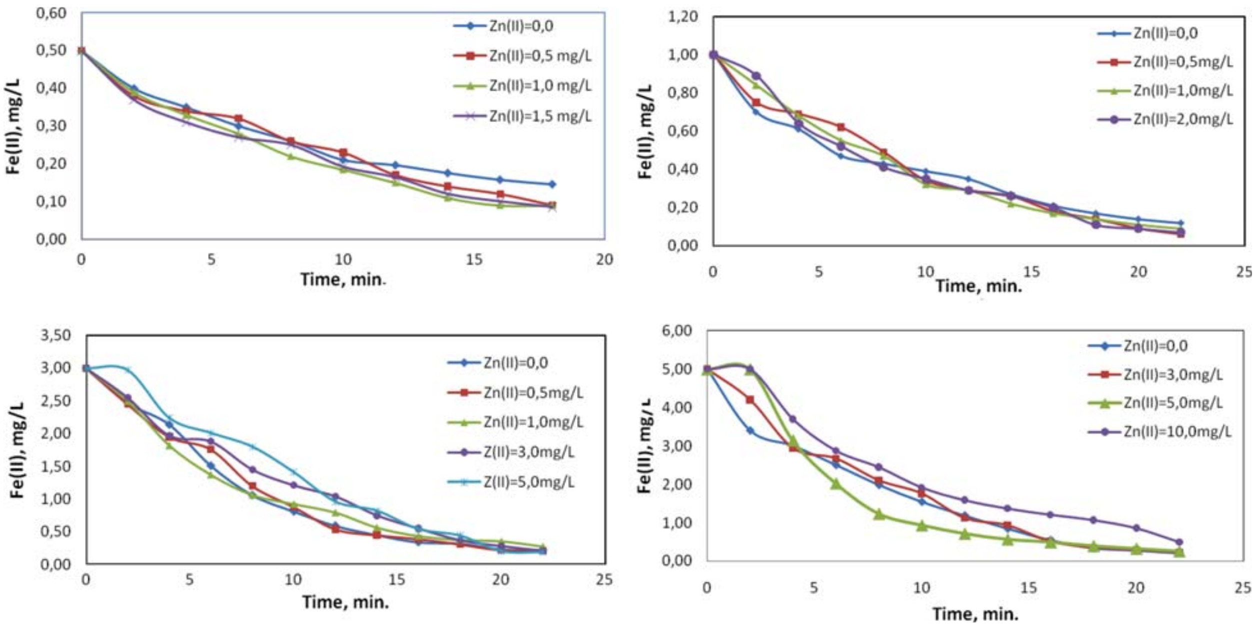

Fig. 5. Effect of Zn(II) on the oxidation of ferrous iron ($[Fe(II)]_0$ = 0.5–5 mg/l, pH = 7, $T$ = 25 °C, alkalinity= 2 × $10^{-2}$ eq/l, $pO_2$ = 0.21 atm.).

