Removal of Iron and Manganese with Ozone

by

Mohammad Younis Abukhudair

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CIVIL ENGINEERING

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King Fahd University of Petroleum and Minerals (Saudi Arabia), 1987

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This thesis, written by MOHAMMAD YOUNIS ABUKHUDAIR under the direction of his Thesis Committee, and approved by all its members, has been presented to and accepted by the Dean, College of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE IN CIVIL ENGINEERING.

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TO
MY PARENTS
AND TO
MY WIFE

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الخلاصة

كان الهدف الاساسي من هذه الدراسة هو تطوير معادلة حركية لأكسدة الحديد(٢) والمنجنيز(٢) بواسطة غاز الأوزون ، وايجاد تأثير المواد العضوية على سرعة أكسدة الحديد(٢) والمنجنيز(٢) . ازالة عنصري الحديد والمنجنيز من الماء ضرورية في أي مصدر لمياه الشرب نظرا لما يسببانه من مشاكل عندما يكون تركيزهما أكثر من ٣ر٠ ملغ (حديد)/لتر و ٥٠ر٠ ملغ (منجنيز)/لتر .

أفادت نتائج الدراسة على أن جميع التجارب التي أجريت في جهاز الماء المقطر كان معدلها صفر وتتمثل في هذه المعادلة :

$$\left(\text{١} - \frac{(\ \text{حديد}\ (\text{٢})\ )}{(\ \text{حديد}\ (\text{٢})\ )_{\text{ب}}}\right) = \grave{\text{ك}}\ \text{ز}$$

حيث أن :

(حديد (٢))$_{\text{ب}}$: التركيز في بداية التفاعل ، (ملغ/لتر) .
ك : سرعة التفاعل ، ملغ/ (لتر . دقيقة) .
ز : الزمن بالدقائق .

كذلك أثبتت الدراسة على أن بعض التجارب التي أجريت في جهاز الماء المقطر والخليط بالمواد العضوية تتمثل في المعادلة السابقة ولكن البعض الآخر يتمثل في معادلة الأكسدة الحركية العامة :

$$\frac{\text{د}\ (\ \text{حديد}\ (\text{٢})\ )}{\text{د}\ (\ \text{زمن}\ )} = -\ \text{ك}\ (\ \text{حديد}\ (\text{٢})\ )^{\text{ن}}$$

حيث أن :

ن : معدل التفاعل

أفادت نتائج هذه الدراسة على أن حديد (٢) لايتبقى في المحلول المائي عندما يتجاوز أل (pH) ٧ درجات ، ولكن المنجنيز (٢) يبقى في المحلول المائي حتى درجة (pH) تصل الى ٩ .

ABSTRACT

The main objective of this study was to develop kinetic expressions for the oxidation of iron(II) and manganese(II) with ozone, and also to determine the effect of organic complexation on the rate of oxidation of iron(II) and manganese(II).The removal of iron and manganese is important in drinking water supply as many problems are associated with presence of these metals in concentrations greater than 0.3 mg/L and 0.05 mg/L, respectively.

The results of the study have shown that all the experiments conducted for the pure water system followed a zero-order reaction with respect to iron(II). The final rate expression is:

$$X = \left(1 - \frac{[Fe(II)]}{[Fe(II)]_o}\right) = k' \, t$$

Some of the reactions for the organic complexation system followed the above expression, but the rest of them followed this general kinetic expression :

$$\frac{d[Fe(II)]}{dt} = -k \, [Fe(II)]^n$$

It has been found out that iron(II) does not remain in solution at pH values above 7. However, complete amount of Mn(II) is found to remain in solution up to pH of 9.

Chapter 1

INTRODUCTION

Iron (II) and manganese (II) are the two most common forms that exist in groundwater under anaerobic conditions, i.e., absence of dissolved oxygen and low pH. These two forms are soluble in water and present many problems to the consumers at concentrations more than 0.3 mg/L and 0.05 mg/L, respectively (1). The common problems associated with iron and manganese are, staining of plumbing fixtures and laundered clothes, foul tastes and odors as a result of growth of iron bacteria in water distribution drains.

The usual and common removal method for iron and manganese is by filtration following aeration and detention. In this method, aeration promotes the oxidation of the iron, detention time allows for the oxidized iron to flocculate, and finally, sand filtration physically removes the iron precipitate from the water.

Other chemicals used in the oxidation of iron & manganese are chlorine and potassium permanganate,which oxidize iron (II) and manganese (II) to their insoluble forms $Fe(OH)_3$ and MnO_2,rspectively.These are finally removed from the solution by filtration (1).

It is reported that some installations using the aeration method in treating groundwater have experienced difficulty in removing iron. This difficulty has been attributed to interference by organic compounds. The substitution of ozonation for simple aeration has been suggested as a better way for overcoming organic interference in iron removal, because it is a more powerful oxidant than is oxygen (2,3). Cromley (3) found out that ozonation of ground water resulted in more rapid and more thorough oxidation of iron (II) than did simple aeration. However, his study was limited to only pure system, and no information was provided about input and output ozone concentrations in the gaseous phases. The purpose of this study is to develop the detailed kinetics of oxidation of iron and manganese with ozone in a semi-batch system under different environmental conditions such as detention times, pH, ozone concentrations, and organic matter.

Chapter 2

LITERATURE REVIEW

2.1 Ozone

Ozone is a gas that is produced by passing air or oxygen between oppositely charged plates or through tubes in which a core and the tube walls serve as the oppositely charged surfaces (6). It was first reported by M. Van Mauren in 1785 when he noticed a peculiar smell in the vicinity of electrical machines. In 1840 the German-Swiss chemist, Christian Schonbein, claimed its presence in the earth's normal atmosphere and named it ozone. The chemical composition of ozone remained uncertain, however, until the definitive work of B. Brodie in 1872 showed it to be a triatomic molecule of oxygen (7). Ozone is unstable and has a tendency to divest itself of its third or nascent oxygen atom through

$$O_3 \rightarrow O_2 + O$$

$$O + O \rightarrow O_2$$

Alder and Hill (25) measured the decomposition rate by iodometric and spectrophotometric methods and obtained very different results. They postulated that the iodometric method gave the total reducible and proposed the following mechanism for O_3 decomposition in pure aqueous solution :

$$O_3 + H_2O \xrightarrow{K_1} HO_3^+ + OH^-$$

$$HO_3^+ + OH^- \underset{}{\overset{K_2}{\rightleftharpoons}} 2\ HO_2$$

$$O_3 + HO_2 \xrightarrow{K_3} HO + 2\ O_2$$

$$HO + HO_2 + \xrightarrow{K_4} H_2O + O_2$$

The free radicals HO_2 and HO that are formed by the previous reactions when ozone decomposes in the aqueous solution have great oxidizing power, that is able to react with any impurities such as metal salts, organic matter, hydrogen and hydroxide ions present in the solution.

2.2 Effects Associated with Presence of Iron (II) and Manganese (II) in Drinking Water

The presence of significant amounts of iron and manganese in concentrations more than 0.3 mg/l and 0.05 mg/l, respectively can cause many problems (1). The problems attributed to iron are:

1. Large concentrations of iron impart a metallic taste to the water.

2. Industrial products such as paper, textiles, or leather may be discolored.

3. Household fixtures such as porcelain basins, bathtubs, glassware, and dishes are stained.

4. Clothes may stain a yellow or brown-yellow color.

5. Iron precipitates clog pipes and promote the growth of gelatinous masses of iron bacteria. These bacteria slough off and create "red water".

6. Iron bacteria may cause odor and taste problems due to low flow conditions.

On the other hand, many problems are associated with manganese such as (1,8):

1. Taste problems at high concentrations.

2. Discoloration of industrial products.

3. Staining of household fixtures and clothes.

4. It causes Parkinson's disease that is associated with the decrease of a neuro-transmitter substance in the brain.

2.3 Application of Ozone in Water Treatment

Ozone has been used commonly in the treatment of water supplies in European countries. The most common objectives are disinfection, oxidation of organic compounds, and removal of iron and manganese by chemical oxidation and subsequent removal of the insoluble oxides or hydroxides which are formed by ozone oxidation. A study was undertaken by the engineering firm, Stevens, Thompson and Runyan (9, 10) to investigate the feasibility of removing the iron and manganese from Moscow, Idaho, City water system that derives its water from two main groundwater aquifers, by using ion exchange, sequestering, ozonation, Cl_2 $KMnO_4$ oxidation using either gravity filtration or pressure filtration, and Cl_2-$KMnO_4$ oxidation followed by manganese greensand contact filtration. Their study indicated that the most promising systems for removal of both the iron and manganese were either ozonation or the Cl_2-$KMnO_4$ greensand system. The first set of data which represents the optimum operating conditions obtained is shown in Table 2.1. This table shows that at a lower ozone dosages, the manganese is not adequately removed even though the iron is removed. Also, they concluded that the excessive high ozone dosage levels did not particularly improve the removal rates but resulted in giving the water a pink color due to oxidation of the manganese to permanganate.

At the optimum conditions, no noticeable pink color was observed.

Table 2.1 : Ozone Removal of Iron and Manganese

Source Well No.	Gas/Liq. (G/L)	Ozone Dose (mg/L)	Raw Water (mg/L)		Treated Water (mg/L)	
			Fe	Mn	Fe	Mn
2	1.7	3.7	3.4	0.6	0.09	< 0.05
3	1.7	8.8	9.5	1.2	0.04	< 0.05
2	1.7	2.8	3.6	0.5	0.02	0.15
3	1.7	6.3	9.9	1.2	0.06	0.11

SOURCE : Kjos, D.J. et al (1973)

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They also measured the amount of ozone actually utilized by the reacting system as shown in Table 2.2.

Table 2.3 shows a comparison of oxygen and ozone oxidation of Fe (II) and Mn (II) for the same pilot unit.

2.4 Oxidation of Iron (II) and Manganese (II)

The most common oxidizing agents for iron (II) and manganese (II) are oxygen, chlorine, and potassium permanganate (1). However, ozone has been applied for the removal of iron and manganese but its detailed kinetics is not worked out.

The oxidation equations for different oxidizing agents are shown below (1,3):

Oxygen:

$4\ Fe^{+2}(aq) + O_2(g) + 10\ H_2O(l) = 4\ Fe(OH)_3(S) + 8\ H^+\ (aq)$

$2\ Mn^{+2}(aq) + O_2(g) + 2\ H_2O(l) = 2\ Mn\ O_2(S) + 4\ H^+\ (aq)$

Potassium Permanganate :

$3\ Fe^{+2}(aq) + KMnO_4(aq) + 7\ H_2O = 3\ Fe(OH)_3(S) + MnO_2(S) + K^+(aq) + 5\ H^+(aq)$

$3\ Mn^{+2}(aq) + 2\ KMnO_4(aq) + 2\ H_2O = 5\ MnO_2(S) + 2\ K^+(aq) + 4\ H^+(aq)$

Ozone (O_3):

Table 2.2: Ozone Concentrations in Pilot Unit

Sample	Equivalent Dose (mg/L)
Gas from generator	2.18
Gas from column	0.34
Liquid from column	0.80
Liquid from filter	0

SOURCE: Kjos, D.J. et al (1973)

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Table 2.3 : Comparison of Oxygen & Ozone Oxidation of Fe (II) and Mn (II)

Sample	Fe (II) (mg/L)	Mn (II) (mg/L)
Raw water	9.54	1.21
O_2 only	3.99	0.71
O_3 (8 mg/L Ozone dose)	0.07	0.05

SOURCE: Kjos, D.J. et al (1973)

$$Fe^{+2} + O_3 + H_2O \rightarrow Fe^{+3} + O_2 + 2\ OH^-$$

$$Fe^{+3} + 3\ H_2O \rightarrow Fe(OH)_3\ (S) + 3\ OH^+$$

$$Mn^{+2} + O_3 + H_2O \rightarrow Mn^{+4} + O_2 + 2\ OH^-$$

$$Mn^{+4} + 4\ OH^- \rightarrow Mn(OH)_4 \rightarrow Mn\ O_2\ (S) + 2\ H_2\ O.$$

As noticed from the above equations, the removal of manganese is more expensive than the removal of iron because manganese needs more oxidant since it has more than one oxidation state, but iron has two oxidation states only $^+2$ and $^+3$.

2.5 Kinetics of Iron (II) and Manganese (II) Oxidation

The rate of oxidation of iron and manganese depends on the type and concentration of the oxidizing agent, pH, alkalinity, organic content, and presence of catalysts (2). The pH for oxidation of iron should be 7.5 or higher and manganese oxidizes readily at pH 9.5 or higher. Organic substances (i.e. humic or tannic acids) can create complexes with iron (II) and manganese (II) ions holding them in the soluble state at higher pH values (2). Organic compounds sometimes interfere in the removal of iron from ground waters by peptizing ferric hyroxide flocs, by forming complexes with ferrous or ferric ions, by reducing the apparent rate of ferrous oxidation by reducing the ferric iron to ferrous iron, or by a combination of these three factors (3).

Copper ions and silica have a catalytic effect on the oxidation of iron and manganese. The presence of 0.1 mg/L of copper increases the rate of iron oxidation 5-6 times (2). Manganese oxides are catalytic in the oxidation of manganese.

Stumm and Lee (11) studied the oxidation of iron (II) by oxygen in bicarbonate solutions in the neutral pH range as shown in Fig. 2.1. The rate law follows the following pattern :

$$\frac{d[Fe(II)]}{dt} = -k\ [Po_2]\ [OH^-]^2\ [Fe(II)] \qquad (1)$$

where:

$\frac{d[Fe(II)]}{dt}$ = rate of oxidation, moles/(liters . min)

k = reaction rate constant. It was found to have a value of $8x10^{13}$ liter^2 mole-^{2} atom^{-1} min^{-1} at 20.5°C. (At 25°C, k = 1.35 x 10^{14} liter^2 mole-^{2} atom^{-1} min^{-1}.)

Po_2 = Partial pressure of O_2 (atm.)

[Fe (II)] = Iron (II) concentration at any time (moles x liter^{-1}).

$$K_{apparent} = \frac{K\ [Po_2]\ (K_W)^2}{[H^+]^2}$$

Hence, Eqn. (1) can be written as :

$$\frac{d[Fe(II)]}{dt} = -\ K_{app}\ [Fe(II)]$$

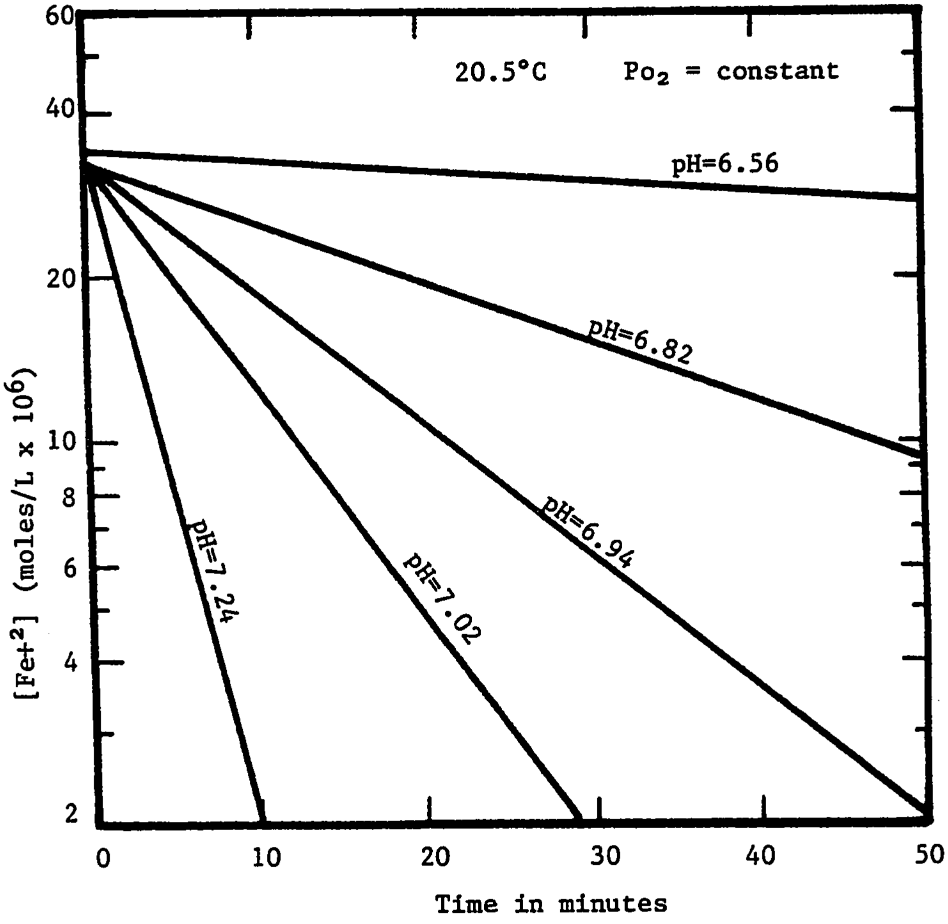


Figure 2.1 : Relationship between the rate of iron (II) oxidation and solution pH (after Stumm and Lee, 1961).

The integrated rate law relationship of manganese (II) oxidation has the following form (1) :

$$\log \left[A\left(\frac{[Mn(II)]_o}{[Mn(II)]} - 1\right)\right] = K_{app}\, t$$

where:

$[Mn(II)]_o$ = Initial Mn(II) concentration, (moles/L)

$[Mn(II)]$ = Mn(II) concentration at any time, (moles/L)

$$A = \frac{C_{Ao}}{(C_T - C_{Ao})}$$

C_{AO} = Initial reactant concentration, (mole/L)

C_T = Concentration of both reactant and product at any time, (mole/L)

$$K_{app} = \frac{(C_{Ao} + C_{Po})\, K_a\, [Po_2]\, (K_W)^2}{2.3\, [H^+]}$$

where:

K_a = Autocatalytic reaction rate constant. (9.63×10^{11} at 25°C and pH of 9.3).

C_{Po} = Initial product concentration, (moles/L).

Fig. 2.2 shows the removal of manganese (II) by oxygenation at different pH values (37).

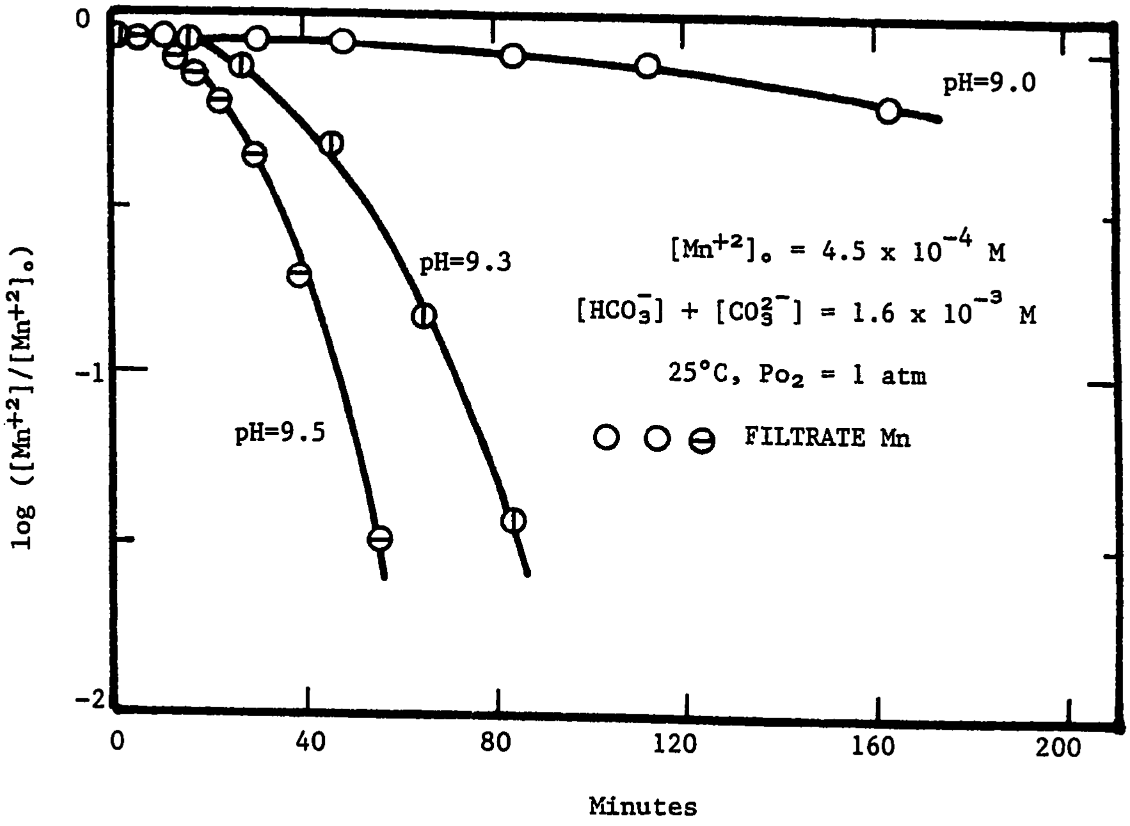


Figure 2.2 : Removal of manganese (II) by oxygenation (after Morgan, 1967b).

2.6 Organic Interference

Organic interference in iron removal was made by Weston in 1909 (12). Weston divided iron-bearing water into two categories : (1) waters that began to precipitate iron immediately after aeration and (2) waters that held iron in solution for an indefinite period following aeration. In the latter case, he believed that organic compounds attached themselves to the dispersed iron and thereby prevented the precipitation of iron.

2.6.1 Peptization

One of the ways that organic compounds can interfere in the removal of iron from ground waters is by peptizing ferric hydroxide flocs (3). Robinson (13) found that certain organic compounds extracted from ground waters caused iron to remain in a filtrable condition in aerated water, whereas the addition of more iron to the same water caused the previously filtrable iron to be retained by filtration. The conclusion was that when the organic compounds chelate the iron, a portion of the chelated iron would remain in solution no matter how much excess iron is added.

2.6.2 Retardation of Oxidation Rate

Another way that organic compounds can interfere in the removal of iron from ground waters is by delaying the rate of ferrous iron oxidation through oxidation-reduction interactions with the iron. Stumm and Singer (14) proposed the following equations to express the oxidation-reduction interactions of iron with organic compounds:

$$\mathrm{Fe(II)} + 1/4\ \mathrm{O_2} + \text{organics} \rightarrow \mathrm{Fe(III)} - \text{Organic complex.}$$

$$\mathrm{Fe(III)} - \text{Organic complex} \rightarrow \mathrm{Fe(II)} + \text{Oxidized organics.}$$

$$\mathrm{Fe(II)} + 1/4\ \mathrm{O} + \text{organics} \rightarrow \mathrm{Fe(III)} - \text{Organic complex.}$$

2.6.3 Complexation

Complexation is the third way by which organic compounds can interfere in the removal of iron from groundwaters. Complexes between orgnaic compounds and iron are believed to be part of the oxidation-reduction cycle between organic compounds and iron, which is responsible for the decrease in the apparent rate of ferrous oxidation. It is also possible that organic complexation with iron may be involved in the peptization of ferric hydroxide flocs (3).

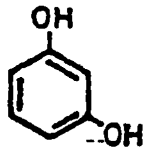
Theis and Singer (15) investigated the effect of model organic compounds which possess the structural features of humic substances on the rate of oxidation of ferrous iron. The model organic compounds that were used in their investigation were : Resorcinol, Phenol, Citric Acid, Tartaric Acid, Histidine, Vanillin, and Glutamic Acid. The structures of these compounds are shown in Figure 2.3.

The complexation sites of the model organic compounds with iron or manganese are shown in Figure 2.4.

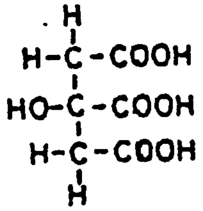
The effects of these organic compounds on the rate of oxidation are shown in Figure 2.5. Gallic acid and pyrogallol completely inhibited Fe (II) oxidation, giving identical results as shown for tannic acid. Glutamic and tartaric acids behaved analogously to glutamine, while vanillic acid, vanillin, phenol, resorcinol, syringic acid, and histidine had no effect on the oxidation rate.

When iron and manganese are present in the form of organic complexes, a powerful oxidant like ozone is used to break down the iron and manganese complexes (21). The continuous oxidation of organic matter results in the formation of alcohols, aldehydes, organic acids and finally to carbon dioxide (22).

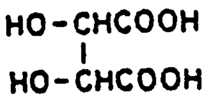
For example, the oxidation of iron (II)-phenol complex will break down the bond between iron and the oxygen of the phenol. The continuous ozonation of phenol proceeds first through dihydroxyaromatic and trihydroxyaromatic compounds and quinones. Continued ozonation breaks the aromatic ring, forming aliphatic



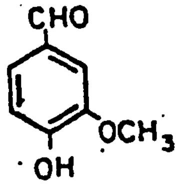
RESORCINOL



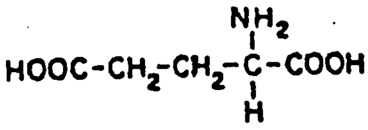
CITRIC ACID



TARTARIC ACID

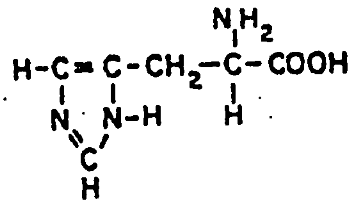


VANILLIN



$HOOC-CH_2-CH_2-\overset{NH_2}{\underset{H}{C}}-COOH$

GLUTAMIC ACID

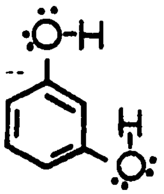


HISTIDINE

PHENOL

Figure 2.3 *Model organic compounds used in this study.*

SOURCE : Theis, T.L. et al (1974)



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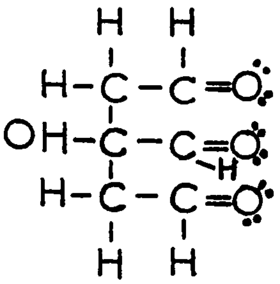
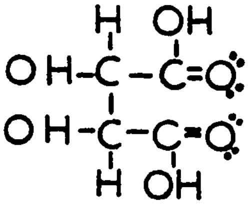


CITRIC ACID



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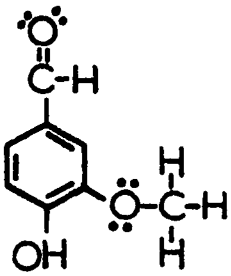

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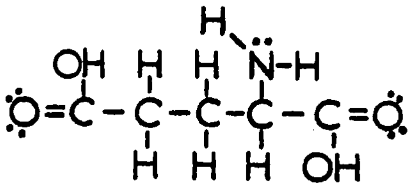
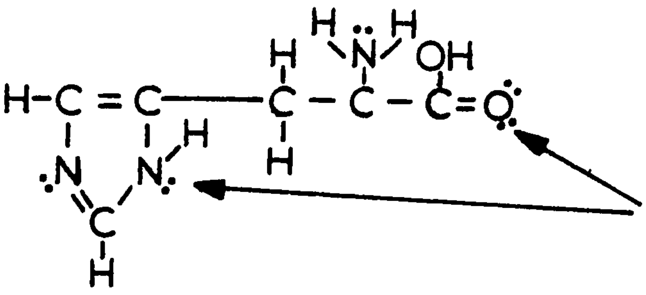


GLUTAMIC ACID



Complexation Sites

HISTIDINE

Figure 2.4 : Complexation Sites of the Model Organic Compounds With Iron or Manganese.

