Removal of Complexed Iron By Chemical

Oxidation and/or Alum Coagulation

by

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(ABSTRACT)

The fate of iron complexed by various organic compounds was investigated as a function of both chemical oxidative and coagulation removal methods. Dissolved organic carbon (DOC) utilized in the studies was obtained from a variety of sources and included humic and fulvic acids, tannic acid and oxalic acid. Oxidants evaluated were potassium permanganate, free chlorine, and chlorine dioxide. Both laboratory-scale and field monitoring studies were performed. The relative molecular weight distribution (MWD) of the DOC present was analyzed to evaluate how changes in this parameter affected the efficiency of soluble iron removal by oxidation. In addition, the MWD of selected coagulated samples was evaluated to determine how this parameter affected the fate of complexed iron during the coagulation of dissolved organic matter with alum.

A high degree of ferrous iron complexation occurred with the DOC dominated by higher molecular weight organics. This complexation rendered the iron stable against the addition of each of the oxidants evaluated. However, soluble Fe(II) complexed by low molecular weight organics was successfully removed by chemical oxidation. Potassium permanganate was found to be the most effective oxidant of the three oxidants utilized in the study.

The results indicated that soluble Fe(II) complexed by high molecular weight DOC can be efficiently removed by alum coagulation. The pH and alum dose utilized to produce effective DOC removal was also found to promote efficient complexed Fe(II) removal.

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INTRODUCTION

Many water treatment facilities are required to implement strategies for Fe(II) removal, either on a seasonal or year-round basis, in order to avoid problems of elevated iron concentrations in the finished water. At natural water pH levels, soluble Fe(II) is quite common and often a difficult contaminant to remove. The problems associated with high concentrations of iron include taste, water discoloration, and staining/discoloration of clothes and plumbing fixtures. In addition, elevated Fe(II) concentrations may cause difficulties in the distribution system by supporting the growth of iron oxidizing bacteria. A secondary maximum contaminant level (SMCL) of 0.3 mg/L was established for iron due primarily to these aesthetic concerns.

In the absence of significant dissolved organic matter, the preferred treatment method for Fe(II) removal is oxidation followed by subsequent solid-liquid separation. Oxidants commonly utilized for this reaction include dissolved oxygen ($O_{2(aq)}$), potassium permanganate ($KMnO_4$), free chlorine (HOCl), and chlorine dioxide (ClO_2). Such treatment processes are often highly efficient, with residual iron concentrations at or below detection limits (<0.03 mg/L as Fe).

When significant amounts of dissolved organic carbon (DOC) are present, Fe(II) complexation often occurs which can retard the oxidation of Fe(II). Prior published data indicate the resistance of complexed Fe(II) to oxidation by $O_{2(aq)}$. However, little published information exists regarding the ability of alternative oxidants (such as those listed above) to promote complexed Fe(II) removal. The limited data that is available suggests that DOC may retard these oxidation reactions as well.

The specific objectives of this study were:

1. To evaluate how the concentration and relative molecular weight distribution (MWD) of the DOC present in water affects the ability of various oxidants (eg., $KMnO_4$, HOCl and ClO_2) to promote removal of complexed Fe(II);

2. To evaluate the fate of complexed Fe(II) during alum coagulation of waters for DOC removal; and

3. To evaluate how the addition of a preoxidant such as $KMnO_4$ might affect the removal of complexed Fe(II) when coupled with alum coagulation.

These objectives were addressed in laboratory-scale oxidation and alum coagulation studies that utilized a variety of sources of DOC for Fe(II) complexation. Monitoring studies at the Williams Water Treatment Plant in Durham, North Carolina, were also conducted to augment the data base regarding iron complexation and subsequent removal during conventional surface water treatment.

LITERATURE REVIEW

WATER QUALITY CONCERNS FOR IRON

The earth's crust is composed of approximately one hundred elements. Iron is the fourth most abundant element and constitutes 8 percent of the earth's crust (1). It occurs in rocks, minerals, clays, soils, and sediments and is a nutrient required by virtually all organisms. Iron is present in many ground water and impounded surface water supplies.

Soluble iron occurs in principally two oxidation states: the divalent ferrous form, Fe(II), and the trivalent ferric form, Fe(III). In waters supplies both soluble and insoluble species of hydrolyzed iron may be present (2). Ferric iron is very insoluble at the pH of natural waters and therefore, under oxidizing conditions, most of the iron is precipitated as ferric hydroxide. In ground water, anaerobic conditions are created by low levels of dissolved oxygen and by the decomposition of organic matter by soil bacteria. In such an environment, ferric iron, a constituent of minerals, may be dissolved and chemically reduced to soluble ferrous iron (3). In addition, iron can form complexes with many organic compounds making its removal from natural waters extremely difficult.

At natural water pH levels, soluble iron is quite common and often a difficult contaminant to remove. In approximately 40% of the public water supplies in the United States, soluble iron concentrations exceed

the secondary maximum contaminant level (MCL) of 0.3 mg/L (4). Primarily, this MCL was established for aesthetic reasons, since humans suffer no known harmful effects from drinking water containing elevated concentrations of iron. The problems associated with high concentrations of iron include taste, water discoloration, and staining and discoloring of clothes and plumbing fixtures. In addition, elevated iron concentration may cause difficulties in distribution systems by supporting growths of iron bacteria.

The amount of iron present plus the intended use of the finished water are important considerations during evaluation of potential raw water sources. Currently, there are three basic methods of treatment for reducing iron concentrations to less than the secondary MCL. The methods include oxidation and precipitation, ion exchange, and stabilization with polyphosphates and silicates. Unfortunately, these conventional treatment methods are not effective in removing iron which has complexed with dissolved organic matter(5).

CHEMISTRY OF IRON

The aqueous chemistry of iron can be very complex since iron enters into several hydrolysis and oxidation-reduction reactions. No simple relationships exist between the iron species, the redox potential, and the solution pH. Therefore, it is necessary to explore the aqueous chemistry of iron in order to better understand and apply the various iron removal techniques available for water supplies. Conditions under

which Fe(II) may be oxidized to Fe(III) by $O_{2(aq)}$ can be determined by examining the pE - pH diagram which describes the predominant or stable boundaries of given iron species (Figure 1). According to the pE - pH diagram, in the absence of electron acceptors such as $O_{2(aq)}$, HOCl or $KMnO_4$, Fe(II) is the predominant iron species in natural waters (5). This is relevant to utilities who practice iron removal through oxidation of Fe(II) and subsequent precipitation and removal of $Fe(OH)_3$. Unfortunately, when significant amounts of dissolved organic carbon (DOC) are present in conjunction with Fe(II), complexation occurs which can retard the oxidation of Fe(II) by oxygen for several days (6). Under such conditions, the oxidation of iron would no longer be a viable method of iron removal for water treatment plants.

Reactions of Fe(II) with Oxygen

The majority of the research initially conducted in the area of iron oxidation utilized dissolved oxygen ($O_{2(aq)}$) as the preferred oxidant. The rate of ferrous iron oxygenation was determined to be first order with respect to both the ferrous iron concentration and the partial pressure of oxygen (5):

$$\frac{-d[Fe(II)]}{dt} = k[Fe(II)][O_{2(g)}]$$

Stumm and Lee (7) determined this reaction to be extremely dependent on solution pH with the reaction rate increasing up to 100-fold per unit increase in pH. Oxygenation studies performed on natural ground waters by Ghosh (8) indicated that pH and alkalinity were the determining

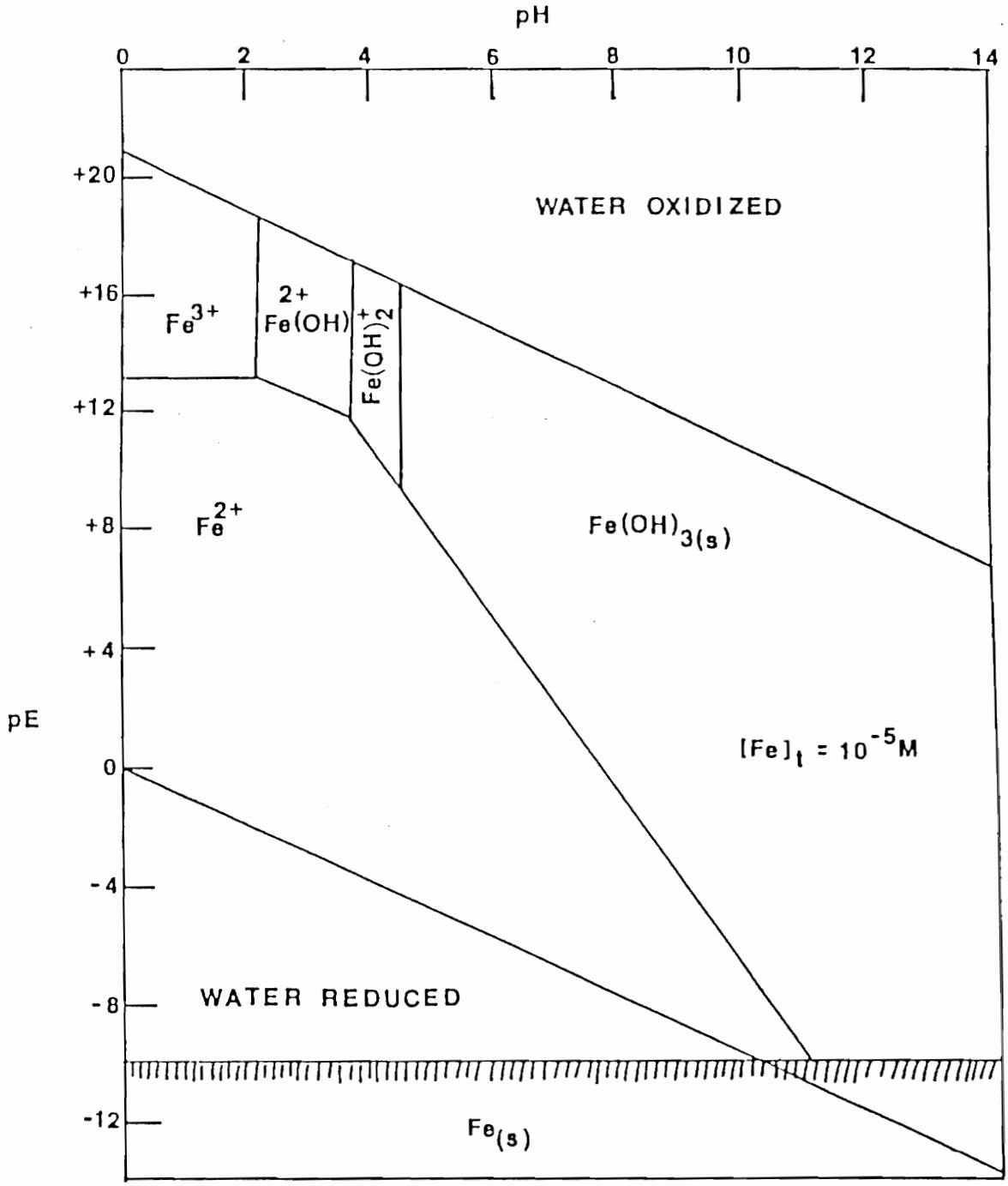


Figure 1. pE-pH diagram for the iron system. Reproduced from Faust and Aly [5] courtesy of Ann Arbor Science Publishers.

factors in the rate of Fe(II) oxidation by $O_{2(aq)}$. Jobin and Ghosh (9) performed additional studies on the oxidation of Fe(II) by $O_{2(aq)}$. They concluded that the buffer intensity of the water had a definite influence on the Fe(II) oxidation rate. In a later study Sung and Morgan (10) warned that the observed correlation between the buffer capacity of the water and the rate of Fe(II) oxidation by $O_{2(aq)}$ may possibly be due only to the changes in the ionic strength of the solution. Andersen et al. (11) reported several treatment facilities in Nebraska which successfully removed iron utilizing aeration under neutral to alkaline pH conditions.

Impact of Organic Matter on Fe(II) Oxidation

In all of the Fe(II) oxidation studies previously reviewed, the waters that were tested contained minimal amounts of dissolved organic matter. Therefore, the results observed indicated the ability of $O_{2(aq)}$ to oxidize uncomplexed Fe(II) only. Unfortunately, a significant amount of the Fe(II) in many surface waters exists in a complexed form with organic matter. This complexation effect has been noted for decades. One of the earliest references to organic complexation was made by Weston (12), who observed that certain waters containing organic matter were able to hold Fe(II) in solution for an indefinite period following aeration. Weston believed that the iron could not be precipitated due to organic compounds which attached to the iron, thereby preventing its removal.

Several researchers have studied the Fe(II) and Fe(III) complexation that occurs when significant DOC is present in conjunction with soluble iron and the potential effect of such complexation on Fe(II) oxidation kinetics. Komolrit (13) indicated during his study of Illinois ground water treatment plants that organic compounds interfered with the removal of iron from ground waters. Shapiro (14) observed that waters with high concentrations of filterable iron frequently had high levels of organic color. Shapiro believed this level of stability was due largely to complexation and peptization reactions. In addition, the author demonstrated the ability of certain yellow organic acids to reduce Fe(III) to Fe(II) when boiled.

Stumm and Singer (15) proposed a set or oxidation-reduction equations which demonstrated the effect of organic matter on the oxygenation of Fe(II):

$$Fe(II) + 1/4\ O_2 + \text{organics} \longrightarrow Fe(III) - \text{organic complex}$$

$$Fe(III) - \text{organic complex} \longrightarrow Fe(II) + \text{oxidized organics}$$

$$Fe(II) + 1/4\ O_2 + \text{organics} \longrightarrow Fe(III) - \text{organic complex}$$

The ferrous - ferric, oxidation - reduction couple serves as an electron transfer catalyst for the oxidation of organic matter. A similar set of equations involving dissolved iron and organic matter were suggested by Oldham and Gloyna (16). In addition, these authors provided evidence for the existence of complexation between organic compounds and iron using polarography and infrared analysis. They showed that naturally

occurring humic acids had significant complexation capacities for both ferrous and ferric iron. Schnitzer and Hansen (17) determined the stability constant, a measurement of the degree to which complexation occurs, for a ferric-fulvic acid complex. They determined the stability constant for the ferric-fulvic acid complex was greater (i.e. more stable) than for any other metallic-fulvic acid complex tested.

The effect of iron-organic complexation on iron oxidation kinetics has been reported by several authors. Hem (18) reported the ability of tannic acids to complex with ferrous iron and thereby significantly retard its subsequent oxidation by oxygen. Jobin and Ghosh (9) demonstrated that both tannic acids and humic acids can complex ferrous iron and retard its oxidation when exposed to $O_{2(aq)}$. Finally, Theis and Singer (19) investigated the ability of various organic compounds to complex iron and retard its removal by contact with $O_{2(aq)}$ (Figure 2). The authors found that tannic acid, gallic acid, pyrogallol, glutamic acid, tartaric acid, and glutamine were able to effectively inhibit the oxidation of Fe(II) for several hours, even in water saturated with $O_{2(aq)}$. In particular, tannic acid was able to inhibit Fe(II) oxidation for several days (Figure 3). In addition, Theis and Singer (19) proposed a schematic diagram of a model to describe the behavior of iron in the presence of humic substances (Figure 4). Because the ferrous - ferric couple can easily sustain reversible oxidation reactions, it seems to adhere to the reactions proposed in this model.

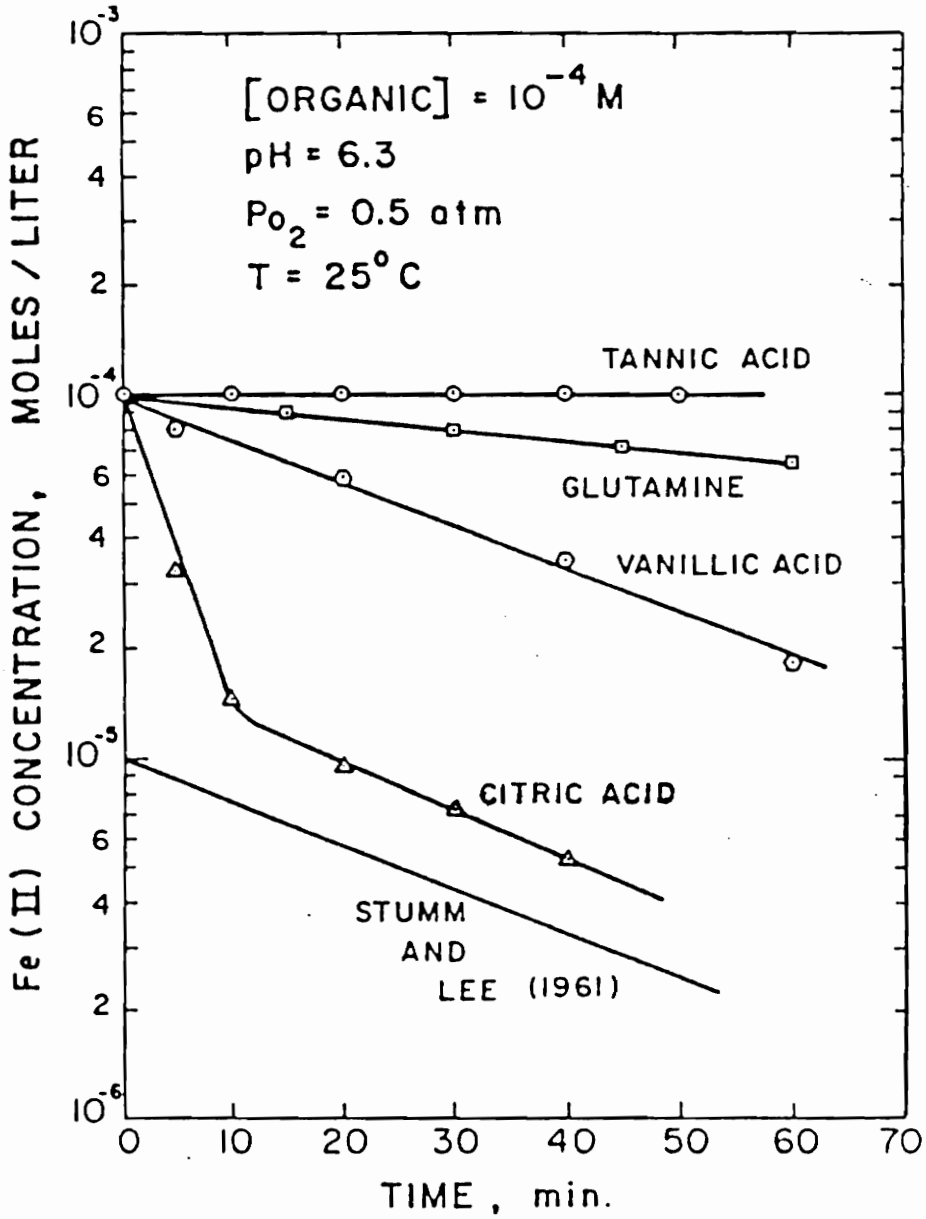


Figure 2. Effects of representative organic compounds on rate of oxidation of ferrous iron at pH = 6.3 P_{O_2} = 0.5 atm. and T = 25°C as compared with rate in simple aqueous media (Stumm and Lee. 1961) (after Theis and Singer. 1973)

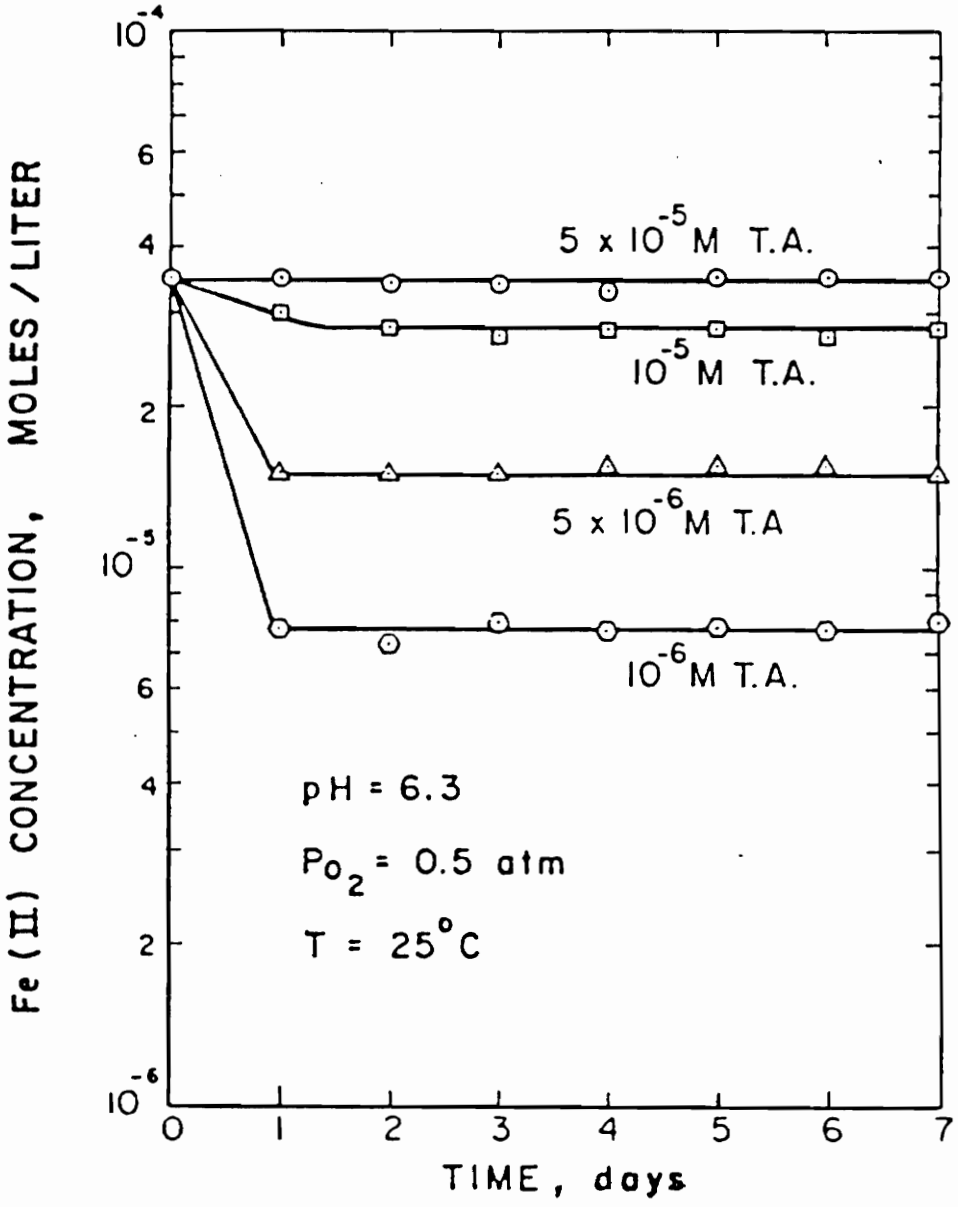
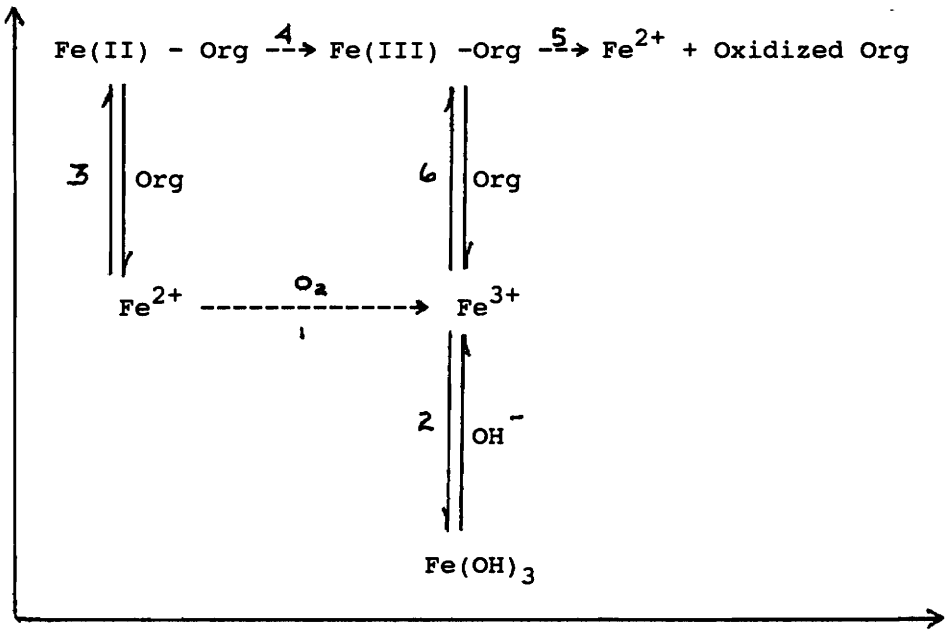


FIGURE 3. Inhibition of ferrous iron oxidation in presence of various concentrations of tannic acid, at pH = 6.3. P_{O_2} = 0.5 atm and T = 25°C (after Theis and Singer, 1973)

Figure 4. Behavior of Iron in the Presence of Humic Substances



Reactions 1 and 2: Ferrous iron is rapidly oxidized by oxygen to ferric iron which precipitates as $Fe(OH)_3$ and is removed from the system.