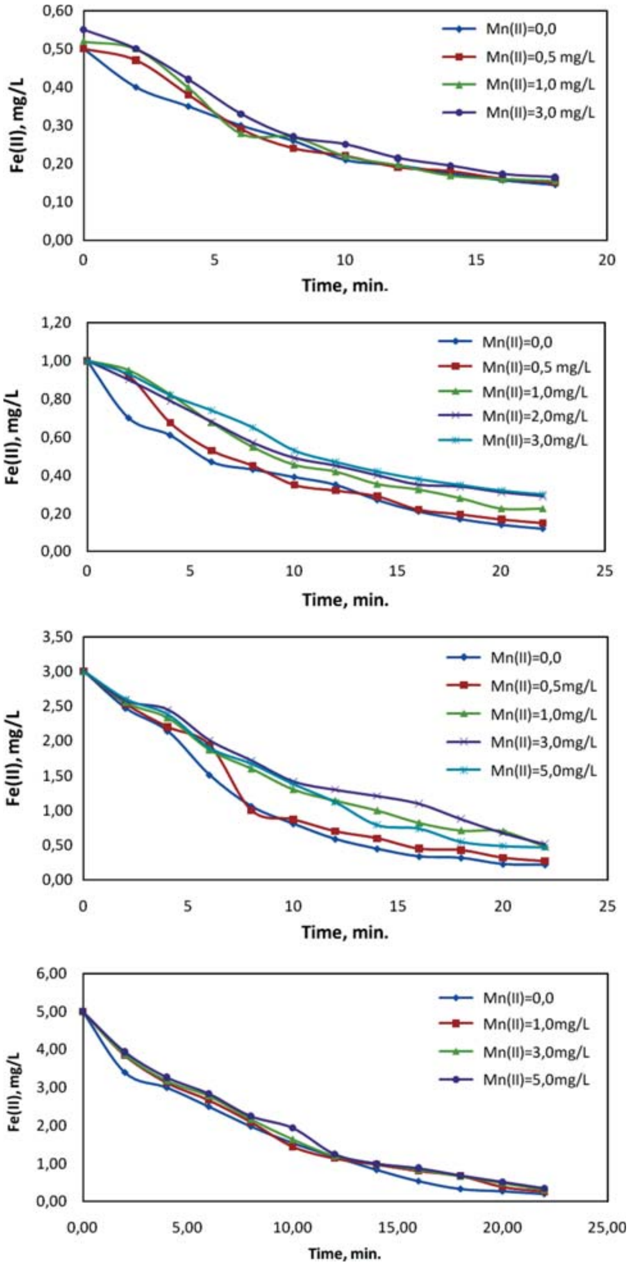

Fig. 6. Effect of Mn(II) on the oxidation of ferrous iron ($[Fe(II)]_0$ = 0.5–5 mg/l, pH = 7, $T$ = 25 °C, alkalinity = $2 \times 10^{-2}$ eq/l, $pO_2$ = 0.21 atm.).

Mn(II) concentrations (0.5–5 mg/l). Effect of Mn(II) on ferrous oxidation was shown in Fig. 6.

According to Eh-pH graphic, $Mn_2O_{3(s)}$ and $Mn_3O_{4(s)}$ were generated at the pH around of 6 and 7, respectively [16]. Oxidation of Fe(II) at the first min was slowed down by presence of Mn(II), which is oxidized to $Mn_2O_{3(s)}$ and $Mn_3O_{4(s)}$ at 7.0 of pH. Oxygen was used by manganese oxidation steps and this can explain the reason of the slowed down oxidation rate of Fe(II). As a rough rule, thumb amorphous ferric oxide is capable of adsorbing 0.5 mmol of ionic material per gram. Mn(II) ions can be absorbed by ferric (hydr)oxide surface and oxidized catalytically by this surface [8]. Thus, autocatalytic oxidation process may be inhibited for ferrous. Formation of ferric hydroxide depends on initial ferrous concentration. Higher catalytic effect of ferric hydroxide was observed clearly during the experiments. This effect was reduced by catalytic effects of Fe(III) in the course of time. Therefore, oxidation rate of Fe(II) at the same Mn(II) concentration increased with elevating of initial Fe(II) concentration. As a result of the study, it was clearly observed that effects of Mn(II) on the oxidation of Fe(II) depended on the ratio of [Mn(II)]/[Fe(II)]. In other words, it is observed evidently that the oxidation is decelerated by Mn(II) at lower values of $[Fe(II)]_0$. This deceleration decreased due to catalytic effect of Fe(III) at relatively higher concentrations of $[Fe(II)]_0$ such as 3–5 mg/l.

## 4. Conclusion

Effects of organic and inorganic materials on the oxidation of Fe(II) were investigated in this study. KHP concentrations have affected the oxidation of Fe(II) at low ferrous concentrations.

KHP slowed down significantly the oxidation for $[Fe(II)]_0$ = 3 mg/l. It was observed that effects of KHP on the oxidation of Fe(II) depended on the ratio of [KHP]/[Fe(II)].

Effects of Ni(II) and Zn(II) on the oxidation of Fe(II) were studied, but no significant effect of Ni(II) and Zn(II) on the oxidation of Fe(II) was observed.