SOURCE : Theis, T.L. et al (1974)

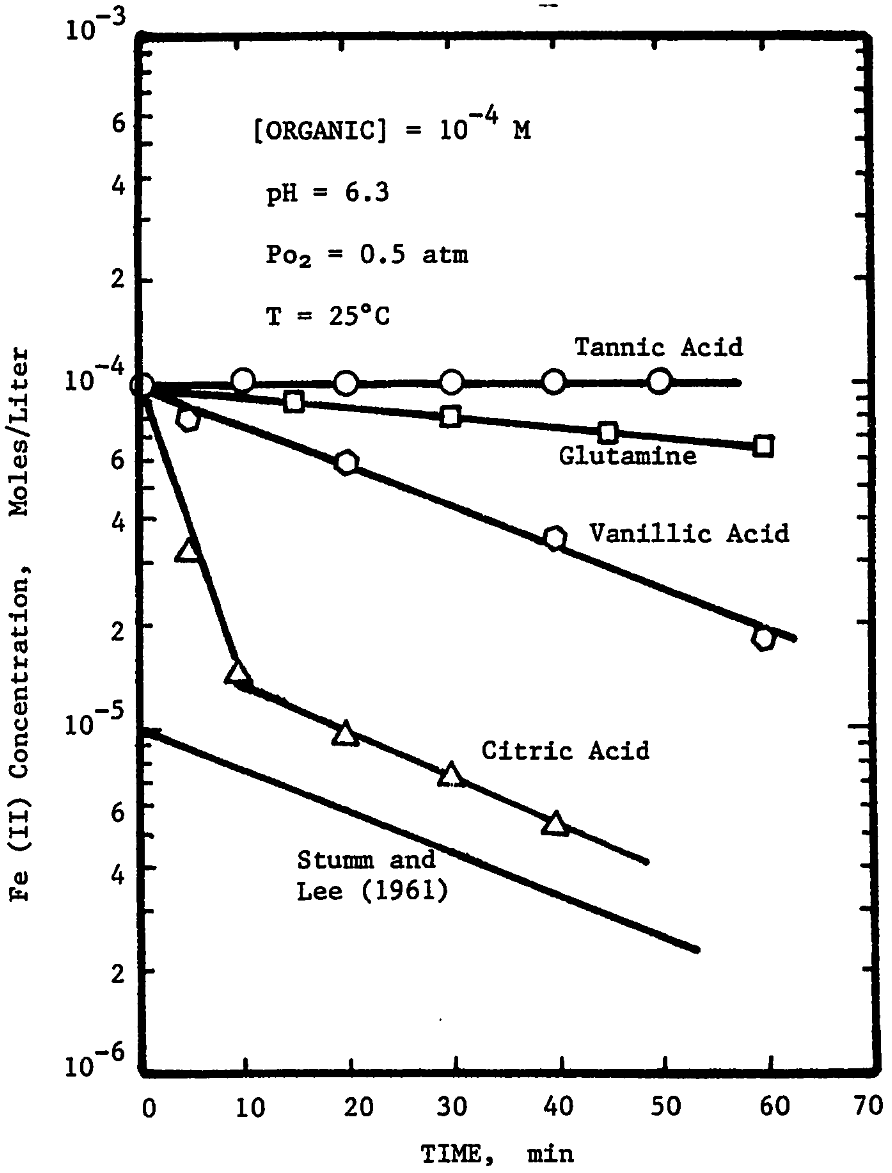


Figure 2.5 : Effects of representative organic compounds on the oxidation rate of ferrous iron.

SOURCE : Theis, T.L., et al (1974)

acids, the most stable end product usually being oxalic acid. Some CO_2 and water are eventually produced by the continuous ozonation after the rupture of the aromatic rings as shown in Fig. 2.6 (21,23).

It can be noticed from the literature that all the studies on oxidation kinetics of iron and manganese have been carried out with oxygen as an oxidant. Limited information is available where other oxidants like ozone, potassium permanganate, and chlorine are used for the oxidation of iron and manganese. Most of the studies are conducted in pure water system under batch experimental conditions, and only removal of iron and manganese are reported. No information is available on removal kinetics under different environmental conditions, which can affect the design of ozone contactor. The objective of this proposed study is to develop detailed oxidation kinetics of iron and manganese with complete ozone balance under different environmental conditions such as pH and organic matter.

This study will be conducted under semi batch condition employing both pure water system, and pure water system with model organic compounds.

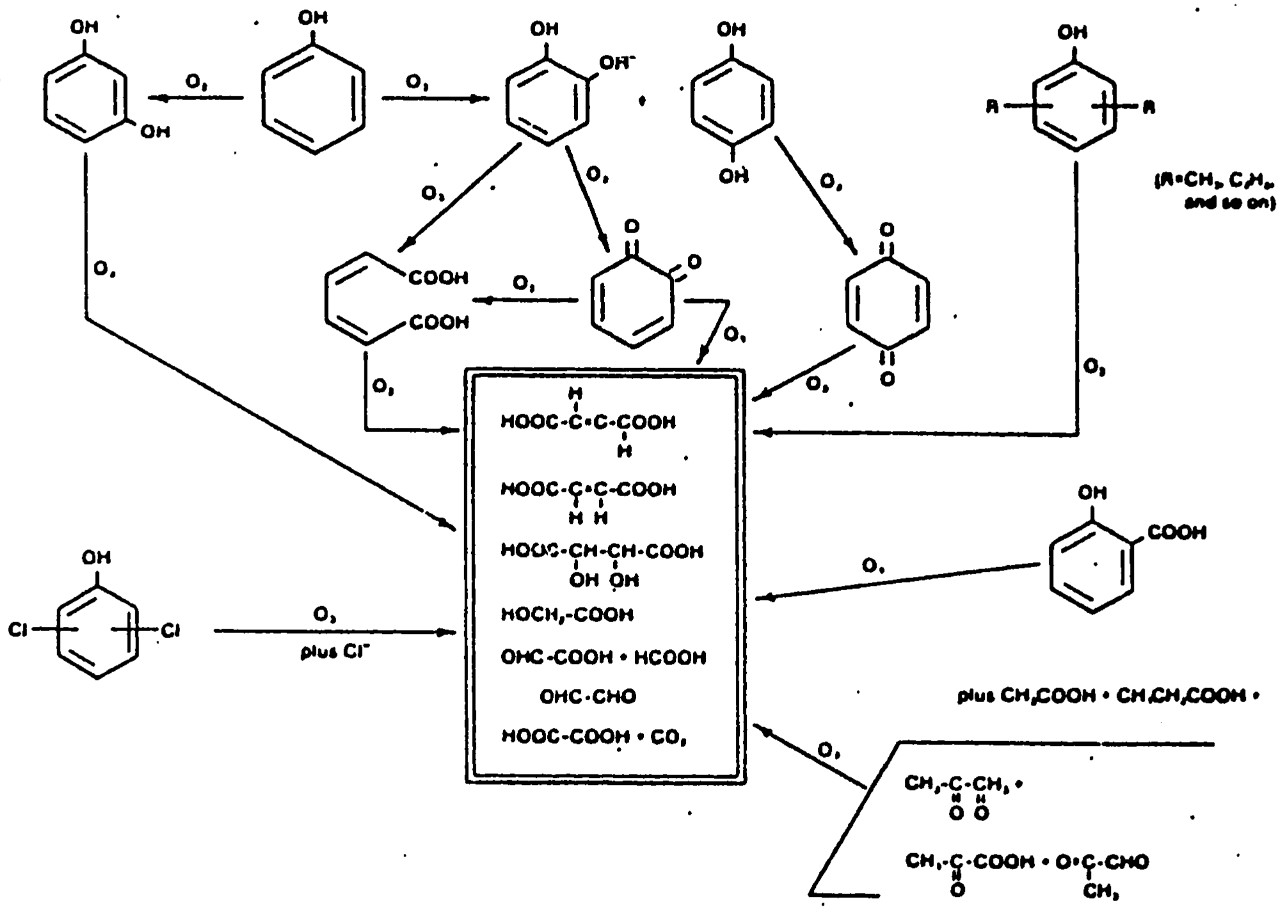


Figure 2.6 : Reactions of Ozone with Phenol After Miller et al. (1978)

Chapter 3

OBJECTIVES

The major objective of this study was to study the effect of ozone on the removal of iron and manganese in a semi batch system under different environmental conditions.

The objectives can be classified as follows:

I. PURE WATER SYSTEM

1. Development of kinetic expressions for oxidation of iron (II) at different pH values, e.g. 5.5, 6.0, and 6.5.
2. Development of kinetic expressions for oxidation of iron (II) at initial iron (II) concentrations of 4, 3, 2, and 1 mg/L and at constant pH of 6.0.
3. Development of kinetic expressions for oxidation of manganese (II) at pH values of 6, 7 and 9.

II. ORGANIC COMPLEXATION SYSTEM

1. Development of kinetic expressions for oxidation of iron

(II) at a pH of 6.5 and different complexing agents such as vanillin, glutamic acid, histidine, resorcinol, phenol, and citric acid.

2. Development of kinetic expressions for oxidation of iron (II) at different pH values:

    a. Development of kinetic expressions for oxidation of iron (II) in the presence of 10^{-4} M tartaric acid at pH values of 5.5, 6.5, and 7.5.

    b. Development of kinetic expressions for oxidation of iron (II) in the presence of 10^{-4} M histidine at pH values of 5.5, 6.5, and 7.5.

    c. Development of kinetic expressions for oxidation of iron (II) in the presence of 10 mg/L TOC of mixture of model organic compounds at pH values of of 5.5, and 6.5.

3. Study of ozone oxidation of manganese (II) in the presence of 10^{-4} M histidine at pH of 6.5.

Chapter 4

MATERIALS AND METHODS

4.1 Water

The distilled water used in this study for dilution was prepared in the Environmental Engineering Laboratory at KFUPM by using a mega-pure system model 11 (Corning Glass Work, New York 14830).

4.2 Air/Ozone

Air was obtained from a cylinder compressed by the Sigas Company in Al-Khobar, Saudi Arabia. Before feeding this air to the Welsbach T-816 ozonator (Plate 4.1), it was passed through a silica gel drier with cotton plugs fitted at the inlet and outlet ends to obtain a dry, particulate-free air supply. The ozonator was operated at a pressure of 8 psi and gas flow rate of 1 liter per minute.

4.3 Glassware

All glassware used in the experiments were cleaned

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thoroughly with washing soap and hot water, then rinsed with hot water to remove all traces of residual washing compound, and finally rinsed with distilled water. The experimental set up was cleaned by rinsing it with distilled water as soon as the experiment is finished.

4.4 Experimental Set-up

A batch-apparatus arrangement that included the following equipment was employed in the study :

1. An electrical discharge ozonator equipped with pressure gauge, pressure regulator, ozone flow meter, ozone valve, sample flow meter, sample valve, voltmeter and water cooling system.
2. A 10-liter plexi glass reaction vessel (reactor).
3. Two half-liter glass bottles filled with 2 percent KI solution to absorb unreacted ozone gas.
4. Clear, flexible tygon tubes to convey the gas between pieces of equipment or to act as a siphon tube for ease in sampling water from the reaction vessel.
5. Medium porosity fritted glass diffusers to distribute the gas in the reaction vessel or in the bottles filled with potassium iodide solution.

6. An air filter to remove moisture from the compressed air, which was the source for the ozonator.

7. An electric pump to pump the iron or manganese solution to the reaction vessel.

8. Automatic cooling system to control the temperature of ozone generator.

9. Wet meters were used to measure the total volume of gas (Plate 4.2) coming into and out of the reactor during a certain time period for determining the ozone concentration in gas phases.

10. Carbon dioxide gas (CO_2) cylinder to buffer the water system at different pH values.

11. Air cylinder for ozone generator.

12. Required glassware, chemicals, and testing equipment.

13. Spectronic-20 spectrophotometer at 1 cm light path for measuring the color intensity (Plate 4.3).

14. Total organic carbon analyzer for measuring the amount of organic matter in the solution.

15. A stop watch for measuring the time.

Plate 4.1 : Welsbach T-816 Ozonator

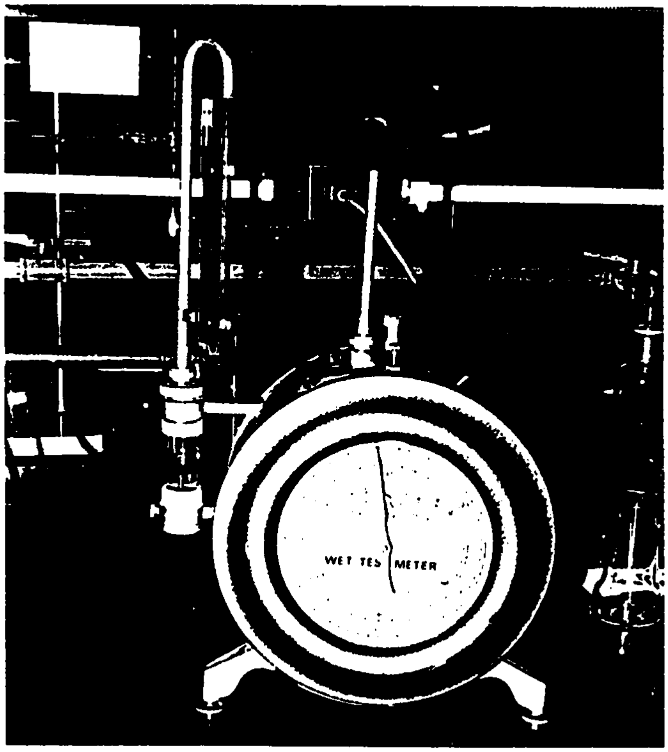

Plate 4.2 : Wet Test Meter

Figure 4.1 and Plate 4.4 show the flow sheet of the batch-apparatus arrangement used in this study. The known amount of water was added in the reactor and ozonated for 10 to 30 minutes with constant flow of ozone gas. The sample aliquots were taken at different time intervals to determine the concentration of remaining iron or manganese along with dissolved ozone.

4.5 Parameters and Analytical Techniques

4.5.1 Temperature

All the experiments for this study were performed at a temperature of 25°C. This temperature was controlled by an automatic cooling system from outside The cooling system was connected to the reactor by a U-tube that was immersed in the solution of the reactor.

4.5.2 Hydrogen Ion Concentration (pH)

The pH values of the solution in the reactor were controlled by a carbonate-bicarbonate buffer solution. The pH of the iron solution was adjusted by adding 28 ml of 1 M sodium carbonate solution so that the final solution was 0.004 M Na_2CO_3. For controlling the pH at lower levels, carbon dioxide gas (CO_2) was bubbled till the final solution reached a specific pH value. Also, CO_2 was diffused at the bottom of the reactor for controlling the pH of

Plate 4.3 : Spectronic-20 Spectrophotometer

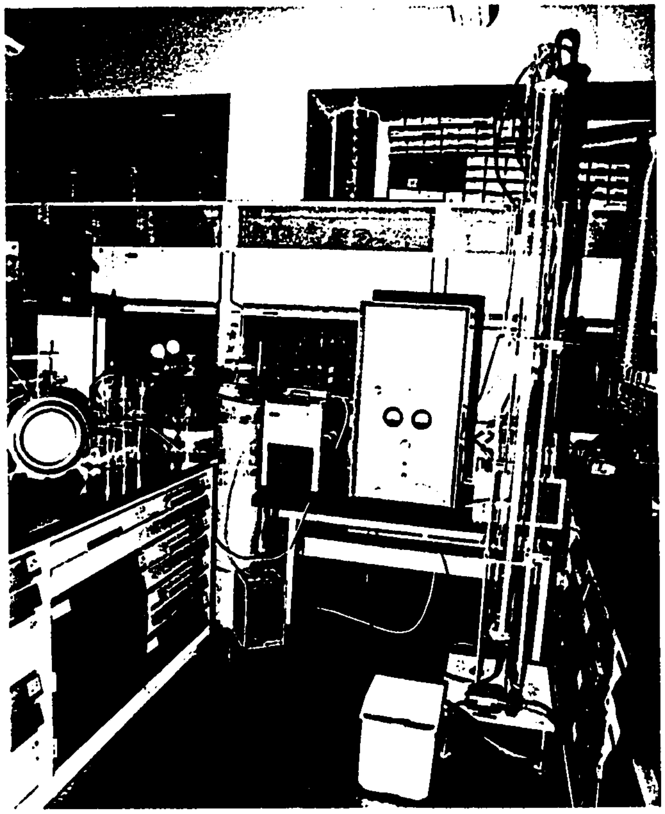

Plate 4.4 : The Experimental System Arrangement Used in this Study.

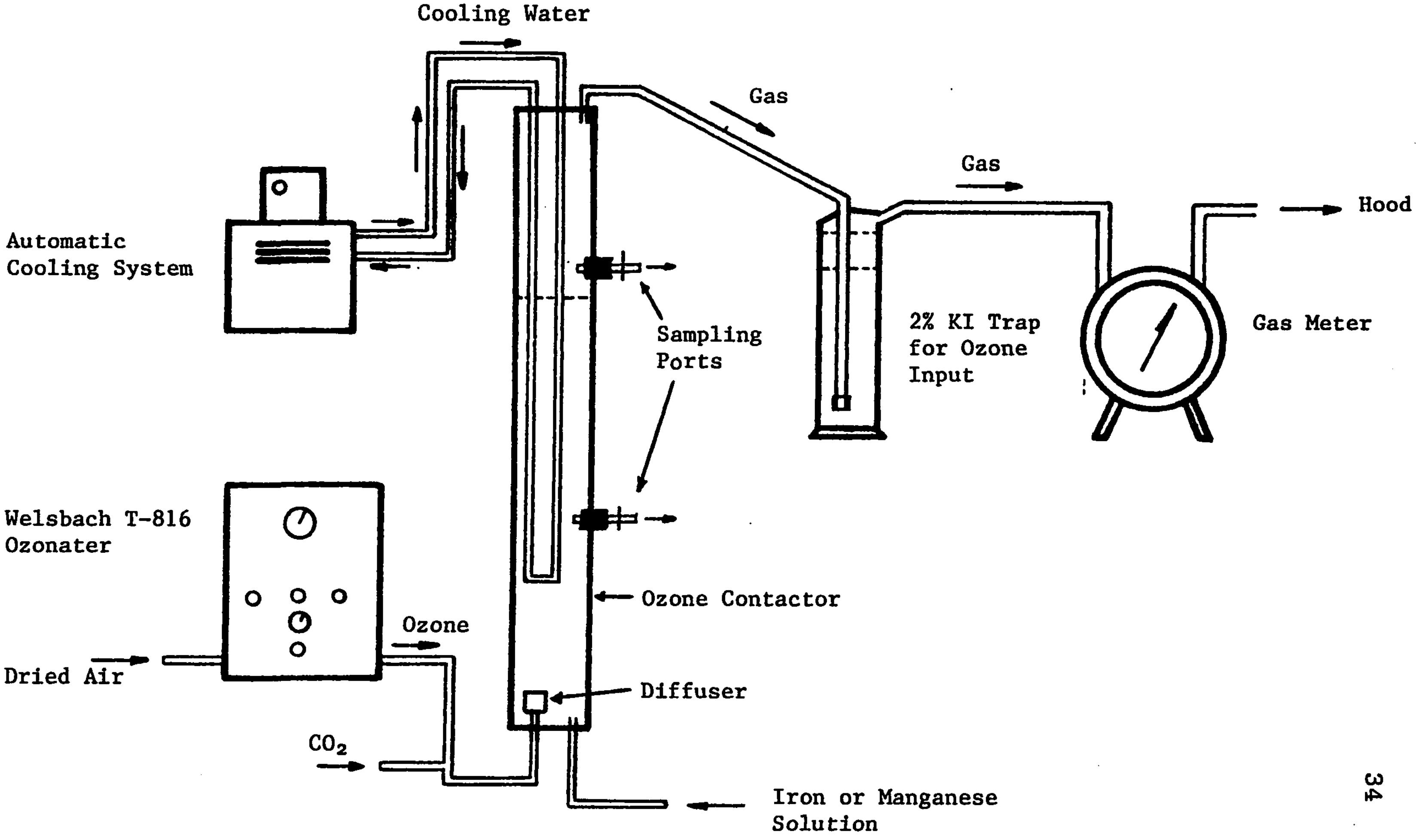

Figure 4.1 : Experimental System for Ozonation

the solution at the required level. At different time intervals water samples were collected for measuring the pH and according to that it was decided if CO_2 was needed to be diffused in the reactor or not. The pH levels were measured by a pH probe that had been recently standardized by a commercial buffer solution having a pH value close to those being monitored.

4.5.3 Ozone Concentration

Ozone concentrations were determined for the following:

1. The concentration of the ozone in the gas coming in and out of the reactor.
2. The ozone residual in the solution in the reactor.

The ozone residual concentration was determined by idometric method as follows:

1. Excess KI crystals were placed in BOD bottles.
2. At the appropriate sampling times, part of the ozonated sample was flushed to clean the sampling part prior to collecting the sample for analysis.
3. After the collection of the sample, 50 mL aliquot was withdrawn immediately from each of those sample bottles and individually titrated against a standard sodium thiosulfate solution ($Na_2S_2O_3$) of normally equal to 0.005. Starch indi-

cator was added to the 50 mL sample before completion of titration to sharpen the end point.

4. Calculation of ozone residual concentration was based on the following relation:

$$\text{mg/L } O_3 = \frac{A \times N \times 24000}{\text{mL of sample}}$$

A = mL of titrant consumed.

N = Normality of the $Na_2S_2O_3$ titrant.

The concentration of ozone in the gas was determined by titrating the KI solution against the sodium thiosulfate solution and the calculations were based on the previous relation, but in this case the volume of the sample was the total volume of the gas that was given by the wet meter in milliliters.

4.5.4 Iron Concentration

At the appropriate sampling times, iron samples were collected. The iron (II) concentrations were measured colorimetrically using the phenanthroline method following "Standard Methods" techniques. Spectronic-20 spectrophotometer was used at a light path of 1 cm for measuring the color intensity. The system was calibrated at various levels of iron and a standard iron (II) vs. absorbance curve was prepared as shown in Figure 4.2. The

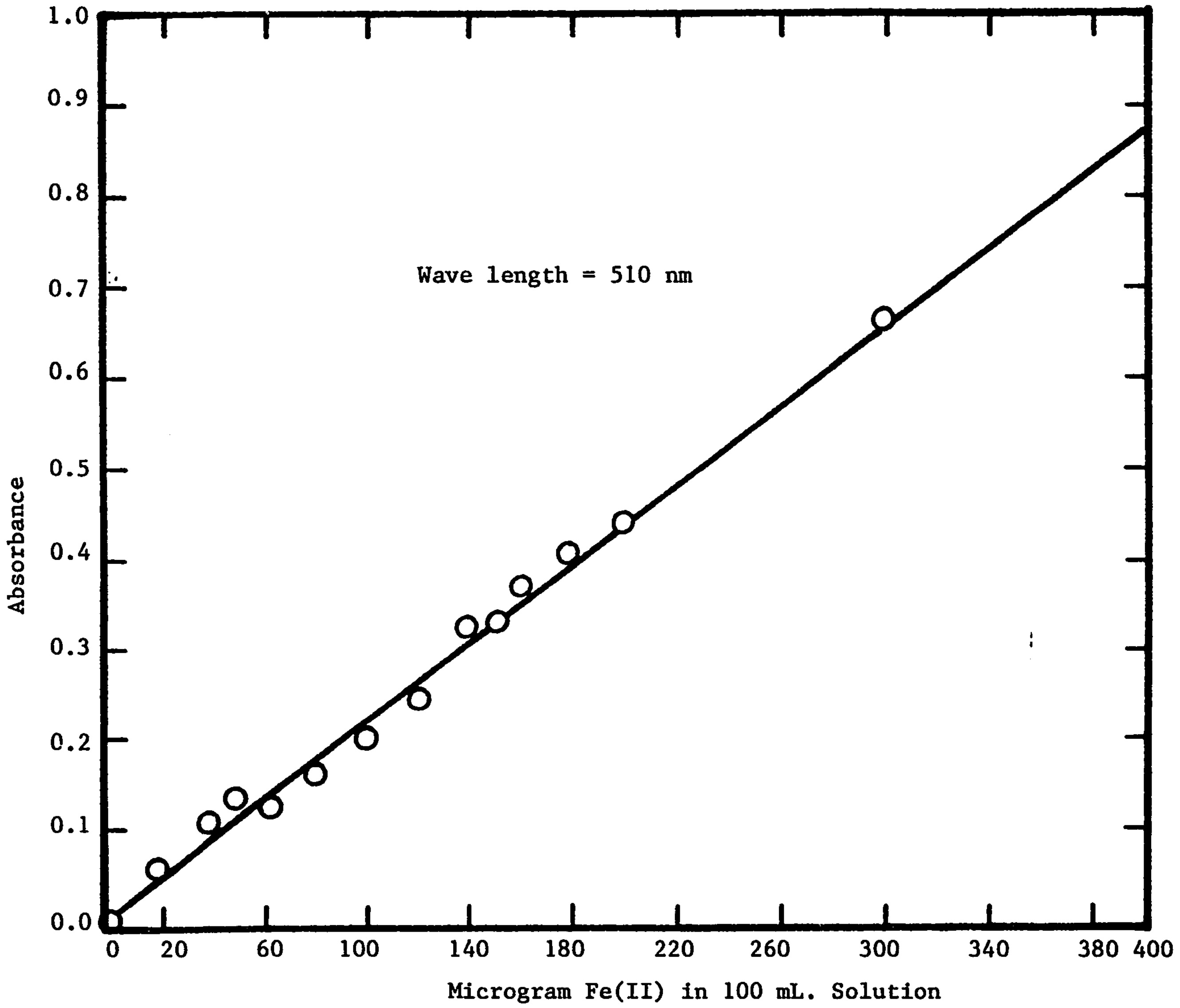

Figure 4.2 : Standard Curve of Absorbance (A) at 510 nm Wave length vs. Iron Added to 100 mL Final Volume.

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experimental procedure that was followed is as below :

1. Prepare and clean a series of 50-ml volumetric flasks.
2. To each flask add 10 ml phenanthroline solution, 5 ml ammonium acetate buffer ($NH_4C_2O_3H_2$), and 10 ml of distilled water.
3. At the appropriate sampling time, fill the flask to the 50 ml mark and shake the sample.
4. Measure color intensity within 5 to 10 minutes by spectronic -20 spectrophotometer at 510 mm providing a light path of one centimeter.

4.5.5 Manganese Concentration

In the other set of experiments, manganese was used instead of iron. Manganese samples were collected at the appropriate sampling times. Each sample was filtered through a filter with a pore size of 0.45 µm, for separating the manganese oxide (MnO_2) from the soluble manganese (II). In the filtrate, manganese was measured colorimetrically by using the persulfate method mentioned in the "Standard Method". Spectronic-20 spectrophotometer was used at a light path of 1 cm for measuring the color intensity of the permanganate color. The system was calibrated at various levels of manganese and a standard manganese (II) vs. absorbance curve was prepared as shown in Figure 4.3.

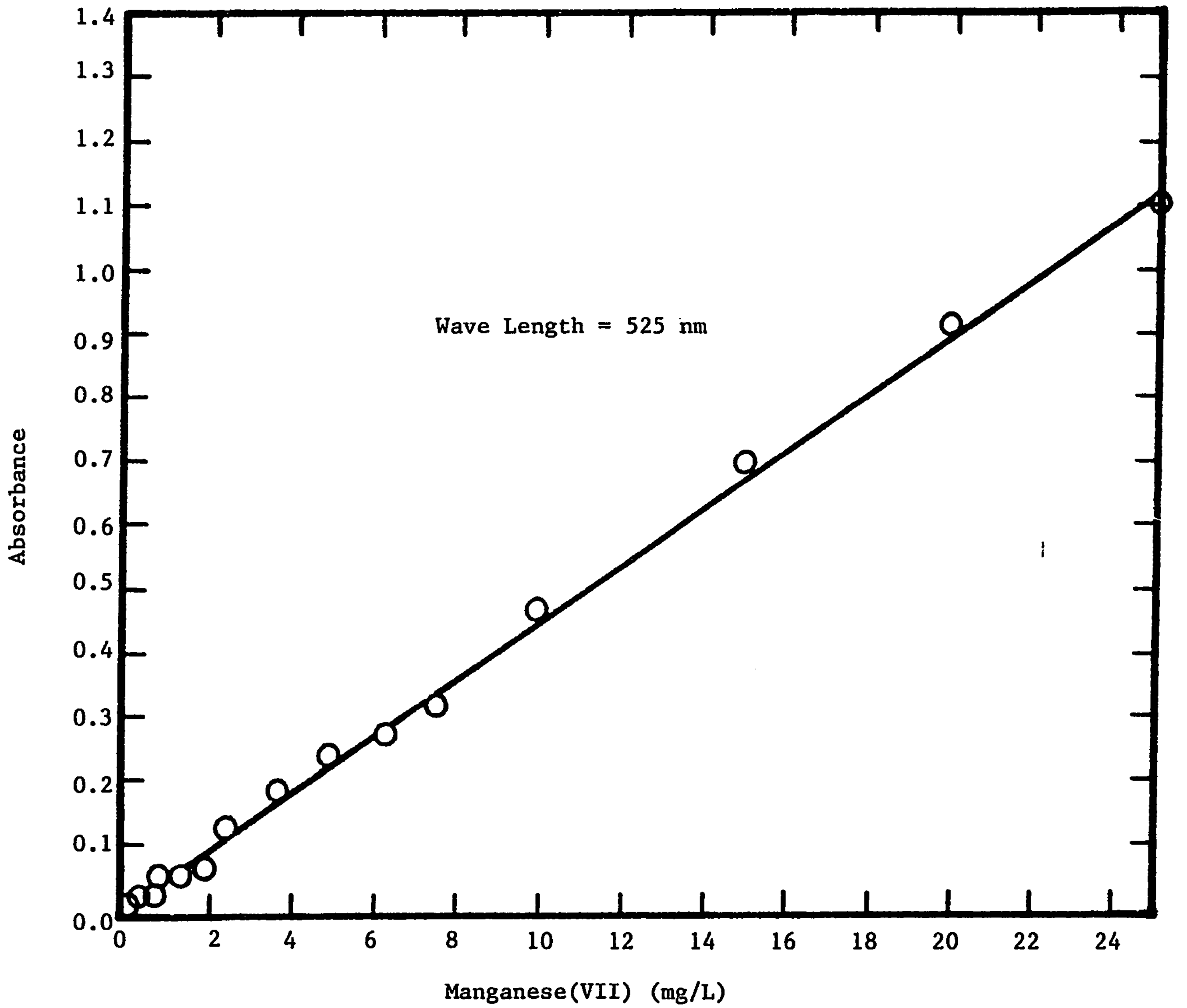

Figure 4.3 : Standard Curve of Absorbance (A) at 525 nm Wave length vs. Manganese Concentration.