Reaction 3: Organic matter (if present) will complex the ferrous iron which will then compete with Reaction 1 for oxygen.

Reaction 4: Oxidation of the complexed iron forms a ferric complex with the organic matter.

Reaction 5: The resultant complex is unstable and is reduced by the organic compound, thereby, allowing ferrous iron to participate in the cycle again.

Reactions of Fe(II) with Alternative Oxidants

There are very few scientific publications available which address the specific use of oxidants other than dissolved oxygen for iron removal. Of those which are available (20, 21, and 22) the information is only semi-quantitative. These studies showed that $KMnO_4$ and HOCl were able to oxidize uncomplexed Fe(II) more rapidly than $O_{2(aq)}$. Unfortunately, little data were provided to demonstrate how effectively either chemical could oxidize complexed Fe(II). A search of the literature provided no additional articles which specifically addressed the use of these oxidants with complexed Fe(II).

REMOVAL OF COMPLEXED IRON DURING COAGULATION

Coagulation/flocculation is the process of coalescing entrained particles by neutralizing repulsive surface charges. Soluble salts of trivalent metals are dispersed and become hydrated, then hydrolyze to form metal hydroxides. The negative surface charges of particles are neutralized by the metal ions. After neutralization, particles coalesce due to weaker Van de Waal's forces. During flocculation particles consisting of hydrated metal oxides and enmeshed particles form and aggregate into "sweep floc". After mixing, the sweep floc settles out of solution capturing clay, silt and organics.

The use of metal ion coagulation to remove organic matter from natural water sources has been thoroughly reviewed in the published literature; therefore, it will not be summarized and presented in this section. However, Edzwald (23) provided an excellent overview of this subject matter. This section will instead provide references which specifically relate to the proposed research study.

Evidence was provided by Rest (24) that alum coagulation preferentially removed higher molecular weight organic material from the water source. Coagulation at pH 5.2-5.3 provided the most efficient removal of DOC. Collins et al. (25) presented an extremely thorough investigation on how the molecular weight distribution of the organic matter effected its removal by alum coagulation. The authors evaluated data from both full-scale and laboratory-scale treatment facilities and likewise concluded that alum coagulation preferentially removed higher molecular weight organic matter. They utilized ultrafiltration techniques to determine the molecular weight distribution. Sinsabaugh et al. (26) provided similar conclusions through the use of iron salts for the removal of organic matter from surface waters. DOC removal by coagulation is related to characteristics of the organic material. Removal processes such as adsorption and direct precipitation may be directly affected by the molecular size and solubility of the DOC.

Although literature exists regarding DOC removal by coagulation, little information is available dealing directly with the fate of iron complexed by DOC during coagulation. Research is needed to understand the fate of complexed iron during alum coagulation of waters for DOC removal. A companion area of interest would be how the addition of a preoxidant might affect the removal of complexed iron when coupled with alum coagulation.

EXPERIMENTAL METHODS AND MATERIALS

EXPERIMENTAL APPROACH

The investigation involved both laboratory and field studies. Three types of laboratory studies were conducted utilizing both synthetically prepared and natural raw water samples.

One set of studies investigated the effectiveness of various oxidants (free chlorine, potassium permanganate and chlorine dioxide) for oxidizing Fe(II) that had been significantly complexed by naturally occurring organic compounds. The oxidants were added to solutions containing complexed Fe(II) and samples were collected over an extended period of time and analyzed for residual soluble Fe(II) concentration. Variables in the experimental matrix included the concentration and type of organic matter present as well as the oxidant dose utilized.

A second set of studies was conducted using alum coagulation to evaluate the removal of both dissolved organic carbon (DOC) and Fe(II). Samples were coagulated, either with or without oxidant addition during the rapid mix phase. Following flocculation and sedimentation, samples were processed through filters of various sizes and analyzed for residual DOC and Fe(II). This aided in evaluating the relationship between the characteristic molecular weight of the complexing organic and the degree of iron removal observed.

The last set of laboratory studies dealt with the bathophenanthroline method (27) for differentiating Fe(III) and Fe(II) species. The experiments were designed to examine if bathophenanthroline could successfully extract complexed Fe(II) from organic matter. This analytical technique, if successful, was to be included in the oxidation experiments to determine whether any iron oxidation occurred following oxidant addition.

Field studies consisted of analyzing data collected by personnel at the Williams Water Treatment Plant located in Durham, N.C., to examine the fate of Fe(II) through various phases of treatment. In addition, water samples were collected at several locations throughout the treatment facility and analyzed for soluble Fe(II) and DOC concentrations.

All the above studies were conducted in the pH range of 6.0 - 6.5. The pH value was chosen as representative of the pH condition anticipated in a treatment plant employing alum coagulation for DOC removal.

TEST SOLUTION PREPARATION

The oxidation experiments, bathophenanthroline tests, and a portion of the alum coagulation experiments were performed using a synthetically prepared water sample to which an organic acid and a sample of soluble Fe(II) were added, resulting in a Fe(II) - organic complex. The target concentration of soluble Fe(II) was 1 mg/L.

The water solutions were prepared using distilled water to which background ions were added to simulate representative freshwater conditions. The amount of water prepared ranged from 2 L for the oxidation experiments to 7 L for the alum coagulation experiments. The background ions and concentrations utilized were 1 meq/L each of sodium bicarbonate ($NaHCO_3$), calcium chloride ($CaCl_2$), and sodium sulfate (Na_2SO_4). DOC was then added from one of several sources at concentrations ranging from 4 mg/L to 5 mg/L. A later section of this chapter details the sources of the DOC used in this study. Prior to the addition of the soluble Fe(II), the water was deaerated by bubbling nitrogen gas ($N_{2\ (g)}$) through the solution for 20 - 30 minutes, thus minimizing the potential oxidation of Fe(II) by molecular oxygen. In addition the pH was adjusted to 5.0 - 5.5 as an extra precaution against oxidation while still allowing for Fe(II) - organic complexation to occur. The required amount of soluble Fe(II) to obtain the desired concentration was pipetted directly from the ferrous stock solution into the test water and mixed gently. The test solution was stored in an air tight container with no head space, with 12 to 24 hours allowed for Fe(II) - organic complexation to occur.

The remaining portion of the alum coagulation experiments were performed using natural water sources. The natural water sources were obtained from two locations, Lake Michie in Durham, North Carolina and the Po River in Spotsylvania County, Virginia. The water from Durham, N.C. contained 0.86 mg/L total iron and 0.43 mg/L soluble iron; the DOC was

7.6 mg/L. The water from the Po River contained 2.1 mg/L total iron and 0.42 mg/L soluble iron; the DOC was 7.1 mg/L. The water samples were not modified nor altered for use in the alum coagulation study.

SIZE FRACTIONATION OF ORGANIC CARBON

Organic matter was fractionated into size categories using a series of filters of decreasing pore size. The series consisted of Amicon Diaflo ultrafiltration membranes, YM series with molecular weight (MW) cut-offs of 30,000, 10,000, 5,000 and 1,000. Each membrane is characterized by its nominal cut-off, i.e., its ability to retain molecules larger than those of a given size. According to the manufacturer (28) the nominal molecular weight cut-off level refers to the molecular weight at which the membrane rejects 90%. The membranes were pretreated with glycerin and sodium azide. The glycerin was used to prevent drying of the membrane while the sodium azide was added as a preservative. Prior to use of each membrane, the glycerine and sodium azide were removed by floating the membrane (skin side down) in a beaker of Milli-Q water for a minimum of one hour. During this time, the water was changed a minimum of three times as per manufacturer's instructions. The membranes were then mounted in 200 mL Amicon ultrafiltration cells (equipped with magnetic stirrer bars) and flushed with Milli-Q water under a $N_{2(g)}$ atmosphere of 40 psi until the DOC concentration of the filtrate was nearly equivalent to the DOC concentration of the Milli-Q influent. The extensive rinsing procedure was performed to minimize the

potential for sample contamination by membrane-associated DOC. After each use the membranes were washed with a mild detergent solution, rinsed, and stored individually in Milli-Q water at 4° C.

Ultrafiltration was accomplished using a prepared YM membrane mounted in a 200 mL, continuously stirred, Amicon ultrafiltration cell operated under a nitrogen atmosphere of 40 psi. The sample was stirred vigorously using a magnetic stirring bar to help prevent clogging of the membrane. The cell was refilled when the water level reached 50-100 mL.

A serial filtration scheme was followed for the Thousand Acre Fulvic Acid. The organic solution was filtered through a YM30 ultrafiltration membrane with a MW cut-off of 30,000. The filtrate was then filtered through a YM10 ultrafiltration membrane with a MW cut-off of 10,000. This method of fractionating the filtrate was repeated using the YM5 ultrafiltration membrane, MW cut-off of 5,000 and the YM2 ultrafiltration membrane, MW cut-off of 1,000. Unfortunately, the serial filtration scheme proved extremely time consuming; therefore, later size fractionations were performed using a parallel filtration scheme where the organic solution was applied directly to each of the above mentioned membrane cut-off levels.

PREPARATION OF STOCK SOLUTIONS AND REAGENTS

Oxidant Preparation

Most oxidants used in the experimental studies were prepared as concentrated stock solutions. The following subsections describe the procedures used to prepare each stock and any subsequent solutions. The specific titration procedures used to quantify the strength of each oxidant are described in a later section of this chapter.

Chlorine Dioxide

A stock solution of chlorine dioxide (ClO_2) was generated in a series of reaction vessels using the sulfuric acid/sodium chlorite generated procedure. The procedure used differed slightly from the ClO_2 generation procedure described in Standard Methods (29). The reagent concentrations were doubled and the temperature of the receiving solution was lowered using an ice bath. These modifications served to decrease the background concentrations of chlorite and chlorine while increasing the yield of chlorine dioxide. The chlorine dioxide generation and absorption system used is shown in Figure 5. Flask A is a 500 mL aspiration flask that was filled with 300 mL Milli - Q water. Bottle B is a 1 L gas generating bottle that contained 20 g of sodium chlorite which had been dissolved in 750 mL Milli-Q water. Bottle C is the scrubber bottle that contained a saturated solution of sodium chlorite. Bottle D is the 2 L gas adsorbtion bottle which was placed in an ice bath and contained 1500 mL of 10^ C Milli-Q water. The graduated cylinder E contained 4 mL concentrated sulfuric acid which had been

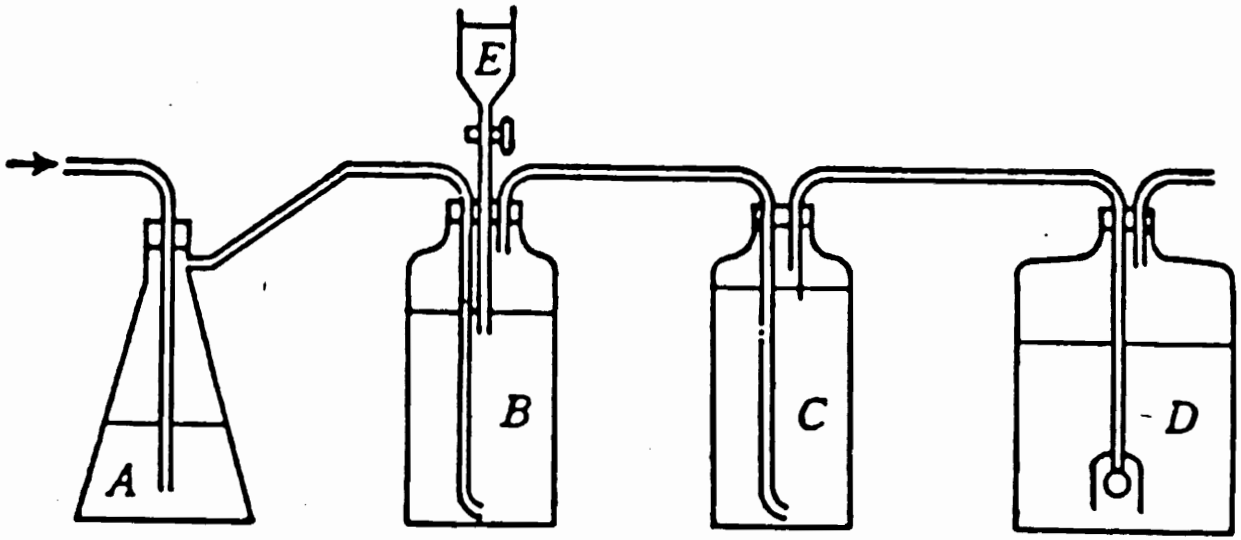


FIGURE 5. Schematic of Chlorine Dioxide Generation Apparatus (from Standard Methods 1985).

diluted to 20 mL with Milli - Q water. The last bottle (F), contained a saturated solution of potassium iodide, which was used to trap any chlorine dioxide gas not transported into solution by reacting to form free iodine. Next the bottles were connected as shown with glass tubing. Flask A was connected to a source of compressed air. The air was bubbled through A, then down through B, through the scrubber bottle C into the collecting bottle D, and finally through F, which contained an outlet for the escape of the moving air. To begin generation, the dilute sulfuric acid was added to bottle B in 5 mL increments at 5 minute intervals. The evolved gas was passed to the scrubber bottle to remove any free chlorine impurity and then passed into the pre-cooled collection bottle to be adsorbed by the Milli-Q water.

The stock chlorine dioxide solution was stored in a brown-colored bottle under dark, refrigerated (4° C) conditions. A 100 mg/L ClO_2 solution was used in the oxidation experiments and was prepared by pipetting an appropriate amount of the ClO_2 stock solution into Milli-Q water. Because ClO_2 is very volatile, the tip of the pipette was submerged below the water surface during preparation of the dilute solution. The dilute solution was prepared just prior to each experiment and its concentration verified using a potentiometric titrator.

Potassium Permanganate

Stock solutions of potassium permanganate were prepared by dissolving an appropriate amount of reagent grade $KMnO_4$ crystals (Fisher Scientific) in Milli-Q water to make a 1 g/L concentration as permanganate. This stock solution was stored in a ground-glass bottle covered in aluminum foil under dark, refrigerated (4° C) conditions. A dilute (100 mg/L) solution of $KMnO_4$ was prepared prior to each experimental study by pipetting an appropriate amount of the permanganate stock solution into Milli-Q water. The titre of this solution was checked by use of potentiometric titration procedures.

Free Chlorine

A free chlorine solution for use in oxidation tests was prepared prior to each experiment. The 100 mg/L solution was prepared by diluting approximately 1.25 mL of 5.25% sodium hypochlorite solution with 500 mL of Milli-Q water. Before each use, the dilute free chlorine solution was titrated for chlorine concentration using a potentiometric titrator.

Organic Acid Preparation

Several organic acids were added individually at varying dosages to water samples to simulate the DOC present in natural waters. These water samples were used in the studies to investigate the effect the DOC concentration and relative molecular weight distribution had on iron complexation, the ability of oxidants to oxidize the complexed Fe(II),

and the fate of complexed iron during the coagulation of DOC. The following subsections describe the sources and the procedures used to prepare the stock DOC solutions used.

Tannic Acid

During the preparation of the tannic acid test solution an appropriate amount of tannic acid granules (Fisher Scientific) were dissolved in distilled water with the background ions, prior to the addition of Fe(II). Concentration of tannic acid in solution was 8.6 mg/L, DOC was 5 mg/L.

Oxalic Acid

Stock solutions of oxalic acid were prepared by dissolving an appropriate amount of oxalic acid crystals (Fisher Scientific) in distilled water to create a 1 mg/mL concentration as oxalic acid. This stock solution was stored in a ground-glass bottle and used to prepare test solutions for oxidation studies. Solutions for use in those tests were prepared by pipetting a required amount of the oxalic acid into distilled water containing background ions prior to Fe(II) addition.

Suwannee River Fulvic Acid

Samples of Suwannee River Fulvic Acid were purchased from the International Humic Substances Society in Arvada, CO. An appropriate amount of the Suwannee River Fulvic Acid was measured and dissolved in

distilled water to obtain the desired DOC concentration. Background ions were added and the resultant test solution was deaerated and adjusted to pH 5.5 prior to soluble Fe(II) addition.

Thousand Acre Fulvic Acid

The Thousand Acre Fulvic Acid is a naturally occurring organic extracted from the Thousand Acre Reservoir in Athol, Massachusetts, and obtained for these studies from Dr. David Reckhow of the University of Massachusetts, Amherst. The concentration of the stock fulvic acid solution was 270 mg/L as DOC. Upon arrival at Virginia Tech the fulvic acid was filtered through Amicon Diaflo ultrafiltration membranes, YM Series with the following nominal molecular weight (MW) cut off levels:

Membrane	Nominal MW Cut-Off
YM 30	30,000
YM 10	10,000
YM 5	5,000
YM 2	1,000

Test solutions were prepared by diluting an appropriate amount from the different MW cut-offs with distilled water to a DOC concentration of 4 mg/L.

Alum Solution

The alum (600 g/mole) used in the coagulation studies was prepared at a 10 mg/mL concentration from reagent grade aluminum sulfate crystals. The alum solution was made prior to each coagulation experiment. During coagulation studies, the required amount of alum was pipetted directly from the stock solution into each water sample.

Soluble Iron Solution

The soluble Fe(II) stock solution was not stable for more than a few days due to $O_{2(aq)}$ intrusion and subsequent Fe(II) oxidation; therefore, it was prepared as needed. The stock solution was prepared using ferrous ammonium sulfate crystals ($Fe(NH_4)_2(SO_4)_2*xH_2O$) to a concentration of 0.5 mg/mL as Fe. The distilled water used in stock solution preparation was initially deaerated by bubbling $N_{2(g)}$ through the water for a minimum of 20 minutes, then acidified by the addition of H_2SO_4 to near pH 2 before Fe(II) addition. The stock solution was stored in a ground-glass bottle which was sealed with parafilm to minimize atmospheric O_2 transfer. During the oxidation studies and Fe(II) complexation studies, the required amount of Fe(II) was pipetted directly from the stock solution into the test water.

Bathophenanthroline Solution

The bathophenanthroline, 0.001 M solution was prepared by dissolving 0.0332 g 4,7-diphenyl-1,10-phenanthroline ($C_{24}H_{16}N_2$) in 50 mL ethyl alcohol and diluting with 50 mL of Milli-Q water. The solution was stored in a glass-stoppered reagent bottle at 25° C.

Sodium Acetate Solution

A 10% sodium acetate solution was prepared by dissolving 10 g sodium acetate in 100 mL of distilled water in a 125 mL separatory funnel. Two (2) mL of 0.001 M bathophenanthroline solution was added to the funnel and mixed very well. Next, 10 mL n-hexyl alcohol was added and mixed vigorously. The liquids were allowed to separate. The sodium acetate layer (the lower aqueous layer) was drawn off into a second separatory funnel and the separation procedure was repeated to insure complete removal of iron. The solution was stored in a glass-stoppered reagent bottle at 25° C.

EXPERIMENTAL PROCEDURES

Oxidation Studies

The oxidation studies were performed to investigate the degree of iron complexation which occurs in the presence of natually occurring organics, and to investigate the ability of various oxidants to oxidize this complexed iron. Organic acids used for this study were tannic

acid, Suwannee Rive Fulvic Acid, oxalic acid, and Thousand Acre Fulvic Acid. The oxidants used were potassium permanganate, chlorine dioxide and free chlorine.

The test solutions were prepared to contain a DOC concentration of 4 mg/L, with the exception that the tannic acid test solution was prepared to a concentration of 5 mg/L DOC. Prior to the start of each oxidation experiment the pH of the test solution was adjusted to 6.3 - 6.5. This pH value was chosen as representative of the pH condition anticipated in a treatment plant employing alum coagulation for DOC removal.

One hundred mL aliquots of the test solution were placed in 125 mL Ehrlenmeyer flasks and dosed with 0%, 30%, 60%, 100%, 150%, 200%, and 300% of the theoretical oxidant dose required to completely oxidize ferrous iron to ferric iron with no other oxidant demand present. The test was conducted over an hour period with the solution being shaken by hand regularly. Samples were taken from each flask at 15, 30, and 60 minute intervals following addition of the oxidant. The samples were passed through a 0.2 um Gelman membrane filter to remove particulates and then acidified with nitric acid (HNO_3) to stop the oxidizing reaction and preserve the sample. The residual Fe(II) concentration was determined using a Model 703 Perkin - Elmer atomic absorption spectrophotometer. The control (0% oxidant dose) sample served to

verify the concentration of Fe(II) at the beginning and end of the experiment, thereby allowing for an accurate measurement of Fe(II) removal by each oxidant.

As a check on the theoretical stoichiometry of reacting with Fe(II), the experiment was repeated with a water sample containing uncomplexed Fe(II) (i.e. no organic acid addition to the test sample). Water samples were dosed with 0%, 30%, 60%, 90%, 120%, and 150% of the stoichiometric requirement for Fe(II) oxidation by the oxidant. Following oxidant addition, the samples were allowed five minutes to react and then filtered through a 0.2 um Gelman membrane filter and acidified for residual Fe(II) analysis. In addition, those samples containing an excess amount of oxidant were titrated for residual oxidant concentration using the potentiometric titrator.

Coagulation Studies

The coagulation studies were performed to evaluate the removal of both DOC and Fe(II). The purpose of the experiments was to determine how the molecular weight of the complexing organics affected the degree of Fe(II) removal observed. The samples used for this study consisted of raw water from Lake Michie (Durham, North Carolina) and the Po River in Spotsylvania County, Virginia. In addition, Suwannee River Fulvic Acid (5.0 mg/L DOC) was used in the preparation of a test solution for alum coagulation. The Suwannee River Fulvic Acid was coagulated both with and without oxidant addition ($KMnO_4$; 1.5 mg/L).

The coagulation/flocculation experiments were performed using a standard Phipps and Bird (Richmond, VA) laboratory jar apparatus and square, glass coagulation jars. A 10 mg/mL stock solution of 600 g/mole alum was used. Sample size was dictated by the amount of sample available; one liter was the preferred sample size and was used with Po River and Durham, N.C. water samples. Due to the limited amount of Suwannee River Fulvic Acid available, sample sizes of 0.4 L were utilized.

The alum was added to the jars in doses which ranged from 0 mg/L to 90 mg/L; the 0 mg/L dose served as an experimental control. Because the Suwannee River Fulvic Acid test sample was not a "river water", two controls were utilized, one stirred on the jar tester, one not. With the stirrer operating at full speed, the alum was added and the samples were rapid mixed for two minutes at approximately 200 revolutions per minute (rpm). If an oxidant was used it was also added to each jar at this time. The pH was adjusted with sodium hydroxide (NaOH) and held constant between 6.0-6.3 throughout the experiment to insure a buffering capacity to allow the formation of $Al(OH)_{3(s)}$ to occur.

Following two minutes of rapid mixing, the paddle speed was reduced to 45 rpm for ten minutes, then to 25 rpm for ten minutes, and finally to 15 rpm for five minutes. The floc was allowed to settle for thirty

minutes. The supernatant was filtered through 0.2 um Gelman membrane filters, with a portion analyzed for DOC and the other portion acidified with HNO_3 and analyzed for residual Fe(II).