Oxidation of Fe(II) was slowed down by the presence of Mn(II). It was clearly observed that the effects of Mn(II) on the oxidation of Fe(II) depended on the ratio of [Mn(II)]/[Fe(II)].

The oxidation of ferrous iron was affected mainly by Mn(II). The higher effects on the oxidation of ferrous iron were accomplished by Mn(II). So, iron and manganese can be found together in many groundwaters and other eutrophic lake water. During the oxidation of ferrous iron, manganese and KHP concentrations must be taken into account.

Initial ferrous concentration and time were the most important parameters that increased the oxidized ferrous iron. Formation of ferric hydroxides might also increase the oxidized ratio. Ferric hydroxide amount increased by time and the hydroxide had catalytic effects on the oxidation of ferrous iron.

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## References

[1] APHA-AWWA-WPCF. Standard methods for the examination of water and wastewater. 18th edition, Washington, DC (1992).

[2] J.M.Wong, Chlorination-Filteration for Iron and Manganese Removal. J. Am. Water Works Assoc., 76 (1984) 76–79.

[3] R. Nayak and JR. Rao, Ferrous-ferric oxidation in pickle liquor, J. Sci. Ind. Res., 62(11) (2003) 1094–1097.

[4] V. Jha, A. Uma, R. Renuka Liquid phase decomposition of organic substrates on birnessites J. Sci. Ind. Res., 59(10) (2000) 829–832.

[5] D.W. King, H.A. Lounsbury and F.J. Miliero, Rates and mechanism of Fe(II) oxidation at nanomolar total iron concnetrations. Environ. Sci. Tech., 29(3) (1995) 818–824.

[6] M.R. Ronnholm, J. Warna, T. Salmi, I. Turunen and M. Luom. Kinetics of oxidation of ferrous sulfate with molecular oxygen. Chem. Eng. Sci., 54(19) (1999) 4223–4232.

[7] L Emmenegger, D.W. King, L. Sigg and B. Sulzberger. Oxidation kinetics of Fe(II) in a eutrophic Swiss lake. Environ. Sci. Tech., 32(19) (1998) 2990–2996.

[8] A. Wolthoorn, E.J.M. Temminghoff, L. Weng, R. Van and H. Willem. Colloid formation in groundwater: Effect of phosphate, manganese, silicate and dissolved organic matter on the dynamic heterogeneous oxidation of ferrous iron. Appl. Geochem., 19(4) (2004) 611–622.

[9] H. Tamura, K. Goto, T. Yotsuyanagi and M. Nagayama, Spectrophotometric line in the Presence of Large Amounts of Iron(III). Talanta, 21 (1974) 314–318.

[10] W. Sung and J.J. Morgan. Kinetics and product of ferrous iron oxygenation in aqueous systems. Environ. Sci. Tech., 14(5) (1980) 561–568

[11] H.Z. Sarikaya, Interactions between ferrous iron oxidation and phosphate (1980) 143–160.

[12] N. Tufekci and H.Z. Sarikaya. Catalytic effects of high Fe(III) concentrations on Fe(II) oxidation. Water Sci. Tech., 34(7–8) (1996) 389–396.

[13] N. Tufekci, G. Demir, G. Ozgul and C. Kinaci. The effect of organic matters on ferrous oxidation. Fresen. Environ. Bull., 12(7) (2003) 771–775.

[14] L. Liang, J.A. McNabb, J.M. Paulk, B. Gu and J.F. McCarthy. Kinetics of Fe(II) oxygenation at low partial pressure of oxygen in the presence of natural organic matter. Environ. Sci. Tech., 27(9) (1993) 1864–1870.

[15] T.L. Theis and P.C. Singer. Complexation of iron(II) by organic matter and its effect on iron(II) oxygenation. Environ. Sci. Tech., 8(6) (1974) 569–573.

[16] J.J. Morgan and W. Stumm. Analytical chemistry of aqueous manganese. J. AWWA, 57 (1965) 107–119.