The experimental procedure that was followed is as under :

1. At the appropriate sampling time, flush into a conical flask about 100 ml sample.
2. Filter the sample through a filter with a pore size of 0.45 µm.
3. Take 50 ml sample from the filtrate.
4. To the 50 ml sample add 5 ml of special reagent and one drop of 30% hydrogen peroxide (H_2O_2) and dilute to 90 ml.
5. Add about 1.2 gms of potassium persulfate. ($K_2S_2O_3$).
6. Boil the solution for one minute.
7. Remove from heat source and let the solution stand for one minute, then cool under the tap.
8. Dilute to 100 ml with distilled water free from reducing substances and mix.
9. Measure the absorbance of the samples by spectronic-20 spectrophotometer at 525 nm providing a light path of one cm.

4.5.6 Total Organic Carbon Concentration

In some of the experiments where model organic compounds were added, the concentrations of the organic substances were measured by using a Beckman Total Organic Carbon Analyzer (Plate 4.5) (TOC).* The TOC samples were collected at the appropriate sampling times and analyzed as mentioned in the manual.

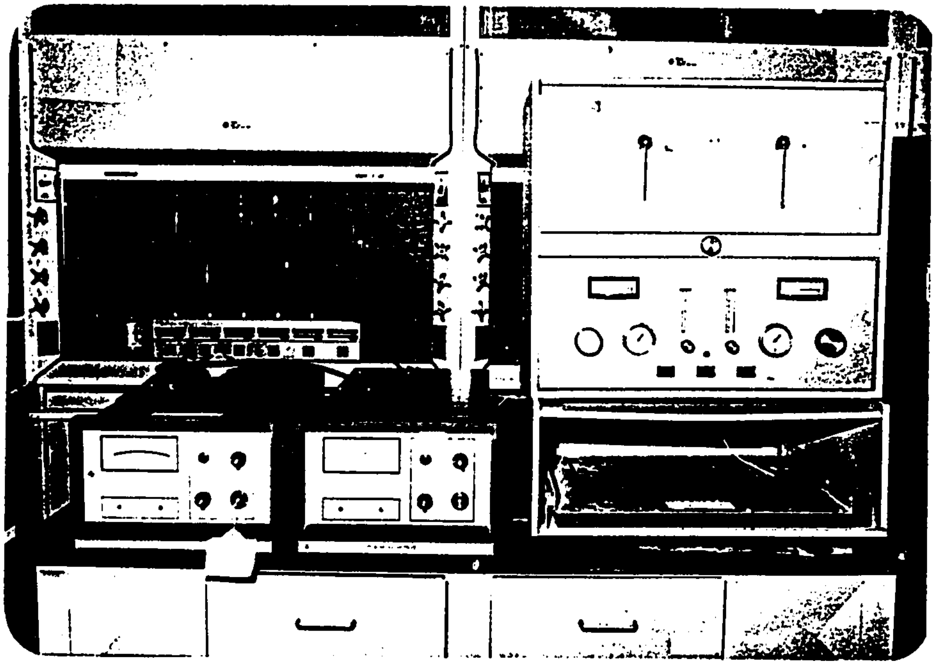

Plate 4.5 : Beckman Total Organic Carbon Analyzer

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*Beckman Instruments, Inc., Fullerton, CA 92634, USA.

Chapter 5

RESULTS AND DISCUSSION

5.1 Pure Water System

5.1.1 Oxidation of Iron (II) at Different pH Values

For the pure water system, the experiments were performed in the absence of any organic matter or complexing agents. Carbonate-bicarbonate buffer solution plus iron or manganese were added to distilled water for preparing the pure system solution.

Three pH values were selected for the oxidation of iron in the pure system. These values are 5.5, 6.0, and 6.5. When the pH was increased above 7, no iron (II) remained in the solution to be oxidized.

Ozone residual was also measured at different time intervals. For all experiments, the results showed that ozone residual increased from zero to 0.25, 0.25, and 0.49 mg/L at pH values of 5.5, 6.0, and 6.5, respectively during the ozonation of 10 minutes. All experiments were performed under similar conditions, i.e., temperature 25°C, iron (II) added 4 mg/L, and ozone concentration in gas phase of 1.96 mg/L. Table 5.1 shows the results of the experiments.

Figure 5.1 shows the oxidation rate of iron (II) at different pH values. By using the statistical analysis (SAS), linear regression gave the best models for fitting the date. Since the oxidation rate is linear with respect to time, the reaction is considered to be zero order.

Stumm and Lee equation for the oxidation of iron with oxygen is (11):

$$\frac{d[Fe(II)]}{dt} - k[Fe(II)][OH^-]^2 \, Po_2$$

The rate of oxidation of Fe(II) is first order with respect to Fe(II) concentration and Po_2, and second order with respect to (OH^-). The above equation could be used as a kinetic equation for the oxidation of iron with ozone. In this study, the pH will be constant in the experiment and ozone dose in the gas phase will also be constant. Therefore, the model that is going to be used is as follows:

$$\frac{d[Fe(II)]}{dt} - k[Fe(II)]^n$$

The above equation is the general equation with n-order with respect to iron (II) concentration.

Since the rate of oxidation is linear with respect to time, the order of the reaction will be zero and, therefore, the above

Table 5.1 : Oxidation of Iron (II) at Different pH Values in Pure Water System

Time (min.)	pH					
	5.5		6.0		6.5	
	Fe(II) (mg/L)	Ozone Resid. (mg/L)	Fe(II) (mg/L)	Ozone Resid. (mg/L)	Fe(II) (mg/L)	Ozone Resid. (mg/L)
0.0	4.0	0.0	3.72	0.0	2.94	0.0
0.5	3.72	0.0	3.4	0.0	2.58	0.0
1.0	3.56	0.0	3.2	0.0	2.36	0.0
2.0	3.0	0.0	2.72	0.0	1.94	0.0
3.0	2.36	0.0	2.16	0.0	1.48	0.0
5.0	1.26	0.0	1.2	0.0	0.52	0.0
6.0	0.84	0.0	0.52	0.0	0.0	0.0
7.0	0.4	0.0	0.04	0.0	0.0	0.0
8.0	0.04	0.0	0.0	0.1	0.0	0.25
10.0	0.0	0.25	0.0	0.25	0.0	0.49
Ozone Output in Gas Phase (mg/L)	0.55		0.633		0.644	

Ozone Inlet in Gas Phase = 1.96 mg/L.

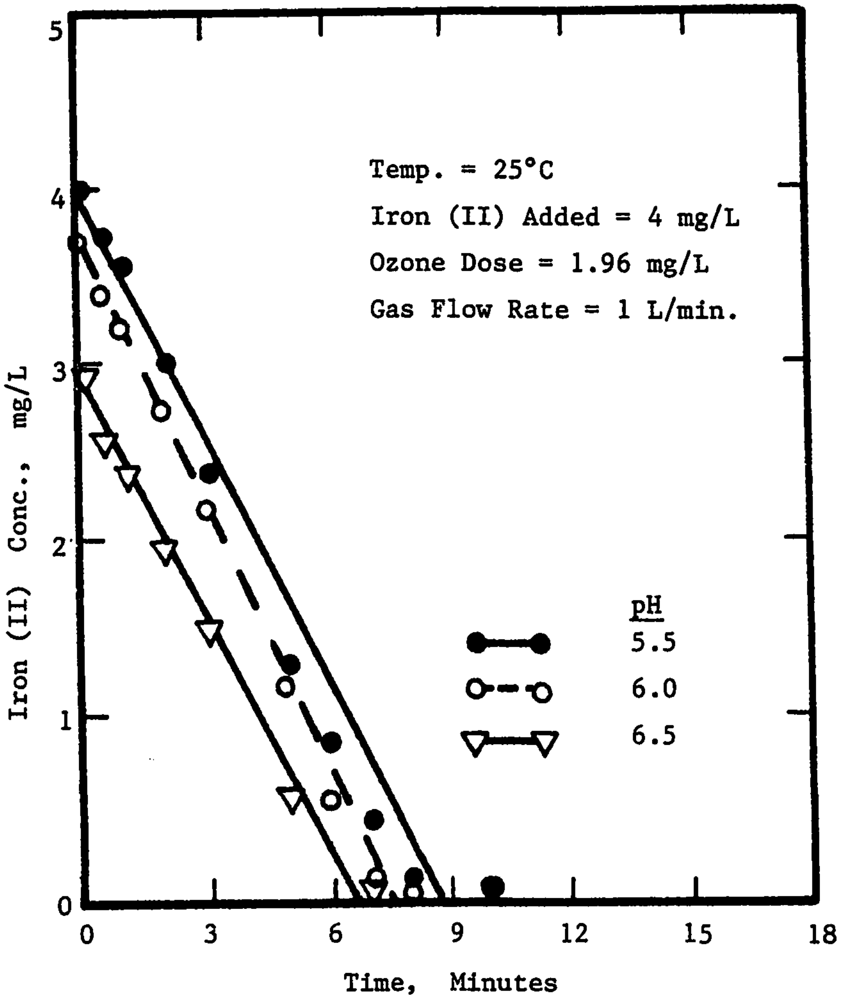


Figure 5.1 : Effect of Ozonation on Concentration of Fe (II) in a Pure Water System at Different pH Values.

equation will be as follows:

$$\frac{d[Fe(II)]}{dt} = -k[Fe(II)]^{\circ} = -k$$

$$\int_{[Fe(II)]_i}^{[Fe(II)]} d[Fe(II)] = -\int_{o}^{t} kdt$$

$$[Fe(II)] - [Fe(II)]_i = -k(t)$$

where, $[Fe(II)]_i$ = the initial Fe(II) conc. in mg/L

$[Fe(II)]$ = the conc. of Fe(II) at time(t) in mg/L

k = the rate of oxidation of Fe(II) in mg/(L.min.)

t = the time in minutes.

Therefore, the general linear regression model is :

$$[Fe(II)] = [Fe(II)]_i - kt$$

"The order of a reaction is the sum of the exponents of concentration factors in an experimental rate law. Reaction order is thus an experimental results for a chemical reaction under specified conditions" (16).

The linear regression models of the oxidation rate of Fe(II) at different pH values are as follows :

(a) At pH = 5.5

Fe(II) = 3.835 - 0.451 t (R^2 = 0.96)

where, Fe(II) = conc. of iron (II) in mg/L

t = time in minutes.

(R^2) is called the coefficient of determination and often used to judge the adequacy of regression model. (R^2) is the square root of the fraction of the sum of squares of deviations of the original data from the regression curve. The value of R^2 will lie between 0 and 1. If the regression curve is a poor fit of the experimental data, R^2 will be close to zero, and vice versa (40). The statistical definition of R^2 is :

$$R^2 = SS_R / SS_{TC}$$

where,

R^2 = Coefficient of determination.

SS_R = Sum of squares due to regression.

SS_{TC} = Total corrected sum of squares.

(b) At pH = 6.0

$$\text{Fe(II)} = 3.67 - 0.49\ t \qquad (R^2 = 0.99)$$

(c) At pH = 6.5

$$\text{Fe(II)} = 2.81 - 0.42\ t \qquad (R^2 = 0.99)$$

The previous three equations show that the intercept (initial

Fe(II) conc.) decreases when the pH increases, but the slopes which are the oxidation rates are more or less the same that range between (0.42 - 0.49) and have an average value of 0.45.

Based on the results of the previous experiments, it is clear that pH plays a vital role in the oxidation of iron. Figure 5.2 shows that when the pH increases, the initial Fe(II) concentration decreases substantially till it reaches zero at a pH of 7. Also, the rate of oxidation initially increases with pH and starts decreasing after reaching the peak at pH of 6 (Figure 5.3). Hence, the optimum pH for oxidation is 6.

5.1.2 Oxidation of Iron (II) at Different Initial Iron (II) Concentrations

On the basis of the results of the previous section, a pH value of 6 was chosen for conducting the experiments of this section. Four different initial concentrations were chosen as shown in Table 5.2. Figure 5.4 shows the oxidation rates of Fe(II) at different initial iron concentrations. The data shown in Table 5.2 and Figure 5.4 show that the concentration of Fe(II) decreases with time till it reaches zero after few minutes of continuous ozonation. Also, the ozone residual increases with time till it reaches a steady state. For example, at an initial Fe(II) concentration of 1 mg/L the ozone residual increases from 0 to a steady state of 0.5 mg/L as shown in Table 5.2.

Linear regression analysis were used for analyzing the data.

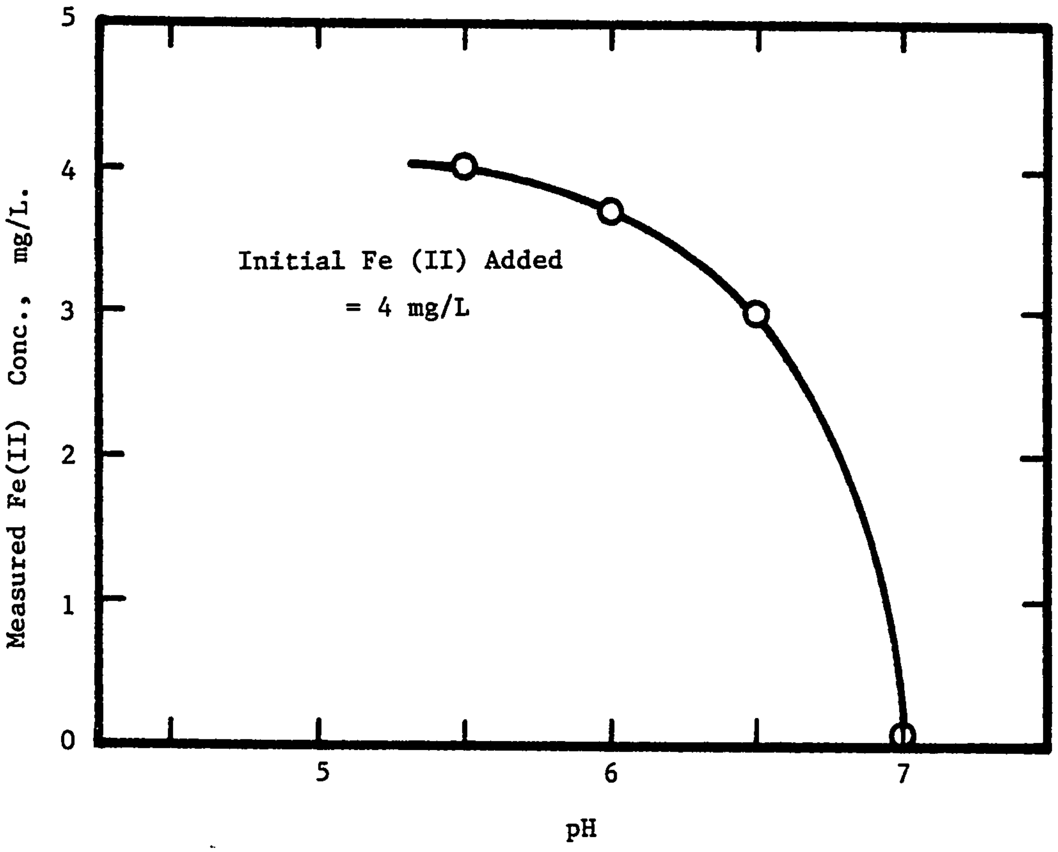


Figure 5.2 : Relationship between the Amount of Fe (II) Added and Measured in Pure Water System at Different pH Values.

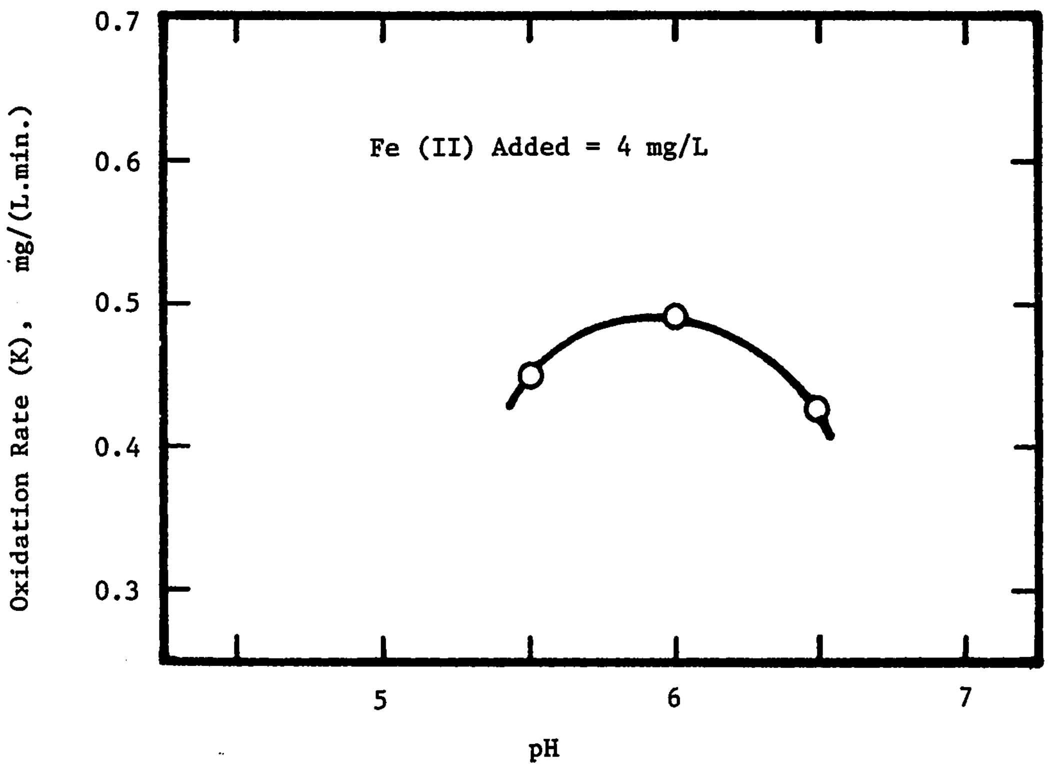


Figure 5.3 : Variation of Oxidation Rate (K) at Different pH Values in Pure Water System.

Table 5.2: Oxidation of Iron (II) at Different Initial Concentrations of Iron (II) Added in Pure Water System

Time in Min.	IRON (II) ADDED (mg/L)							
	1.0		2.0		3.0		4.0	
	Fe(II) (mg/L)	Ozone Res. (mg/L)	Fe(II) (mg/L)	Ozone Res. (mg/L)	Fe(II) (mg/L)	Ozone Res. (mg/L)	Fe(II) (mg/L)	Ozone Res. (mg/L)
0.0	0.96	0	1.8	0	2.72	0	3.72	0
1.0	0.88	0	1.56	0	2.36	0	3.2	0
2.0	0.76	0.05	1.4	0	2.2	0	2.72	0
3.0	0.6	0.1	0.8	.05	1.84	0	2.16	0
4.0	0.04	0.37	0.44	0.1	1.44	0	1.6	0
5.0	0.0	0.37	0.0	0.2	0.36	0.05	1.2	0
6.0	0.0	0.4	0.0	0.25	0.04	0.1	0.52	0
7.0	0.0	0.5	0.0	0.5	0.0	0.2	0.04	0
8.0	0.0	0.5	0.0	0.5	0.0	0.25	0.0	0.1
9.0	0.0	0.5	0.0	0.5	0.0	0.35	0.0	0.15
Ozone Outlet in Gas Phase (mg/L)	1.075		0.795		0.702		0.633	

Ozone Inlet in Gas Phase = 1.96 mg/L

pH = 6.

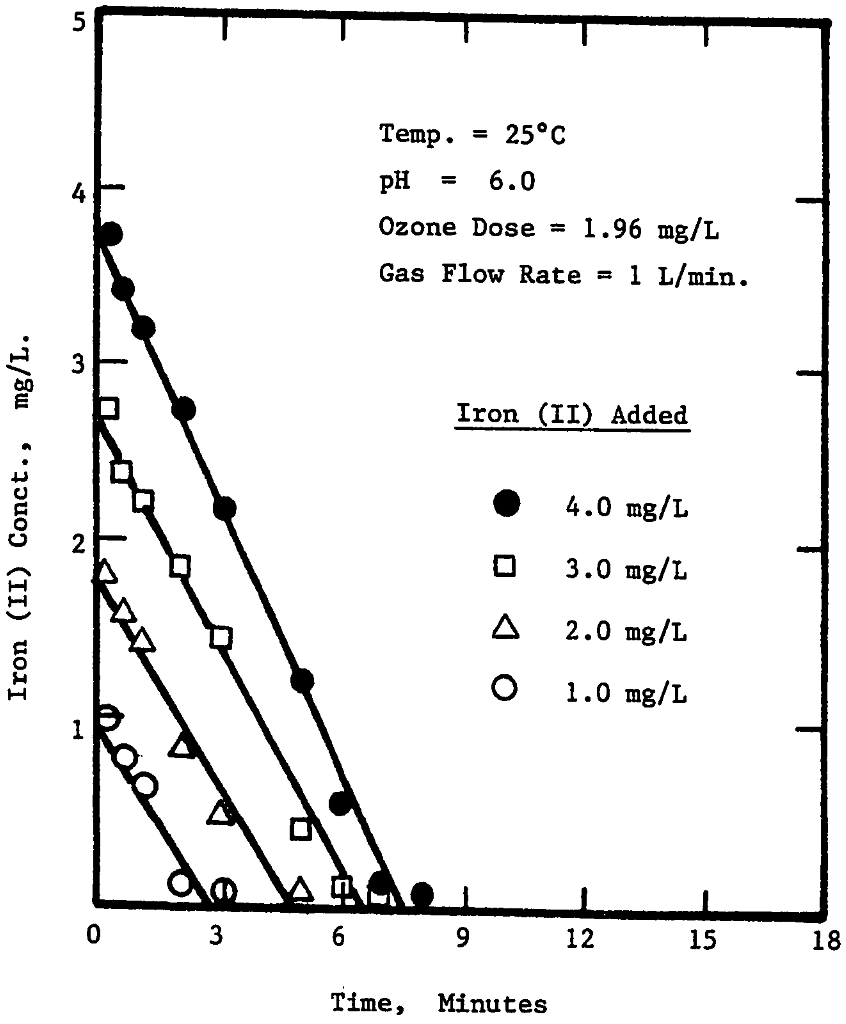


Figure 5.4 : Effect of Ozonation on Different Initial Concentrations of Fe (II) in a Pure Water System.

The models that are obtained from the analysis are as follows:

(a) At pH = 6, Fe(II) added = 4 mg/L

Fe(II) = 3.67 - 0.49 t $\quad$ (R^2 = 0.99)

(b) At pH = 6, Fe(II) added = 3 mg/L

Fe(II) = 2.623 - 0.41 t $\quad$ (R^2 = 0.98)

(c) At pH = 6, Fe(II) added = 2 mg/L

Fe(II) = 1.712 - 0.372 t $\quad$ (R^2 = 0.96)

(d) At pH = 6, Fe(II) added = 1 mg/L

Fe(II) = 0.936 - 0.352 t $\quad$ (R^2 = 0.94)

The above equations have R^2 values greater than 0.9, which means that linear models are the best models for fitting the data. The order of the reaction is zero because the rate of change of iron (II) with respect to time is constant. Hence,

$$\frac{d[Fe(II)]}{dt} = -k$$

The rate constants in the previous equations are noticed to be different. The rate constant which is the oxidation rate (k) increases with increase in initial iron (II) concentration at constant pH (Figure 5.5).

In a similar study conducted by Cromley and O'Conner (3), the oxidation rate, using their data and similar approach, was calculated and the value is very much similar to the values obtained by this study for the pure water system. Based on the ozonation data given by Cromley and O'Conner, the oxidation rate of iron (II) is calculated as follows:

$$\frac{\Delta\ \mathrm{Fe(II)}}{\Delta\ t} = \frac{1.33 - 0.14}{2 - 0} = 0.6\ \mathrm{mg/(L.min.)}$$

The above rate of oxidation of iron (II) is more or less similar to the optimum rate of oxidation of iron in the pure water system at a pH of 6 which is about 0.5.

However, the details of their experimental results are given in Table 5.3. The results of their experiment show that the pH increases gradually with time from a value of 7.13 to 7.59 at the end of the 60 minutes. The ozone residual increases during the first ten minutes and starts decreasing after termination of ozonation at the end of 10 minutes. Iron (II) concentration drops substantially during the first two minutes of ozonation from a value of 1.33 mg/L to a value of 0.14 mg/L and after that it remains steady and eventually it drops to 0.09 mg/L at the end of the 60 minutes as shown in Figure 5.6.

The rate constants (k) in the previous equations are noticed to be different varying from 0.352 to 0.49 mg/(L.min) for different initial concentrations, although orders of the reaction is zero (Figure 5.4). Therefore, the rate of oxidation of iron(II) depends on the initial concentration of iron(II) as follows:

$$\frac{d[Fe(II)]}{dt} = -k' \, [Fe(II)]_o$$

where, $[Fe(II)]$: iron(II) concentration at any time, (mg/L)

$[Fe(II)]_o$: initial iron(II) concentration, (mg/L)

k' : reaction rate constant, $(min.^{-1})$

t : any time, (min.)

The integration of the above equation gives :

$$-\int_{[Fe(II)]_o}^{[Fe(II)} d[Fe(II)] = k'[Fe(II)]_o \int_{o}^{t} dt$$

$$[Fe(II)]_o - [Fe(II)] = k'[Fe(II)]_o \, t$$

Therefore, the general kinetic expression for the oxidation of iron(II) can be represented by the following expression :

$$X = (1 - \frac{[Fe(II)]}{[Fe(II)]_o}) = k' \, t$$

For determining the value of k' a plot of X versus time (Figure 5.6A) for all the data points is supposed to give a straight line. The slope of that line is the value of k'. The data points shown in Figure 5.6A do not lie on the same line, and this scatter can be attributed to the experimental error. Therefore, for determining the best fit, linear regression analysis (SAS) package is employed. The linear regression kinetic expression obtained is :

$$X = 0.026 + 0.13\ t \qquad (R^2 = 0.77)$$

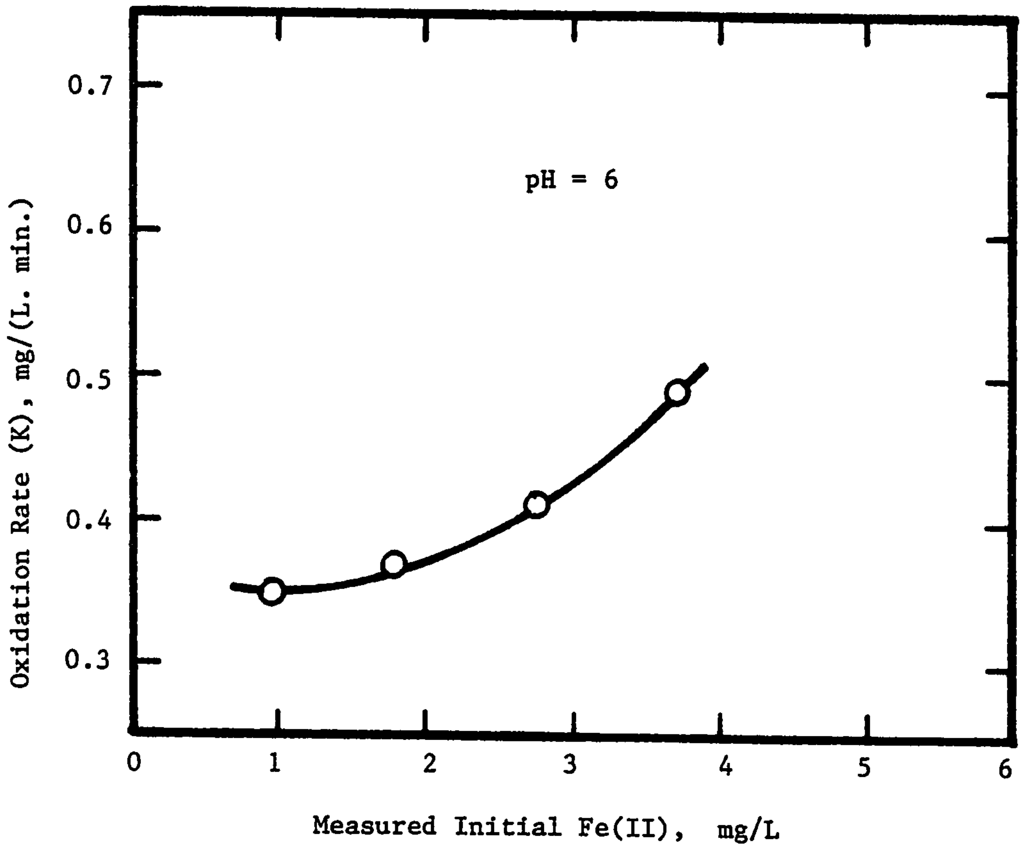


Figure 5.5 : Variation of Oxidation Rate (K) at Different Initial Concentrations (measured) of Fe(II) in Pure Water System.