Additional analyses were performed on the supernatant from Po River and the Suwannee River Fulvic Acid jar tests. In the studies using the Po River, these samples were fractionated through the Amicon Diaflo ultrafiltration membranes, YM series: the raw water sample (control); the supernatant from the highest alum dose which coagulated color (70 mg/L); and the lowest alum dose which gave good iron removal (20 mg/L). The soluble iron and DOC of the fractionated samples was measured shortly after fractionation. In the experiments with the Suwannee River Fulvic Acid, the unstirred control sample (0 mg/L alum dose) and the 70 mg/L alum dose sample were fractionated with the Amicon Diaflo ultrafiltration membranes, YM series. The fractionated samples were analyzed for residual Fe(II) and DOC.

Bathophenanthroline Method for Differentiating Fe(II) and Fe(III) Species

Experiments using the bathophenanthroline method were designed to determine if bathophenanthroline could successfully extract complexed Fe(II) from organic matter. The organic sources included Thousand Acre Fulvic Acid, Suwannee River Fulvic Acid, oxalic Acid, tannic acid,

citric acid, glycine, and sodium glutamate. The test solutions were prepared to contain DOC concentrations which ranged between 3.0 mg/L and 10.0 mg/L.

Ten mL of the test solution was pipeted into a 125 mL separatory funnel. Four mL of 10% sodium acetate solution was added to the funnel to bring the pH to 4.0 (optimum pH for complexation to occur between Fe(II) and bathophenanthroline). Next, 15 mL of bathophenanthroline solution, 0.001 M, was added to the funnel and mixed. A 10 mL dose of n-hexyl alcohol was then added to the funnel, the stopper was placed on the funnel and the mixture was shaken thoroughly. The liquids were allowed at least five minutes to separate. After the liquids separated into two distinct layers, the lower aqueous layer was drawn off and discarded. The n-hexyl layer was drained into a 50 mL volumetric flask. The sides of the funnel and stopper were rinsed with ethyl alcohol which also drained into the volumetric flask. The rinsing procedure was performed twice. The solution in the flask was diluted to 50 mL by ethyl alcohol addition and mixed by shaking. The absorbancy of the solution was determined using a spectrophotometer with a wavelength of 533 mu.

The iron-bathophenanthroline color follows Beer's law; therefore, a plot of absorbance versus Fe(II) concentration yields a straight line. Using the bathophenanthroline method and uncomplexed iron standards a standard curve was developed to enable measurement of the Fe(II) extracted from the complexed samples.

ANALYTICAL TECHNIQUES

Residual Iron Concentration

All samples were preserved after filtration with the addition of 10% HNO_3. Fe(II) analysis was performed using a Perkin-Elmer (Norwalk, CT) atomic absorption spectrophotometer equipped with an air - acetylene flame and a low - level detention furnace. The Fe(II) was analyzed using the impact bead attachment which increased the sensitivity of the instrument. Fe(II) standards preserved in 10% HNO_3 were used to generate a standard calibration curve.

DOC Analysis

The DOC concentration of each sample was determined using a Dohrmann Envirotech Model DC - 54 Ultralow Level TOC analyzer. The operation and maintenance instructions prescribed by the manufacturer were adhered to. Duplicate measurements were made for each sample.

Oxidant Concentration

Oxidant concentrations were determined by the potentiometric titration method (Orion Autochemistry 960, Orion Research, Inc.) which utilized a Computer Aided Titrator (Fisher Model 465) equipped with a platinum - platinum electrode. The sample was titrated with a standard PAO titrant (0.00564N), with the endpoint automatically detected by a sign change in the second derivative of the titration curve.

Each oxidant was analyzed using potentionmetric titration procedures. Initially, the pH of the samples was adjusted using 1 mL of a pH 7.0 phosphate buffer. Next, 1 g of potassium iodide was added to the sample. The KI reacted with any residual oxidant present to form $I_{2(aq)}$, which was then titrated with the PAO titrant. Species concentrations were then determined from appropriate mathematical equations derived on the principle of chemical equivalence.

EXPERIMENTAL RESULTS

This chapter will present the results of both laboratory studies and field studies which were conducted to address the research objectives previously stated. The results are summarized into four subsections which include: Evaluation of the Bathophenanthroline Method for Differentiating Complexed Ferrous and Ferric Iron Species; Stoichiometry of Fe(II) Oxidation; Complexed Fe(II) Removal Studies; and Alum Coagulation for Complexed Fe(II) and DOC Removal. These subsections are further divided into various subheadings to present the data in an organized and concise manner.

EVALUATION OF THE BATHOPHENANTHROLINE METHOD FOR DIFFERENTIATING COMPLEXED FERROUS AND FERRIC IRON SPECIES

The bathophenanthroline method of Lee and Stumm (27) was examined for its potential use in differentiating complexed Fe(II) and Fe(III) iron species. Such information would be helpful in evaluating the ability of various oxidants to oxidize Fe(II) that was bound by DOC. Therefore, experiments were undertaken using known amounts of Fe(II) addition to deaerated water samples containing different concentrations of various DOC source compounds. The results from these experiments (shown in Table 1) indicate that the bathophenanthroline method was not able to extract or recover all of the Fe(II) that had been complexed by organic matter. In most of the experiments, bathophenanthroline addition extracted only 10% - 50% of the ferrous iron regardless of the

Table 1

Representative Data for the Recovery of Complexed Fe(II) Using the Bathophenanthroline Method

Organic Source	Organic Concentration (mg/L as DOC)	Fe(II) Added (mg/L)	Fe(II) Extracted w/ Bathophenanthroline Method (mg/L)
Thousand Acre Fulvic Acid MW>30k	5.27	1.0	0.37
Thousand Acre Fulvic Acid 5k>MW>1k	6.07	1.0	0.31
Thousand Acre Fulvic Acid MW>1k	4.0	1.0	0.40
Suwannee River Fulvic Acid	4.0	1.0	0.85
Oxalic Acid	4.0	1.0	0.84
Tannic Acid	10.0	1.0	0.50
	3.0	1.0	0.72
Citric Acid	10.0	1.0	0.23
	3.0	1.0	0.30
Glycine	5.0	1.0	0.13
Sodium Glutamate	5.0	1.0	0.11

Note: Temperature = 25 C, pH=4.0, which is the optimum pH for bathophenanthroline and Fe(II) complexation.

concentration of the organic matter present. In a few instances, it was able to extract more than 50% of the ferrous iron, but in no case was it able to extract 100%. Based upon the results obtained, it was decided that bathophenanthroline would not be used during the study.

Therefore, in the following oxidation experiments, the amount of iron removed following oxidant addition and subsequent sample filtration (0.2 um) was utilized as a method to determine the efficiency of each oxidant. The residual soluble iron concentration was measured and served as an indirect indicator of the effectiveness of the oxidant to oxidize complexed Fe(II).

STOICHIOMETRY OF FE(II) OXIDATION

Experiments were performed utilizing uncomplexed Fe(II) in an effort to verify the stoichiometry of Fe(II) oxidation by each of the oxidants used. Solutions were prepared by deaerating the background water prior to Fe(II) addition at pH 5.0. The experiment was performed at pH 5.0 using the following theoretical stoichiometry for each oxidant:

Fe:	$KMnO_4$	0.94 mg $KMnO_4$/ mg Fe
Fe:	HOCl	0.64 mg HOCl / mg Fe
Fe:	ClO_2	1.20 mg ClO_2 / mg Fe

The results of these studies are presented in Figures 6 - 8. The results verify the theoretical stoichiometry of reacting with iron and indicate complete removal of uncomplexed iron by each oxidant at doses between 100% and 110% of the stoichiometric requirement.

An item of importance regarding reaction stoichiometry was related to the use of ClO_2 for Fe(II) oxidation. Experiments involving Fe(II) oxidation by ClO_2 (Figure 9) indicated that a significant portion of the ClO_2 was being reduced to Cl^-, with a resulting transfer of 5 electrons. This result was verified by oxidation tests involving direct chlorite addition which resulted in significant amounts of Fe(II) oxidation (Figure 10). Therefore, further discussion related to stoichiometric dosages for ClO_2 are expressed on the basis of the five electron transfer reaction, 0.24 mg ClO_2 / mg Fe.

COMPLEXED FE(II) REMOVAL STUDIES

The purpose of these studies was to investigate the degree of iron complexation which occurs in the presence of naturally occurring organics and to investigate the ability of various oxidants to oxidize the complexed iron. The organics used for this study were tannic acid, Suwannee River Fulvic Acid, oxalic acid, and Thousand Acre Fulvic Acid. The oxidants used were $KMnO_4$, HOCl and ClO_2. Subsections have been established to initially present the laboratory results by considering each organic source separately. Iron was complexed with each organic using deaerated water at pH 5.0 - 5.5 for at least 12 - 24 hours. Prior

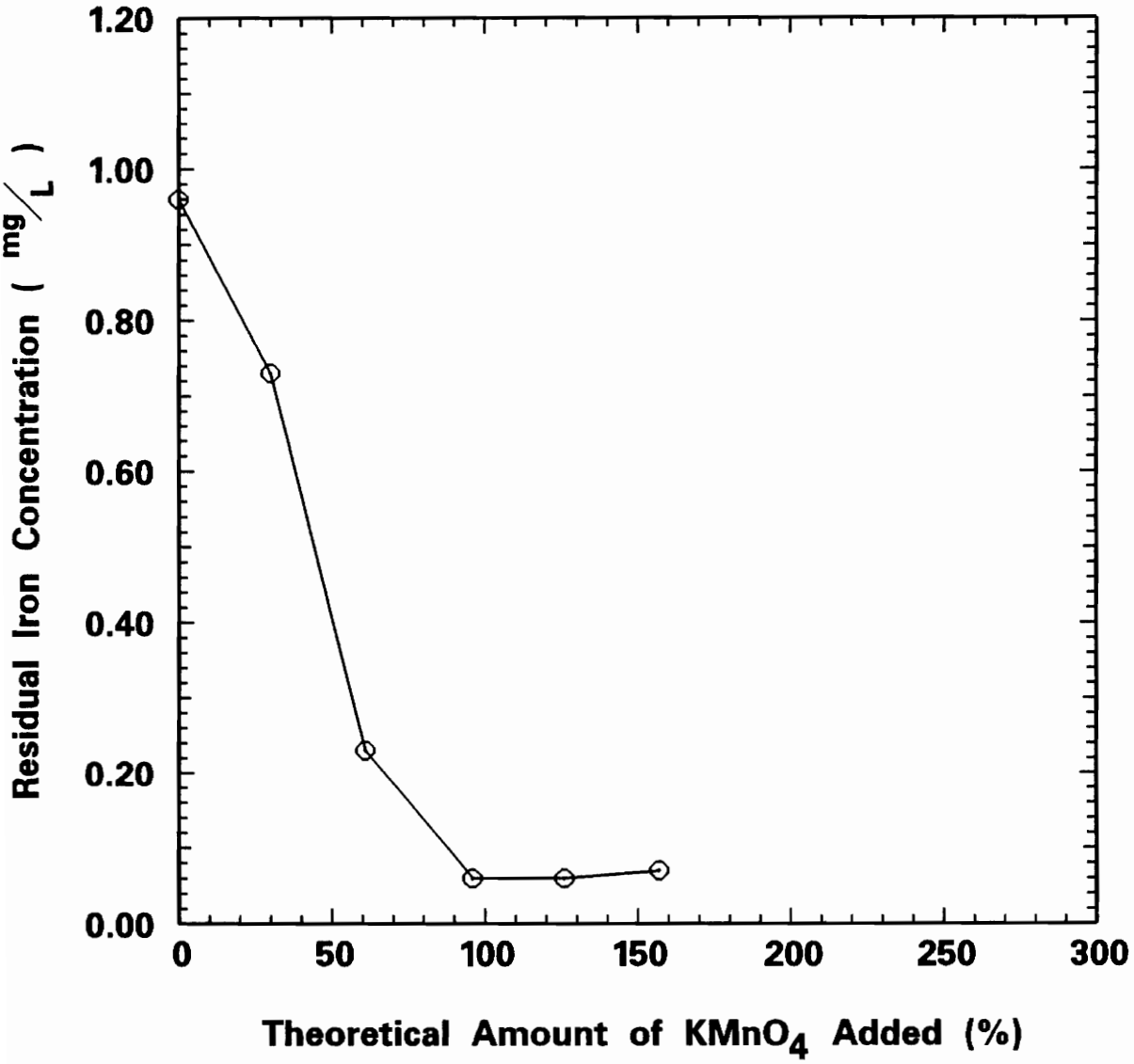


Figure 6 . Removal of Fe (II) by Permanganate at pH 5.Ø: [Initial Concentration of Fe (II) = Ø.96 mg/L, 1ØØ% Stoichiometric Dosage = Ø.94 mg/L $KMnO_4$, No Organic Added, Temperature = 25° C]

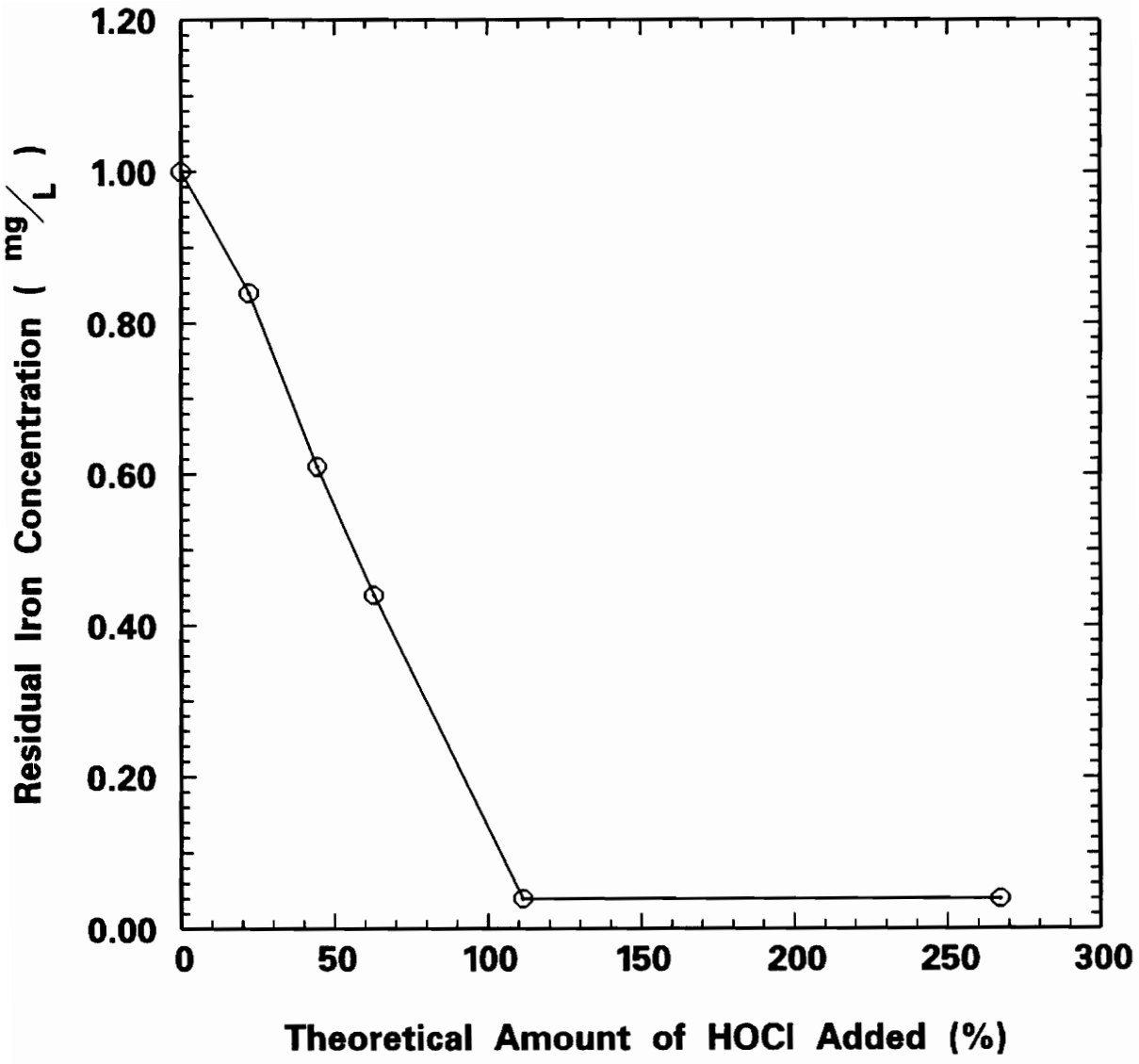


Figure 7 . Removal of Fe (II) by Chlorine at pH 5.Ø: [Initial Concentration of Fe (II) = 1.ØØ mg/L, 1ØØ% Stoichiometric Dosage = Ø.64 mg/L HOCl, No Organic Added, Temperature = 25° C]

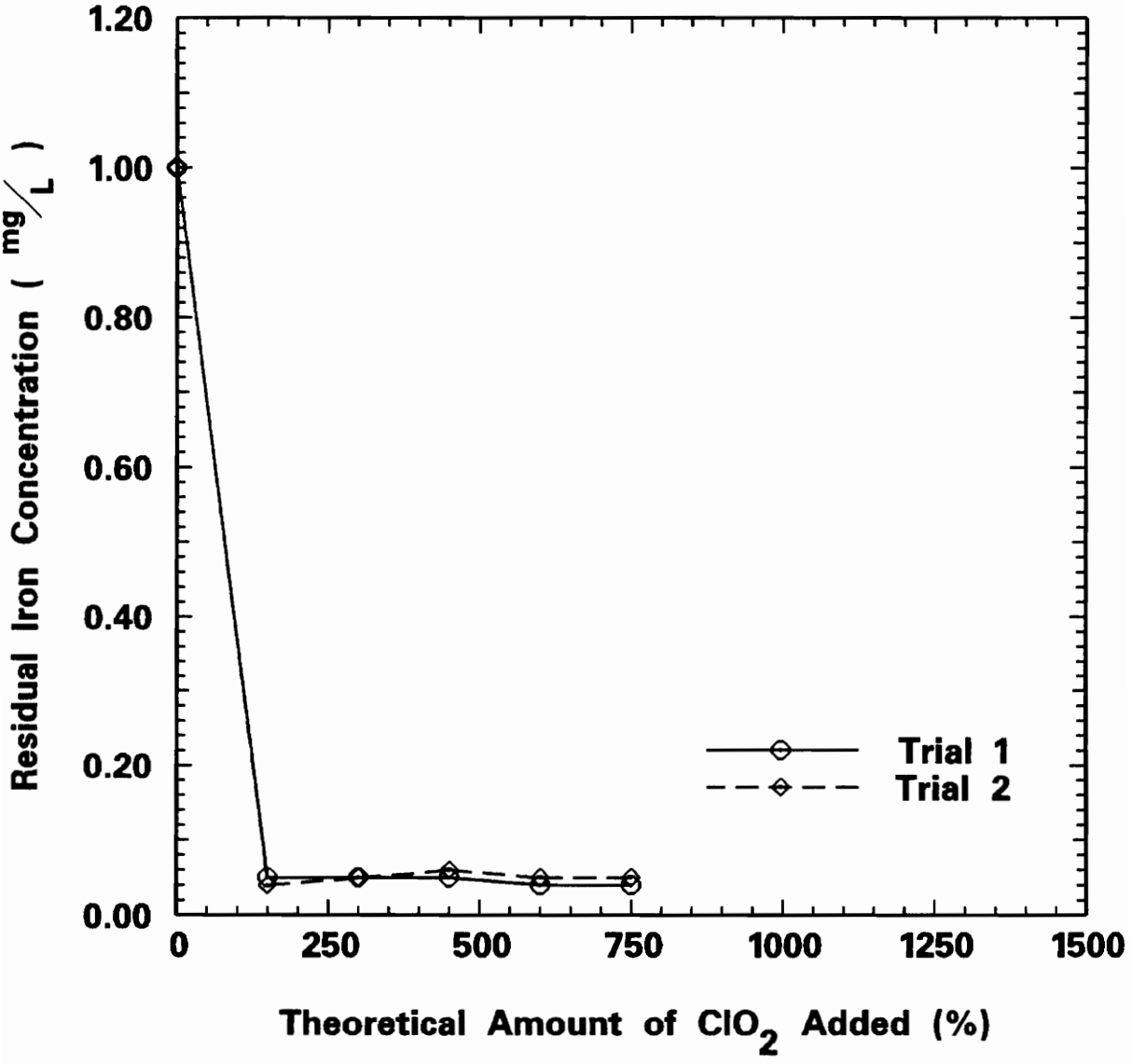


Figure 8. Removal of Fe (II) by Chlorine Dioxide at pH 5.Ø: [Initial Concentration of Fe (II) = 1.ØØ mg/L, 1ØØ% Stoichiometric Dosage = Ø.24 mg/L ClO_2, No Organic added, Temperature = 25° C]

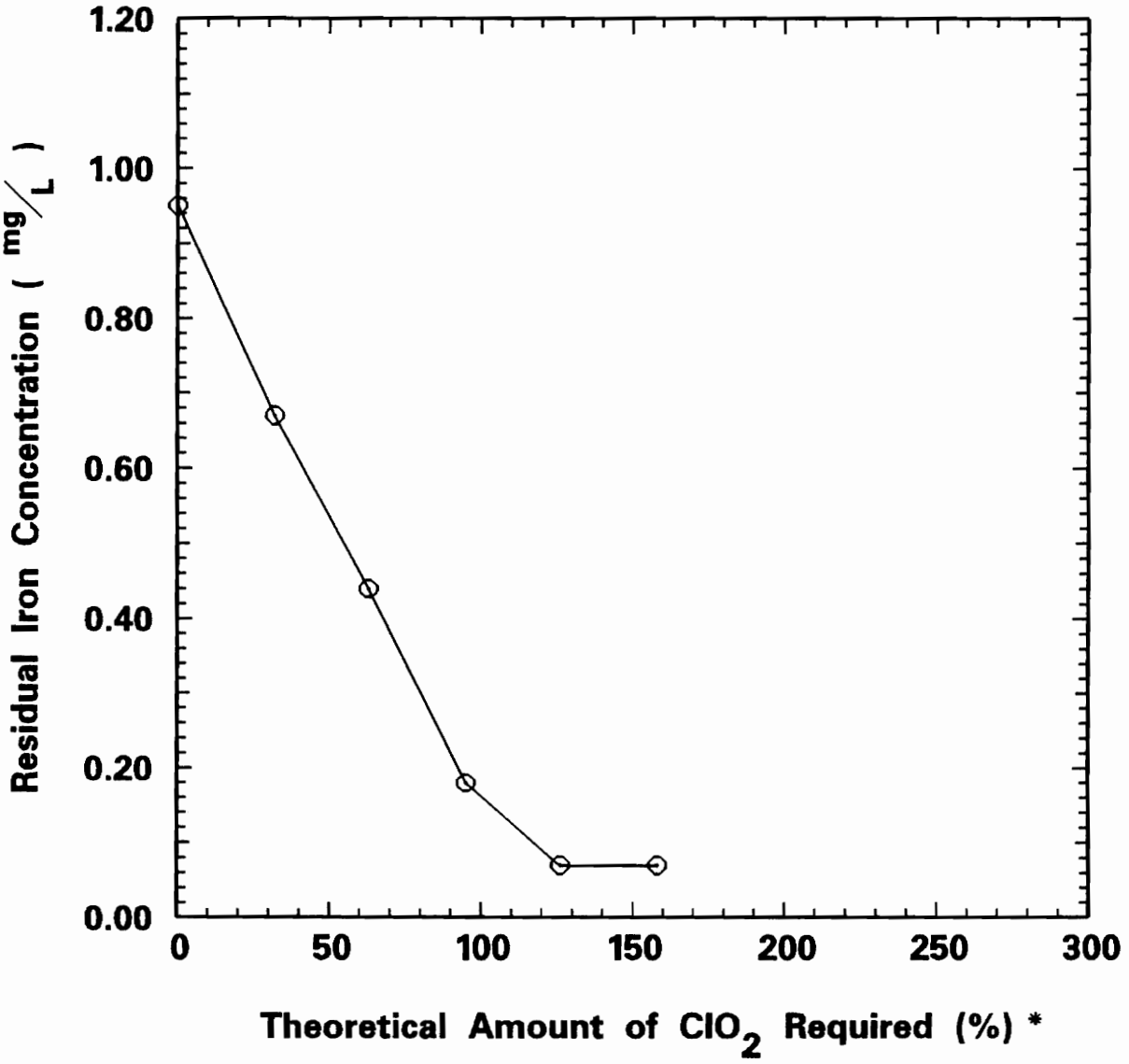


Figure 9. Removal of Fe (II) by Chlorine Dioxide at pH 5.Ø: [Initial Concentration of Fe (II) = Ø.95 mg/L, No Organic added, Temperature = 25° C]