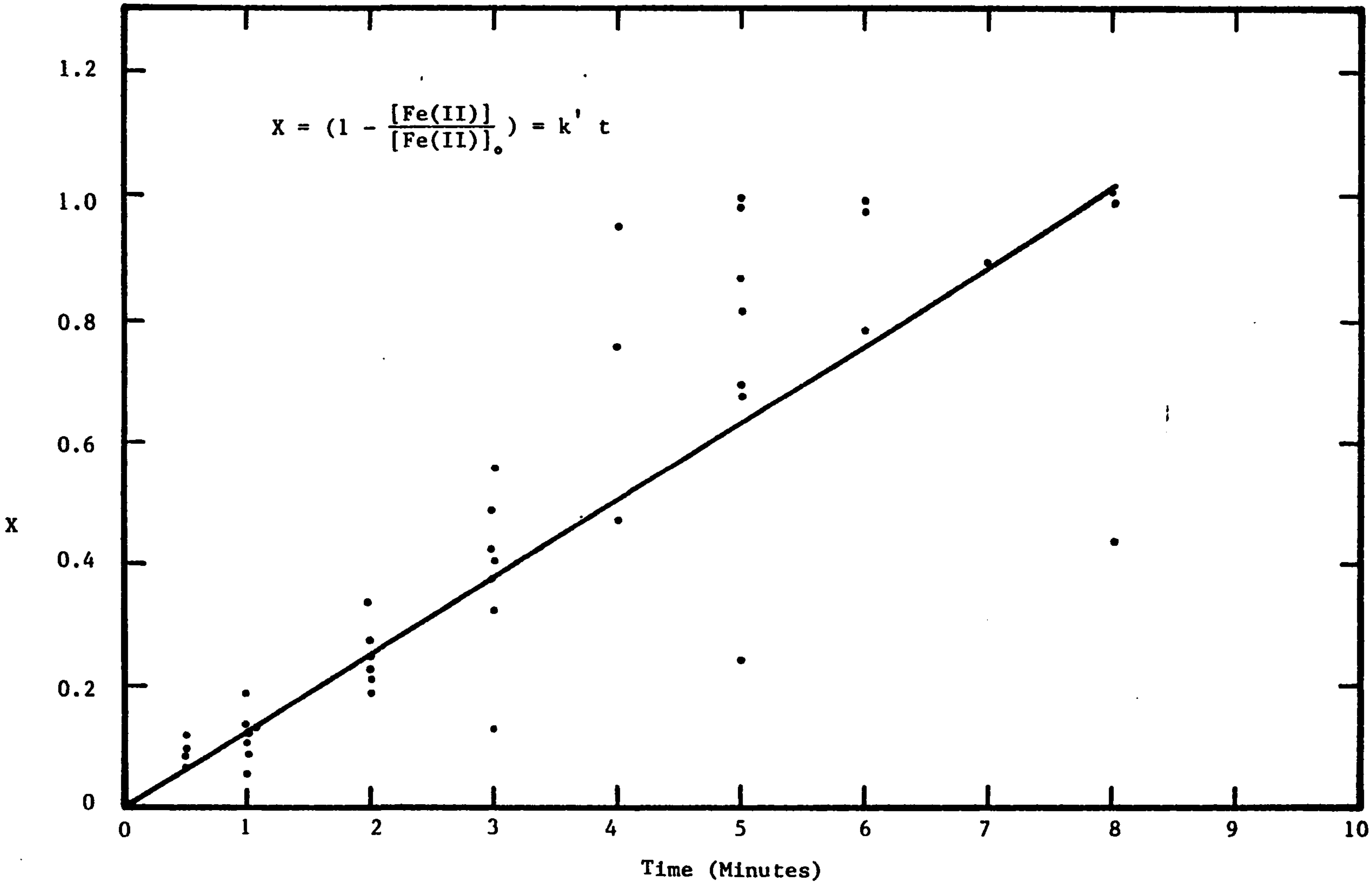
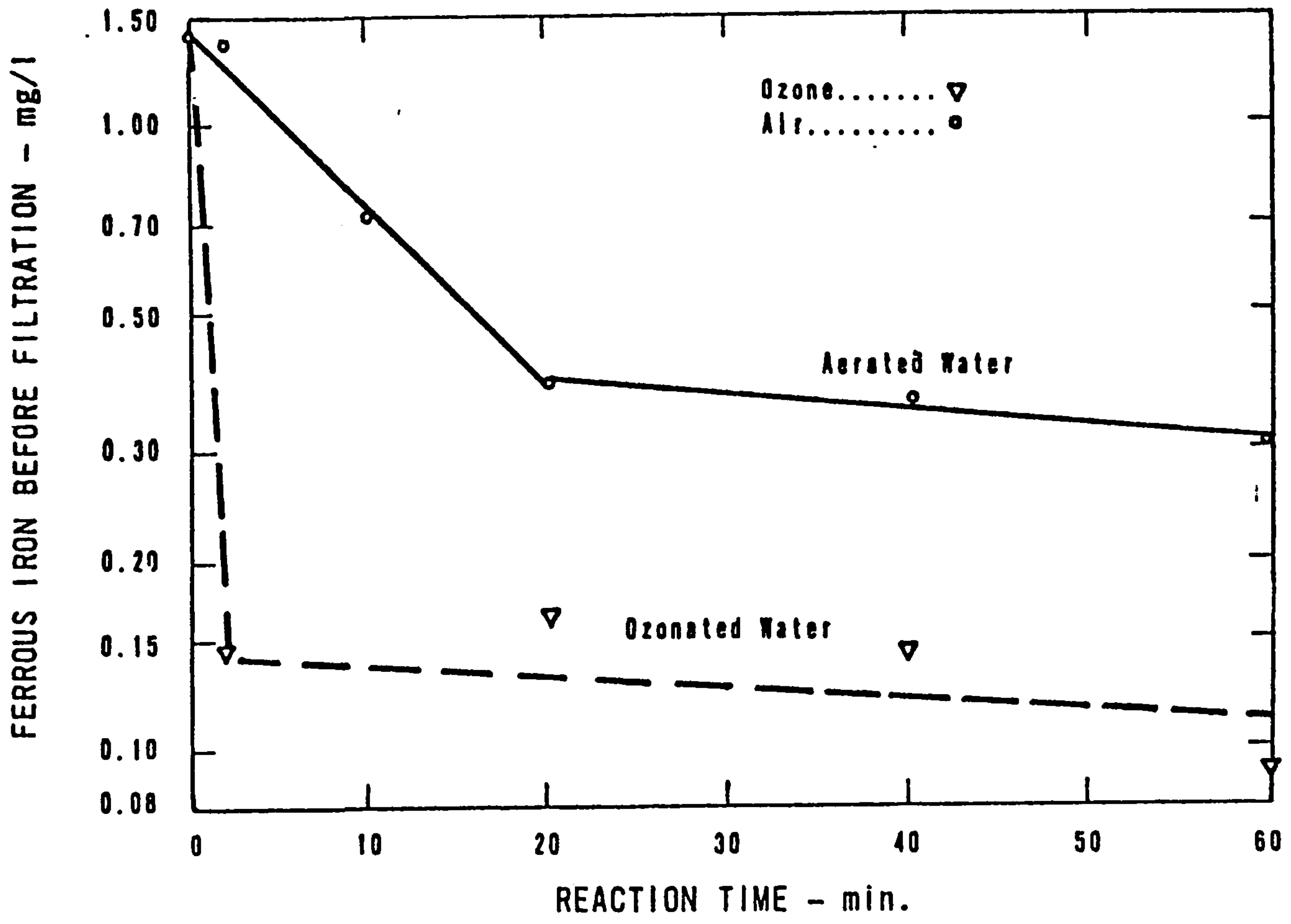


Figure 5.6A : Linear Regression Plot of X vs. Time.

Figure 5.6 : COMPARISON OF THE FERROUS IRON CONCENTRATIONS IN AN AERATED AND OZONATED GROUND WATER



SOURCE: Cromley, J.T., et al (1976)

Table 5.3 : **RESULTS FROM OZONATION OF GROUNDWATER**

Time min.	Ozone mg/l	pH	Iron		TOC mg/l	Remarks
			Fe^{+2} mg/l	Total mg/l		
0	0.0	7.13	1.33	1.34	3.5 ± 1.8	Ozonation Initiated
2	1.27	7.30	0.14		5.6 ± 3.3	
10	4.18	7.52				Ozonation Terminated
20	3.42	7.54	0.16			
40	2.60	7.56	0.14		2.4 ± 0.4	
60	2.44	7.59	0.09		1.2 ± 1.1	

SOURCE : Cromley, J.T., et al (1976)

Meanwhile, TOC data are quite erratic as it decreases from 3.5 ± 1.8 mg/L to 1.2 ± 1.1 mg/L during ozonation. This gives approximate TOC removal of about 70 percent in 60 minutes. However, the TOC removal is only 30 percent in our study during 30 minutes of ozonation.

5.1.3 *Oxidation of Manganese (II) at Different pH Values*

Manganese (II) was oxidized by ozone at pH values of 6, 7, and 9. The results of the experiments are given in Table 5.4. The data given in Table 5.4 show that the concentration of manganese (II) decreases by ozonation at all pH values. The idometric method used in this study for measuring ozone residual was found inadequate as it interferes with the presence of manganese. Most of the sodium thiosulfate titrant was utilized by manganese (IV) to be reduced to manganese (II) instead of being utilized by the iodine ions to be reduced to iodide ions.

The results (Figure 5.7) show that at pH values of 6 and 7 the concentrations of manganese (II) are linear with respect to time. The linear regression analysis give the best model for the data with R^2 values greater than 0.9. Since the oxidation rates are constant at pH values of 6 and 7, the orders of the reactions are considered to be zero with a constant rate of oxidation.

The linear regression models that were obtained are as follows:

Table 5.4 : Oxidation of Manganese (II) at Different pH Values in Pure Water System

Time in minutes	pH 6 Mn(II) Conc. (mg/L)	pH 7 Mn(II) Conc. (mg/L)	pH 9 Mn(II) Conc. (mg/L)
0.0	4.0	4.0	4.0
1.0	3.53	3.55	1.022
2.0	3.25	3.24	0.9
3.0	2.96	2.92	0.8
4.0	2.67	2.6	0.7
5.0	2.38	2.28	0.5
6.0	2.1	1.97	0.55
7.0	1.81	1.65	0.45
8.0	1.52	1.33	0.4
9.0	1.23	1.02	0.3
10.0	0.94	0.7	0.2
11.0	0.65	0.38	0.1
12.0	0.366	0.07	0.0
Ozone Outlet in Gas Phase (mg/L)	0.18	0.347	0.356

Ozone Inlet in Gas Phase = 1.96 mg/L

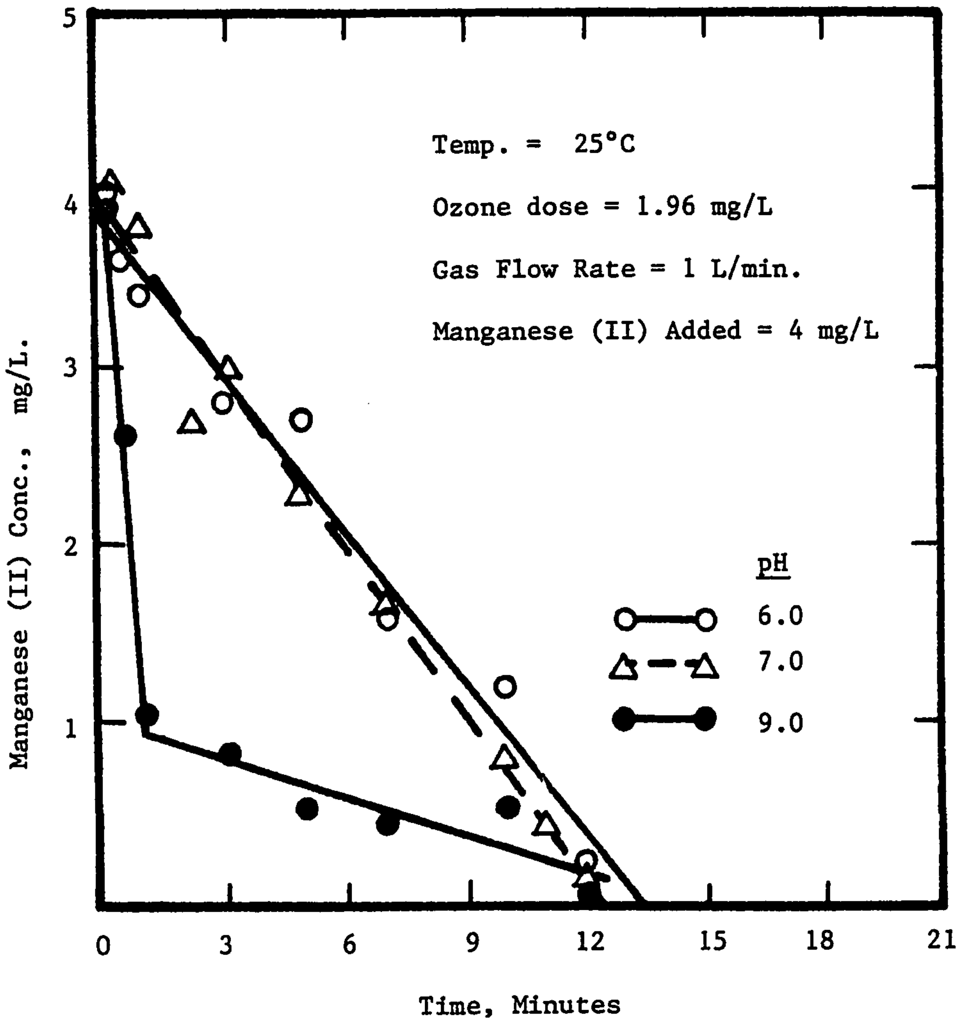


Figure 5.7 : Effect of Ozonation on Concentration of Mn(II) in a Pure Water System at Different pH Values.

(a) At pH = 6

Mn(II) = 3.822 - 0.29 t (R² = 0.97)

(b) At pH = 7

Mn(II) = 3.87 - 0.317 t (R² = 0.977)

At a pH of 9, the oxidation rate of manganese (II) is different and has two linear stages as shown in Figure 5.7. During the first minute of oxidation, which is the first stage, the rate of oxidation is fast and has a slope of -3. The second stage of oxidation starts after the first minute with a rate of oxidation of -0.077. Linear regression model is the best model that fits the data.

The regression models for the two stages are as follows:

(a) First Stage

Mn(II) = 4.0 - 3 t (R² = 0.99)

(b) Second Stage

Mn(II) = 1.02 - 0.076 t (R² = 0.84)

Figure 5.7 shows that at a pH value of 9, the oxidation of manganese (II) occurs in two stages and that is due to the presence of high concentration of hydroxide ions (OH^-). During the first minute of ozonation, most of the manganese (II) exist in the form of $Mn(OH^-)_3$, therefore, it is much faster for manganese (II) to be converted to manganese (IV). But after the first minute, the rate of oxidation decreases because the concentration of (OH^-) ions is less than before. The chemical equation for the oxidation of manganese with ozone is as follows (1,21):

$$Mn^{+2} + O_3 + H_2O \rightarrow Mn^{+4} + O_2 + (OH)^-$$

$$Mn^{+4} + 4\ (OH)^- \rightarrow Mn(OH)_4 \rightarrow MnO_2 + 2\ H_2O.$$

5.2 Organic Complexation System

Some model organic compounds were selected from literature for studying the effect of organic complexation on the oxidation rates of iron and manganese (15). These organic compounds were added to the pure water solution separately at concentration of 1.0×10^{-4} M. The model organic compounds that were used are : Histidine, Glutamic acid, Citric Acid, Tartaric Acid, Phenol, Vanillin, and Resorcinol. The initial iron (II) added for all experiments was 4 mg/L. Also, total organic carbon (TOC) was measured with respect to time in all cases, which was approximately 10 mg/L in all cases.

5.2.1 Oxidation of Iron (II) in the Presence of Different Complexing Agents

In this set of experiments, all the experiments were conducted at a pH of 6.5 and applied ozone dosage of 5.1 mg/L in gaseous phase. The results of the experiments are discussed separately for each organic compound.

5.2.1.1 Vanillin

The results of the experiments for the oxidation of iron when vanillin was added to the pure water system are shown in Table 5.5. The differential method is employed for calculating the kinetic constants from the data in all cases (1). The procedure is explained as follows:

$$\frac{dFe(II)}{dt} = - k\, [Fe(II)]^n \qquad (1)$$

where n is the order of the reaction and k is the reaction constant. Figure 5.8 shows that the rate of oxidation of iron is linear after six minutes and has a slope of-0.04. The rate of oxidation is curvilinear during the first six minutes of oxidation.

Table 5.5 : Oxidation of Iron (II) in the Presence of 10^{-4} M Vanillin

Time (Min.)	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)
0	3.26	0	10.7
1	2.44	0	10.4
2	2.36	0	10.4
3	2.08	0	10.4
4	2.0	0	10.3
5	1.88	0	10.3
10	1.88	0	10.3
20	1.4	0	8.7
30	0.9	0.49	7.2

Ozone Inlet in Gas Phase = 5.1 mg/L

Ozone Outlet in Gas Phase = 0.973 mg/L

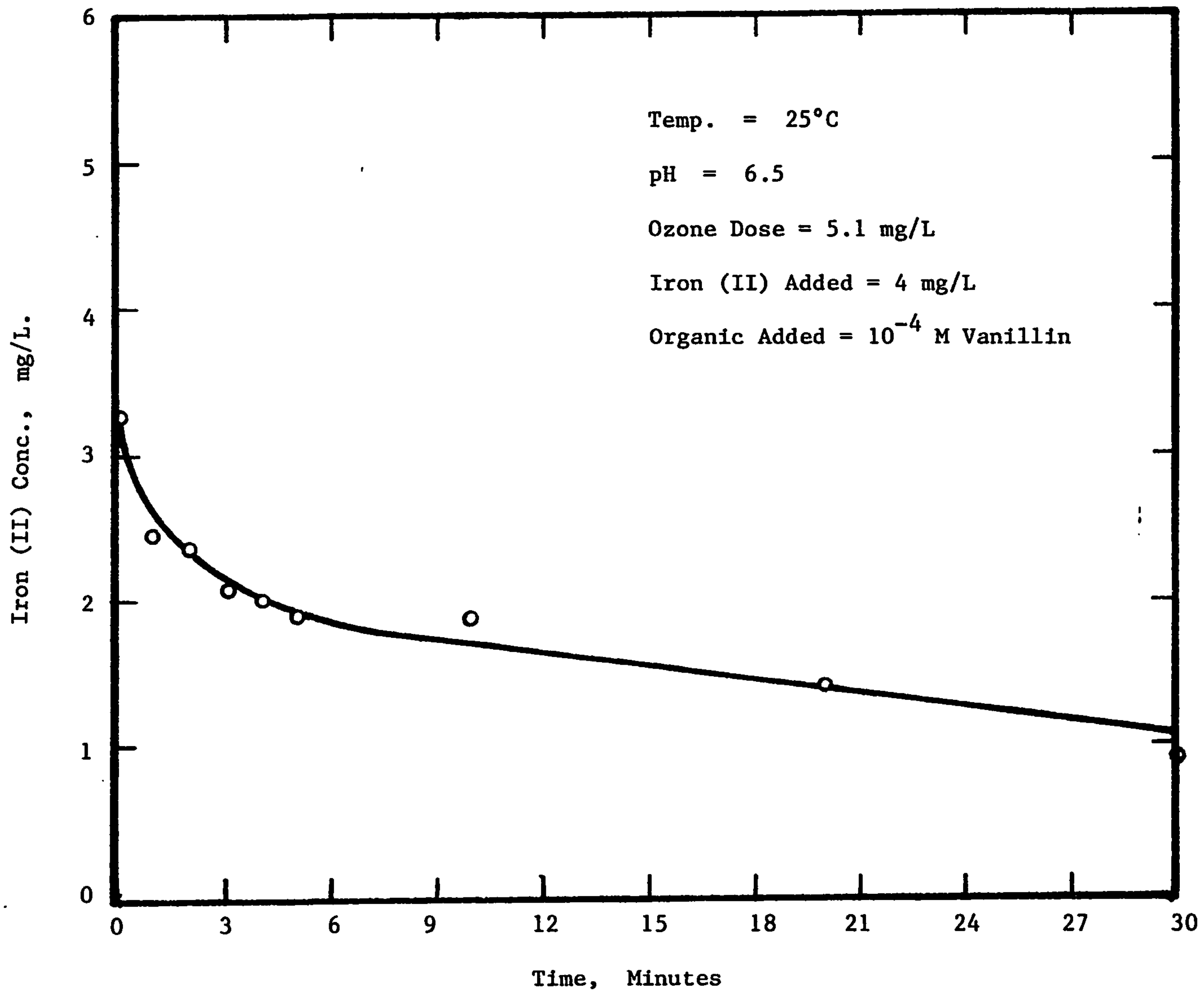


Figure 5.8 : Oxidation of Iron (II), in the presence of 10^{-4} M Vanillin.

From Equation (1):

$$\log \left(- \frac{dFe(II)}{dt}\right) = \log k + n \log [Fe(II)] \text{..........(2)}$$

Using the data in Tables 5.5 and 5.6, a plot of $\frac{\Delta Fe(II)}{\Delta t}$ vs. time produces a smooth curve as shown in Figure 5.9. By using the curve in Figure 5.9, a plot of $\frac{dFe(II)}{dt}$ vs. Fe(II) on a log-log paper produces a straight line having a slope of n and intercept k as shown in Figure 5.10. The respective values of n and k are found to be 4.49 and 0.0045 respectively.

The first two columns in Table 5.6 are obtained from Table 5.5 and the third column of Table 5.6 is determined from the data of columns 1 and 2. For example, the first value given in column 3 is calculated as follows :

$$\frac{3.26 - 2.55}{1 - 0} = 0.71$$

The data that have been obtained in column 3 are plotted as shown in Figure 5.9 and a smooth curve is drawn as shown in the same Figure. The data in column 4 of Table 5.6 are obtained from the curve shown in Figure 5.9.

Hence, the kinetic model for the oxidation of iron in presence of vanillin at 10^{-4}M is :

$$\frac{dFe(II)}{dt} = - k[Fe(II)]^n = 0.0045\ [Fe(II)]^4$$

Table 5.6 : Differential Method Calculations for Vanillin

Fe(II) Conc. (mg/L.)	Time (Min.)	$\frac{\Delta\ Fe(II)}{\Delta t}$ [mg/(L.min)]	$\frac{d\ Fe(II)}{dt}$ [mg/(L.min)]
3.26	0	-	0.9
2.55	1	0.71	0.4
2.3	2	0.25	0.19
2.15	3	0.15	0.13
2.0	4	0.15	0.1
1.9	5	0.1	0.08
1.82	6	0.08	0.07
1.8	7	0.02	0.04
1.78	8	0.02	0.04
1.75	9	0.03	0.04
1.7	10	0.05	0.04
1.68	11	0.02	0.04
1.65	12	0.03	0.04
1.6	13	0.05	0.04
1.58	14	0.02	0.04
1.55	15	0.03	0.04
1.5	16	0.05	0.04

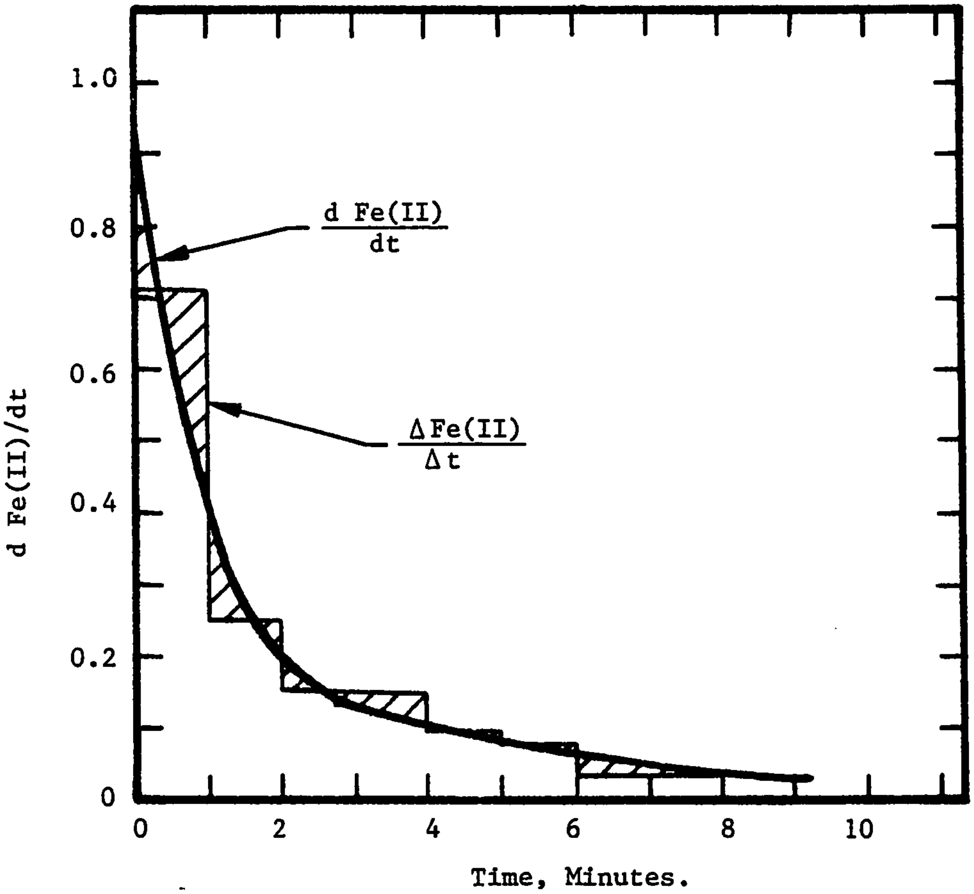


Figure 5.9: d Fe(II)/dt vs. Time at 10^{-4} M Vanillin.

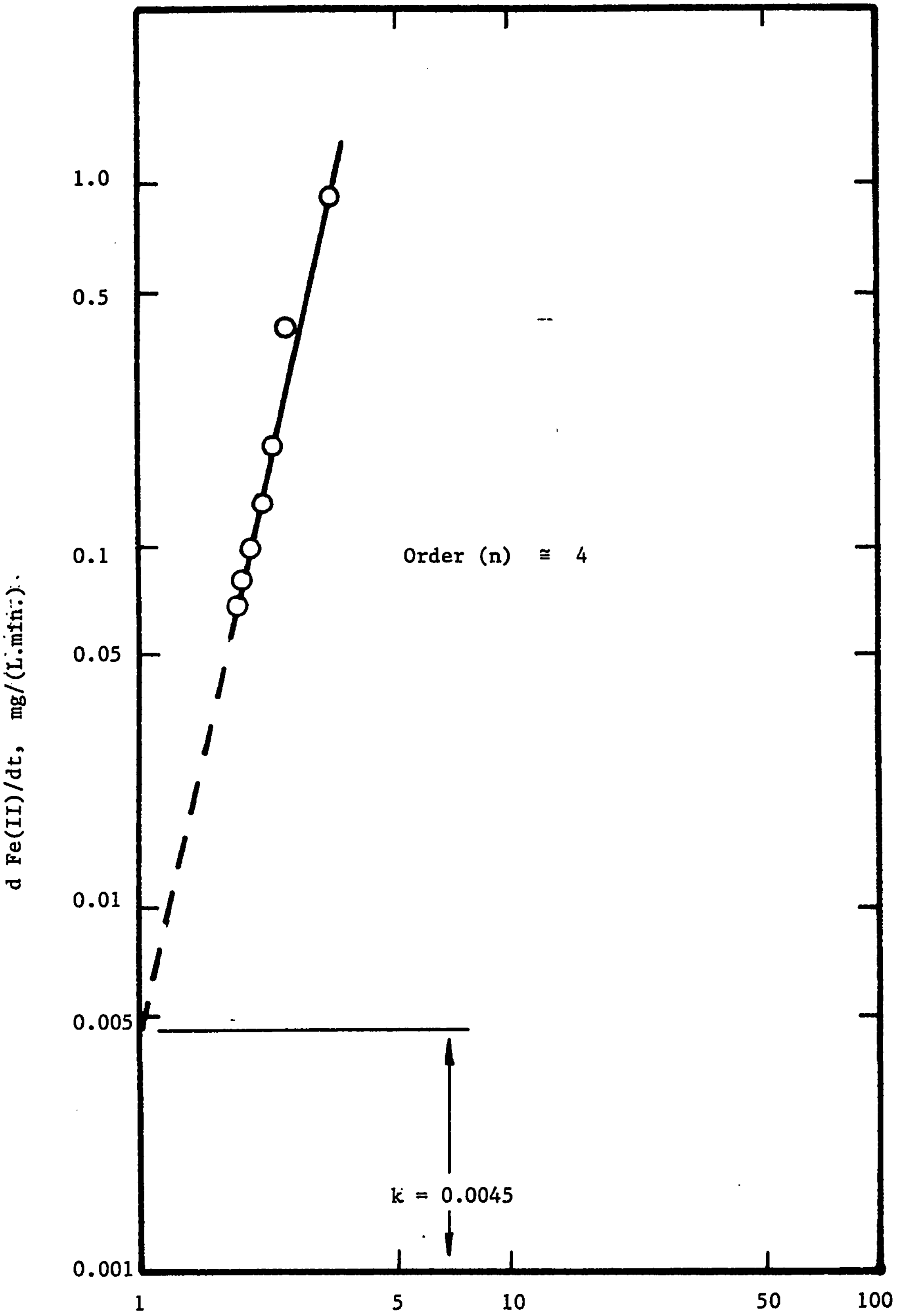


Figure 5.10: Log d Fe(II)/dt vs. Log Fe(II) at 10^{-4} M Vanillin.

This model is appropriate for the oxidation period from 0 to 7 minutes, but beyond the seventh minute, the order of the reaction is essentially zero.

Also, the TOC was measured and the results show that the concentration of TOC decreases by about 32% at the end of 30-minute duration of ozonation.

It is noticed that the order of the reaction (n) in the presence of vanillin is quite high indicating that probably the reaction rate is fast. Therefore, our method is not applicable here and other methods for fast reaction kinetics such as Stop-flow techniques or T-Jump procedures are necessary for determining the kinetic constants for such reactions.

5.2.1.2 *Glutamic Acid*

The results of the oxidation of iron (II) at a 10^{-4} M glutamic acid are given in Table 5.7 and Figure 5.11. The results show that the rate of oxidation of iron (II) is linear with respect to time for the first three minutes of oxidation. After the third minute, the concentration of iron (II) starts to appear in the solution till it reaches a steady state of about 0.4 mg/L. The possible reason for this increase in Fe(II) concentration can be explained as follows:

Table 5.7 : Oxidation of Iron (II) in the Presence of 10^{-4} M Glutamic Acid

Time (Min.)	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)
0	3.64	0	7.3
1	2.44	0	7.3
2	1.08	0	7.3
3	0	0.123	7.3
4	0.2	0.37	7.3
5	0.36	0.48	7.2
10	0.4	0.72	7.0
20	0.38	0.72	6.0
30	0.48	0.72	5.8

Ozone Inlet in Gas Phase = 5.1 mg/L

Ozone Outlet in Gas Phase = 2.92 mg/L

pH = 6.5

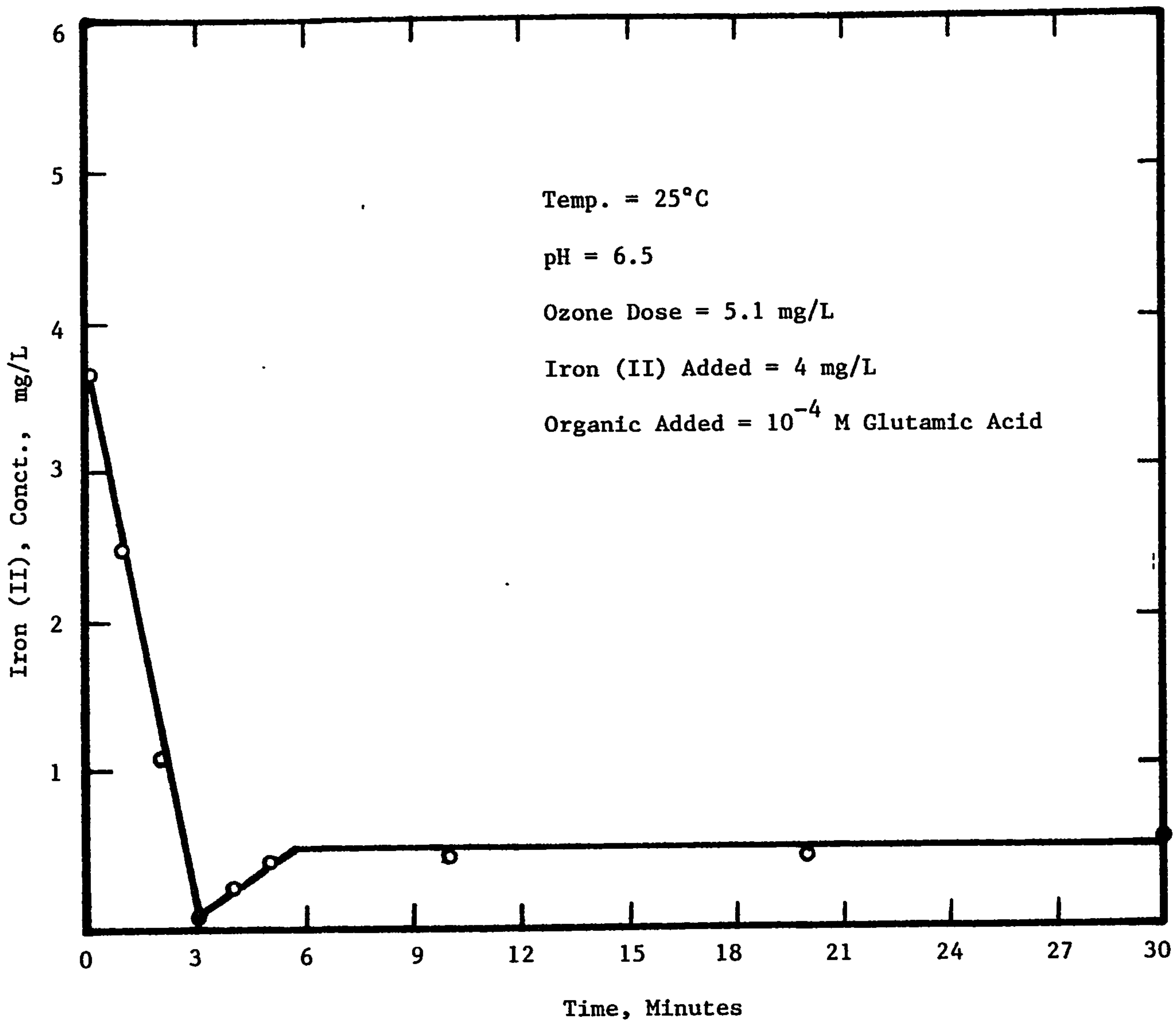
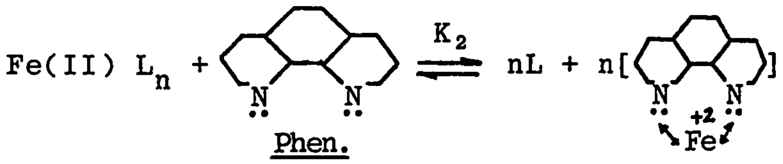


Figure 5.11 : Oxidation of Iron (II) in the Presence of 10^{-4} M Glutamic Acid.

(1) The method used for measuring ferrous ion is a colorimetric method called the Phenanthroline Method. The ferrous ion when it is complexed with phenanthroline gives orange color. Also, when the organic compound reacts with iron (II), it forms iron (II)-organic complex. The above two reactions can be represented in the following equations:

$$\mathrm{Fe(II)} + \mathrm{L} \xrightleftharpoons{K_1} \mathrm{Fe(II)} - (\mathrm{L})_n \quad n=1,2,..$$



L : represents the model organic compound (Ligand).

K_1 and K_2 are called stability constants.

The continuous oxidation of Fe(II) - Organic complex by ozone breaks part of it, and when the phenanthroline is added, it gets complexed with Fe(II) and gives the orange color again. For example, the stability constant between Fe (II) and histidine is K_1 = 5.88 and the stability constant between Fe(II) and phenanthroline is 5.88 which are almost similar. Therefore, the continuous oxidation breaks part of the Fe(II) - Histidine complex and when the phenanthroline is added, it gets complexed with Fe(II) and gives the orange color again.

color again.

(2) On the other hand, the ferric iron can be reduced by humic substances to generate ferrous iron that is more soluble (18,19). Table 5.8 gives the extent of reduction of Fe(III) by model organic compounds (20).

Generally, the kinetic stability of ferrous iron may be due either to the formation of Fe(II)-Organic complexes which resist oxidation or to the reduction of the resultant Fe(III) by the organic species (20).

The linear regression model for the first part of oxidation is :

$$\text{Fe (II)} = 3.64 - 1.21\ t \qquad (R^2 = 0.99)$$

Also, TOC was measured and has been observed that the TOC is reduced by about 21% after the 30-minute duration of ozonation.

5.2.1.3 Histidine

The oxidation of iron II in the presence Of 10^{-4} M histidine and pH of 6.5 gave similar results as those for glutamic acid as shown in Table 5.9 and Figure 5.12. The results indicate that the rate of oxidation of iron (II) for the first 4 minutes of oxidation is linear with respect to time. Hence, the order of the reaction is

Table 5.8 :

*Reduction of Fe(III) by Model Organic Compounds**

Compound, 10^{-4} M	*Fe(III) Reduced,† M/l*
Tannic acid	7.9×10^{-5}
Pyrogallol	6.9×10^{-5}
Gallic acid	3.4×10^{-5}
Syringic acid	2.6×10^{-5}
Resorcinol	5.2×10^{-6}
Citric acid	4.7×10^{-6}
Tartaric acid	1.9×10^{-6}
Vanillic acid	9.0×10^{-7}
Vanillin	7.0×10^{-7}

*pH 6.3; Fe(III) added = 8.0×10^{-5} M.

†Reduction was virtually instantaneous.

SOURCE: Theis, T.L. et al (1974)

Table 5.9 : Oxidation of Iron (II) in the Presence of 10^{-4} M Histidine

Time (Min.)	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)
0	3.6	0	10
0.5	2.88	0	-
1	2.44	0	9.1
2	1.64	0	9
3	0.8	0	9
4	0.2	0	8.9
5	0	.25	8.7
10	0.54	.49	-
20	0.54	.49	7.7
30	0.54	.49	7.3

Ozone Inlet in Gas Phase = 5.1 mg/L

Ozone Outlet in Gas Phase = 2.33 mg/L

pH = 6.5

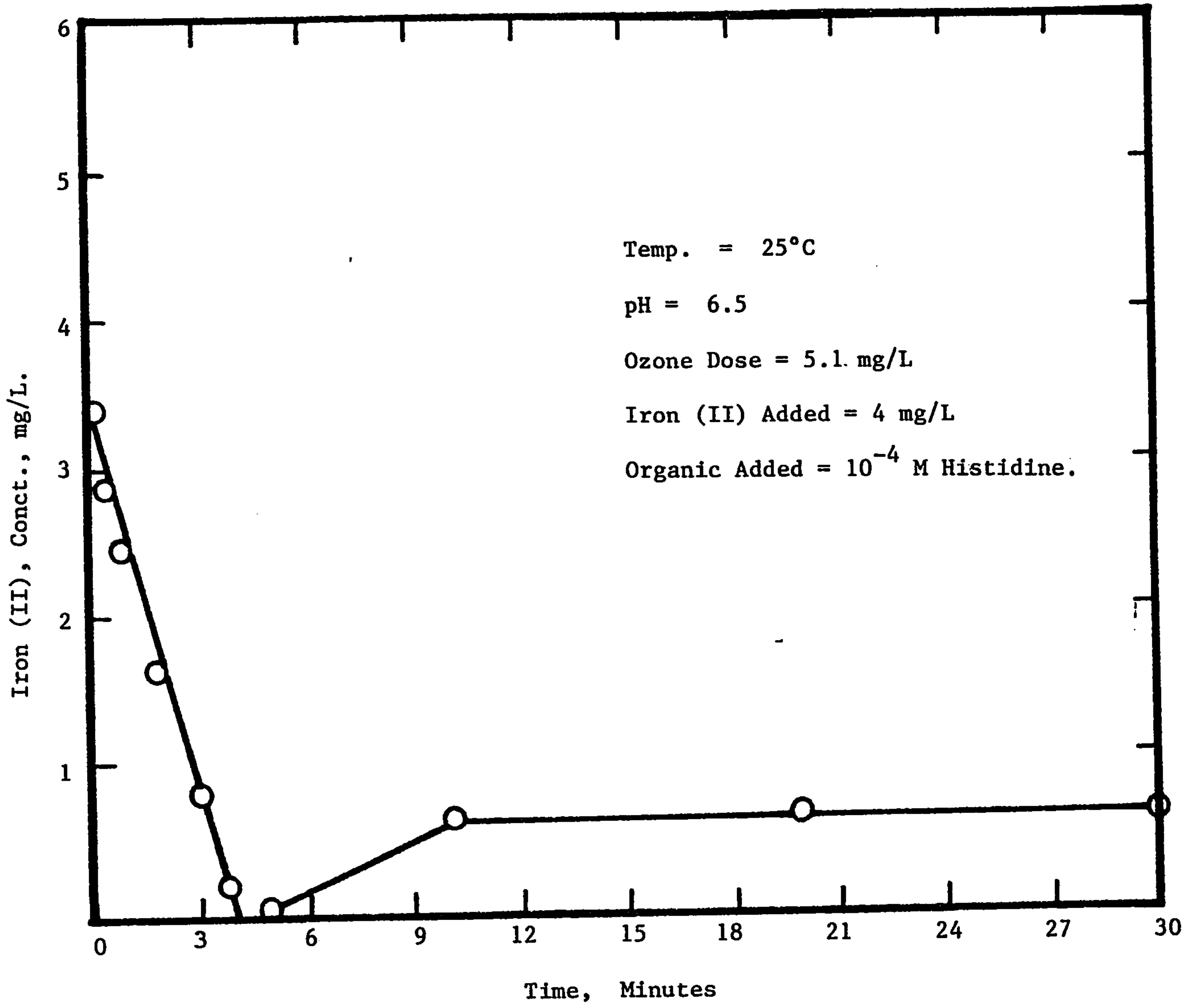


Figure 5.12 : Oxidation of Iron (II) in the Presence of 10^{-4} M Histidine.

zero. Therefore, the linear regression model of the oxidation is :

$$\text{Fe (II)} = 3.6 - 0.9 \; t \qquad (R^2 = 0.97)$$

where, Fe(II) : conc. of iron, (mg/L)

t : time in minutes.

TOC was reduced by about 27% at the end of the 30-minute duration of oxidation.

5.2.1.4 *Resorcinol*

The results of the oxidation of iron (II) in the presence of 10^{-4} M of resorcinol are shown in Table 5.10. The curve of the rate of oxidation in Figure 5.13 shows that the rate of oxidation is variable with respect to time, i.e., the slope is curvilinear up to the third minute of oxidation. Between the third and the tenth minute, the concentration of iron (II) increases a little bit and then it is oxidized again at a constant rate of about 0.021. The calculations for determining the kinetic model for the oxidation of iron (II) at 10^{-4} M resorcinol for the first stage of oxidation (0 to 3 minutes) are shown in Figures 5.14 and 5.15 and Table 5.11.

$$\frac{dFe(II)}{dt} = - k \, [Fe(II)]^n = [Fe(II)]^3$$

The order of the reaction, n = 2.783 = 3

Reaction constant, k = 0.14

Table 5.10: Oxidation of Iron (II) in the Presence of 10^{-4} M Resorcinol

Time (Min.)	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)
0	2.8	0	8.4
0.5	1.84	0	-
1	1.54	0	8.1
2	1.2	0	7.4
3	1.0	0	7.4
4	0.9	0	7.3
5	1.0	0	7.3
10	1.12	0	6.1
20	0.9	0.123	5.2
30	0.56	0.24	3.8

Ozone Inlet in Gas Phase = 5.1 mg/L

Ozone Outlet in Gas Phase = 1.64 mg/L

pH = 6.5

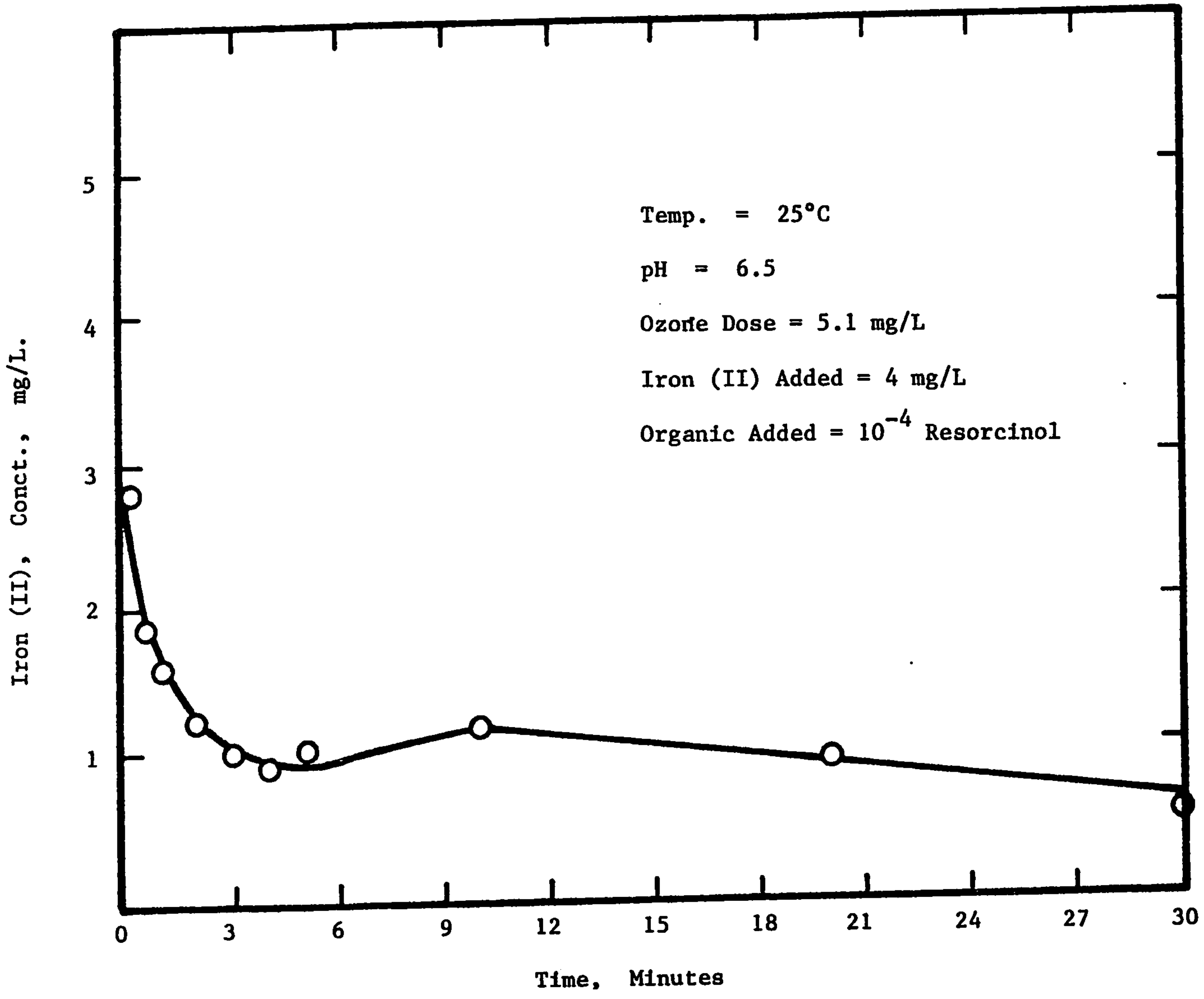


Figure 5.13 : Oxidation of Iron (II), in the Presence of 10^{-4} M Resorcinol.

Table 5.11 : Differential Method Calculations for Resorcinol

Fe(II) Conc. (mg/L.)	Time (Min.)	$\frac{\Delta \text{Fe(II)}}{\Delta t}$ [mg/(L.min)]	$\frac{d \text{Fe(II)}}{dt}$ [mg/(L.min)]
2.54	0	-	1.8
1.84	0.5	1.4	0.87
1.54	1	0.6	0.54
1.33	1.5	0.42	0.36
1.2	2	0.26	0.24
1.08	2.5	0.24	0.16
1.0	3.0	0.16	0.1
0.95	3.5	0.1	0.06
0.92	4.0	0.06	0.03
0.9	4.5	0.04	0.02
0.89	5.0	0.02	0.02

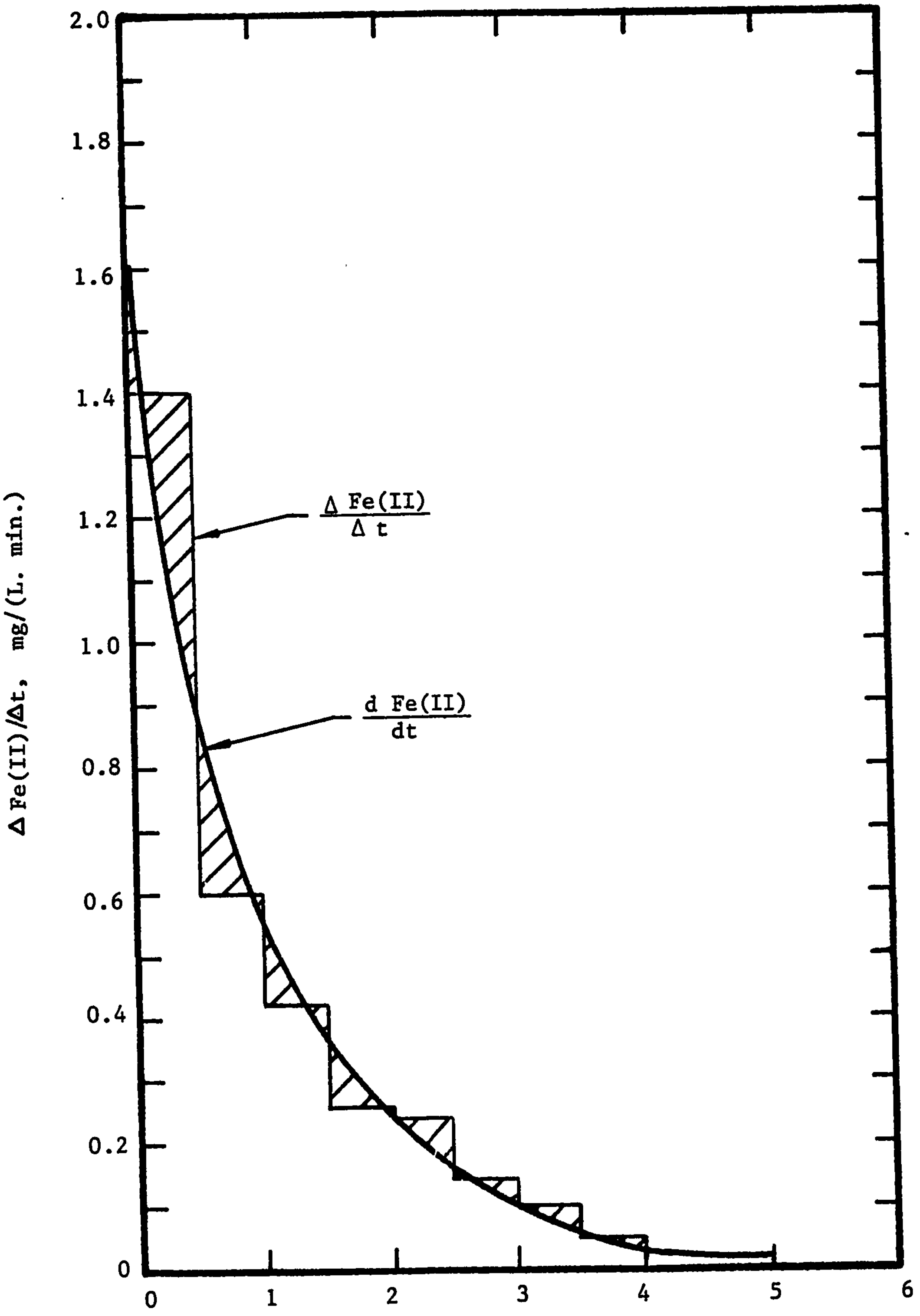


Figure 5.14: Δ Fe(II)/Δt Vs. Time in the presence of 10^{-4} M Resorcinol.

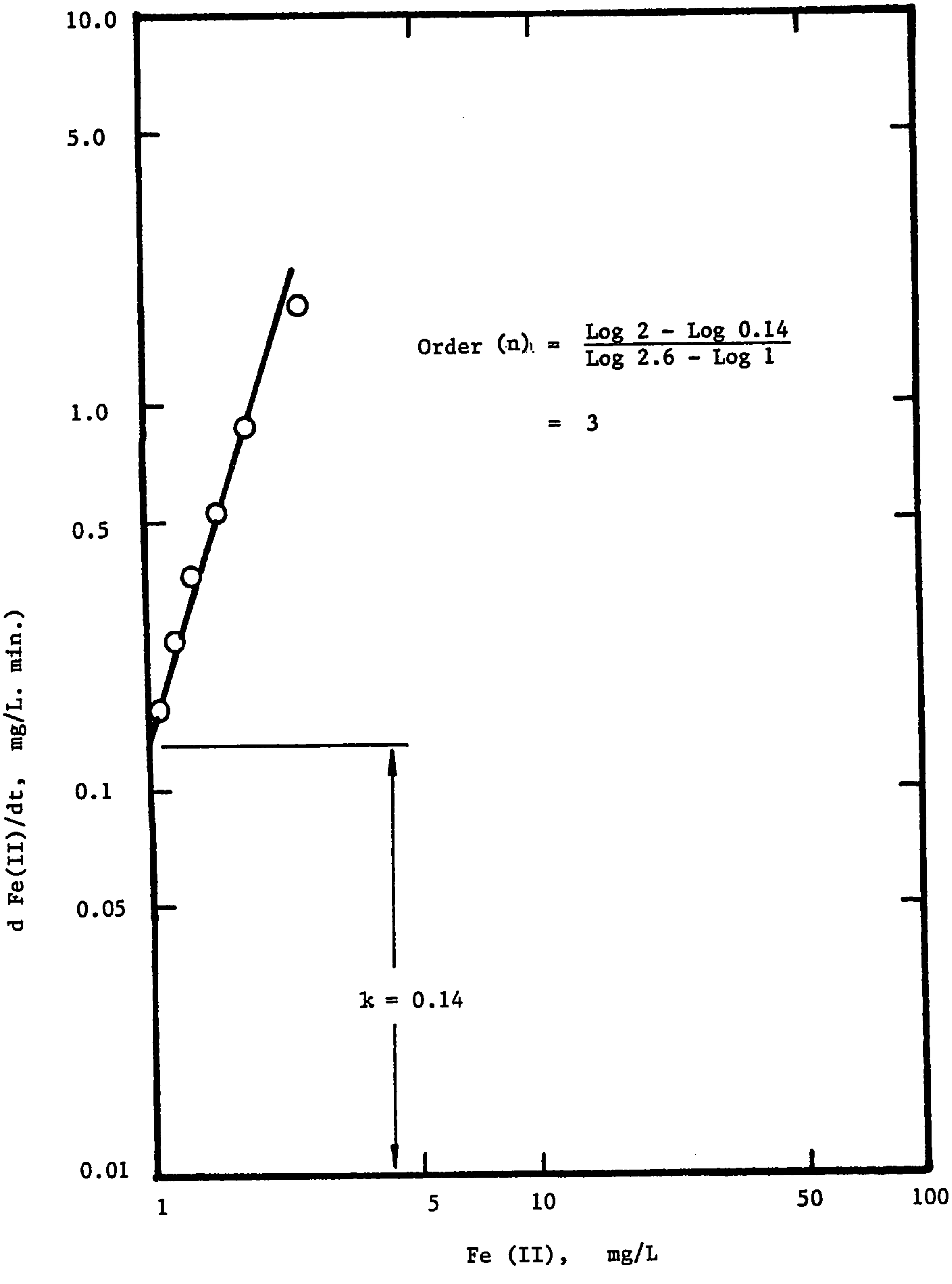


Figure 5.15: $\frac{d\ Fe(II)}{dt}$ vs. Fe(II) in the presence of 10^{-4} M Resorcinol.

TOC was reduced by about 55% at the end of the 30-minute ozonation period.