* Amounts of ClO_2 based on reduction of $ClO_2 \xrightarrow{5e^-} Cl^-$

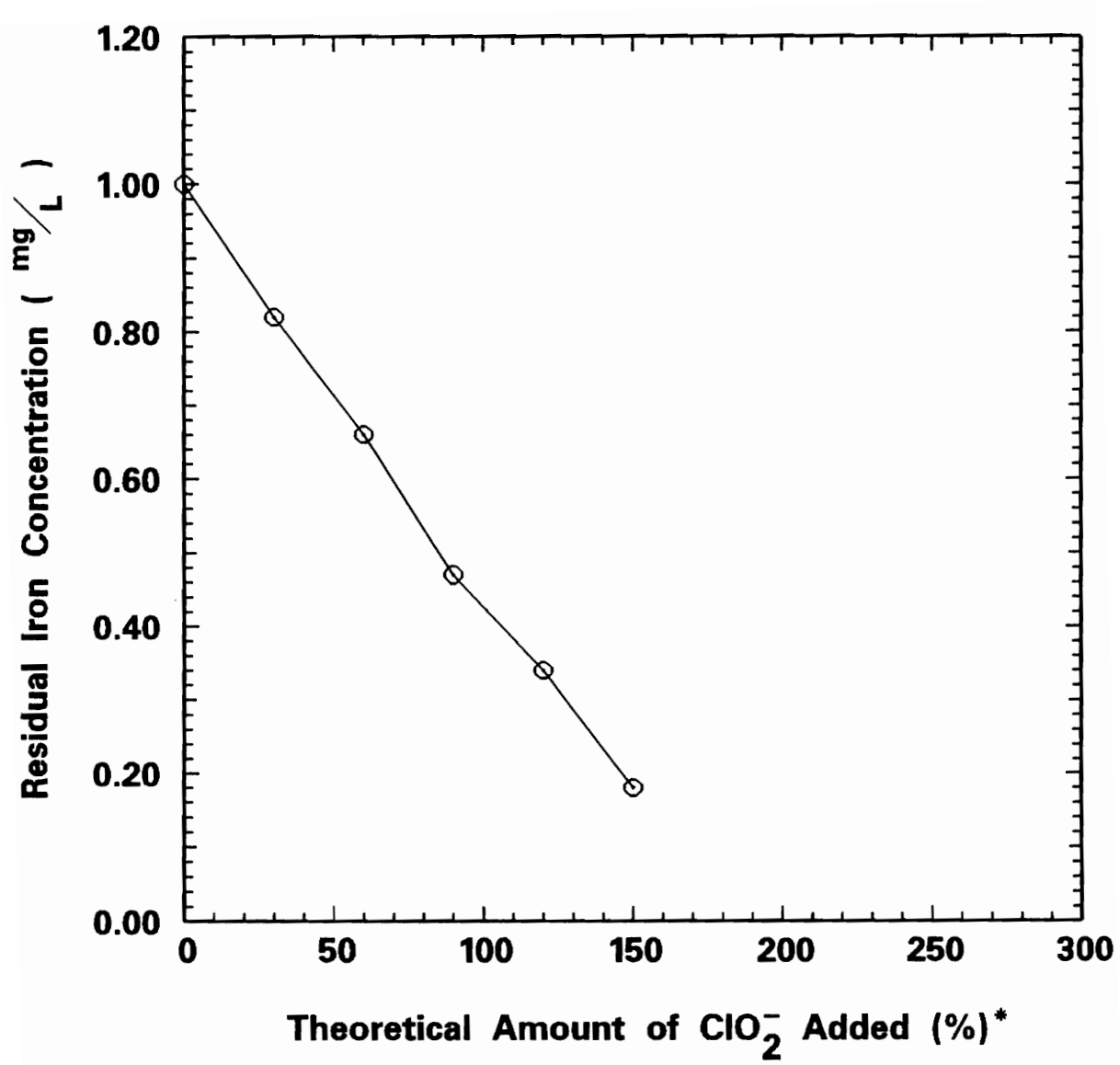


Figure 10. Removal of Fe (II) Complexed by Chlorite at pH 5.Ø: [Initial Concentration of Fe (II) = 1.ØØ mg/L, 1ØØ% Stoichiometric Dosage = Ø.3Ø mg/L ClO_2, No Organic Added, Temperature = 25° C]

* Amounts of ClO_2^- based on reduction of $ClO_2^- \xrightarrow{4e} Cl^-$

to the start of the experiment the pH was increased to 6.3 - 6.5, which is representative of the pH condition anticipated in a treatment plant employing alum coagulation for DOC removal.

Fe(II) Complexation by Tannic Acid

Data presented in Figures 11 through 13 indicate the ability of $KMnO_4$, HOCl, and ClO_2 to oxidize Fe(II) which had been complexed with tannic acid. The data demonstrate that the iron complexed with the tannic acid was not effectively removed by either $KMnO_4$, HOCl or ClO_2, regardless of the oxidant dose utilized. The largest amount of iron removed by $KMnO_4$ addition occurred after thirty minutes using a dose of 1.41 mg/L (150% of the stoichiometric dose, based on Fe(II) oxidation alone). HOCl addition yielded only 10% Fe(II) removal using a 200% stoichiometric dose and a sixty minutes reaction time. Less than 10% of the Fe(II) was removed by ClO_2 using a 1500% stoichiometric dose regardless of the reaction time.

These data indicate only a minimal amount of Fe(II) is removed between the sampling periods. This result indicated the possibility of a very slow rate of oxidation for the Fe(II) - tannic acid complexes. Theis and Singer (19) demonstrated a similar inhibitory effect of tannic acid on Fe(II) oxidation by dissolved oxygen. The authors showed that the rate of oxygen consumption was much slower for the Fe(II) - tannic acid system than for uncomplexed Fe(II), indicating a reduced rate of Fe(II) oxidation.

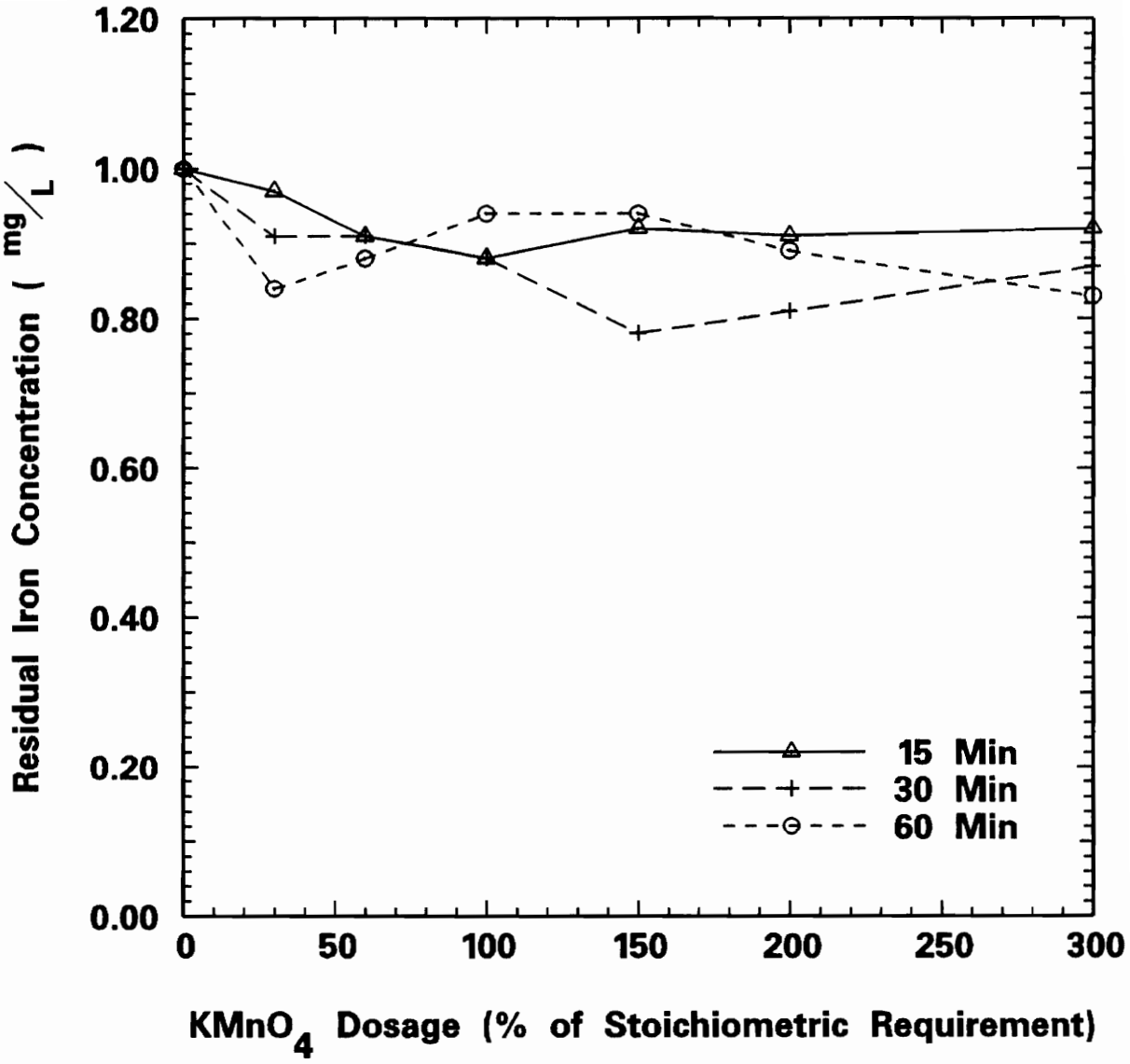


Figure 11. Removal of Fe (II) Complexed with Tannic Acid by Permanganate at pH 6.4: [Initial Concentration of Fe (II) = 1.ØØ mg/L, 1ØØ% Stoichiometric Dosage = Ø.94 mg/L $KMnO_4$, Concentration of Tannic Acid = 5 mg/L, Temperature = 25° C]

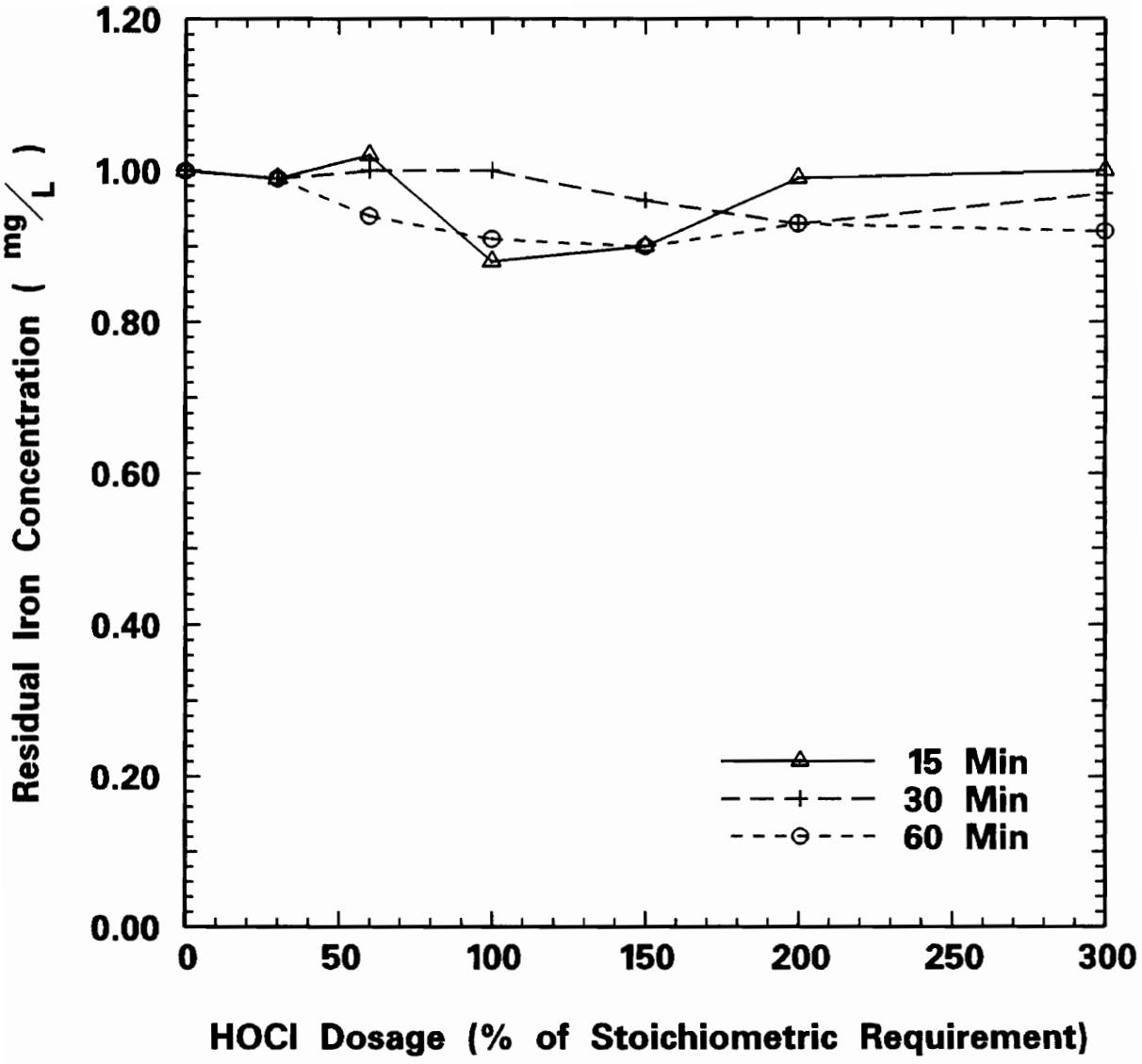


Figure 12. Removal of Fe (II) Complexed with Tannic Acid by Chlorine at pH 6.4: [Initial Concentration of Fe (II) = 1.ØØ mg/L, 1ØØ% Stoichiometric Dosage = Ø.64 mg/L HOCl, Concentration of Tannic Acid = 5 mg/L, Temperature = 25° C]

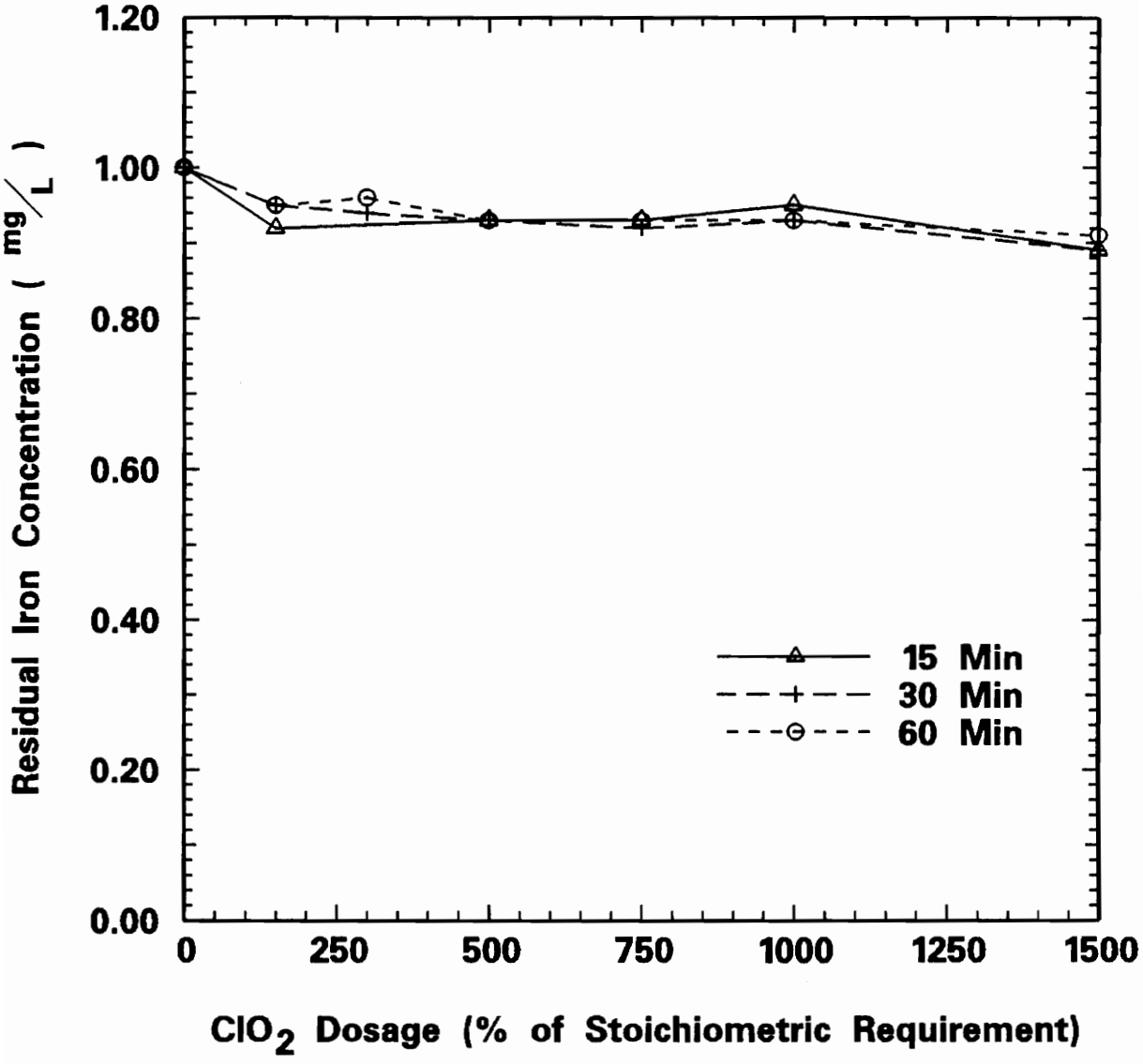


Figure 13. Removal of Fe (II) Complexed with Tannic Acid by Chlorine Dioxide at pH = 6.5: [Initial Concentration of Fe (II) = 1.ØØ mg/L. 1ØØ% Stoichiometric Dosage = Ø.24 mg/L ClO_2. Concentration of Tannic Acid = 5 mg/L. Temperature = 25° C]

Fe(II) Complexation by Suwannee River Fulvic Acid

Data presented in Figures 14 through 16 demonstrate the ability of $KMnO_4$, HOCl, and ClO_2 to remove Fe(II) which has been complexed with Suwannee River Fulvic Acid. Complexed Fe(II) was successfully removed by $KMnO_4$ to a residual iron concentration less than 0.3 mg/L using a 300% stoichiometric dose with a fifteen minute reaction time, a 150% dose with a thirty minute reaction time, or a 100% dose with a sixty minute reaction time (Figure 14). After sixty minutes, the 300% dose effectively removed 98% of the complexed Fe(II), indicating that the ability of $KMnO_4$ to promote Fe(II) removal complexed by Suwannee River Fulvic Acid was much greater than that observed for the Fe(II)-tannic acid system.

Free chlorine also removed Fe(II) complexed by Suwannee River Fulvic Acid but to a lesser degree than that observed with $KMnO_4$, (Figure 15). The secondary MCL of 0.3 mg/L was not obtained, but approximately 40% of the Fe(II) was removed following the sixty minute reaction time. Apparently, HOCl did not oxidize the complexed Fe(II) as effectively as $KMnO_4$.

Unfortunately, ClO_2 was not an effective oxidant for the Fe(II)-Suwannee River Fulvic Acid complex (Figure 16) as it removed less than 10% of the iron regardless of the dose or time increment. However,

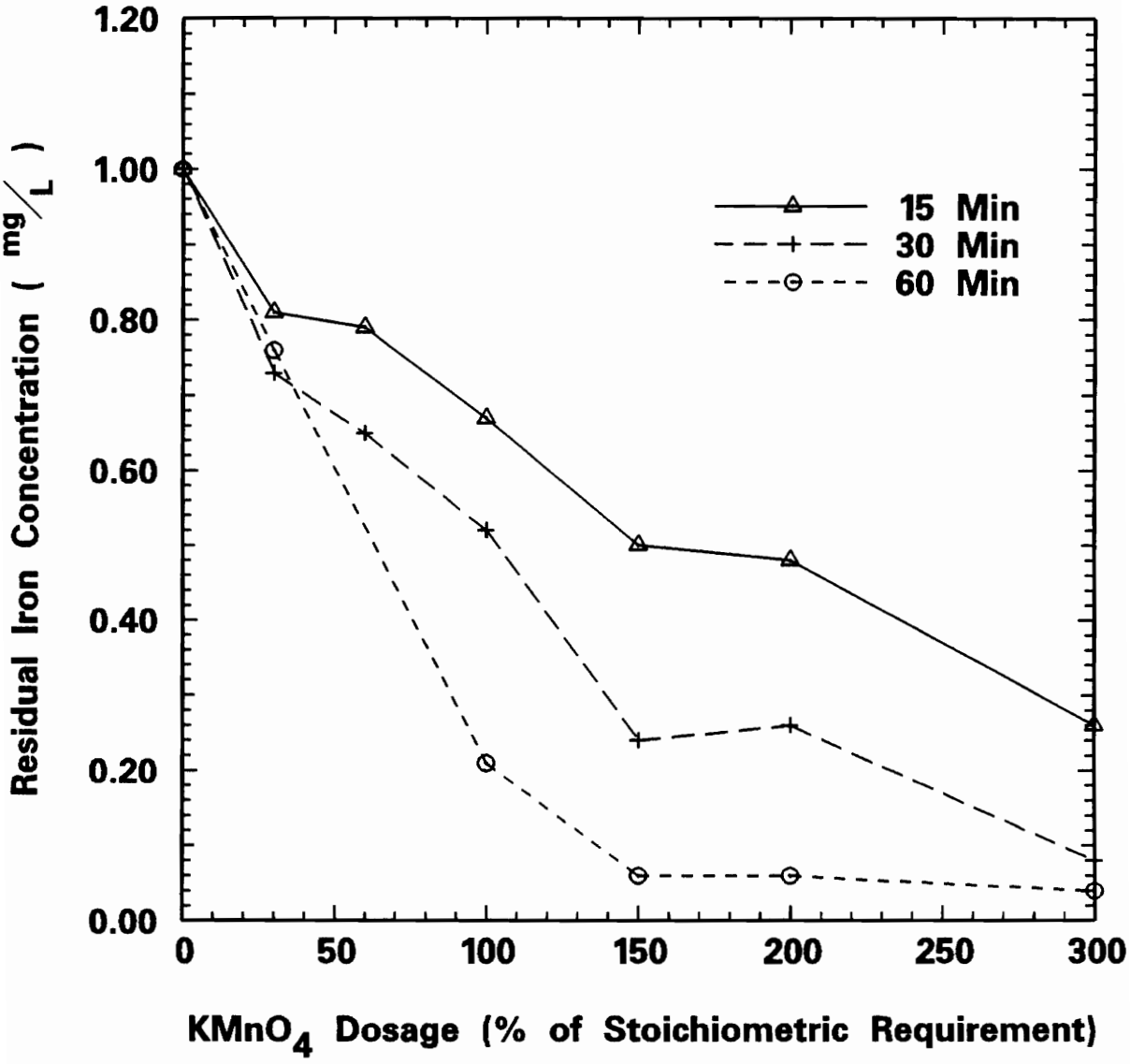


Figure 14. Removal of Fe (II) Complexed with Suwannee River Fulvic Acid by Permanganate at pH 6.4: [Initial Concentration of Fe (II) = 1.00 mg/L, 100% Stoichiometric Dosage = 0.94 mg/L $KMnO_4$ Concentration of Suwannee River Fulvic Acid = 4 mg/L, Temperature = 25° C]

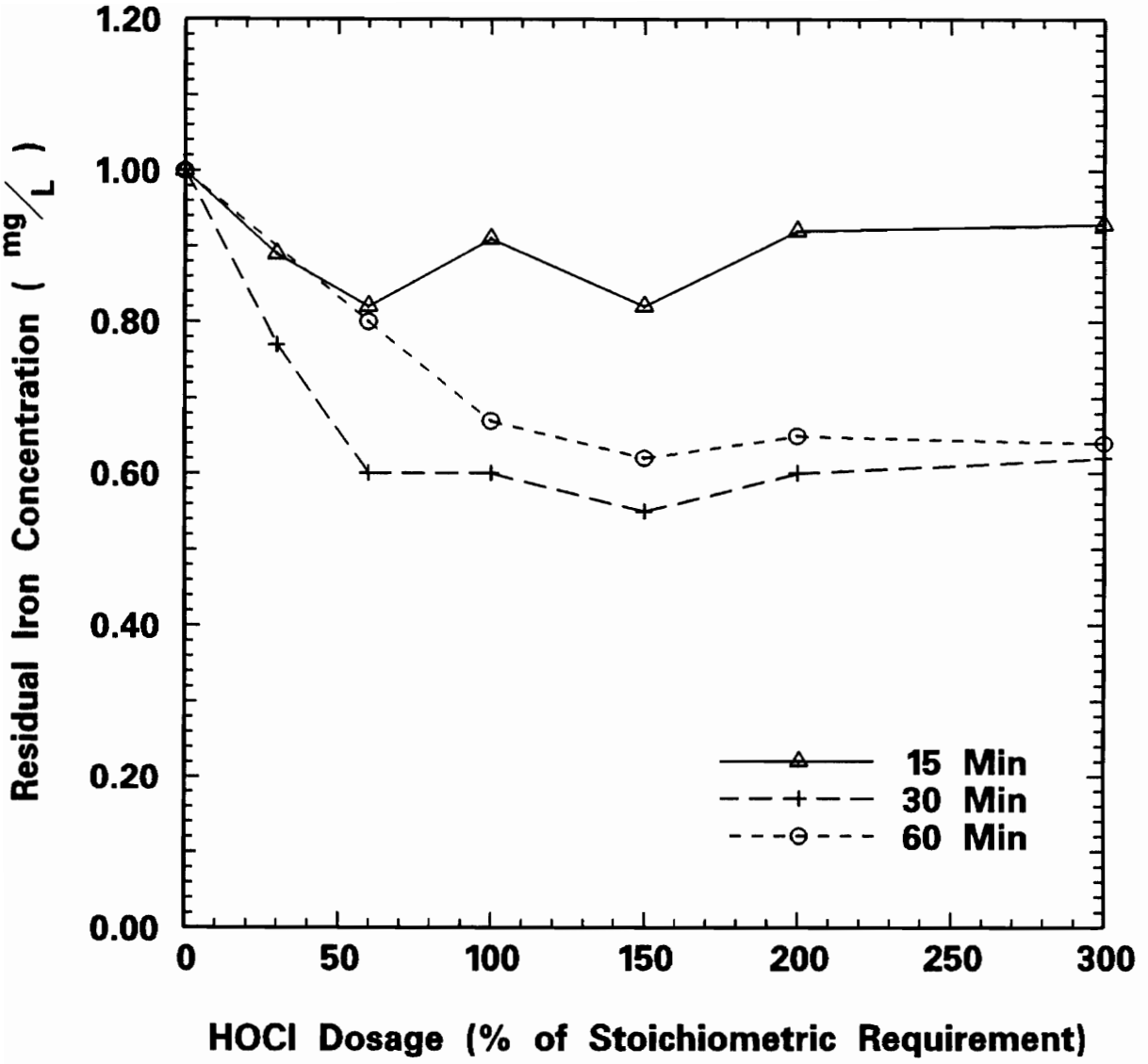


Figure 15. Removal of Fe (II) Complexed with Suwannee River Fulvic Acid by Chlorine at pH 6.4: [Initial Concentration of Fe (II) = 1.ØØ mg/L, 1ØØ% Stoichiometric Dosage = Ø.64 mg/L HOCl, Concentration of Suwannee River Fulvic Acid = 4 mg/L, Temperature = 25° C]

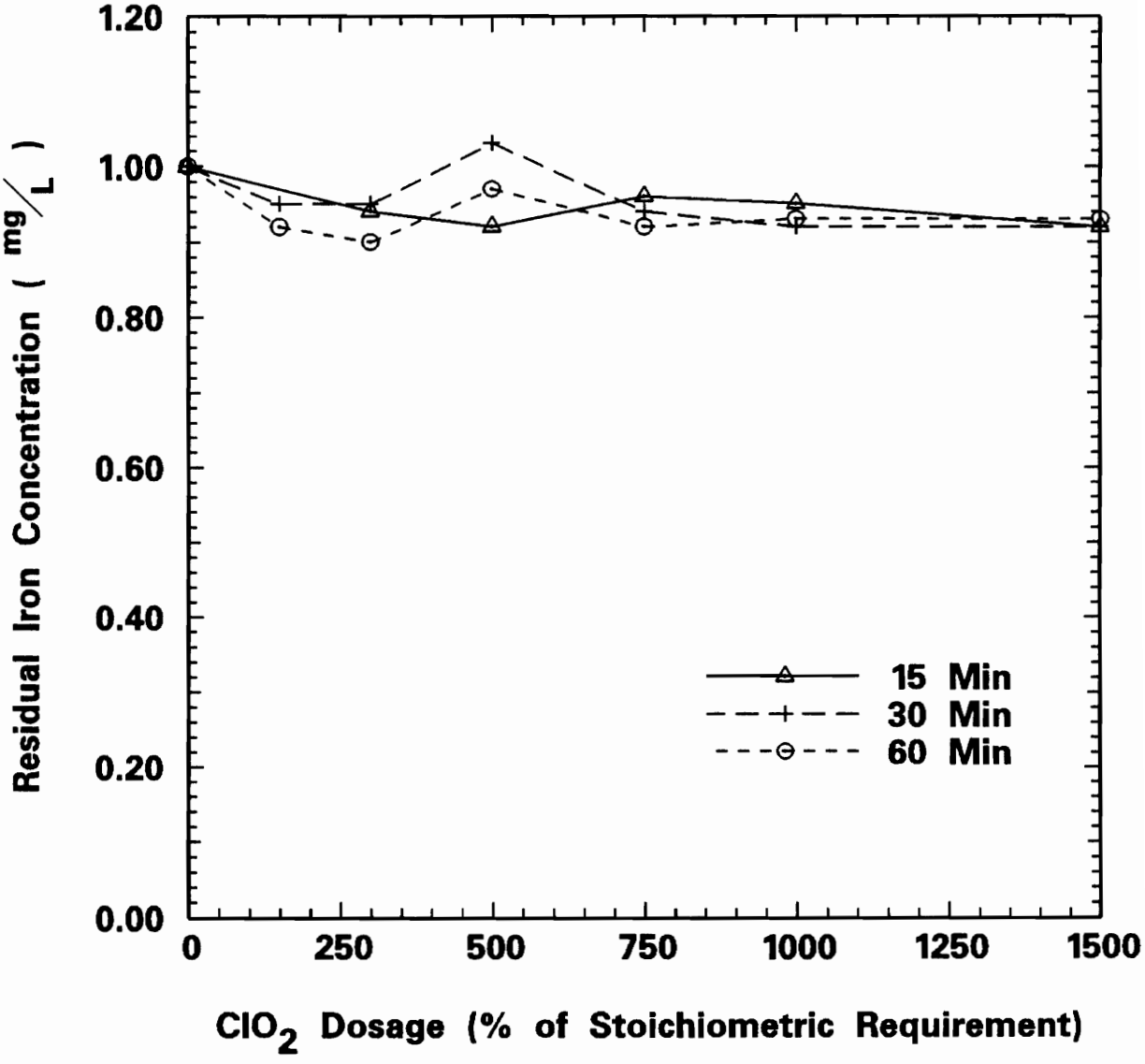


Figure 16. Removal of Fe (II) Complexed with Suwanee River Fulvic Acid by Chlorine Dioxide at pH = 6.3: [Initial Concentration of Fe (II) = 1.ØØ mg/L, 1ØØ% Stoichiometric Dosage = Ø.24 mg/L ClO_2 Concentration of Suwannee River Fulvic Acid = 4 mg/L. Temperature = 25° C]

based upon the amount of Fe(II) removed by $KMnO_4$ and HOCl, it was concluded that complexation by Suwannee River Fulvic Acid did not retard the removal of Fe(II) as strongly as the tannic acid complex.

Fe(II) Complexation by Oxalic Acid

The Fe(II) complexed with oxalic acid was very successfully removed by $KMnO_4$, HOCl, and ClO_2; typical data are contained in Figures 17 through 19. Permanganate addition removed 89% of the Fe(II) with a 100% stoichiometric dose and a fifteen minute reaction time. Removal increased to 98% following an additional fifteen minute reaction time.

Complexed Fe(II) was efficiently removed to concentrations below 0.3 mg/L using a 150% dose with a fifteen minute reaction time, a 105% dose with a thirty minute reaction time, or a 95% dose with a sixty minute reaction time. Essentially complete Fe(II) removal was achieved in sixty minutes using a 200% stoichiometric dose of HOCl.

Using ClO_2, 98% of the complexed Fe(II) was removed by a 200% stoichiometric dose and a thirty minute reaction time. Essentially 100% removal of the complexed Fe(II) was observed after sixty minutes. It would appear since each oxidant was able to successfully remove large percentages of complexed Fe(II) in rather short reaction times, the oxalic acid does not retard the oxidation of Fe(II) as strongly as the tannic acid complex and the Suwannee River complex.

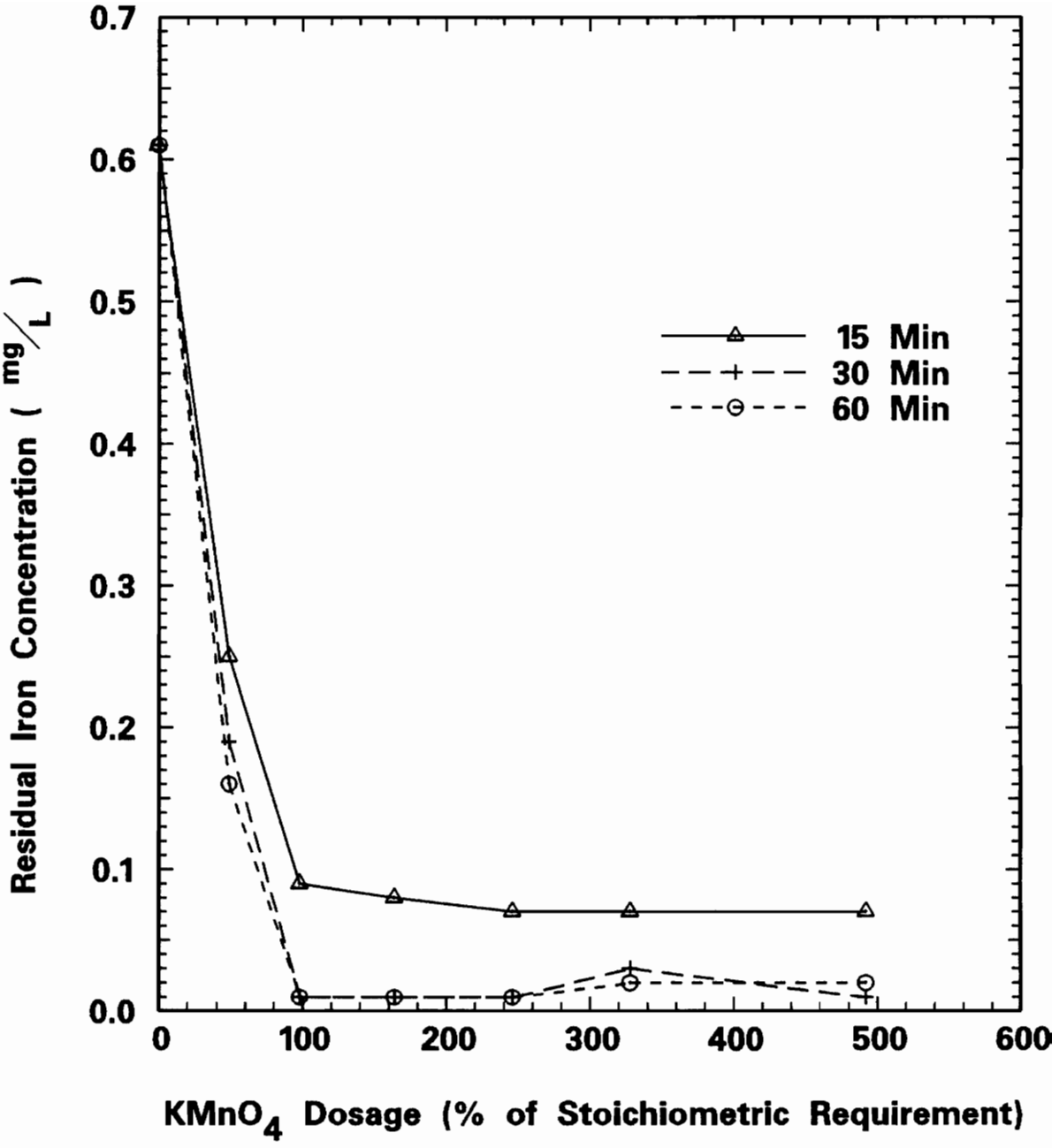


Figure 17. Removal of Fe (II) Complexed with Oxalic Acid by Permanganate at pH = 5.3: [Initial Concentration of Fe (II) = Ø.61 mg/L, 1ØØ% Stoichiometric Dosage = Ø.57 mg/L $KMnO_4$, Concentration of Oxalic Acid = 4 mg/L, Temperature = 25° C]

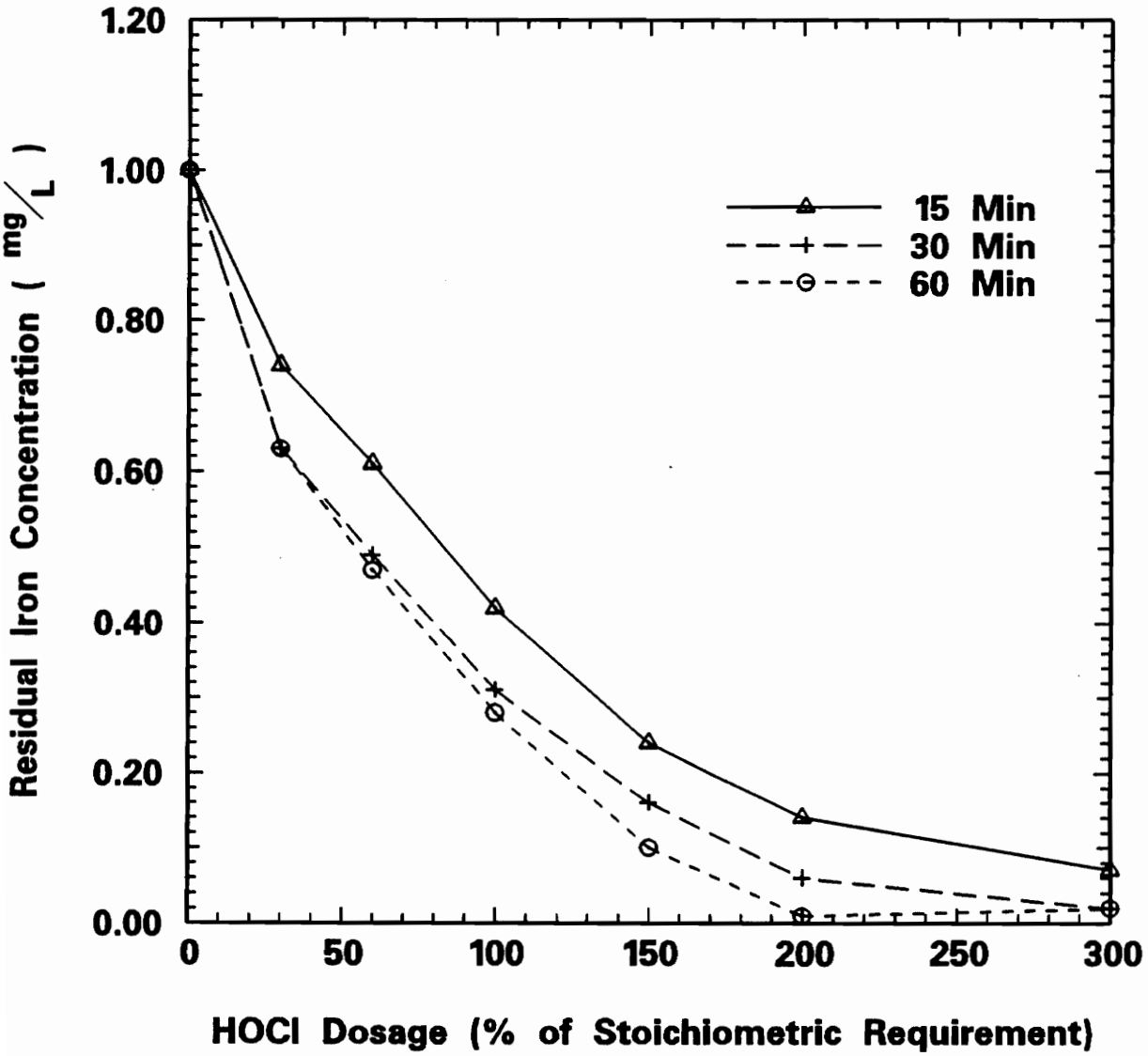


Figure 18. Removal of Fe (II) Complexed with Oxalic Acid by Chlorine at pH = 5.1: [Initial Concentration of Fe (II) = 1.ØØ mg/L, 1ØØ% Stoichiometric Dosage = Ø.64 mg/L HOCl, Concentration of Oxalic Acid = 4 mg/L, Temperature = 25° C]

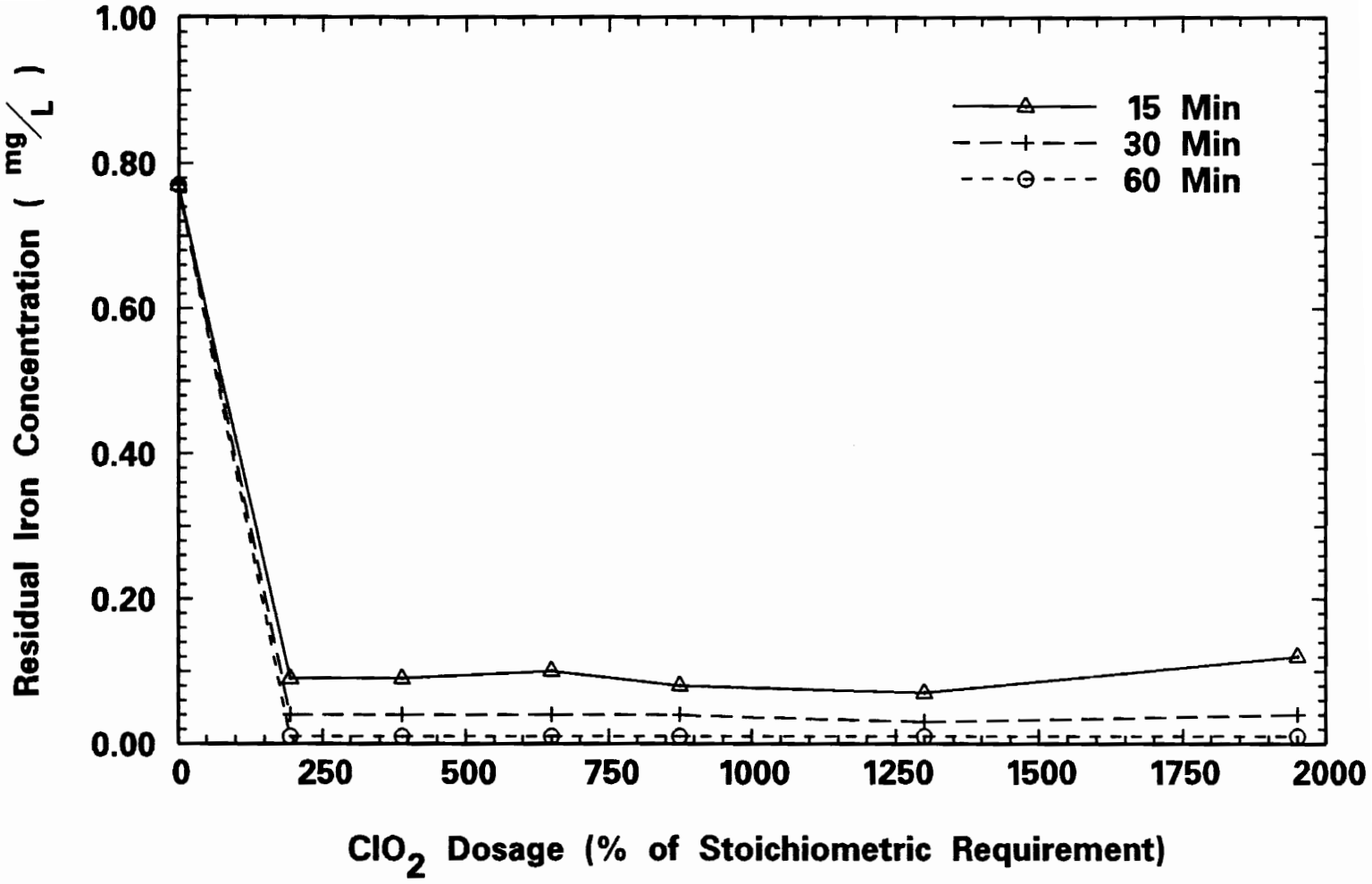


Figure 19. Removal of Fe (II) Complexed with Oxalic Acid by Chlorine Dioxide at pH 5.5: [Initial Concentration of Fe (II) = Ø.77 mg/L, 1ØØ% Stoichiometric Dosage = Ø.18 mg/L ClO_2. Concentration of Fe (II) = Ø.77 mg/L. Concentration of Oxalic Acid = 4 mg/L. Temperature = 25° C]

Fe(II) Complexation by Thousand Acre Fulvic Acid

The Thousand Acre Fulvic Acid was separated by molecular weight (MW) using Amicon Diaflo ultrafiltration membranes (YM Series) with the following nominal molecular weight cut-off levels: MW > 30,000, MW > 10,000, MW > 5,000, MW > 1,000. According to the manufacturer (28) the nominal molecular weight (MW) cut off level refers to the MW at which the membrane rejects 90% of the compound.

Data presented in Figure 20 are the results of studies involving $KMnO_4$ addition to oxidize Fe(II) that was complexed by the highest molecular weight (MW > 30k) fraction of the Thousand Acre Fulvic Acid. $KMnO_4$ was only able to remove 18% of the complexed Fe(II) following a sixty minute reaction time and a 300% stoichiometric dose. Previously mentioned studies have shown that HOCl and ClO_2 were not able to remove the complexed Fe(II) as effectively as $KMnO_4$; therefore, these oxidants were not evaluated for this molecular weight fraction.

Data in Figures 21 through 23 show the relative potential for each oxidant to remove Fe(II) that was previously complexed by the 30k > MW > 10k fraction of the Thousand Acre Fulvic Acid. $KMnO_4$ was able to remove 22% of the complexed Fe(II) with essentially no change in removal between the 100% dose and the 300% dose. In addition, reaction time made no significant difference in Fe(II) removal. Free chlorine addition had virtually no effect on the complexed Fe(II), resulting in less than 5% Fe(II) removal regardless of reaction time or HOCl dose.