5.2.1.5 *Phenol*

The results of the oxidation of iron (II) at 10^{-4} M phenol are shown in Table 5.12. The curve in Figure 5.16 shows that iron (II) concentration drops from 2.44 mg/L to 1.2 mg/L during the first 30 seconds of oxidation. After the thirty seconds, the rate of oxidation remains constant, i.e., the concentration of iron (II) is linear with respect to time and has a slope of (-0.023). This linear regression model for the oxidation period after the thirty second is :

$$\text{Fe (II)} = 1.2 - 0.023\, t \qquad (R^2 = 0.97)$$

The rate of oxidation for the first thirty seconds of oxidation is -2.48 and the linear regression model is:

$$\text{Fe (II)} = 2.44 - 2.48\, t \qquad \text{1st 30 seconds.}$$

The order of the reaction in this case is zero, hence, the kinetic model for the oxidation will be :

$$\frac{d\text{Fe(II)}}{dt} = -k = -2.48 \qquad \text{1st 30 seconds.}$$

$$\frac{d\text{Fe(II)}}{dt} = -k = -0.023 \qquad \text{beyond the 30 seconds.}$$

Table 5.12 : Oxidation of Iron (II) in the Presence of 10^{-4} M Phenol

Time (Min.)	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)
0	2.44	0	7.2
0.5	1.2	0	7.2
1	1.26	0	7.2
2	1.16	0	7.1
3	1.12	0	7.1
4	1.08	0	7.1
5	1.1	0	7.0
10	0.96	0	6.8
20	0.76	0.126	6.4
30	0.52	0.37	5.3

Ozone Inlet in Gas Phase = 5.1 mg/L

Ozone Outlet in Gas Phase = 1.446 mg/L

pH = 6.5

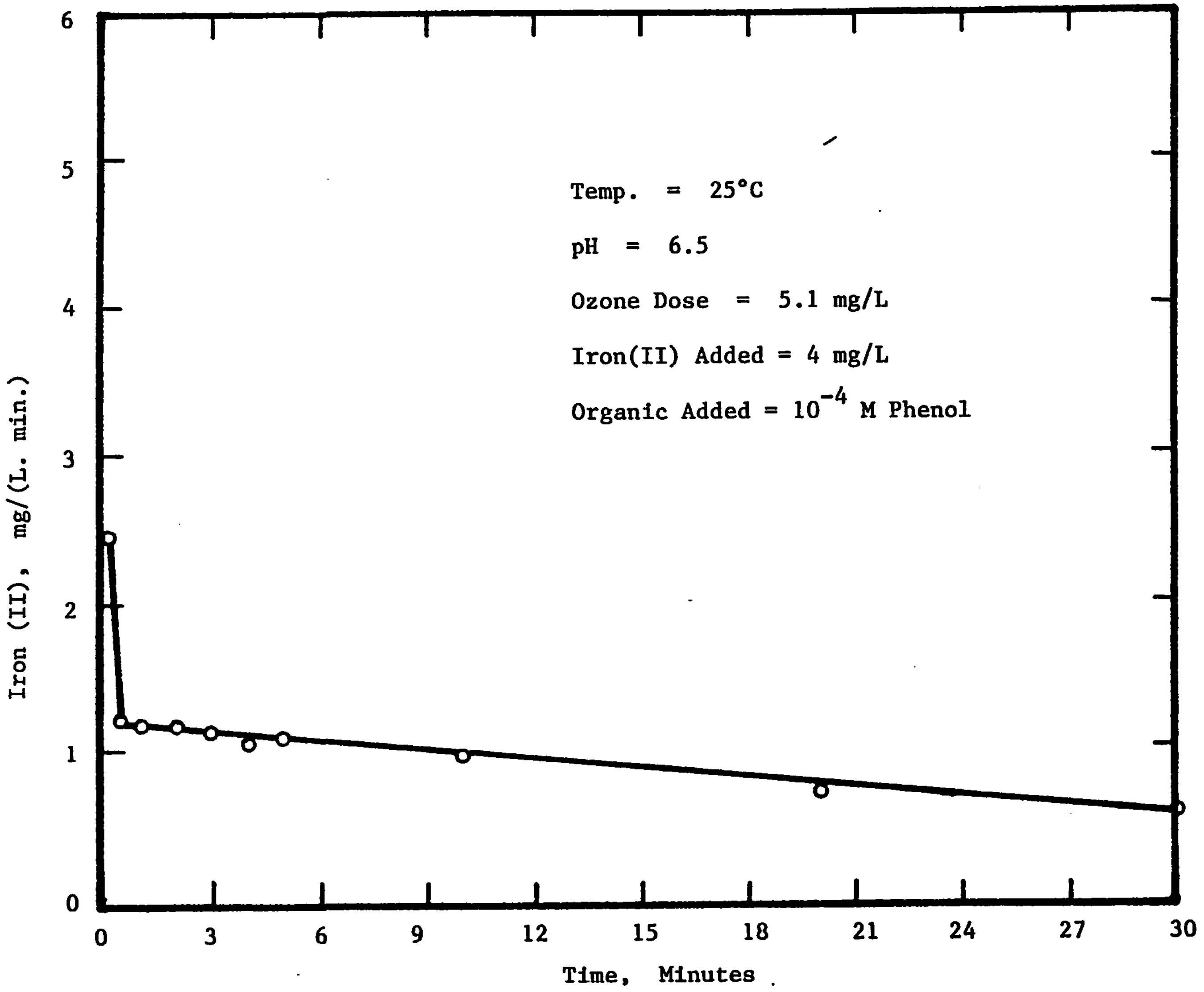


Figure 5.16 : Oxidation of Iron (II) in the Presence of 10^{-4} M Phenol.

TOC was reduced by about 26% at the end of the 30-minute ozonation period.

5.2.1.6 Citric Acid

The results of the experiment (Table 5.13 and Figure 5.17) show that only 1.28 mg/L of iron (II) appears in the solution out of the 4 mg/L that were added initially. During the first minute of oxidation, iron (II) concentration was reduced from 1.28 mg/L to 0.26 mg/L and after that the concentration of iron (II) starts increasing till it reaches a steady state of about 0.85 mg/L. This increase in concentration of iron (II) is due to the increase in concentration of phenanthroline- iron (II) complex due to breaking up of the iron (II) citric acid complex.

TOC was reduced by about 27 percent at the end of the 30-minute period of ozonation.

5.2.2 Oxidation of Iron (II) at Different pH Values in the Presence of Model Organic Compounds

The second set of experiments were conducted at different pH values while other experimental parameters were left constant such as temperature, organic added, initial iron added and ozone input. The results of the experiments for the different organic compounds added are explained in the following sections.

Table 5.13: Oxidation of Iron (II) in the Presence of 10^{-4} M Citric Acid

Time (Min.)	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)
0	1.28	0	8.85
1	0.26	0	8.4
2	0.4	0.25	8.4
3	0.52	0.49	8.4
4	0.56	0.74	8.3
5	0.68	0.74	8.3
10	0.8	0.99	8.2
20	0.9	1.23	7.7
30	0.84	1.23	7.1

Ozone Inlet in Gas Phase = 5.1 mg/L

Ozone Outlet in Gas Phase = 3.72 mg/L

pH = 6.5

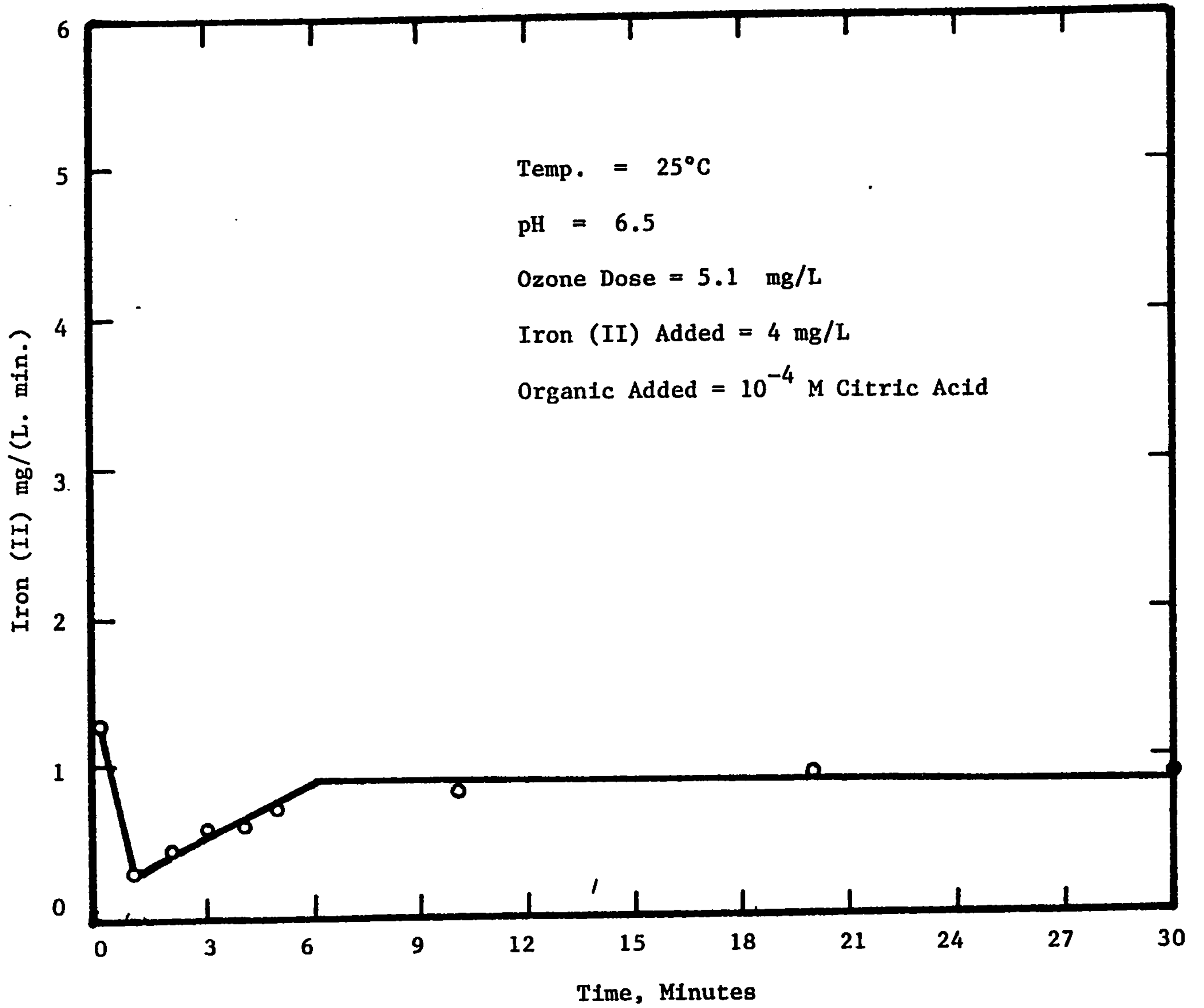


Figure 5.17: Oxidation of Iron (II) in the Presence of 10^{-4} M Citric Acid

5.2.2.1 Tartaric Acid

Tartaric acid was selected according to the results of the previous set of experiments. The experiments were conducted at three pH values of 5.5, 6.5 and 7.5. The results are shown in Table 5.14.

The data given in Table 5.14 show that at the end of the 30-minute ozonation period, the concentration of iron (II) does not reach zero and that is due to the presence of organic matter. Also, the ozone residual increases from zero till it reaches a steady state value, e.g., at the pH of 6.5, the ozone residual increases from zero to a steady state value of 0.6 mg/L.

The results shown in Figure 5.18 shows that at pH value of 5.5, the initial reading is 4 mg/L of Fe(II) and then it decreases gradually by oxidation, but at pH values of 6.5 and 7.5, the initial readings of iron (II) are much less and the iron (II) increases with oxidation. TOC was reduced by 28%, 36.4% and 30% at pH values of 5.5, 6.5 and 7.5 respectively. The best set of data for the analysis to determine the kinetic model will be for pH of 5.5. Therefore,the given kinetic calculations are for the data at pH of 5.5.

From the results of Table 5.15 and Figures 5.19 and 5.20 ,the order of the reaction of the first eight minutes of oxidation would be 2.0 and the reaction constant is 0.09. Therefore, the

Table 5.14 : Oxidation of Iron (II) in the Presence of 10^{-4} M Tartaric Acid

TIME (min.)	pH = 5.5			pH = 6.5			pH = 7.5		
	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)
0	4	0	5.3	2.0	0	5.5	0.36	-	7.2
0.5	3.76	0	5.3	1.2	0	5.5	0.18	-	7.2
1	3.44	0	5.3	0.92	0	5.4	0.20	-	7.2
2	2.88	0	-	0.52	0.12	5.3	0.48	0.72	7.2
3	2.44	0	5.2	0.56	0.24	5.3	0.64	0.84	7.2
4	2.16	0.12	-	0.72	0.37	5.3	0.76	0.84	7.0
5	1.9	0.25	5.2	0.9	0.6	5.3	0.8	0.84	6.7
10	1.26	0.37	5	1.26	0.6	5.2	1.2	0.96	6.1
20	0.96	0.49	4.1	1.48	0.6	4.4	1.12	0.6	5.8
30	0.84	0.49	3.8	1.48	0.6	3.5	1.36	0.84	5.0
Ozone Outlet in Gas Phase (mg/L)		2.66			2.83			2.78	

Ozone Inlet in Gas Phase = 5.1 mg/L

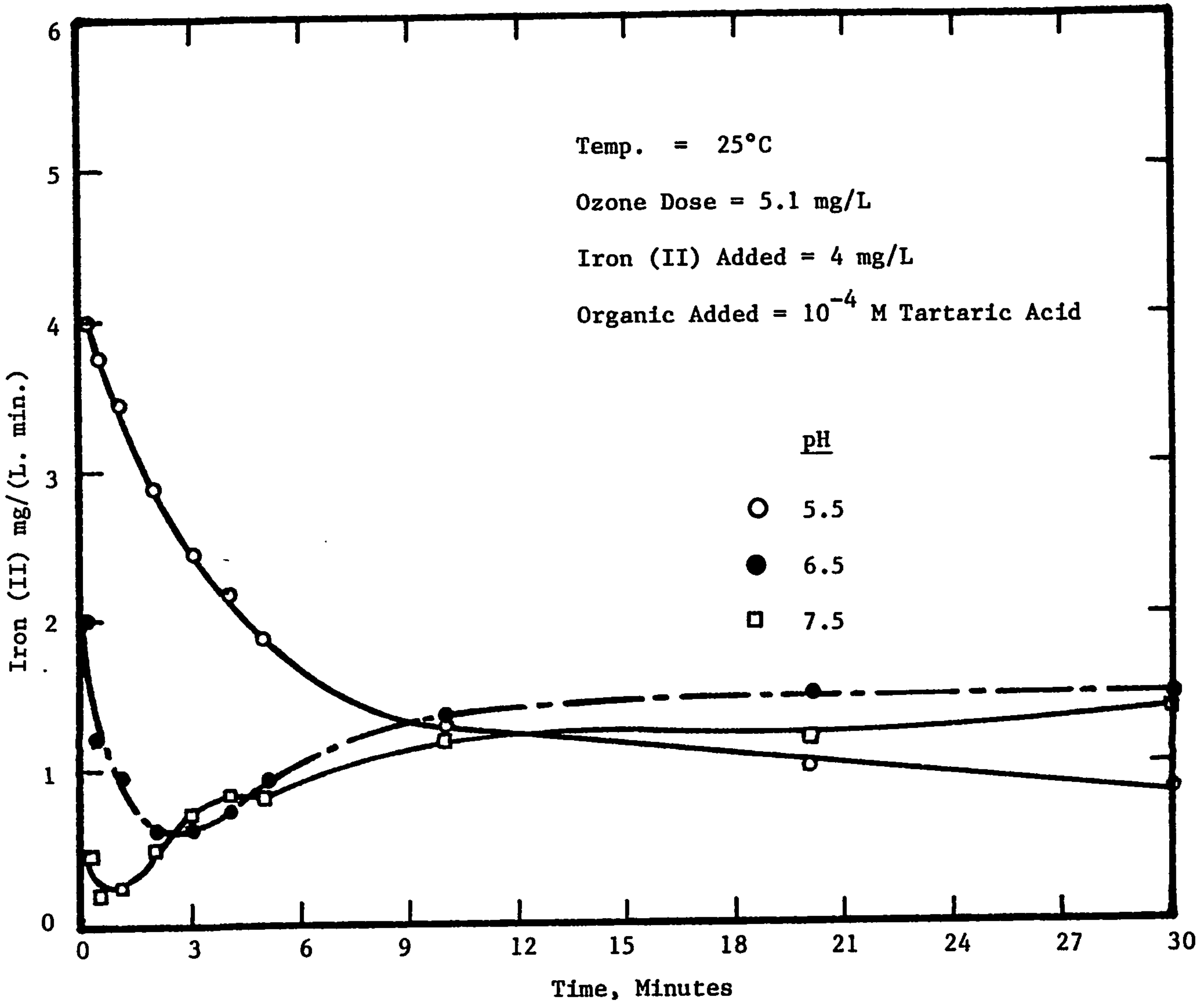


Figure 5.18: Oxidation of Iron (II) in the presence of 10^{-4} M Tartaric Acid and Different pH Values.

Table 5.15: Differential Method Calculations for Tartaric Acid, pH=5.5

Fe(II) Conc. (mg/L.)	Time (Min.)	$\frac{\Delta \text{Fe(II)}}{\Delta t}$ [mg/(L.min)]	$\frac{d\,\text{Fe(II)}}{dt}$ [mg/(L.min)]
4.0	0	-	0.7
2.88	2	0.56	0.45
2.16	4	0.36	0.29
1.68	6	0.24	0.18
1.4	8	0.14	0.1
1.26	10	0.07	0.055
1.18	12	0.04	0.035
1.1	14	0.04	0.025
1.05	16	0.025	0.02
0.98	18	0.035	0.015
0.96	20	0.01	0.01
0.95	22	0.005	0.01
0.92	24	0.015	0.01
0.88	26	0.02	0.01
0.87	28	0.005	0.01
0.84	30	0.015	0.01

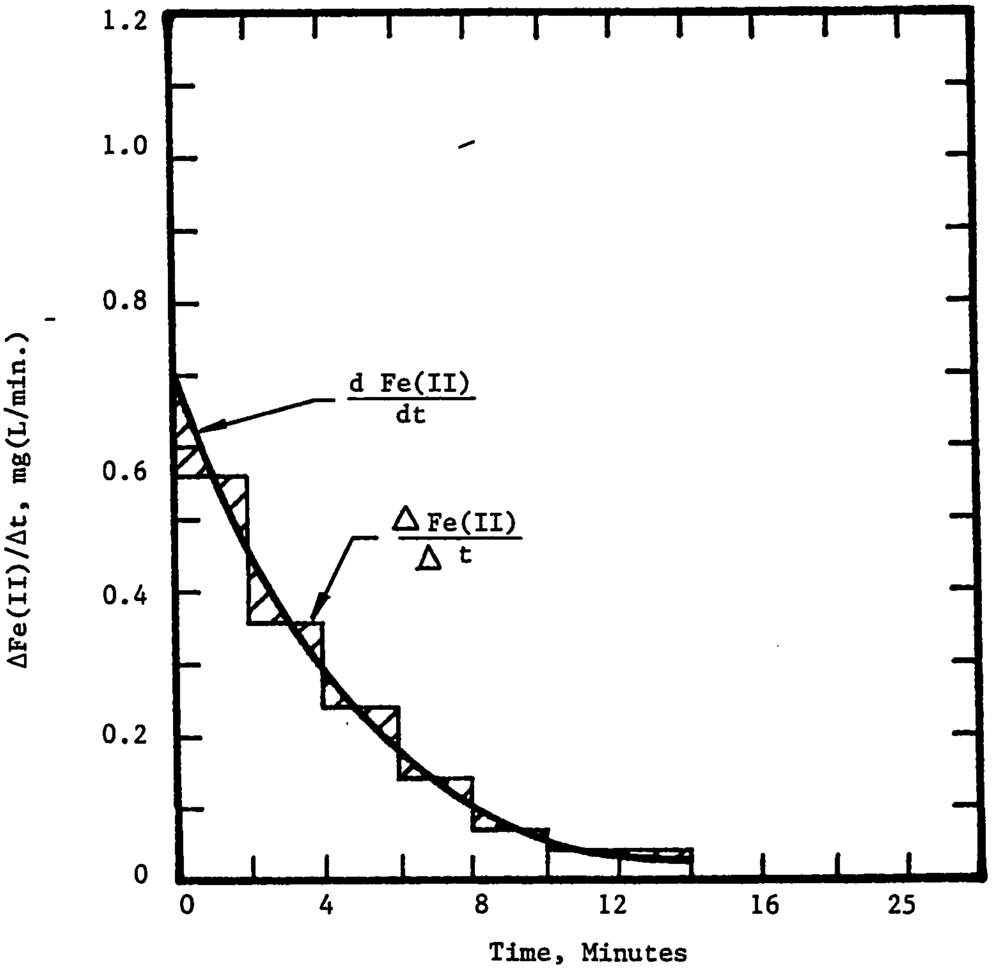


Figure 5.19: $\frac{\Delta \text{ Fe(II)}}{\Delta t}$ vs. Time in the presence of 10^{-4} M Tartaric Acid and pH of 5.5

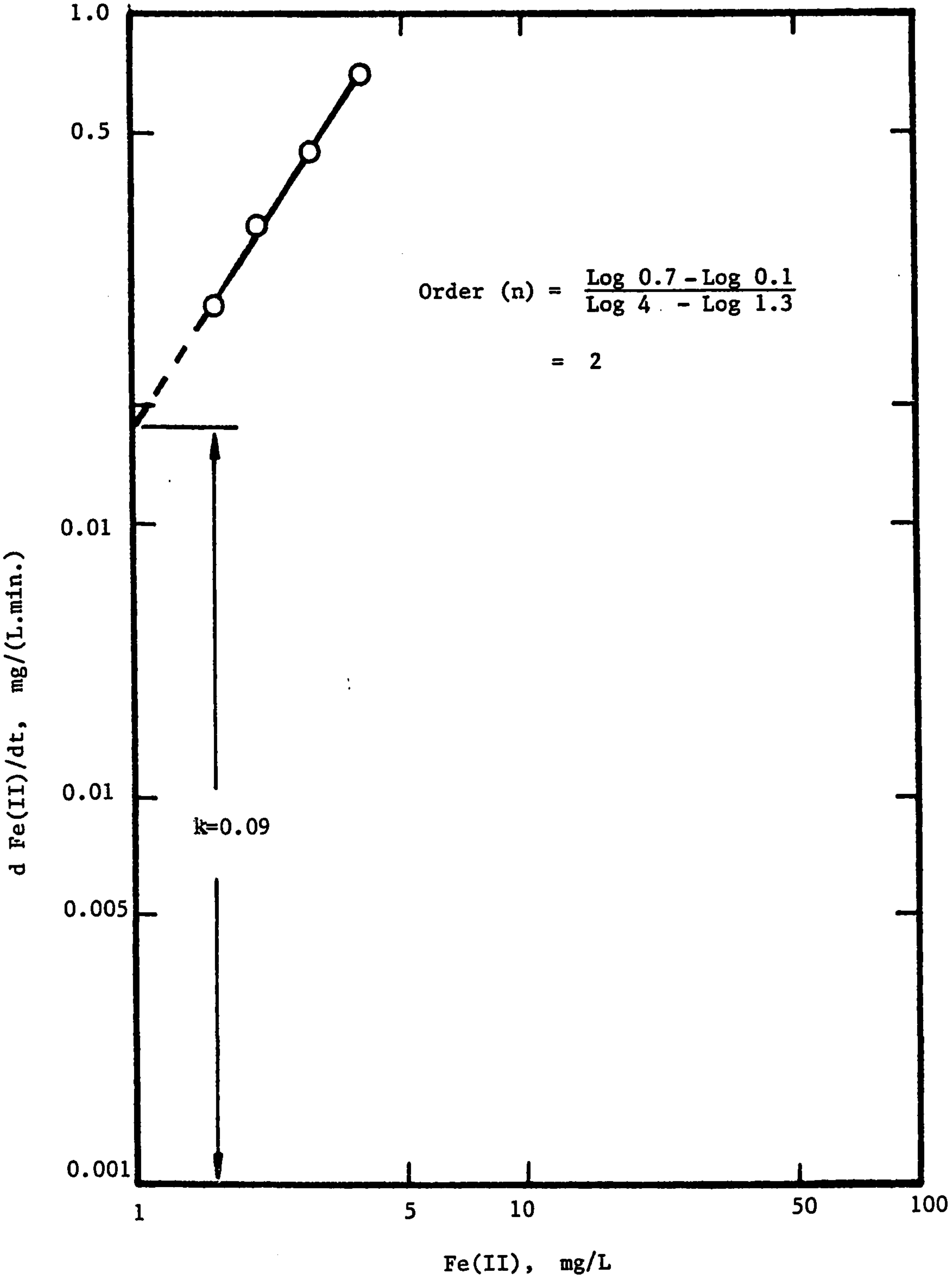


Figure 5.20: $\frac{d\,Fe(II)}{dt}$ vs. Fe(II) in the Presence of 10^{-4} M Tartaric Acid and pH of 5.5.

Table 5.16: Oxidation of Iron (II) in the Presence of 10^{-4} M Histidine

	pH = 5.5			pH = 6.5			pH = 7.5		
TIME (min.)	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)
0	4.0	0	10.1	3.6	0	10	0.08	0	9.0
0.5	3.8	0	9.2	2.88	0	-	0	0.12	-
1	3.26	0	9.2	2.44	0	9.1	0	0.24	8.4
2	2.36	0	9.1	1.64	0	9	0.18	0.4	-
3	1.2	0	9.0	0.8	0	9	0.32	0.6	8.1
4	0.32	0	8.8	0.2	0	8.9	0.32	0.72	-
5	0	0.48	8.7	0	.247	8.7	0.4	0.92	7.5
10	0	1.44	8.1	0.54	.49	-	0.4	1.08	7.5
20	0.32	1.44	7.8	0.54	.49	7.7	0.36	1.9	7
30	0.4	1.44	7.5	0.54	.49	7.3	0.2	1.9	6.1
Ozone Outlet in Gas Phase (mg/L)		2.1			2.33			2.5	

Ozone Inlet in Gas Phase = 5.1 mg/L

kinetic model of oxidation is:

$$\frac{dFe(II)}{dt} = -k[Fe(II)]^n$$

$$= -0.09\ [Fe(II)]^2$$

After the eighth minute of oxidation, the reaction has different order with a value of about 5.64 and a reaction constant of (k=0.018).

5.2.2.2 Histidine

The results of the oxidation of iron (II) at pH values of 5.5, 6.5, and 7.5 are shown in Table 5.16. At pH of 7.5, the results are insignificant and not good for kinetic studies, but at pH values of 5.5 and 6.5, the results have more or less the same oxidation rate which is linear with respect to time as shown in Figure 5.21. Hence, the linear regression kinetic models for both reactions at pH of 5.5 and 6.5 have the same slope but different initial measured concentrations.

$Fe\ (II) = 4.0 - 0.9\ t$ pH=5.5 ($R^2 = 0.95.$)

where, Fe (II) = Iron (II) conc. (mg/L)

t = time (minutes).

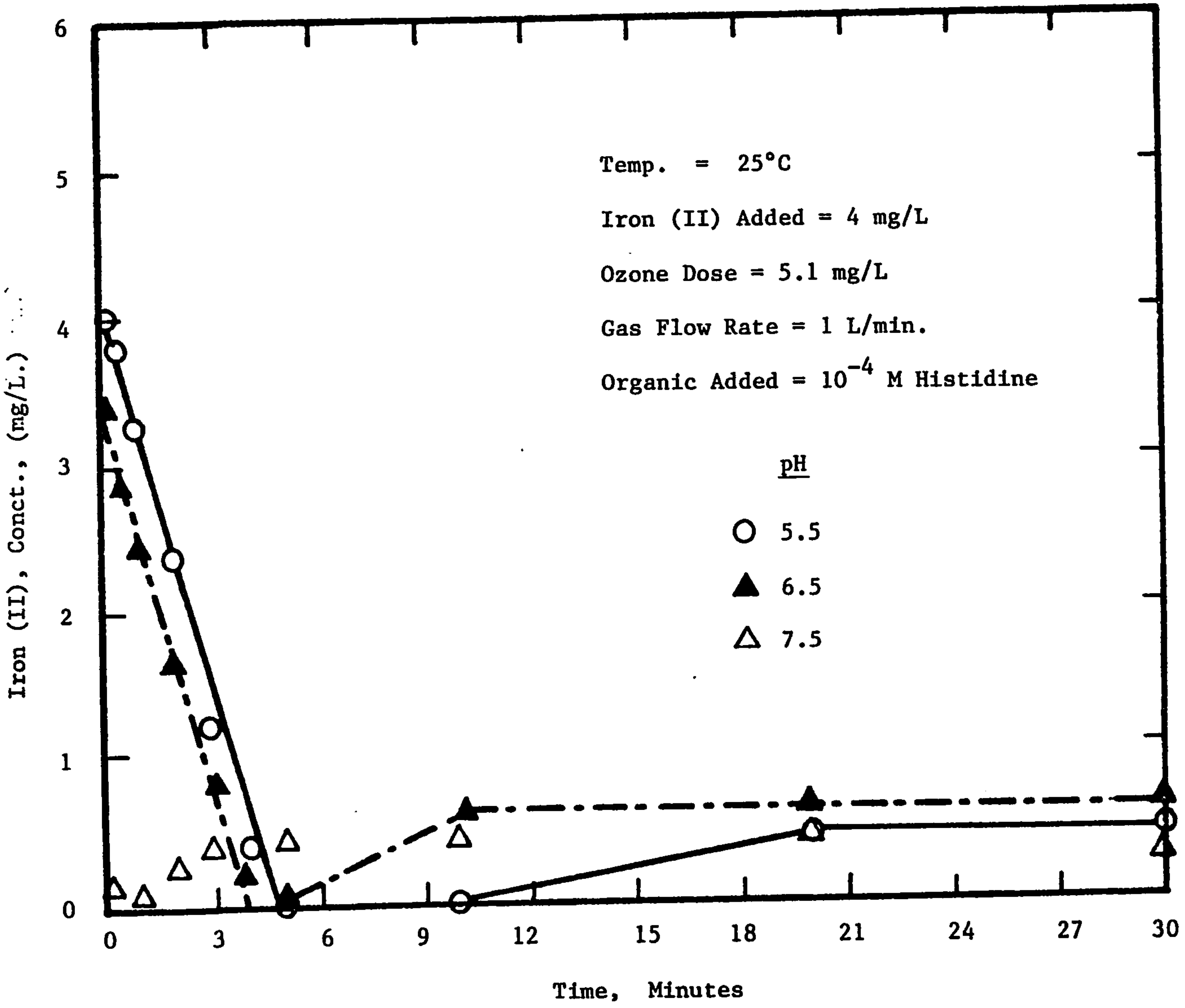


Figure 5.21: Oxidation of Iron (II) in the Presence of 10^{-4} M Histidine and Different pH Values.