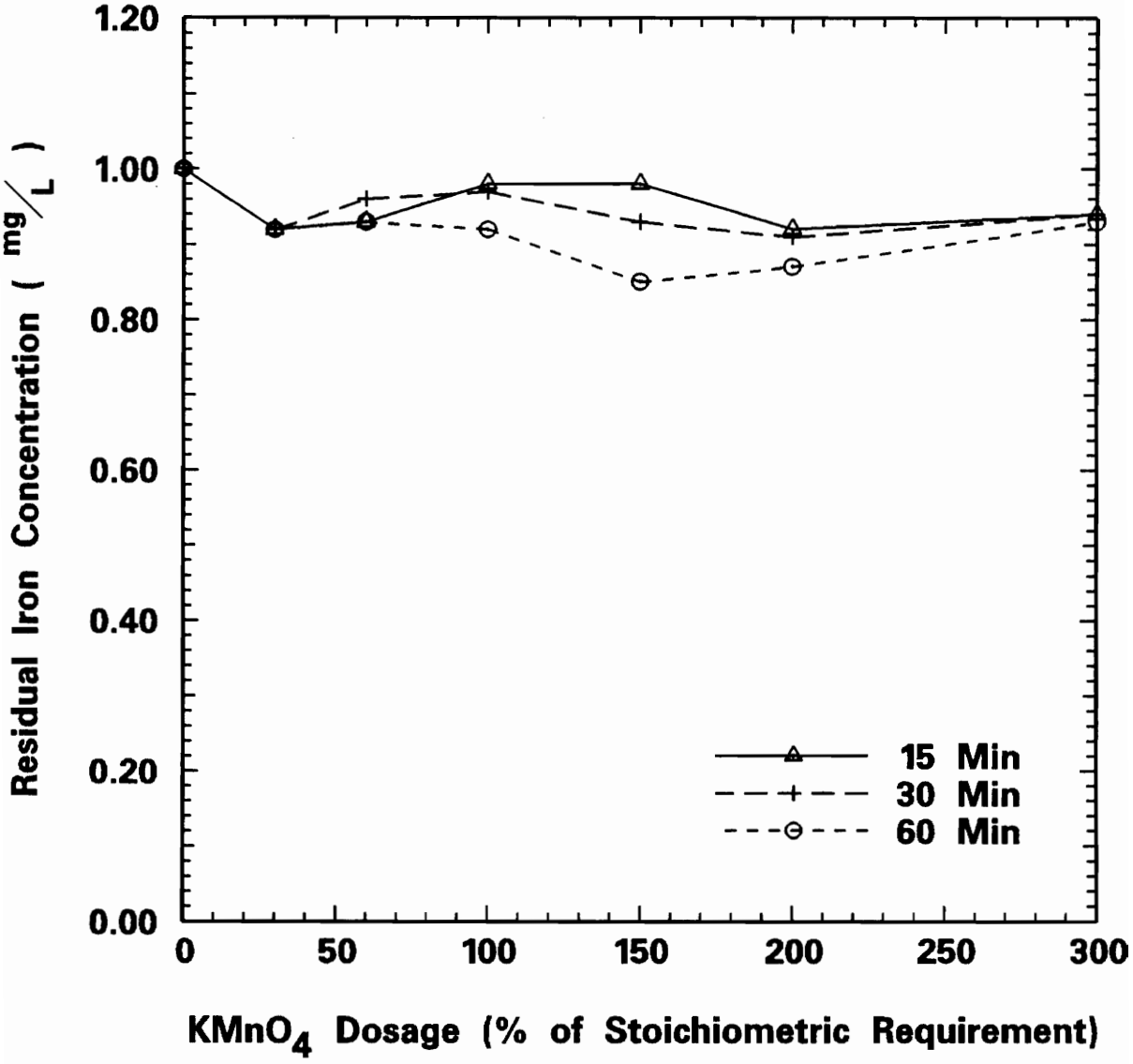


Figure 20. Removal of Fe (II) Complexed with Thousand Acre Fulvic Acid, MW>30k, by Permanganate at pH 6.4: [Initial Concentration of Fe (II) = 1.00 mg/L, 100% Stoichiometric Dosage = 0.94 mg/L $KMnO_4$, Concentration of Thousand Acre Fulvic Acid = 4 mg/L, Temperature = 25° C]

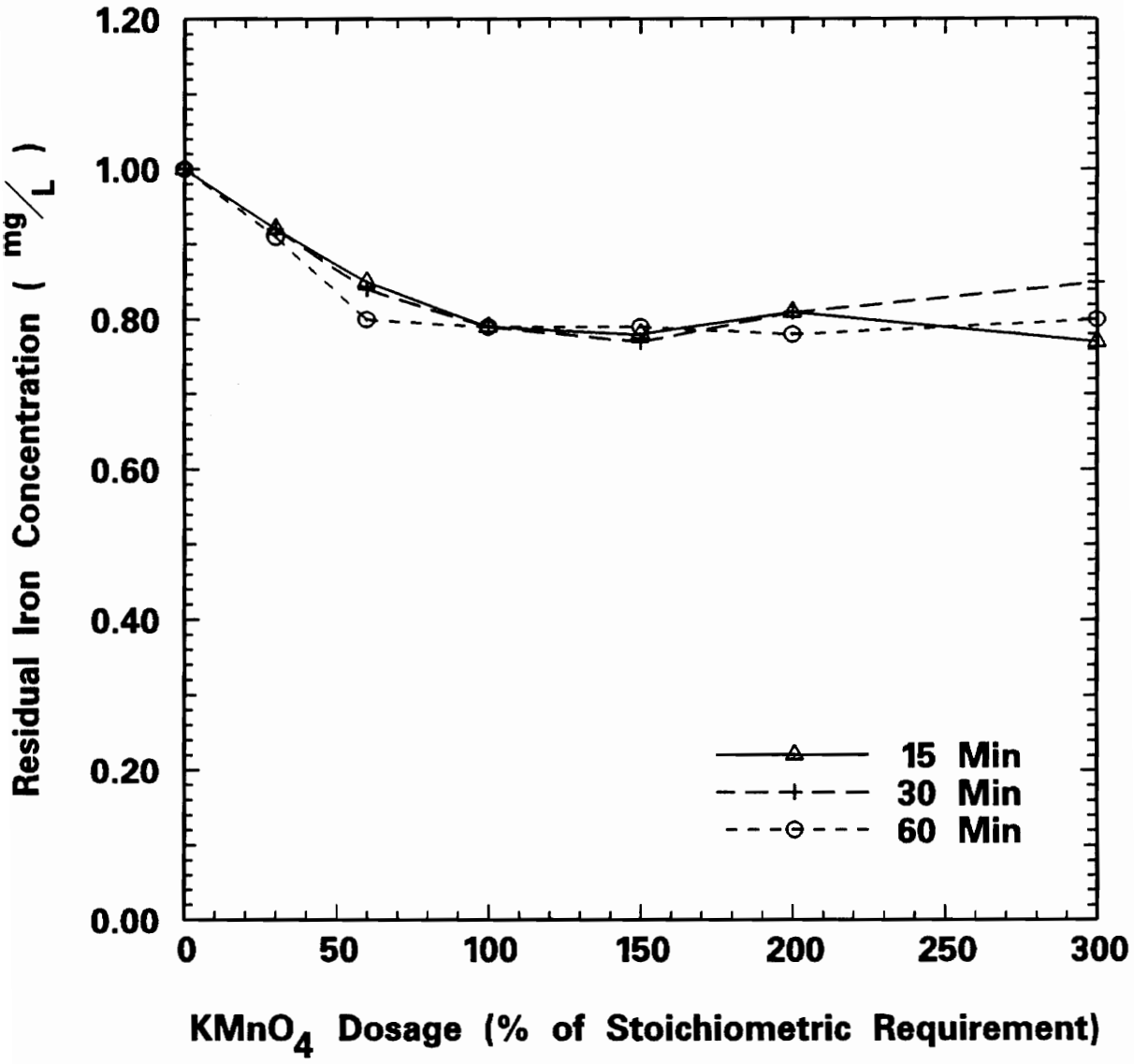


Figure 21. Removal of Fe (II) Complexed with Thousand Acre Fulvic Acid, 30k>MW>10k, by Permanganate at pH 6.4: [Initial Concentration of Fe (II) = 1.00 mg/L, 100% Stoichiometric Dosage = 0.94 mg/L $KMnO_4$, Concentration of Thousand Acre Fulvic Acid = 4 mg/L, Temperature = 25° C]

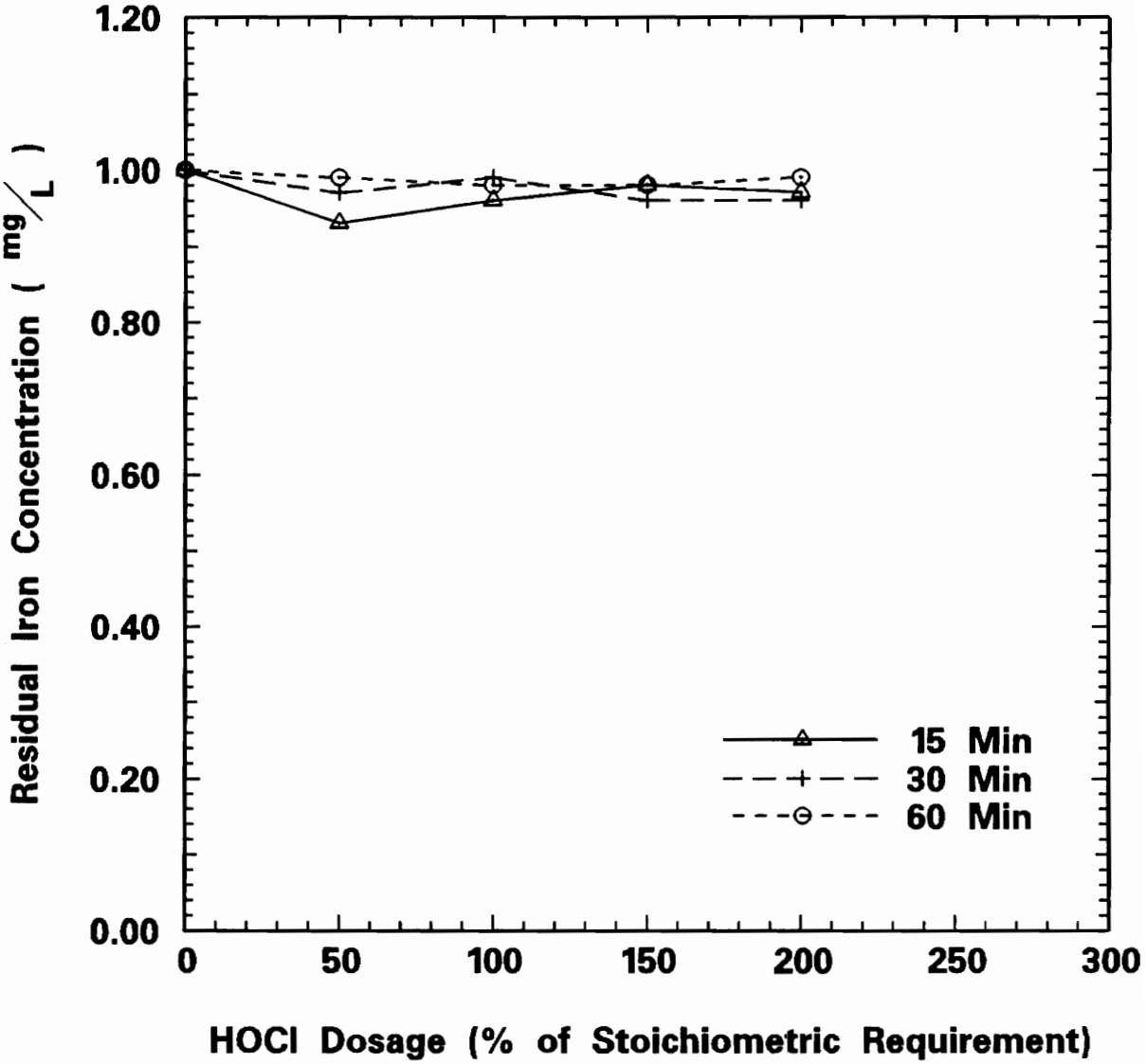


Figure 22. Removal of Fe (II) Complexed with Thousand Acre Fulvic Acid, 3ØK > MW > 1ØK, by Chlorine at pH = 6.4: [Initial Concentration of Fe (II) = 1.ØØ mg/L, 1ØØ% Stoichiometric Dosage = Ø.64 mg/L HOCl, Concentration of Thousand Acre Fulvic Acid = 4 mg/L, Temperature = 25° C]

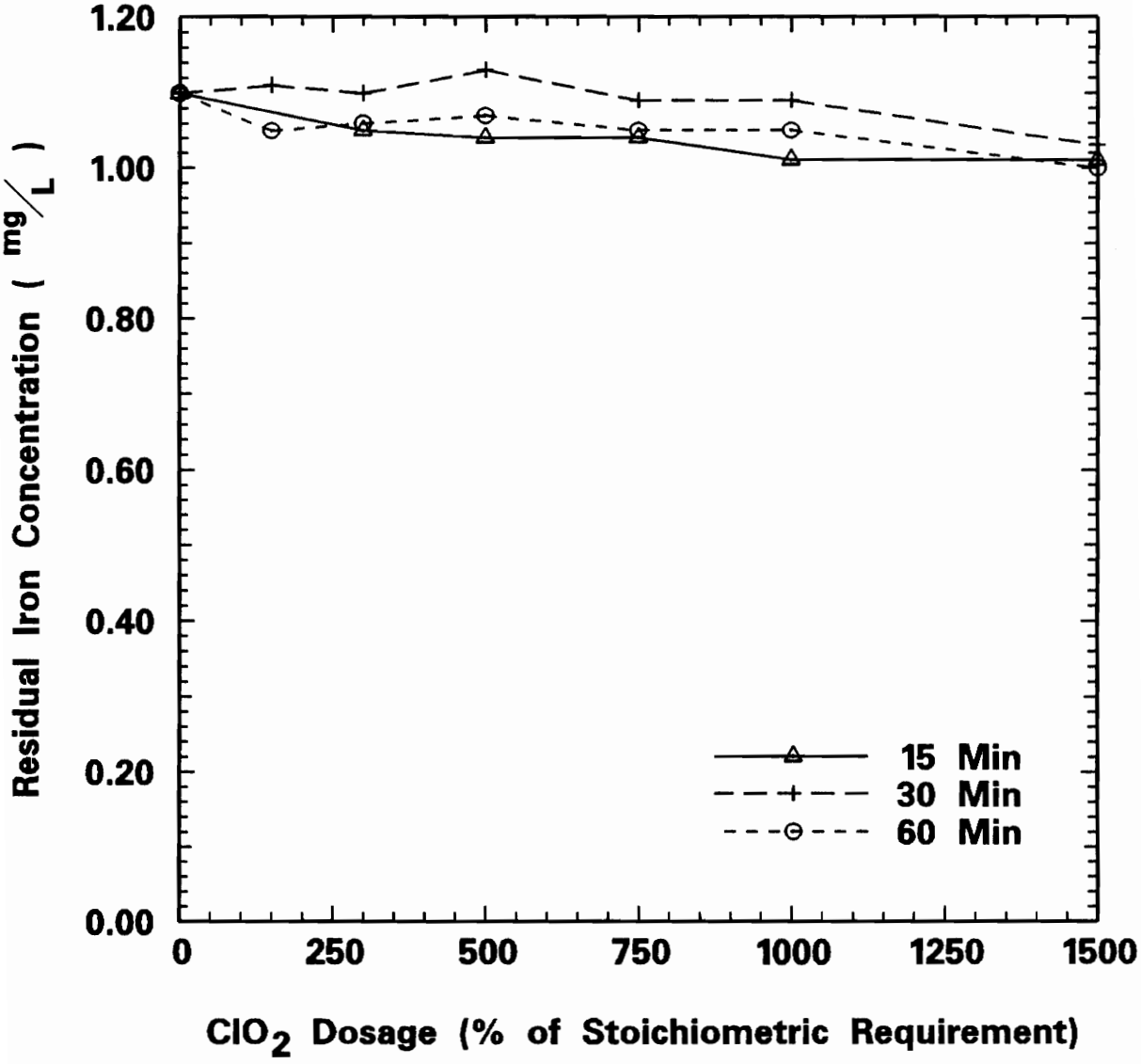


Figure 23. Removal of Fe (II) Complexed with Thousand Acre Fulvic Acid 30K > MW > 10K, by Chlorine Dioxide at pH 6.4: [Initial Concentration of Fe (II) = 1.10 mg/L, 100% Stoichiometric Dosage = 0.26 mg/L ClO_2, Concentration of Thousand Acre Fulvic Acid = 4 mg/L, Temperature = 25° C]

Minimal (< 10%) Fe(II) removal was obtained using ClO_2 at a 1500% stoichiometric dose regardless of reaction time provided. It appears the Fe(II) complexed by the larger molecular weight fractions was not removed successfully by any of the oxidants utilized during the study. The ability of $KMnO_4$ to oxidize Fe(II) that was complexed by the 10k> MW >5k fraction of the Thousand Acre Fulvic Acid was also evaluated (Figure 24). With a sixty minute reaction time and a 300% stoichiometric dose, $KMnO_4$ was only able to remove approximately 25% of the complexed Fe(II). Due to the poor results obtained for $KMnO_4$, HOCl and ClO_2 were not tested with this molecular weight fraction.

The results of $KMnO_4$ tests utilizing a lower MW fraction (5k> MW >1k) are shown in Figure 25. Oxidation of Fe(II) complexed by the small molecular weight fraction of the Thousand Acre Fulvic resulted in 94% removal of Fe(II) at a 100% stoichiometric dose. Unfortunately, there was only enough complexed 5k> MW >1k solution (due to a freezer accident) to perform one experiment. Although $KMnO_4$ is the stronger oxidant, the amount of Fe(II) removed was so substantial it is believed that HOCl and ClO_2 would have successfully removed a significant portion of the complexed Fe(II) (as seen in previous experiments with both complexed Suwannee River Fulvic Acid and oxalic acid).

In summary, the ability of $KMnO_4$ to promote removal of Fe(II) that was complexed by Thousand Acre Fulvic Acid increased as the apparent molecular weight of the fulvic acid decreased.

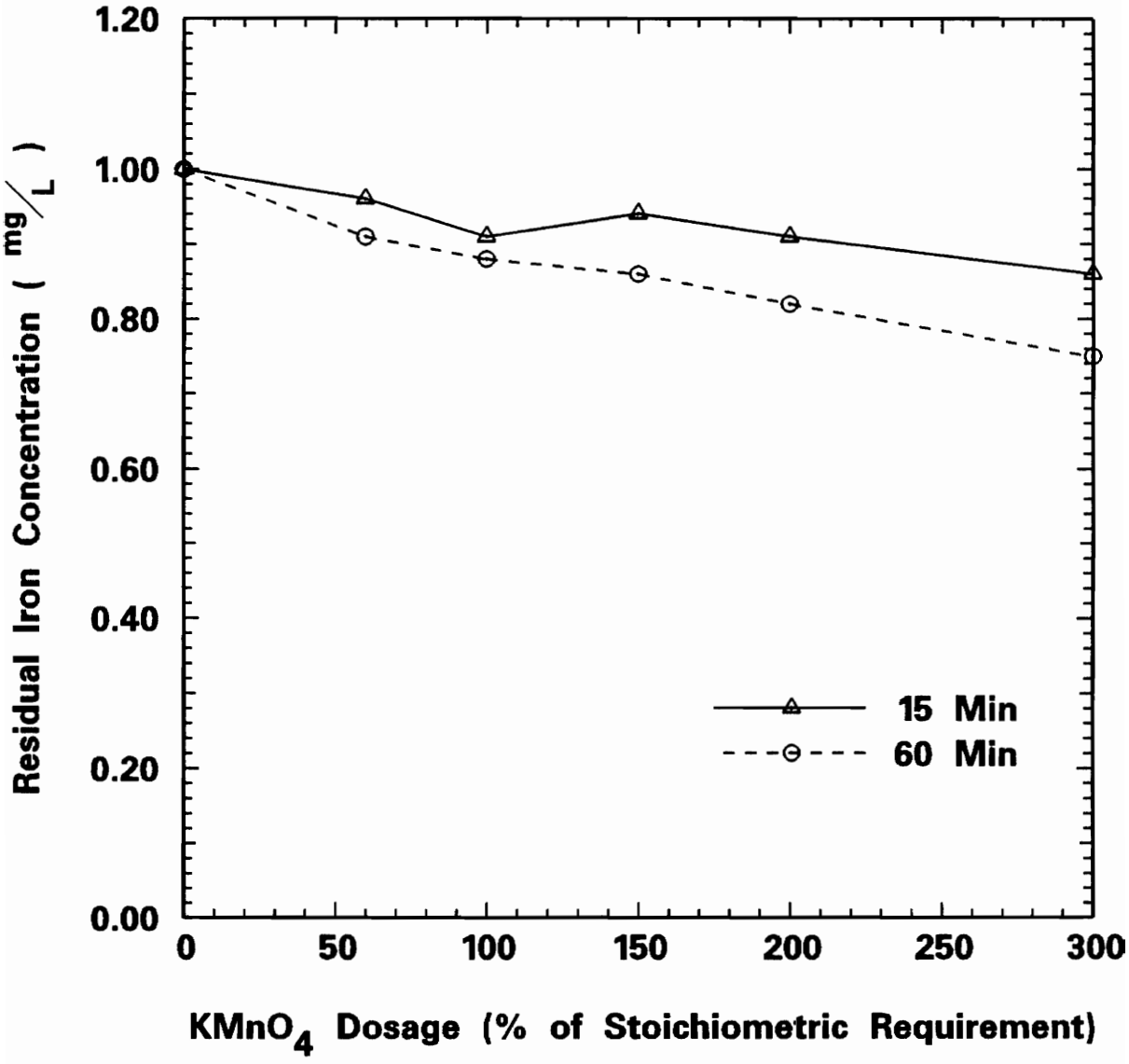


Figure 24 . Removal of Fe (II) Complexed with Thousand Acre Fulvic Acid, 10K>MW>5K, by Permanganate at pH 6.4: [Initial Concentration of Fe (II) = 1.00 mg/L, 100% Stoichiometric Dosage = 0.94 mg/L, $KMnO_4$ Concentration of Thousand Acre Fulvic Acid = 4mg/L, Temperature = 25° C]

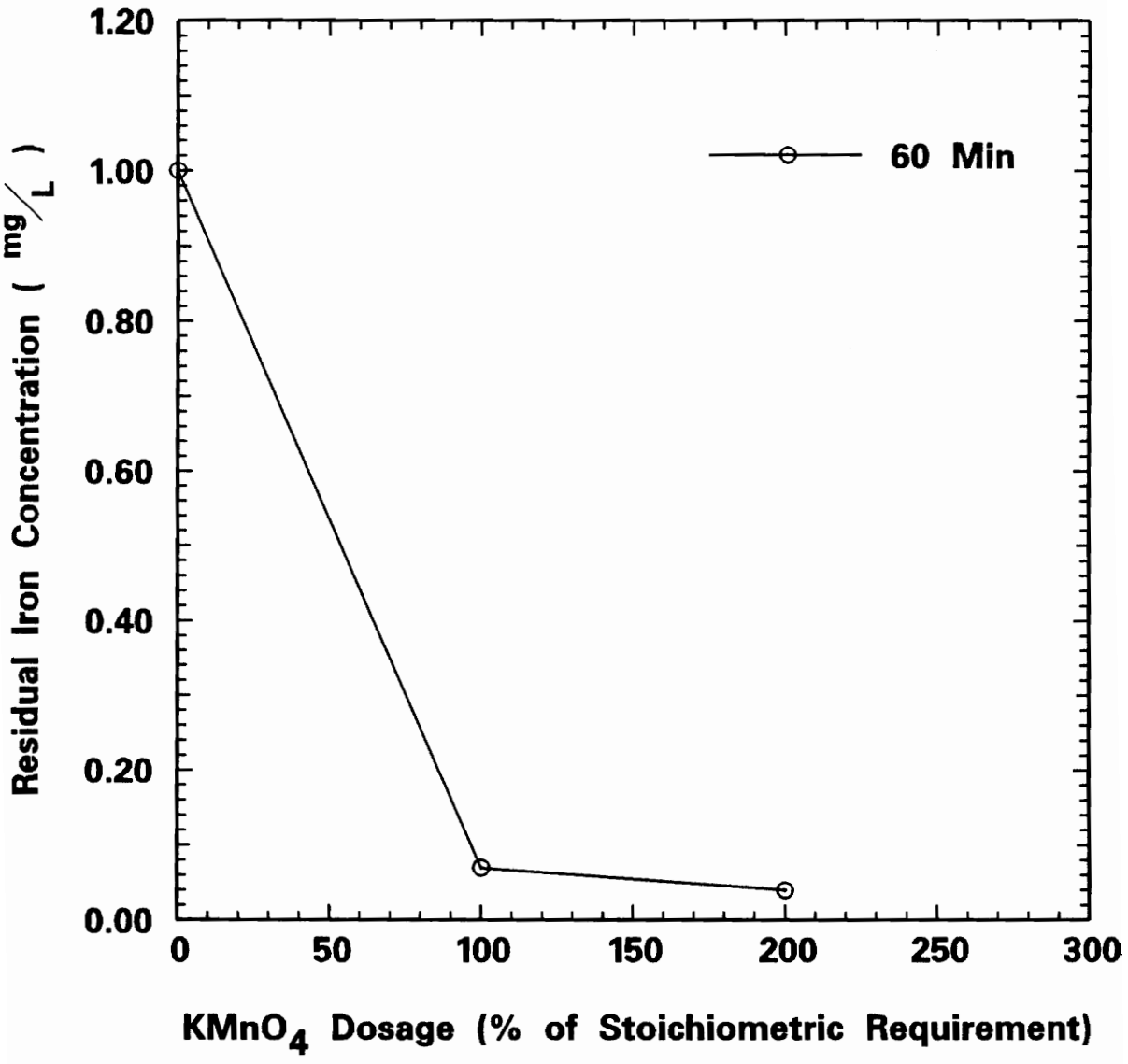


Figure 25. Removal of Fe (II) Complexed with Thousand Acre Fulvic Acid, 5k>MW>1k by Permanganate at pH 6.4: [Initial Concentration of Fe (II) = 1.ØØ mg/L, 1ØØ% Stoichiometric Dosage = Ø.94 mg/L $KMnO_4$. Concentration of Thousand Acre Fulvic Acid = 4mg/L. Temperature = 25° C]

Comparison of Complexed and Uncomplexed Fe(II) Oxidation

The results of complexed and uncomplexed Fe(II) oxidation studies have been summarized in Figures 26 through 29. Several points are noteworthy. First, all three oxidants successfully removed the uncomplexed Fe(II) from solution using doses which ranged between 100% - 110% of the stoichiometric dose. However, the Fe(II) which had been complexed by high molecular weight organics such as tannic acid and Thousand Acre Fulvic Acid (30k> MW >10k) experienced no significant removal regardless of the oxidant and the dose utilized. Secondly, Fe(II) complexed by the low molecular weight organics such as oxalic acid and Thousand Acre Fulvic Acid (5k> MW >1k) was almost completely removed by all three oxidants tested using essentially the same dose as the stoichiometric dose for uncomplexed Fe(II). Thirdly, the Fe(II) complexed by Suwannee River Fulvic Acid appeared to be the only complex which was affected by the type of oxidant utilized. Approximately 90% of the Suwannee River complexed Fe(II) was removed by $KMnO_4$ at a 300% dose; 40% of this complexed Fe(II) was removed by HOCl at dosages ranging from 60% to 300%; and 10% of the Suwannee River complexed Fe(II) was removed by ClO_2 at a dose of 1500%. This would indicate that the Fe(II) which is being complexed by the low molecular weight portion of the organic matter may be effectively removed by any of the three oxidants. However, Fe(II) complexed by the higher MW organic matter may not be as easily removed.