The TOC was reduced by 26%, 27% and 32.2% at pH values of 5.5, 6.5 and 7.5, respectively at the end of the 30-minute oxidation period.

Figure 5.22 shows the relationship between the amount of iron(II) added and measured in a pure water system as well as in the presence of histidine and tartaric acid,at different pH values.In the presence of about 10^{-4} M histidine or tartaric acid,iron(II) remains in solution as the pH exceeds 7,but in the pure water system iron(II) concentration drops very fast when the pH starts approaching 7. It is noticed that,both,histidine and tartaric acid curves are fltter than the pure water system curve(Figure 5.21).This happens because of the iron(II)-organic complexation that holds iron(II) in solution.

5.2.2.3 Mixture of Organic Compounds

In this set of experiments, all the model organic compounds that were used previously were added together in the preparation (Table 5.17) to give final TOC concentration of 10 mg/L. For each organic compound, 1.5×10^{-4} moles were added in seven liters of distilled water to give the organic solution with about 10 mg/L of TOC.

Two sets of experiments were conducted at pH values of 5.5 and 6.5.The results are shown in Figure 5.23 and Table 5.18. TOC

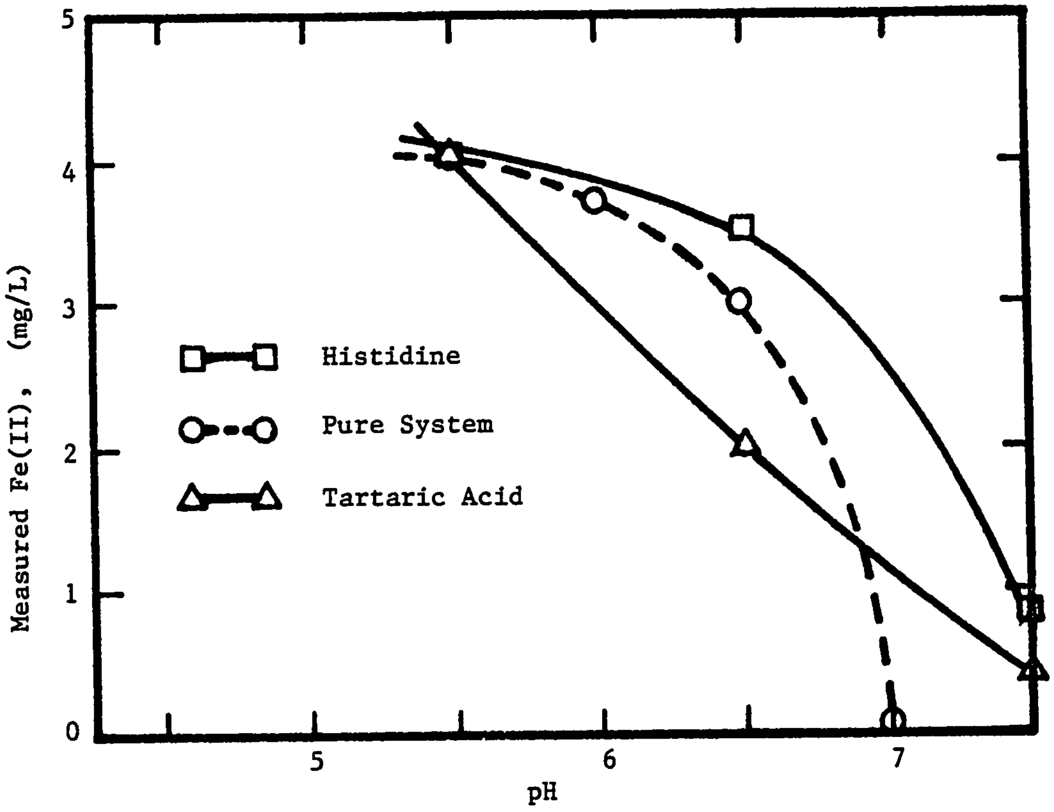


Figure 5.22 : Relationship between the amount of Fe(II) added and measured in Organic Complexation System as well as in Pure Water System at Different pH Values.

Table 5.17 : Various Amounts of Model Organic Compounds Used in Preparing the Mixture

Organic Compound	Weight (mg)
Histidine	23.27
Phenol	14.12
Citric Acid	31.52
Vanillin	22.82
Glutamic Acid	22.07
Resorcinol	16.52

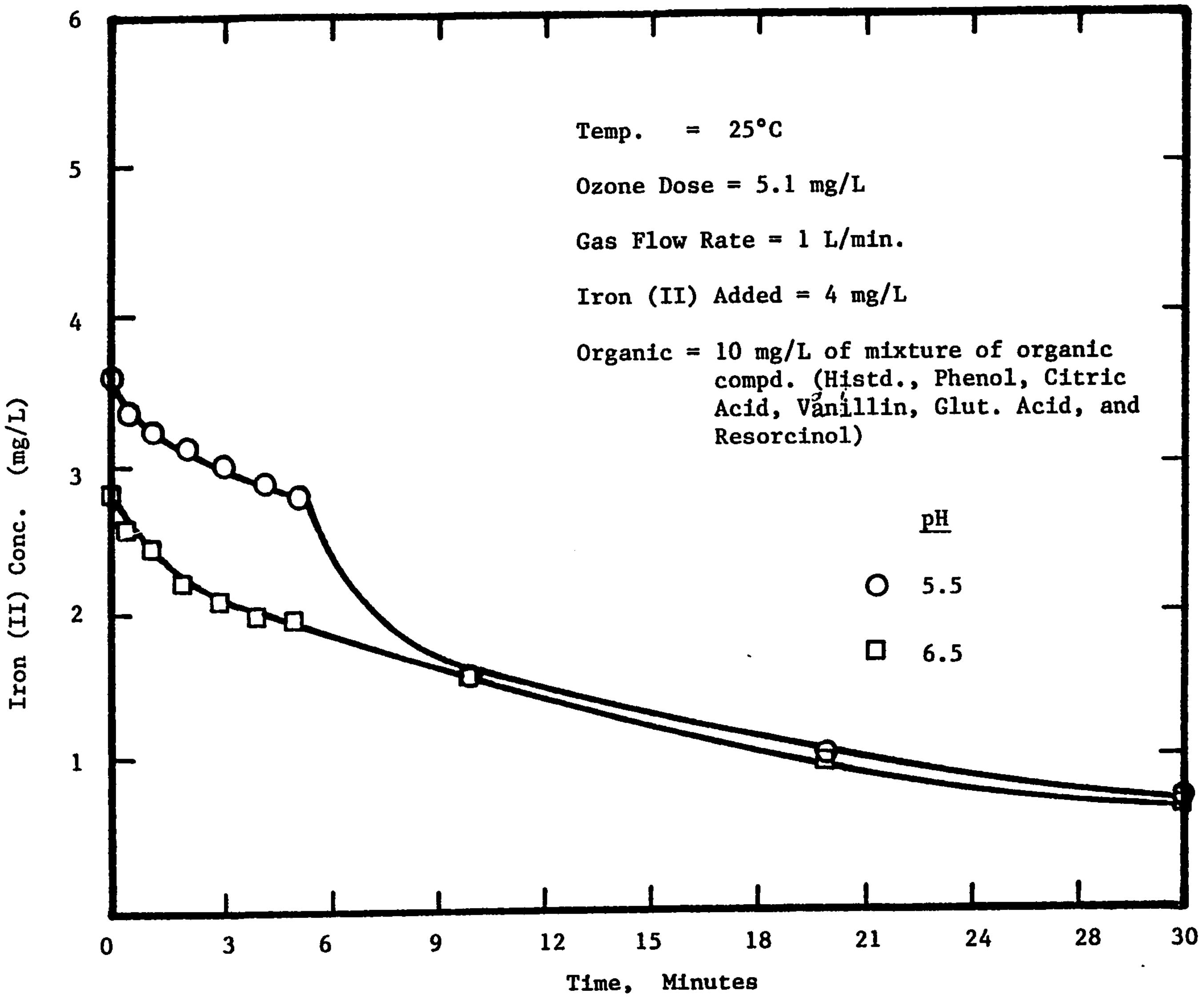


Figure 5.23 : Oxidation of Iron (II) in the Presence of 10 mg/L TOC of mixture of Organic Compounds and Different pH Values.

Table 5.18: Oxidation of Iron (II) at 10 mg/L TOC of the Mixture of Model Organic Compounds

TIME (Min.)	pH = 5.5			pH = 6.5		
	Fe(II) (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)	Fe(II) (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)
0	3.6	0	10.7	2.8	0	9.9
0.5	3.36	0	10.7	2.56	0	9.9
1	3.26	0	10.7	2.44	0	9.8
2	3.12	0	10.7	2.2	0	9.9
3	3.0	0	10.7	2.08	0	9.9
4	2.88	0	10.7	2	0	9.9
5	2.8	0	10.7	1.92	0	9.9
10	1.54	0.12	9.6	1.48	0.12	9.9
20	1.0	0.37	8.4	1.0	0.37	8.7
30	0.72	0.48	7.6	0.76	0.48	7.0
Ozone Outlet in Gas Phase (mg/L)		2.82			3.36	

Ozone Inlet in Gas Phase = 5.1 mg/L

was reduced by 29% and 29.3% at pH values of 5.5 and 6.5 respectively. The results of the experiments show that at pH of 6.5, the rate of oxidation is curvilinear from zero to 10 minutes and has constants rate, i.e., linear relationship, from 10 to 30 minutes. But at pH of 5.5, the rate of oxidation of iron (II) with respect to time has two stages as shown in Figure 5.23. The first stage is between 0 and 5 minutes and the second stage is between 5 and 30 minutes. The kinetic analyses will be done separately for each stage as follows:

(1) At pH = 5.5

(a) First Stage (0-5 min.)

The first stage of oxidation is from 0 to 5 minutes. The analyses for determining the kinetic constants are given in Table 5.19 and Figures 5.24 and 5.25. It is noticed that the order of the reaction (n) is very high and the k value is very small which means that the results are insignificant.

(b) Second Stage (5-30 min.)

The kinetic analysis for this stage are given in Table 5.20 and Figures 5.26 and 5.27. The values of n and k obtained from the analyses are 2 and 0.045, respectively. Hence, the final kinetic expression for the second stage is :

$$\frac{dFe(II)}{dt} = -k\,[Fe(II)]^n = -0.045\,[Fe(II)]^2$$

Table 5.19 : Differential Method Calculations for Mixture, pH=5.5 First Stage

Fe(II) (mg/L)	Time Min.	$\frac{\Delta \text{Fe(II)}}{\Delta t}$ [mg/(L.min)]	$\frac{d \text{Fe(II)}}{dt}$ [mg/(L.min.)]
3.6	0	-	0.44
3.26	1	0.34	0.255
3.05	2	0.21	0.15
2.92	3	0.13	0.07
2.88	4	0.04	0.025
2.8	5	0.08	0.01

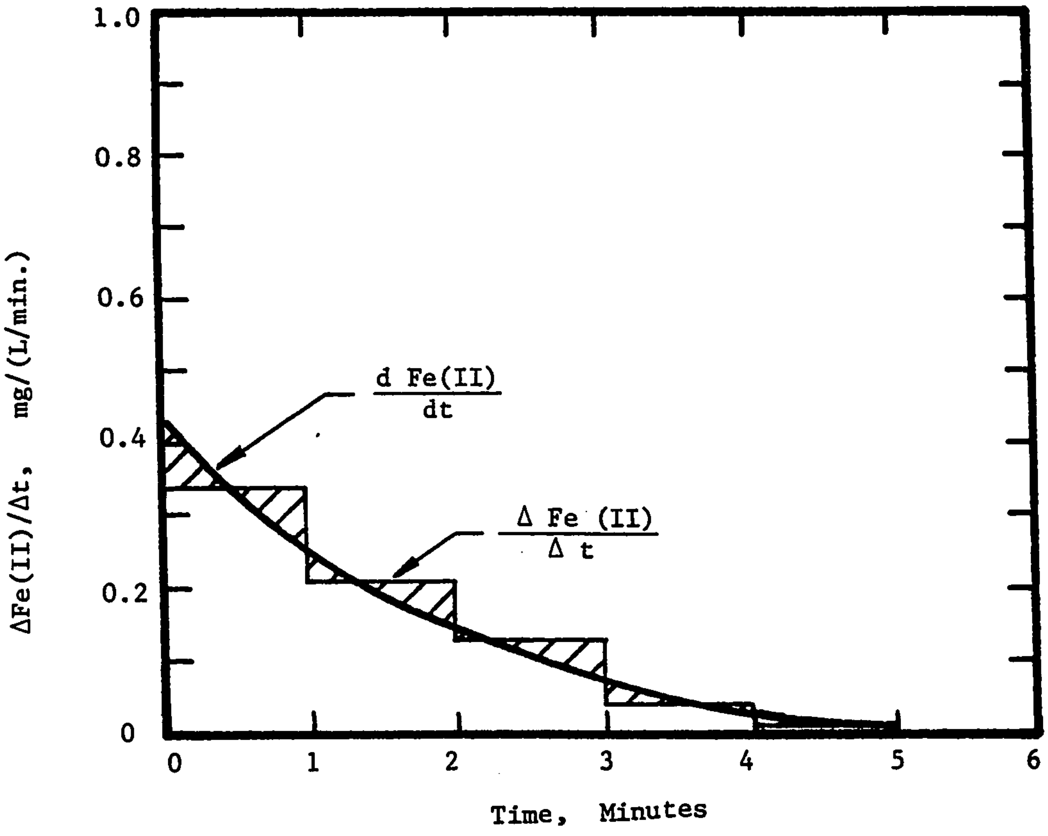


Figure 5.24: $\frac{\Delta \text{Fe(II)}}{\Delta t}$ vs. Time in the presence of 10 mg/L. TOC of mixture of organics and pH of 5.5. First Stage (0-5 minutes).

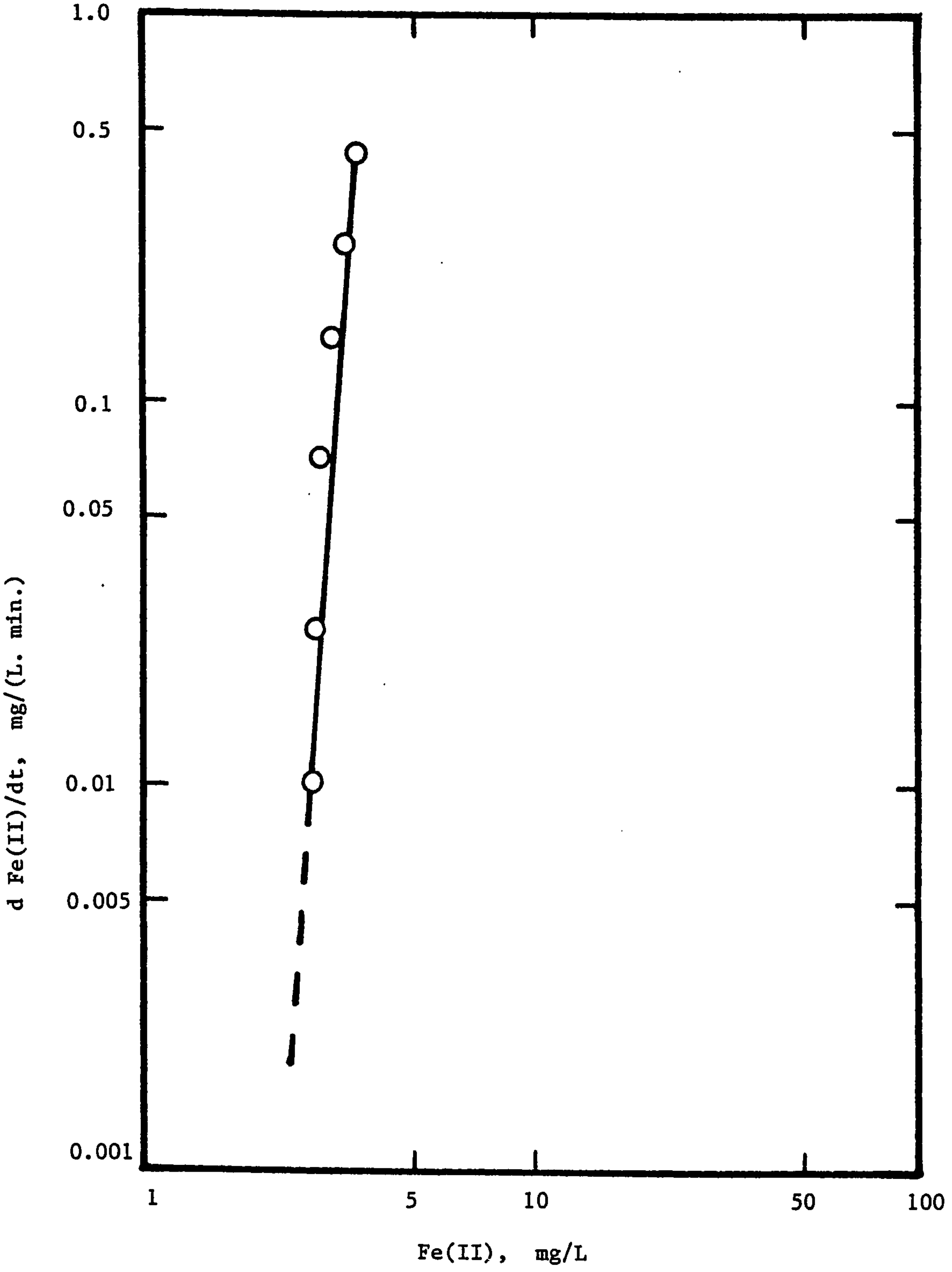


Figure 5.25 : $\frac{d\ Fe(II)}{dt}$ vs. Fe(II) for the first stage of oxidation (0-5 min.). pH = 5.5, TOC = 10 mg/L of Mixture of Organic Compounds.

Table 5.20: Differential Method Calculations for Mixture, pH=5.5, Second Stage.

Fe(II) Conc. (mg/L.)	Time (Min.)	$\frac{\Delta \text{Fe(II)}}{\Delta t}$ [mg/(L.min)]	$\frac{d\,\text{Fe(II)}}{dt}$ [mg/(L.min)]
2.8	5	-	0.46
2.05	7	0.38	0.26
1.65	9	0.02	0.165
1.45	11	0.1	0.11
1.25	13	0.1	0.065
1.05	15	0.05	0.035
1.0	19	0.025	0.01
0.95	21	0.025	0.01
0.9	23	0.025	0.01
0.82	25	0.04	0.01
0.77	27	0.025	0.01
0.7	29	0.035	0.01

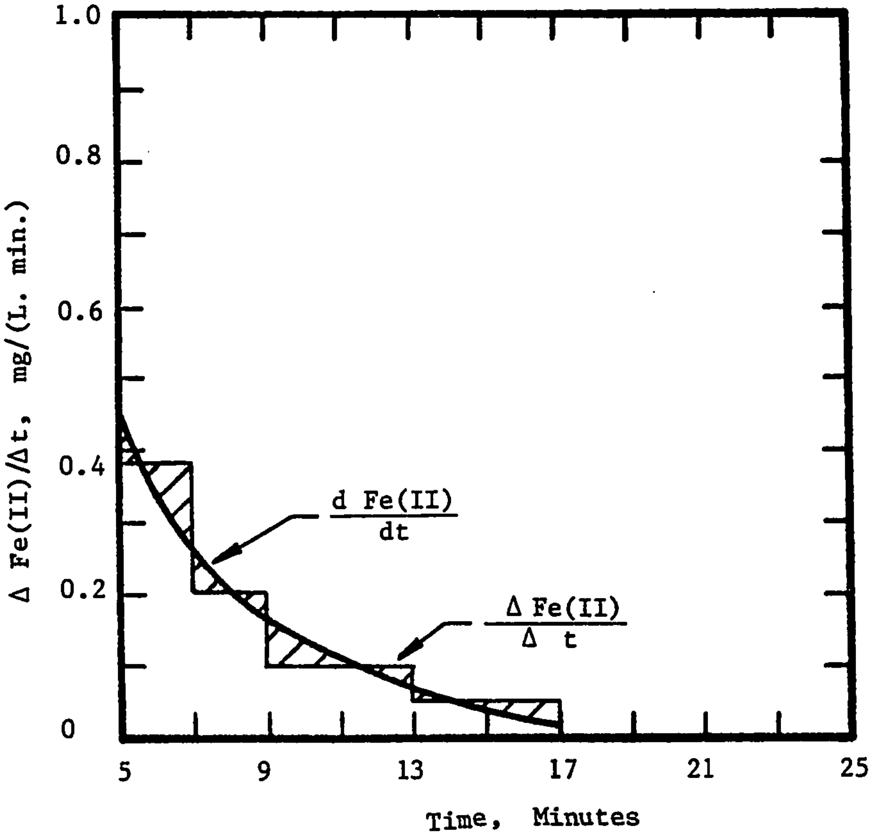


Figure 5.26 : $\frac{\Delta\,Fe(II)}{\Delta\,t}$ vs. Time. pH = 5.5.

TOC=10 mg/L of Mixture of organics.
Second Stage (5-30 min.)

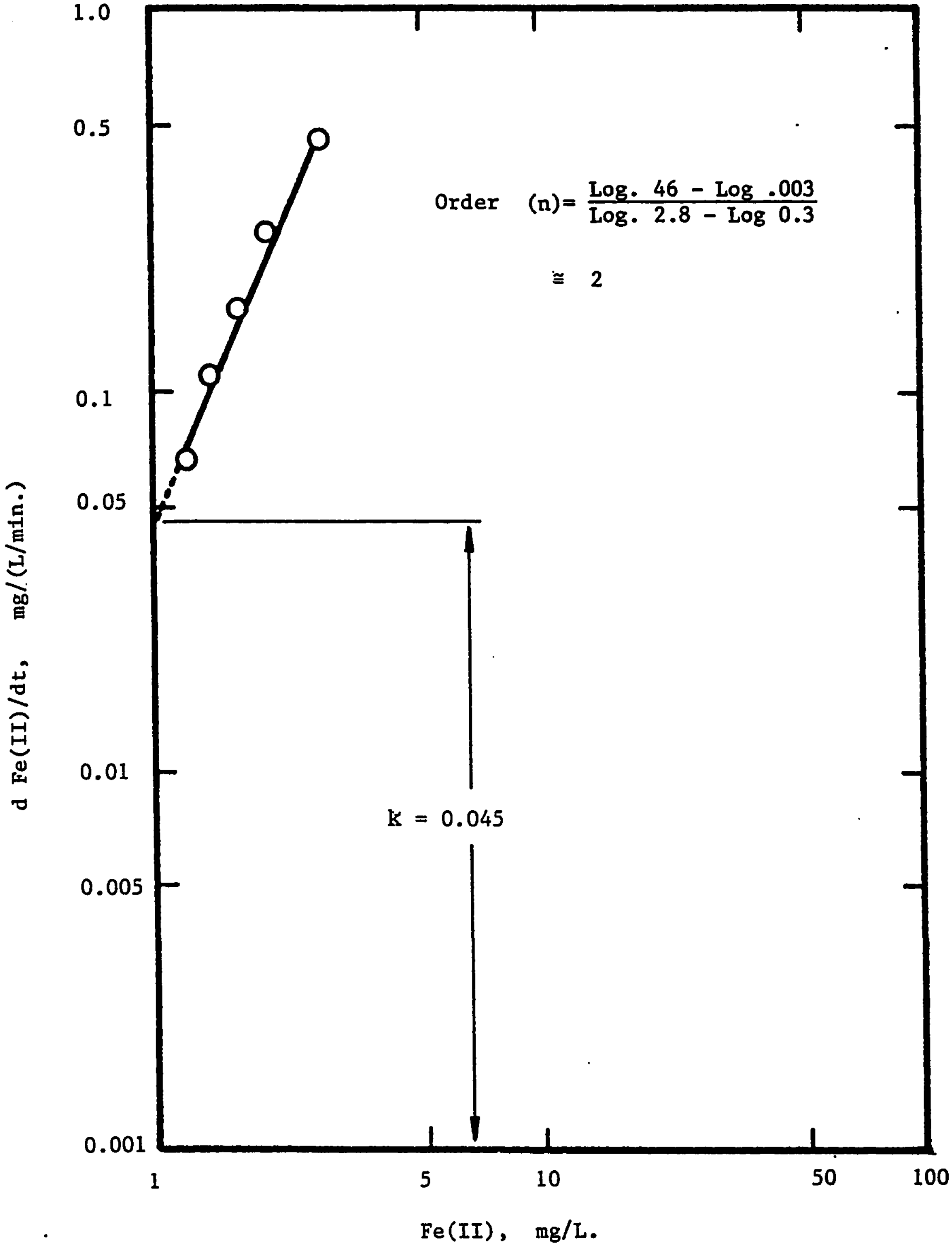


Figure 5.27: $\frac{d\,Fe(II)}{dt}$ vs. Fe(II). pH = 5.5. TOC = 10 mg/L of Mixture of Organics. Second Stage (5-30 minutes).

(2) At pH = 6.5

The kinetic analyses for determining the kinetic constants are given Table 5.21 and Figures 5.28 and 5.29. The values of n and k obtained are 4.66 and 0.0038, respectively. Since the value of n is high, the results are considered to be insignificant.

Figure 5.30 shows that the oxidation rate of manganese(II) is slower than the oxidation rate of iron(II), under the same environmental conditions. This difference could be due to the difference in the oxidation states of both iron and manganese. It is shown that iron (II) is oxidized within a short period of about 5 minutes but manganese (II) remains in solution for a longer period. Therefore, manganese needs more dosages of ozone to be oxidized than iron.