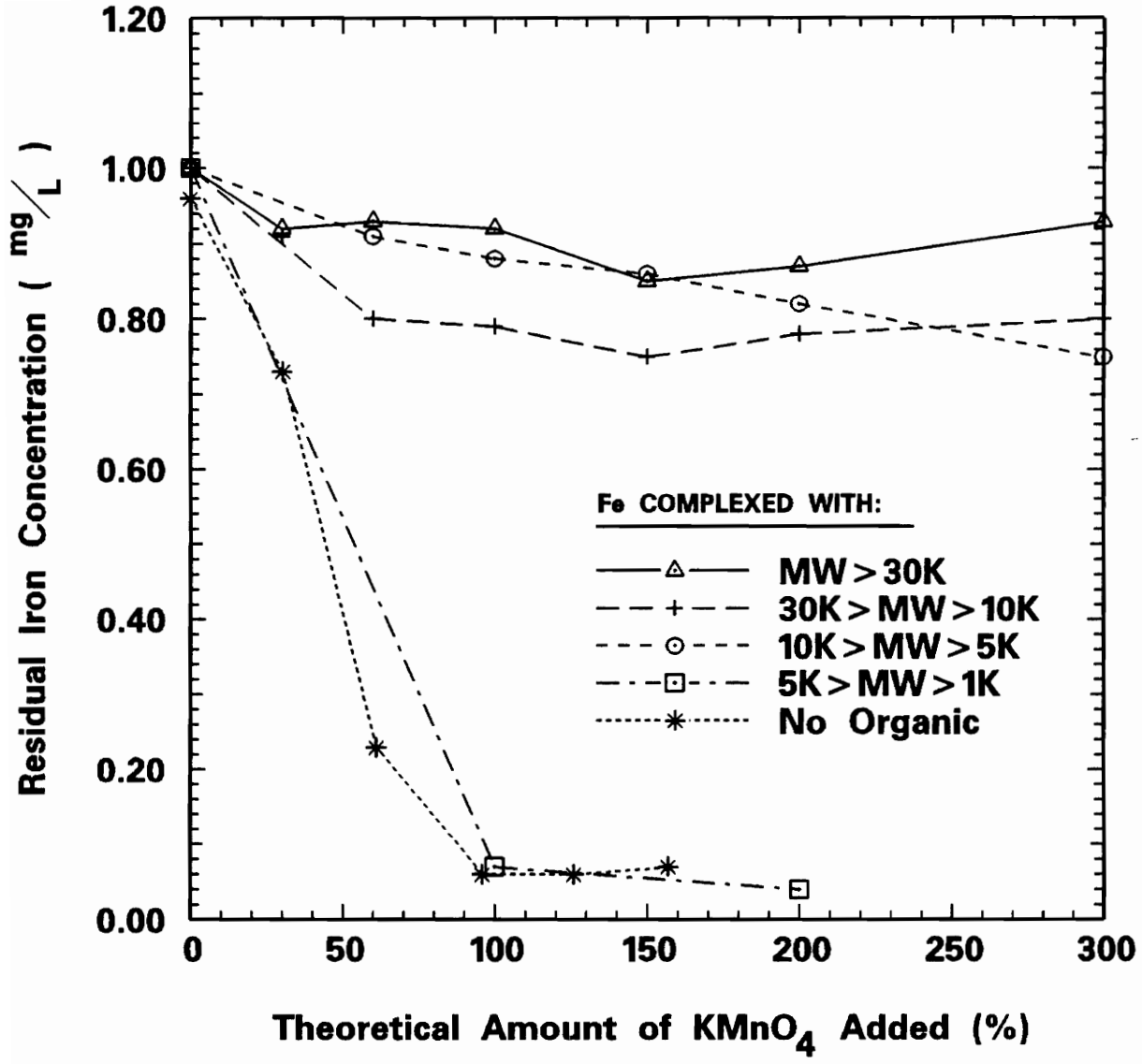


Figure 26. Removal of Fe (II) Complexed with Thousand Acre Fulvic Acid and with no Organic by Permanganate [Initial Concentration of Fe (II) varies, 100% Stoichiometric Dosage for $KMnO_4$ =0.94 mg $KMnO_4$ /mg Fe. Concentration of Thousand Acre Fulvic Acid = 4 mg/L, Temperature = 25° C]

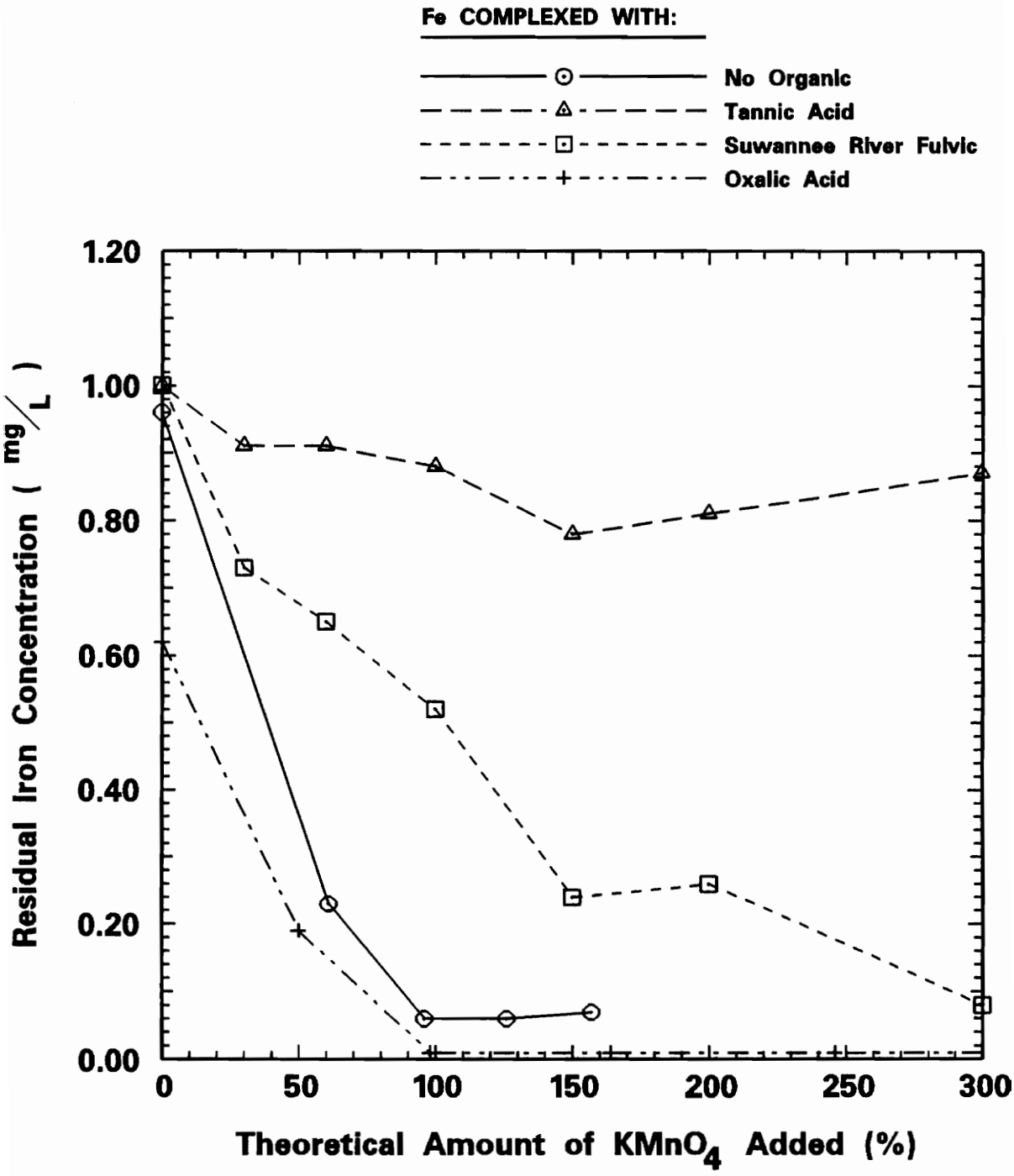


Figure 27. Removal of Fe (II) Complexed with Different Organics and with No Organic by Permanganate. [Initial Concentration of Fe (II) Varies, 100% Stoichiometric Dosage for $KMnO_4$ = 0.94 mg $KMnO_4$ / mg Fe, Concentration of Tannic Acid = 5 mg/L, Concentration of Suwannee River Fulvic Acid and Oxalic Acid = 4 mg/L, Temperature = 25° C]

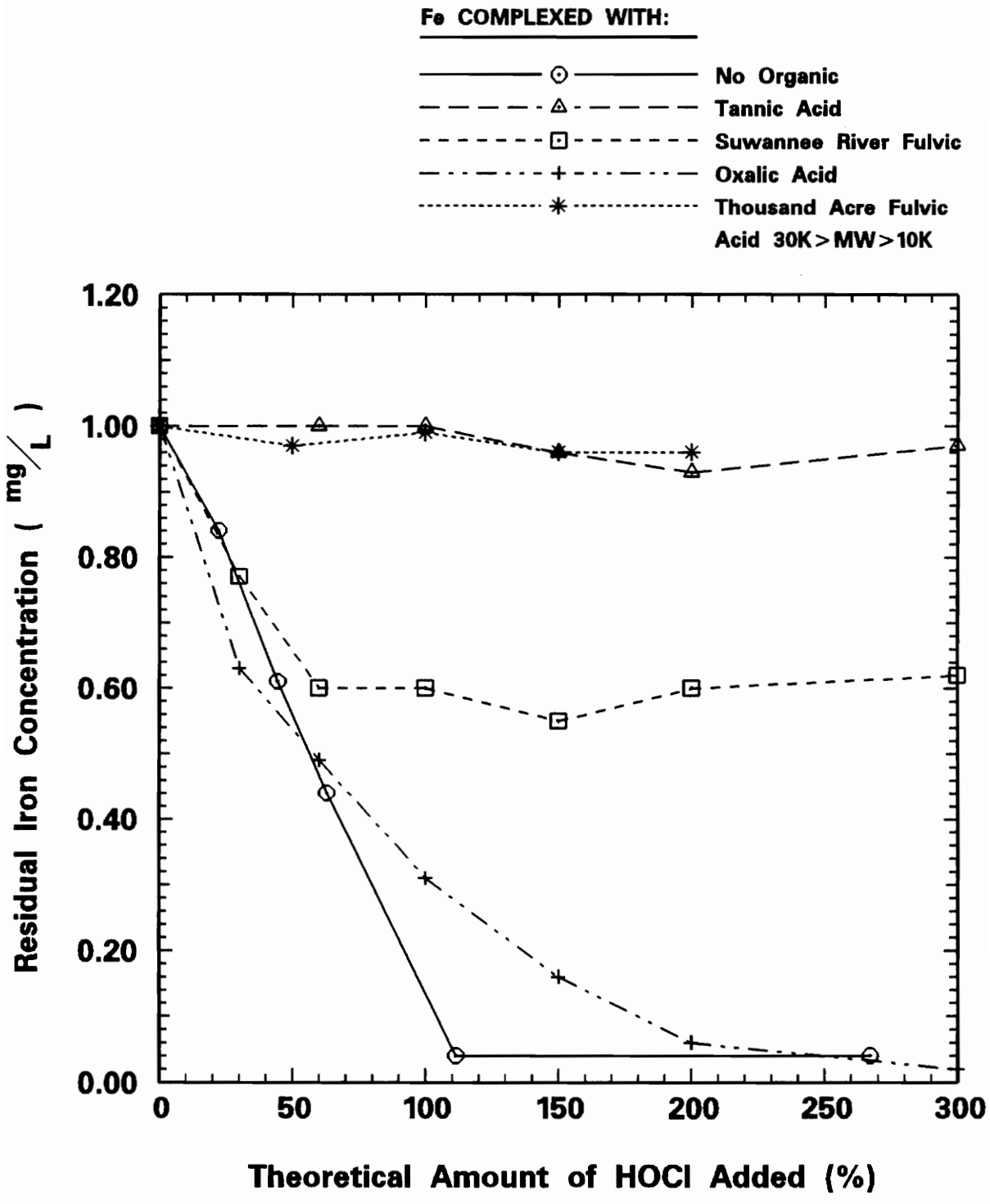


Figure 28. Removal of Fe (II) by Chlorine at pH 5.Ø: [Initial Concentration of Fe (II) = 1.ØØ mg/L, 1ØØ% Stoichiometric Dosage = Ø.64 mg/L HOCl, No Organic Added, Temperature = 25° C]

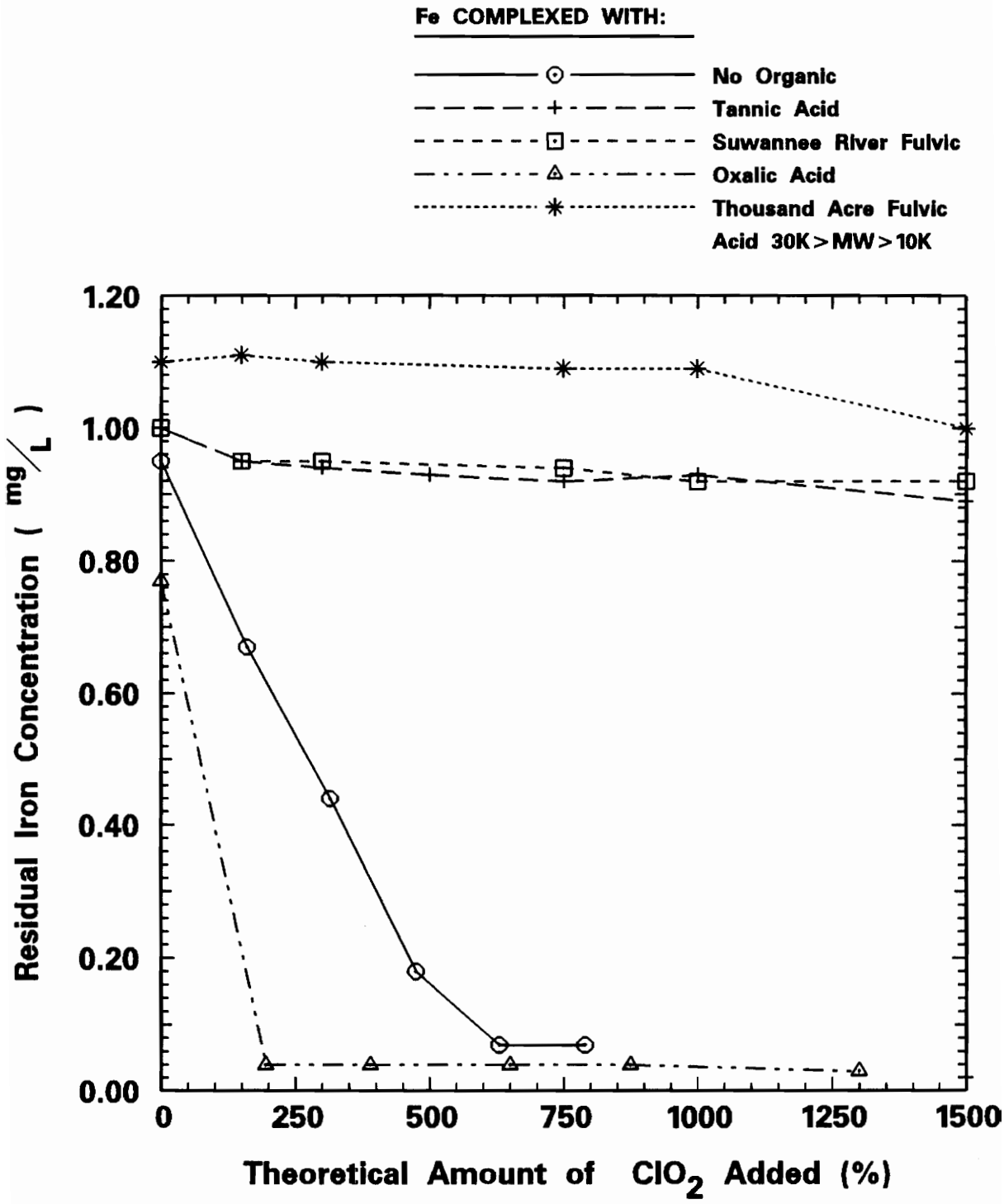


Figure 29. Removal of Fe (II) by Chlorine Dioxide, [Initial Concentration of Fe (II) Varies, 100% Stoichiometric Dosage for ClO_2 =0.24 mg ClO_2 /mg Fe, Temperature = 25° C]

ALUM COAGULATION FOR COMPLEXED FE(II) AND DOC REMOVAL

The coagulation studies were performed to evaluate the removal of both DOC and complexed Fe(II). The purpose of the experiments was to determine how the molecular weight of the complexing organics affected the degree of iron removal observed. Natural water samples from the Po River (Spotsylvania County, Virginia) and Durham, North Carolina, were used. Furthermore, water samples from the Durham water treatment facility were collected at several locations during the treatment scheme and analyzed by sequential ultrafiltration. Water samples were also prepared containing 1.0 mg/L Fe(II) complexed by Suwannee River Fulvic Acid (5 mg/L DOC). Alum coagulation tests were conducted at a pH of 6.0 - 6.5 to evaluate removal of both constituents. In addition, control samples were evaluated to verify that no significant loss of Fe(II) due to O_2 (aq) transfer during solution mixing. The Suwannee River Fulvic Acid was coagulated both with and without oxidant addition ($KMnO_4$; 1.5 mg/L).

Alum coagulation results for the Po River water sample (Figure 30) indicate that approximately 97% of the Fe(II) and 47% of the DOC were removed with an alum dose of 20 mg/L. The fractionated coagulation samples (0 mg/L, 20 mg/L, and 70 mg/L alum) indicate the degree of Fe(II) complexation relative to the Molecular Weight distribution (Table 2). The 20 mg/L alum dose was the lowest dose which gave good Fe(II) removal, whereas the 70 mg/L alum dose produced the most efficient DOC

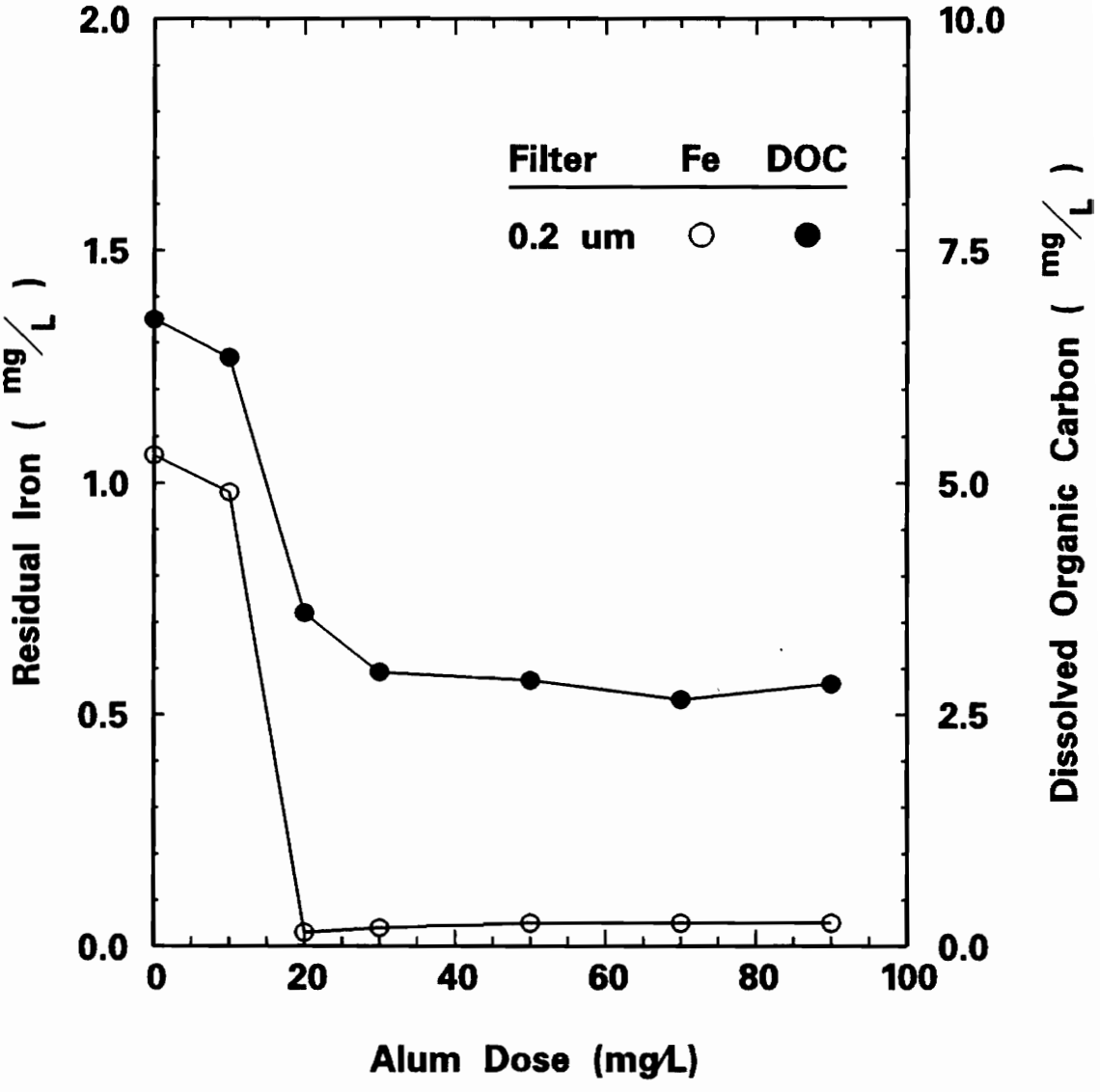


Figure 30. Removal of Soluble Iron and DOC by Alum Coagulation at pH 6.Ø - 6.3 (Temperature = 25° C, no oxidant addition, source of DOC - Po River, Spotsylvania County, Va.)

Table 2

Fractionation of Coagulated Po River Sample

	Alum Dose					
	0 mg/L		20 mg/L		70 mg/L	
Filter	Fe(II) mg/L	DOC mg/L	Fe(II) mg/L	DOC mg/L	Fe(II) mg/L	DOC mg/L
0.2 um	1.06	6.8	0.03	3.6	0.05	2.7
30 k	0.02	5.6	0.01	3.6	0.03	2.5
10 k	0.01	3.8	0	2.7	0.03	2.0
5 k	0.02	2.0	0	1.7	0.03	1.4
1 k	0.02	0.9	0	0.8	0.03	0.6

removal. Comparison of the Fe(II) concentrations obtained after 0.2 um filtration and 30K ultrafiltration for the 0 mg/L alum dose indicate that approximately 98% of the dissolved Fe(II) was associated with DOC of very high molecular weight. The DOC concentrations obtained after 0.2 um filtration and 30K ultrafiltration for the 20 mg/L and 70 mg/L alum doses indicate that essentially all DOC of very high molecular weight was removed by alum coagulation. Therefore, it seems clear that essentially all Fe(II) associated with high molecular weight organics was removed by alum addition. Further, minimal Fe(II) was associated with lower molecular weight organic material.

Results from the coagulation of Durham raw water (Figure 31) likewise indicate that significant dissolved Fe(II) removal can be achieved through alum addition. A 20 mg/L dosage of alum removed nearly 90% of the Fe(II) and 50% of the DOC. The results of the ultrafiltration characterization test (Table 3) for in-plant samples indicate that over 80% of the dissolved Fe(II) in the Durham raw water was associated with high molecular weight DOC, However, this high molecular weight DOC represents less than 30% of the DOC present in the raw water. After coagulation and passage through flocculation and sedimentation, the settled water contained only insignificant amounts of both soluble Fe(II) and high molecular weight DOC.

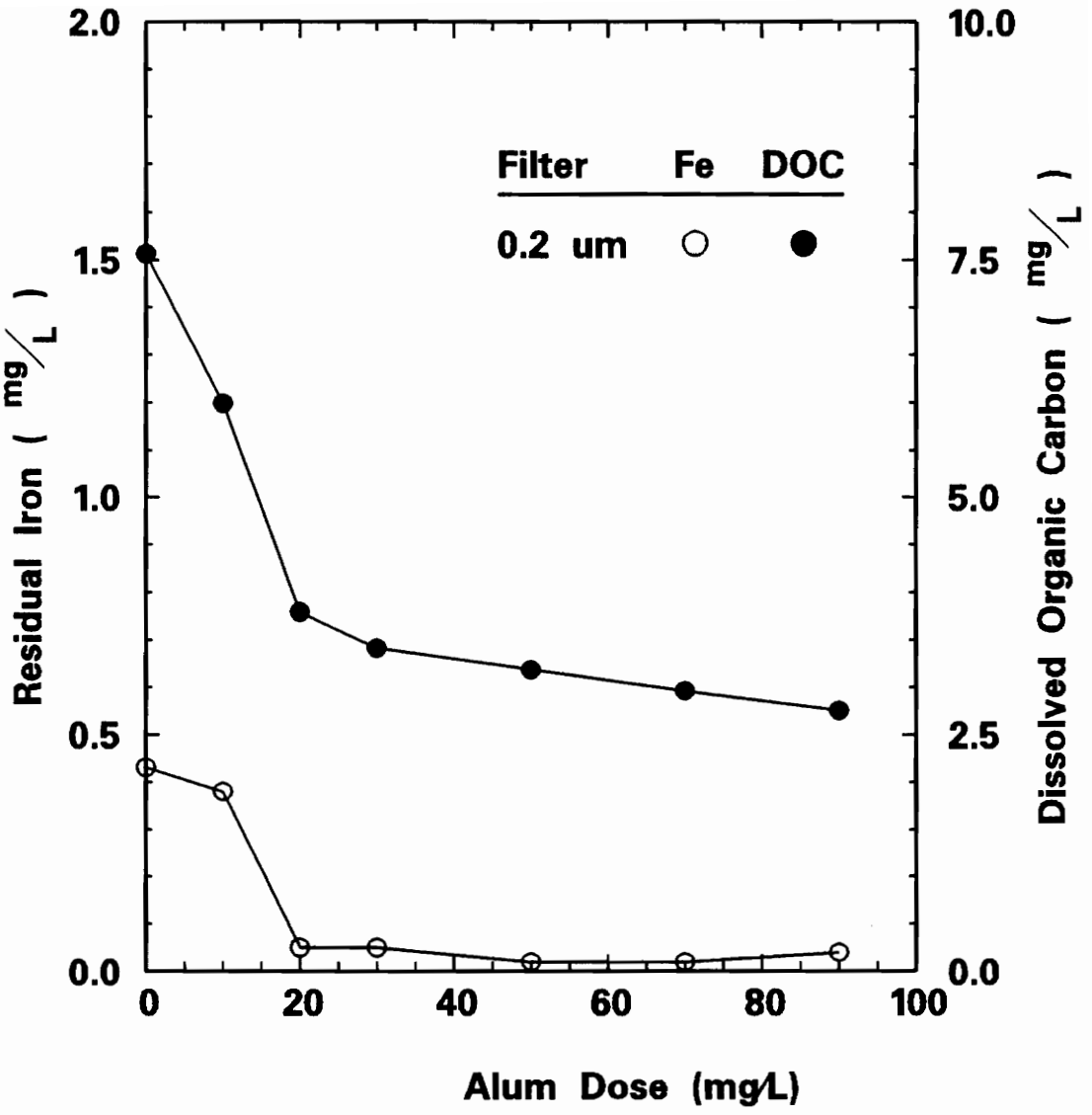


Figure 31. Removal of Soluble Iron and DOC by Alum Coagulation at pH 6.Ø - 6.3 (Temperature = 25° C, no oxidant addition, source of DOC - Durham, N.C.)

Table 3

Fractionation of Water Samples Collected at Various Locations in the Williams Water Treatment Plant

	Raw Water		Settled Water		Filtered Water	
Filter	Fe(II) mg/L	DOC mg/L	Fe(II) mg/L	DOC mg/L	Fe(II) mg/L	DOC mg/L
0.2 um	0.43	7.6	0.03	3.2	0.03	3.1
30 k	0.08	5.6	0.01	2.9	0.03	2.9
10 k	0.07	3.9	0.01	2.6	0.04	2.9
5 k	0.01	1.8	0.02	2.1	0.04	2.5
1 k	<0.01	0.8	0.01	1.2	0.04	1.6

A similar study was undertaken wherein Suwannee River Fulvic Acid provided the source of DOC. Alum coagulation in the absence of an oxidant resulted in DOC removal along with Fe(II) removal (Figure 32). Comparison of the Fe(II) concentrations obtained after 0.2 um filtration and 30 k ultrafiltration (Table 4) indicate that the majority of dissolved iron present was complexed by high molecular weight DOC. Less than 30% of the DOC present was retained by a 30k ultrafilter; however, nearly 80% of the dissolved iron was associated with this very high molecular weight fraction of the DOC. In addition, essentially complete Fe(II) removal was accomplished by alum coagulation alone. The impact of $KMnO_4$ addition was minimal for the treatment of this sample water (Figure 33). In addition, the fractionated coagulation samples (Table 5) show little impact of oxidant addition. The removal percentage of both Fe(II) and DOC was essentially the same regardless of $KMnO_4$ addition.

Both experiments demonstrated that significant dissolved iron removal can be accomplished purely by alum addition.

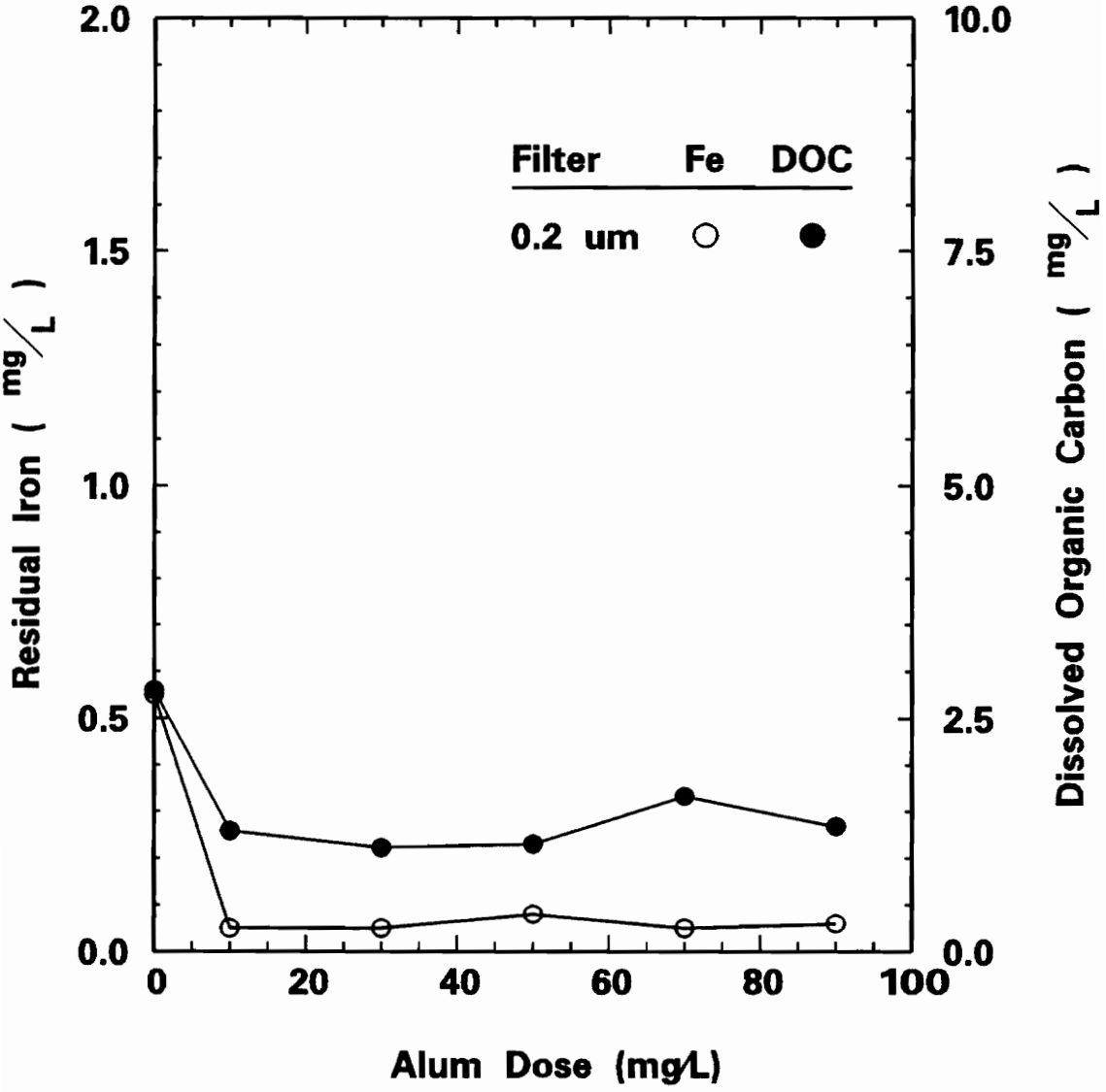


Figure 32. Removal of Soluble Iron and DOC by Alum Coagulation at pH 6.Ø - 6.3 (Temperature = 25° C, no oxidant addition, source of DOC - Suwannee River Fulvic Acid)

Table 4

Fractionation of Coagulated Suwannee River Fulvic Acid Samples

	Alum Dose			
	0 mg/L		70 mg/L	
Filter	Fe(II) mg/L	DOC mg/L	Fe(II) mg/L	DOC mg/L
0.2 um	0.55	2.8	0.05	1.7
30 k	0.14	2.2	0.01	1.5
10 k	0.11	1.6	0.01	1.7
5 k	0.08	0.9	<0.01	1.3
1 k	0.05	0.5	<0.01	<0.3

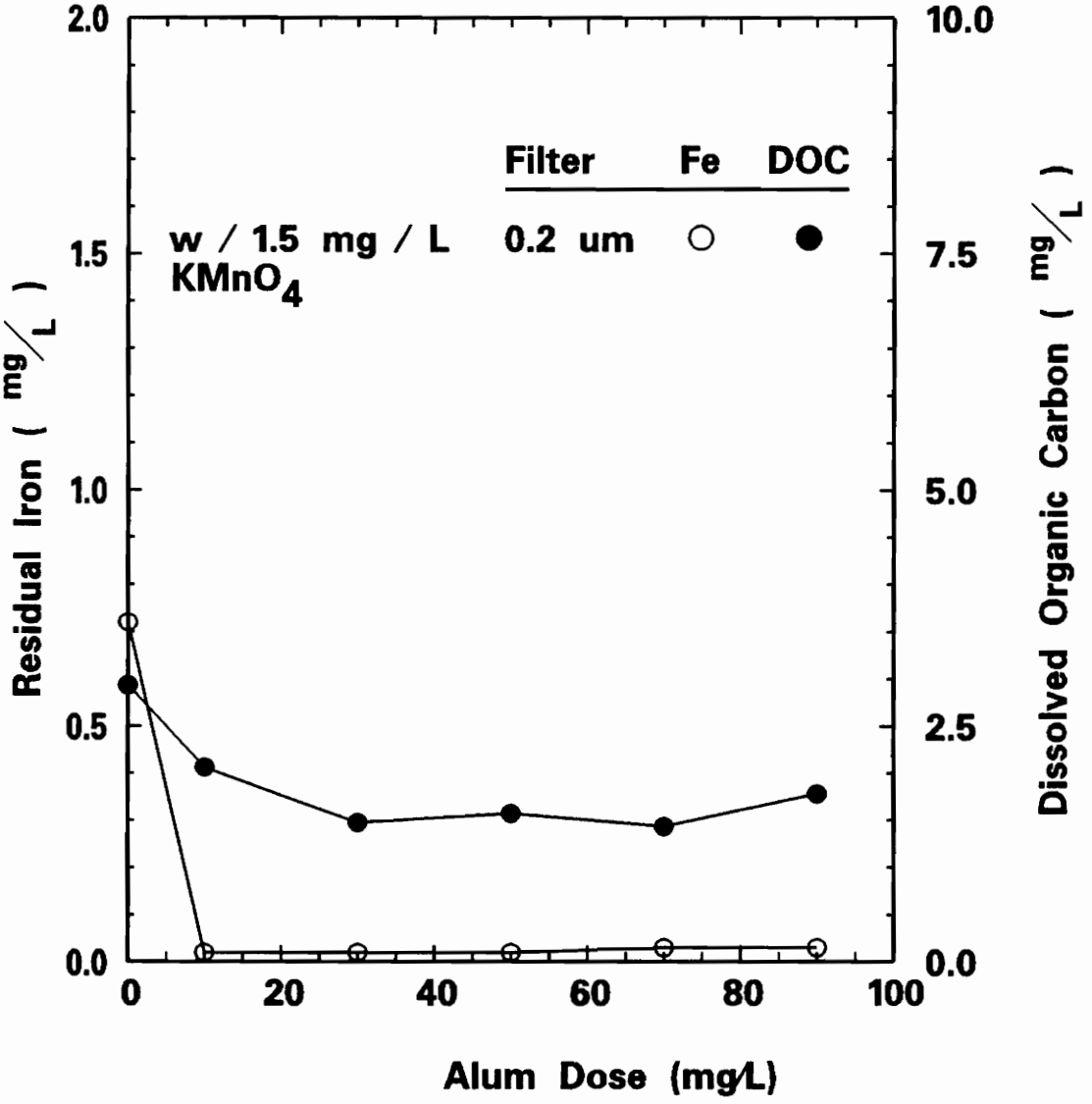


Figure 33. Effect of Potassium Permanganate Addition on the Removal of Dissolved Iron and DOC by Alum Coagulation (Temp. = 25° C, ph 6.Ø - 6.3, source of DOC - Suwannee River Fulvic Acid)

Table 5

Fractionation of Coagulated Suwannee River Fulvic Acid Water Sample Following Oxidation and Alum Coagulation

	Alum Dose			
	0 mg/L		70 mg/L	
Filter	Fe(II) mg/L	DOC mg/L	Fe(II) mg/L	DOC mg/L
0.2 um	0.72	2.9	0.03	1.4
30 k	0.32	2.3	0.01	1.2
10 k	0.28	1.7	0.01	1.1
5 k	0.23	1.0	0.01	1.0
1 k	0.06	0.3	0.01	0.6

Note: $KMnO_4$ Dose = 1.5 mg/L

DISCUSSION

Experimental results are further explained in the following sections. This chapter presents a discussion into the results of the previous chapter and is organized into three subsections: Complexed Fe(II) Removal by Chemical Oxidation, Complexed Fe(II) Removal by Alum Coagulation and Applications to Water Treatment Operations.

COMPLEXED FE(II) REMOVAL BY CHEMICAL OXIDATION

The results of the complexed Fe(II) removal studies indicate that Fe(II) complexed by high molecular weight DOC (ex. tannic acid, Thousand Acre Fulvic Acid, MW>30k, and Thousand Acre Fulvic Acid 30k>MW>10k) was not efficiently removed by the addition of any of the oxidants used in the study. The $KMnO_4$ and HOCl doses utilized were 300% of the stoichiometric requirement for complete Fe(II) oxidation, while ClO_2 doses were over 1500% of the stoichiometric requirement.

In contrast to results observed using high molecular weight organics, experiments involving Fe(II) complexed by low molecular weight organics (ex. Suwannee River Fulvic Acid and Thousand Acre Fulvic Acid, 5k>MW>1k) demonstrate that Fe(II) removal by oxidant addition is possible. Unfortunately for the oxidants to be effective they require relatively long contact times and dosages well above the stoichiometric requirement

for Fe(II) oxidation. It is interesting to note that although Fe(II) removal was obtained with all three oxidants studied, $KMnO_4$ achieved the highest degree of Fe(II) removal with the shortest contact time (60 minutes). Fe(II) complexed with oxalic acid, a low molecular weight organic, was also successfully removed by oxidant doses close to the stoichiometric requirements and contact times between 15 and 60 minutes. Contact time appears to be very important in the successful removal of Fe(II) complexed by low molecular weight organics. One possibility may be the reduced rate of interaction between the oxidant and the complexed Fe(II) due to the DOC present. Another possible explanation, which would require further exploration, is the additional mixing time allowed any colloidal iron particles present to aggregate and be retained on the 0.2 um filter.

A summary of the data regarding the effect of DOC molecular weight on complexed Fe(II) removal is presented in Table 6. Minimal Fe(II) removal was observed in the solutions containing high molecular weight organics, while significant Fe(II) removal was achieved in the solution containing low molecular weight organics. The effectiveness of a specific oxidant for removing complexed Fe(II) appears to be a direct function of the molecular weight of the DOC present. Therefore, specific characteristics such as the type and the molecular weight distribution of the DOC may be just as important in determining oxidant effectiveness as DOC concentration.

Table 6

Effects of DOC Type and/or Molecular Weight on Iron Removal Achieved by Various Oxidants

	Low Molecular Weight Organics			High Molecular Weight Organics		
	Oxalic Acid	Thousand Acre Fulvic 5k>MW>1K	Suwannee River Fulvic	Thousand Acre Fulvic 30k>MW>10k	Thousand Acre Fulvic MW>30k	Tannic Acid
Oxidant	Residual Soluble Iron (mg/L)					
$KMnO_4$	0.01	0.04	0.07	0.80	0.87	0.90
HOCl	0.01	----	0.65	0.99	----	0.93
ClO_2	0.01	----	0.94	1.05	----	0.92

Note: Fe(II) quantified by residual sample filtration through a 0.2 um membrane filter. $KMnO_4$ and HOCl doses 200% of stoichiometric dose required for complete oxidation of 1 mg/L uncomplexed Fe(II); ClO_2 dose 1000% of stoichiometric dose. Sixty minute reaction time; pH 6.0-6.5; temperature 25^ C.

COMPLEXED FE(II) REMOVAL BY ALUM COAGULATION

The results of the alum coagulation studies demonstrated that soluble Fe(II) complexed by high molecular weight organics could be successfully removed by alum coagulation.

The studies with the Po River water samples indicated that 98% of the Fe(II) was associated with high molecular weight DOC. As alum dose increased, residual Fe(II) decreased to values below 0.05 mg/L. DOC removal also increased with additional alum doses, attaining a maximum removal of 60-70% with alum doses of 70 mg/L. The remaining DOC was considered to be of low molecular weight since the DOC concentration obtained using the 0.2 um and 30k filters were essentially the same.

Similar results were obtained using alum coagulation for complexed Fe(II) and DOC removal from the Durham raw water samples. The results demonstrated again that Fe(II) complexed by higher molecular weight organics could be efficiently removed using alum coagulation. Complexed Fe(II) removal was achieved at the alum doses which optimize DOC removal.

Alum coagulation of the Suwannee River Fulvic Acid samples produced results similar to the other alum coagulation studies. Efficient Fe(II) removal was obtained with the optimum alum dose for DOC removal. Again, the ultrafiltration analysis indicated that most of the Fe(II) was associated with DOC which had a MW>30k.

APPLICATION TO WATER TREATMENT OPERATIONS

These results are important to the design and operation of water treatment facilities which function for Fe(II) removal. The results of the studies contained herein indicate that the removal of soluble Fe(II) complexed by high molecular weight organics (MW>10k) is extremely poor following the addition of $KMnO_4$, HOCl, or ClO_2. However, soluble Fe(II) complexed by low molecular weight organics (MW<10k) is successfully removed by chemical oxidation. The results indicate that soluble Fe(II) complexed by high molecular weight DOC can be efficiently removed by alum coagulation. The pH and alum dose utilized to produce effective DOC removal will also promote efficient complexed Fe(II) removal.

CONCLUSIONS

The purpose of this research was to assess the removal of complexed Fe(II) by chemical oxidation and alum coagulation. An experimental matrix was established which utilized various types of organic matter and various oxidants. The different DOC sources were utilized to evaluate the ability of $KMnO_4$, HOCl, and ClO_2 to promote complexed Fe(II) removal. The various complexing organics aided in evaluating the relationship between the molecular weight distribution of the organic and the degree of iron removal observed. In addition, the fate of complexed iron during the coagulation of DOC with alum was undertaken with and without direct oxidant addition. Based on the results and discussion of the accumulated data, the following conclusions were reached:

1. Fe(II) complexed by DOC dominated by higher molecular weight organics (>10k MW) was not efficiently removed by the addition of $KMnO_4$, HOCl, or ClO_2. Fe(II) complexed by lower molecular weight DOC (<5K MW) was more readily removed by direct oxidant addition.

2. Fe(II) complexed by higher molecular weight DOC can effectively be removed by alum coagulation. Efficient Fe(II) removal can be obtained with the optimum alum dose and pH utilized for effective DOC removal.

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