5.2.3 The Effect of Organic Complexation on Manganese (II) Oxidation

Oxidation of manganese (II) at 10^{-4} M of histidine was conducted at a pH of 6.5 and ozone dose of 5.1 mg/L. The results are shown in Table 5.22 and plotted in Figure 5.30. TOC was reduced by 25 percent at the end of the 30-minute oxidation period. The Mn(II) curve of Figure 5.30 shows that manganese (II) concentration remains fairly constant during the first 7 minutes

Table 5.21: Differential Method Calculations for Mixture, pH=6.5

Fe(II) Conc. (mg/L.)	Time (Min.)	$\frac{\Delta \text{Fe(II)}}{\Delta t}$ [mg/(L.min)]	$\frac{d\,\text{Fe(II)}}{dt}$ [mg/(L.min)]
2.8	0	-	0.46
2.44	1	0.36	0.275
2.2	2	0.24	0.165
2.08	3	0.12	0.1
1.92	4	0.16	0.07
1.81	5	0.11	0.055
1.72	6	0.09	0.045
1.65	7	0.07	0.045
1.58	8	0.07	0.045
1.52	9	0.06	0.045
1.48	10	0.04	0.045

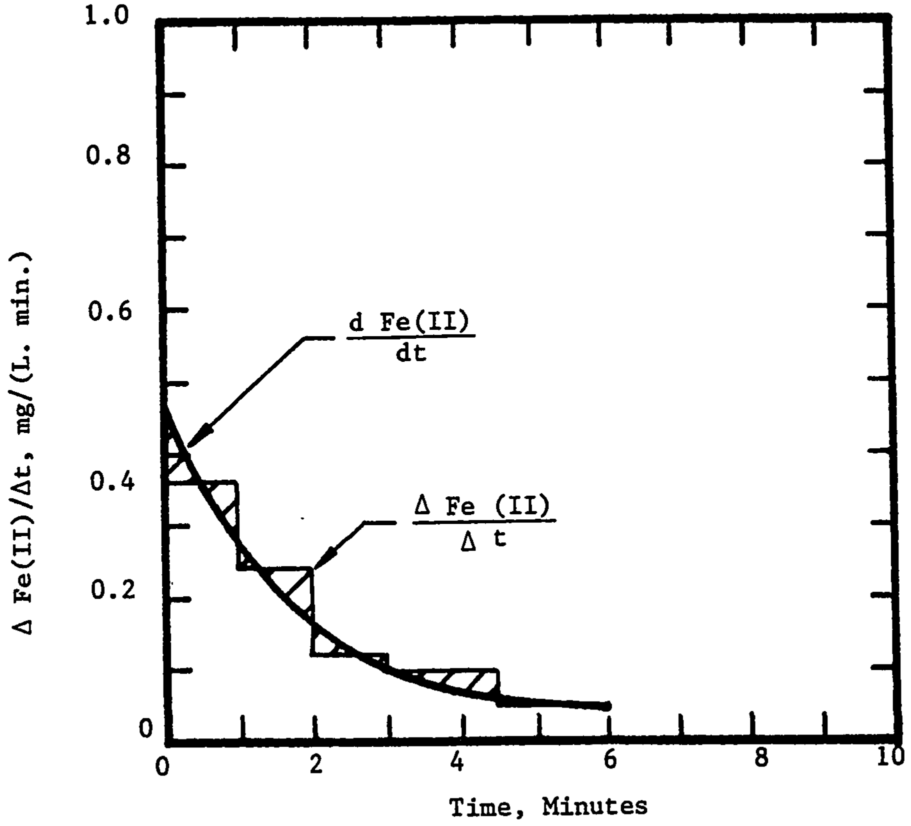


Figure 5.28 : $\frac{\Delta Fe(II)}{\Delta t}$ vs. Time. pH = 6.5, TOC = 10 mg/L of Mixture of Organic Compounds (0-6 min.)

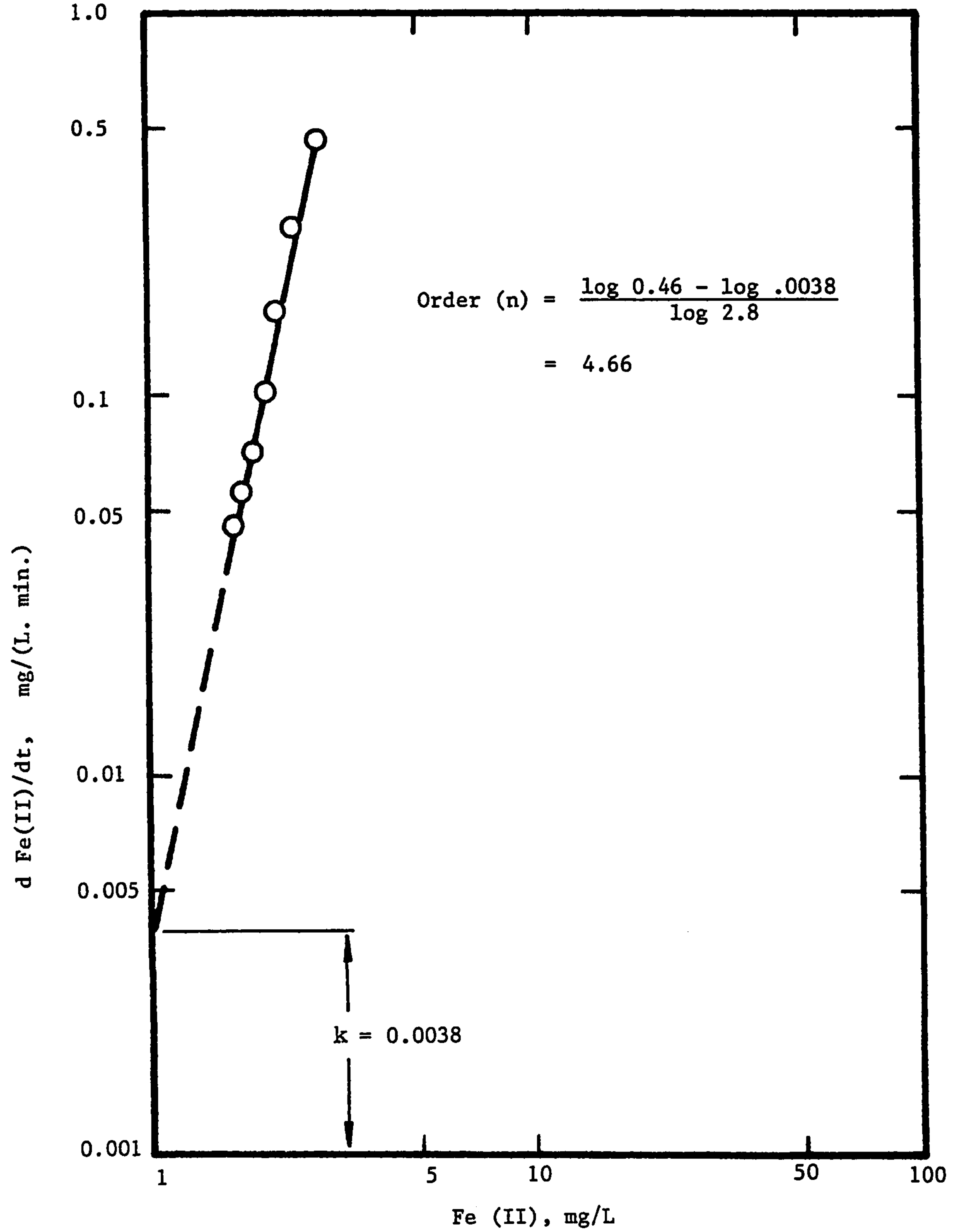


Figure 5.29: $\frac{d\ Fe(II)}{dt}$ vs. Fe(II). pH = 6.5. TOC=10 mg/L of Mixture of Organic Compounds.

Table 5.22 : Oxidation of Manganese (II) in the Presence of 10^{-4} M Histidine and pH of 6.5

TIME (Min.)	Mn(II) (mg/L)	TOC (mg/L)
0	4.0	10
0.5	4.0	9.5
1	4.0	9.1
3	3.9	9
5	3.9	9
7	3.9	8.7
10	3.28	8.5
12	2.73	8.3
15	2.0	8.2
20	1.4	8.0
30	1.4	7.5

Ozone Inlet in Gas Phase = 5.1 mg/L

Ozone Outlet in Gas Phase = 1.18 mg/L

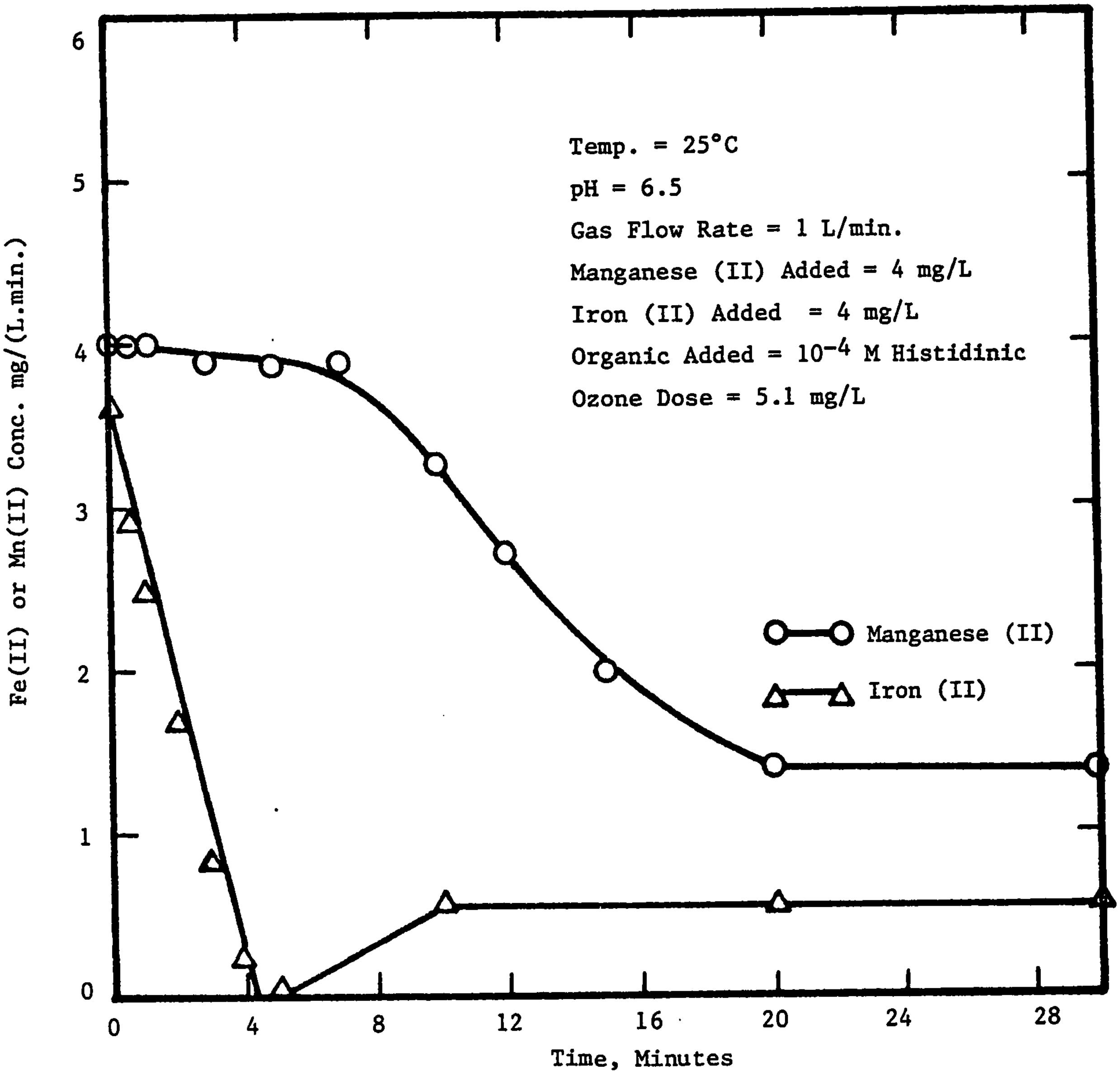


Figure 5.30: Oxidation of Iron (II) as well as Manganese (II) in the Presence of 10^{-4} M Histidine.

followed by rapid oxidation, and eventually reaches a constant value of 1.4 mg/L after 20 minutes (Figure 5.30).This behaviour could be due to the formation of MnO_2,which catalyses the following secondary reaction (41):

$$3\ Mn^{+2}\ (aq) + MnO_2\ (S) + 4\ H_2O\ = 2\ Mn_2O_3\ (S) + 8\ H^+\ (aq)$$

Therefore,when the MnO_2 is formed during the first few minutes the oxidation of Mn(II) would be much faster after the seventh minute due to the formation of Mn_2O_3 .Eventually, Mn(II) concentration reaches a steady state and that could be due to the stability of Mn(II)-histidine complex.

Chapter 6

CONCLUSIONS

In the light of the results obtained in this study, the following conclusions may be drawn:

A. Pure Water System

All the experiments conducted for the pure water system for the oxidation of iron and manganese followed similar kinetic expression. This expression is a zero-order regression model. This expression is:

$$[Fe(II)] = [Fe(II)]_i - k\,t$$

1. The oxidation rates (k) of iron(II) at initial iron(II) added of 4 mg/L and ozone dosage of 1.96mg/L are 0.45, 0.49, and 0.42 mg/(L.min.) at pH values of 5.5, 6.0, and 6.5, respectively.

2. The oxidation rates (k) of iron(II) at pH of 6, ozone dosage of 1.96 mg/L, and initial iron (II) added of 4, 3, 2, and 1 mg/L are 0.49, 0.41, 0.372, and 0.352

mg/(L.min.), respectively.

3. The oxidation rates (k) of manganese (II) at initial Mn(II) added of 4 mg/L, ozone dosage of 1.96 mg/L, and pH values of 6 and 7 are 0.29 and 0.317 mg/(L.min.), respectively. At pH of 9, the oxidation of Mn(II) has two stages, the first stage has a rate of 3 mg/(L.min.) and the second stage has a rate of 0.077 mg/(L.min.).

B. Organic Complexation System

Some of the experiments in this system followed the zero-order kinetic expression and some of them did not. The order (n) and reaction constant (k) for each experiment are summarized in Table 6.1. The general kinetic expression used is :

$$\frac{dFe(II)}{dt} = - k\,[Fe(II)]^{n}$$

C. It has been found that iron (II) does not remain in solution at pH values above 7 in the pure water system as well as in the presence of model organic compounds. However, complete amount of manganese (II) is found to remain in solution up to pH of 9 in pure water system as well as in the presence of model organic compounds.

Table 6.1: Summary for the Results of Oxidation of Iron (II) in the Presence of Different Complexing Agents

ORGANIC COMPOUND	ORDER OF THE REACTION (n)	REACTION CONSTANT (k)	TOC REDUCTION (%)	pH
1. Vanillin (10^{-4} M)				6.5
0-6 min.	Insignificant	Insignif.		
6-30 min.	0	-0.04	32	
2. Glutamic Acid (10^{-4} M)	0	-1.21	21	6.5
3. Histidine (10^{-4} M)	0	-0.9	26-27	5.5 & 6.5
4. Resorcinol (10^{-4} M)				6.5
0-5 mint.	3	-0.14		
5-30 mint.	0	-0.021	55	
5. Phenol (10^{-4} M)				6.5
0-0.5 Mint.	0	-2.48		
0.5-30 Mint.	0	-0.023	26	
6. Tartaric Acid (10^{-4} M)	Insignificant	Insignif.	36.4	6.5
0-8 mint.	2	-0.092		5.5
8-30 mint.	Insignificant	Insignif.	28	5.5
7. Mixture (10 mg/L TOC)			28.9	
0-5 mint.	Insignificant	Insignif.		5.5
5-30 mint.	2	-0.045		5.5
	Insignificant	Insignif.	29.3	6.5
8. Citric Acid	Insignificant	Insignif.	27	6.5

Chapter 7

RECOMMENDATIONS

Based on the present study, more comprehensive investigations may be carried out for which the following recommendations have been forwarded:

1. Very little kinetic information is available where oxidants other than oxygen are employed in kinetic studies. Further studies need to be conducted employing oxidants other than ozone or oxygen such as potassium permanganate and chlorine.
2. The measurement of ozone residual by the idometric method is not accurate in the presence of manganese because of manganese interference. Therefore, other methods are recommended for measuring the ozone residual when manganese is present.
3. More advanced kinetic studies could be conducted in detail including the value of pH, TOC in the mathematical model.

4. Other advanced, quick, and reliable methods such as Stop-Flow Techniques or T-Jump Procedures, are recommended for measuring iron(II) and manganese(II) at different time intervals for conducting kinetic studies.

Chapter 8

ENGINEERING SIGNIFICANCE

Detention time and ozone dosage are two most important parameters for the design of any ozonation treatment plant. The detention time and ozone dosage required to allow complete oxidation of iron and manganese are controlled by the kinetics of the reaction. Based on the present kinetic study, it can be concluded that:

(1) For the removal of iron(II) at a pH range of 6 to 7, the detention time and ozone dosage required are 10-15 minutes and 3-5 mg/L ozone dose in the gas phase, respectively.

(2) For the removal of manganese(II) at a pH range of 6 to 9, the detention time and ozone dosage required are 20-30 minutes and 4-6 mg/L ozone dose in the gas phase, respectively.

(3) The operating experience available in literature indicates that only about 2.1 mg/L of ozone dosage is required to obtain the maximum contaminant levels of iron and manganese at pH range of 6.5-7.5. The detention time that is recommended is at least 30 minutes (10,24).

Thus, the recommended values of pH and ozone dosages compare reasonably with the values available in literature.

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APPENDIX

Oxidation of Iron(II) in Presence of Humic Substances

Some preliminary experiments were conducted in the presence of a mixture of the model organic compounds and humic substances at different pH values, to compare the results with model organic compounds.

The humic substances are divided into three major fractions (42,43) : (i) Humic Acid, (ii) Fulvic Acid, and (iii) Humin. These three humic fractions are similar to each other but they differ in molecular weight and functional group content. Molecular weights ranging from a few hundreds to several millions have been reported for humic substances.

The humic substances used in this study were extracted from sea water by Tawabini (42) and were borrowed in small quantity to conduct preliminary studies. The method used by him involved resin adsorption as proposed by Mantoura and Riley (42,44). The procedure is explained in the following steps:

1. Before using the Amberlite XAD-2 resin, it is washed with distilled water and extracted with acetone in a soxhlet apparatus for one hour.
2. Pack the resin into 12 cm x 0.5 cm^2 column.
3. Wash the resin with 10 bed volumes of 0.5 M NaOH and finally with 1-2 liters of distilled water.
4. Filter the sea water and acidify it with 1 N HCL to a pH of about 2.2
5. Drain 5 liters of sea water through the column at a flow rate of about 3.5 mL/min.
6. Wash the resin with 1-2 liters of distilled water to remove the salt impurities.
7. Fill the extraction column with 1 M methanol-ammonia solution (eluant) and let stand overnight.
8. Collect the eluant in evaporating dishes and evaporate in a steam-water bath.

9. Dissolve the yellowish residue (humic substances) in 60 mL distilled water and keep in a refrigerator at a temperature of 4°C.

The quantity of humic substances obtained from Tawabini was so small that a mixture of model organic compounds as described under Section 5.2.2.3 was added to get the final TOC of 10 mg/L. Other experimental conditions were same as in case of model organic compounds. The results of this study are given in Table A1.

Oxidation of Iron(II) in Pure Water System

Table A2 shows the results of the oxidation of iron(II) at high initial added iron(II). The results show that, even at high initial concentration of iron(II), the oxidation pattern remains the same, i.e. zero-order reaction. The linear regression kinetic expression for the data shown in Table A2 is:

$$[Fe(II)] = 21.45 - 1.074\ t \qquad (R^2 = 0.99)$$

Table A1 : Oxidation of Iron (II) at 10 mg/L TOC of a Mixture of Model Organic Compounds and Humic Substances

Time (Min.)	pH = 5.5			pH = 6.5		
	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)	Fe(II) Conc. (mg/L)	Ozone Res. (mg/L)	TOC (mg/L)
0	3.8	0	10.2	2.56	0	10.2
0.5	3.64	0	-	2.44	0	-
1	3.6	0	10.2	2.44	0	10.2
2	3.36	0	-	2.36	0	-
3	3.26	0	10.2	2.32	0	10.2
4	3.26	0	-	2.16	0	-
5	3.18	0	10.2	2.12	0	10.1
10	2.36	0	10.1	1.68	0	10.0
20	1.2	0.37	10.0	1.26	0.48	8.7
30	0.9	0.48	8.7	1.04	0.48	7.0
Ozone Outlet in Gas Phase (mg/L)		2.48			2.64	

Ozone Inlet in Gas Phase = 5.1 mg/L
Iron(II) Added = 4 mg/L

Table A2 : Oxidation of Iron (II) at Initial Iron (II) Added of 20 mg/L in Pure Water System

Time (Min.)	Fe(II) Conc. (mg/L)
0	21.4
1	20.4
3	18.6
5	16.3
8	12.08
11	10
14	6
17	3
20	0.4
25	0

Ozone Inlet in Gas Phase = 1.96 mg/L

Ozone Outlet in Gas Phase = 0.14 mg/L

pH = 6

Temp. = 25°C

Gas Flow Rate = 1 L/min.

Oxidation of Iron(II) in Continuous Flow System

Some preliminary experiments were conducted in continuous flow system to study the oxidation of iron(II) under similar environmental conditions that were used in semi-batch system previously. The volume of ozone contactor was 3 liters. The flow rates were varied from 0.37 L/min. to 2.3 L/min. The results of the experiments are shown in Table A3 and Figure A1.

The values of steady state iron(II) concentrations for different detention times obtained from Figure A1, are plotted in Figure A2 against their respective detention times. This results in straight line as shown in Figure A2 with a k value of 0.88 mg/(L.min). The results also follow the zero order reaction as are determined previously in case of semi-batch system.

Table A3 : Effect of Ozonation on Iron(II) Concentration in a Continuous Flow System

Time (min.)	Detention Time (min.)				
	1.3	2.33	3.83	4.67	8.12
	Fe(II) (mg/L)	Fe(II) (mg/L)	Fe(II) (mg/L)	Fe(II) (mg/L)	Fe(II) (mg/L)
1	4.0	4.0	4.0	4.0	4.0
2	3.44	2.56	2.92	2.8	2.9
2.5	-	-	-	-	1.48
3	3.0	2.0	1.76	1.52	-
5	2.96	-	1.26	-	0.54
6	-	1.84	-	0.6	-
7	-	-	-	-	0.04
7.5	3.0	-	-	-	-
8	-	-	0.8	-	-
9	-	-	-	0.08	-
10	-	2.0	-	-	0.08
11	-	-	-	0.04	-
12	-	-	0.6	-	-
12.5	-	1.8	-	0.04	0.04
15	-	-	-	-	-
17	-	-	0.6	-	-
21	-	-	0.6	-	-

Ozone Dosage in Gas Phase = 1.96 mg/L

pH = 6.0.

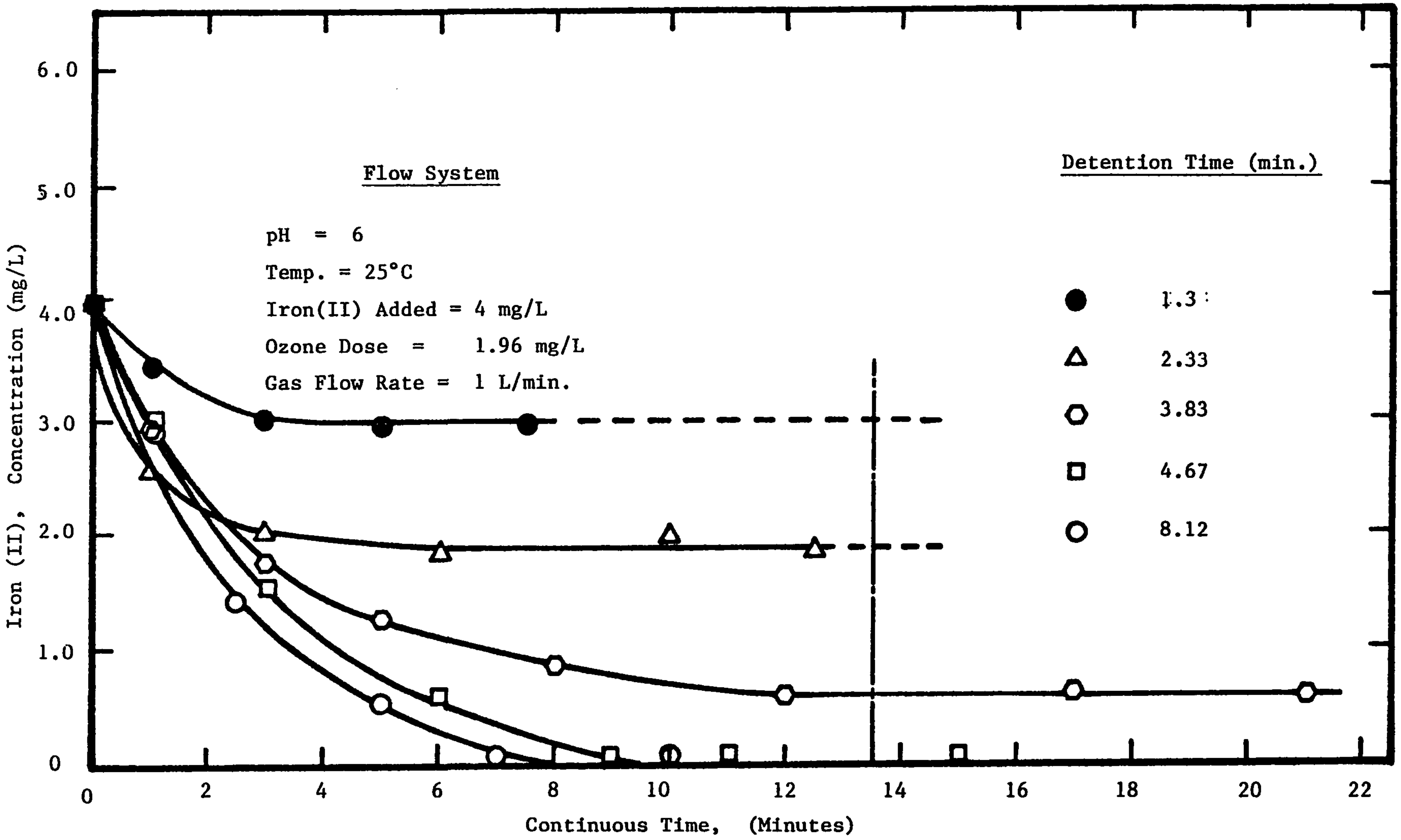

Figure A1 : Effect of Ozonation on Iron(II) Concentration in a Continuous Flow System

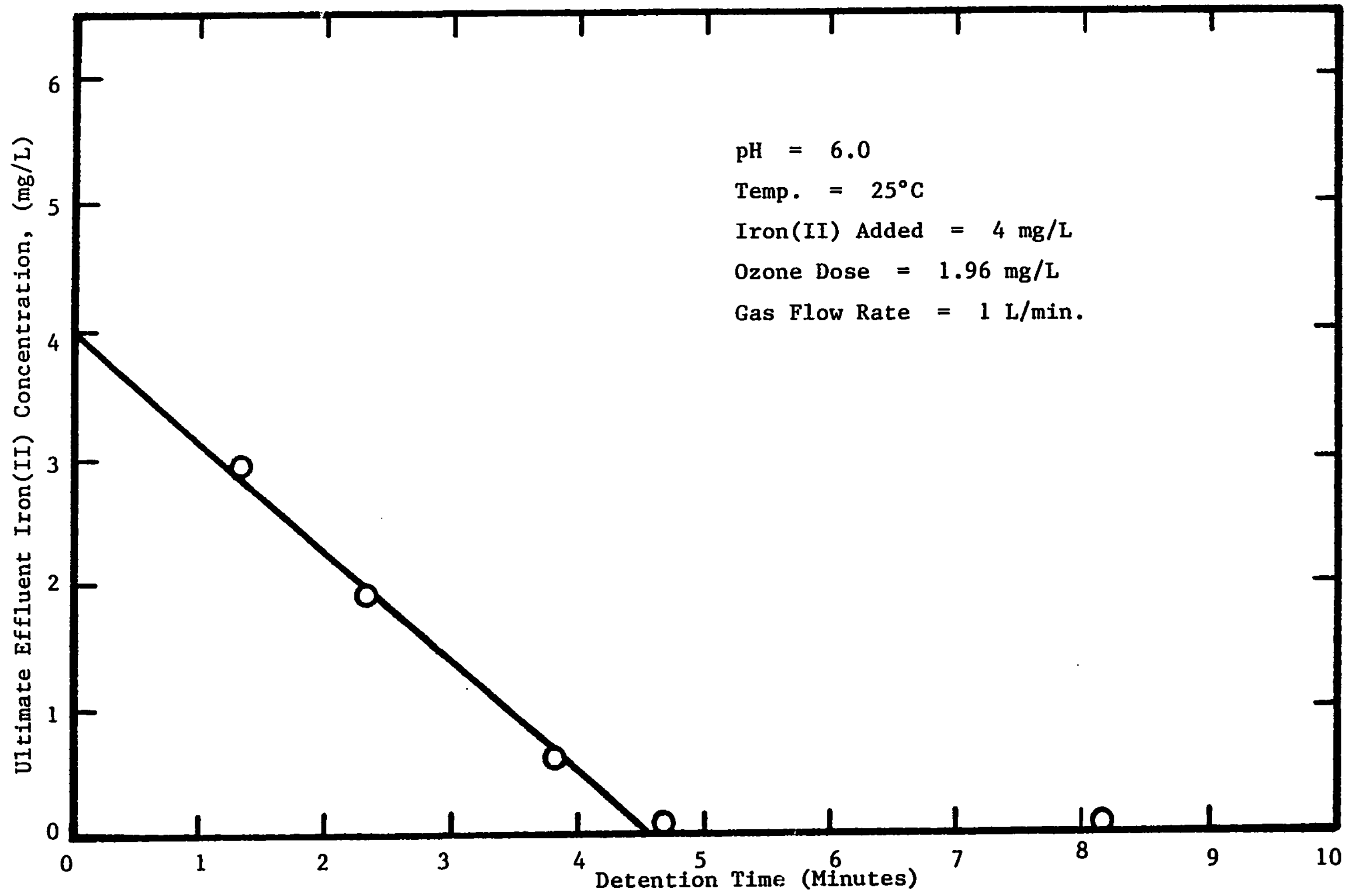

Figure A2 : Effect of Ozonation on Ultimate Effluent Concentration of Iron(II) in a Continuous Flow System