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Removal Of Refractory Tkn From An Effluent Wastewater Using Sodium Ferrate

Lucia Lettie
University of Central Florida

REMOVAL OF REFRACTORY TKN FROM AN EFFLUENT WASTEWATER USING SODIUM FERRATE

by

LUCIA ANTONIETA LETTIE
B.S. Universidad Estatal de Guayaquil, 1994

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ABSTRACT

This research addresses refractory forms of nitrogen that, even with advanced biological nitrification-denitrification systems are not removed completely from domestic wastewater. TKN (Total Kjeldahl Nitrogen), ammonia plus organic nitrogen, is one of the forms to measure the levels of nitrogen present in effluent wastewaters. Ferrate, a strong oxidant, was used for the treatment of these nitrogen forms with the objective of producing nitrogen compounds that can be removed by subsequent biological processes.

Bench-scale experiments were performed on effluent samples taken prior to chlorination from an Orlando, FL wastewater treatment facility, using a biological nutrient removal process. The samples were treated with doses of ferrate ranging from 1 to 50 mg/L as FeO_4^{-2} under unbuffered conditions. TKN removal as high as 70% and COD removal greater than 55% was observed. The TSS production after ferrate treatment was in a range of 12 to 200 mg/L for doses between 10 and 50 mg/L FeO_4^{-2}.

After an optimum dose of ferrate was determined, three bench-scale reactors were operated under anoxic conditions for 10 to 12 days, two as duplicates containing the treated effluent and one as a control with untreated sample. Two different doses of ferrate were used as optimum dose for these experiments, 10 and 25 mg/L as FeO_4^{-2}. The purpose of these reactors was to determine the potential for biological removal of remaining nitrogen after ferrate oxidation of refractory nitrogen.

Treated and raw samples were analyzed for Total Kjeldahl Nitrogen (TKN) (filtered and unfiltered), chemical oxygen demand (COD) (filtered and unfiltered), total

suspended solids (TSS), nitrate (NO_3-N), nitrite (NO_2-N), and heterotrophic plate count (HPC). As a result, more than 70% of the soluble TKN was removed by chemical and biological oxidation for a sample treated with a dose of 25 mg/L FeO_4^{-2}, and less than 50% when treated with 10 mg/L FeO_4^{-2}. For the control samples run parallel to the ferrate treated samples, a maximum of 48% of soluble TKN and a minimum of 12% was removed. A three-log increase was observed in heterotrophic bacteria numbers for both doses during the operation of the reactors. Sodium ferrate was found to be an effective oxidant that can enhance the biodegradability of recalcitrant TKN present in municipal wastewaters. As mentioned before this research was develop using batch reactor units at bench-scale, therefore it is recommended to follow the investigation of the biodegradability of recalcitrant TKN of a ferrate treated sample under continuous flow conditions so that results can be extrapolated to a full-scale treatment facility.

…….to the two most important persons in my life; my Mom, for all the sacrifices she made raising me alone, encouraging me to have an education, so I can have a better life; and to my dearest husband who with all his love, has given me not only a better but a wonderful life. I love you so much.

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1. INTRODUCTION

There is increasing public concern regarding the level of nutrients in waters. Eutrophication of surface water is one of the most obvious problems that the increase of nutrients presents. Chronic symptoms of over-enrichment include low dissolved oxygen, fish kills, cloudy, murky water, and the depletion of desirable flora and fauna. This accumulation of nutrients, especially nitrogen, comes from certain types of organic matter being discharged from wastewater treatment facilities. Nitrogen in wastewater is present in inorganic and organic forms, but there are some forms of organic nitrogen that are recalcitrant to conventional treatments (nitrogen forms that cannot be biologically processed in wastewater treatment plants within their existing resident time). Little information is known about their source, characteristics or fate. Studies conducted based on extraction and fractionation to characterize these organic forms have been published, finding that only 22% in treated water or wastewater, more than 50% in wastewater, and 63% in activated sludge, were possible to characterize (Dignac et al., 1999).

Even though municipal wastewater treatment facilities are frequently designed for nitrification and denitrification, typically these processes only remove approximately 95% of inorganic forms of nitrogen with significantly less efficiency for the organic nitrogen (Mantas et al., 2006). Some of the refractory forms of organic nitrogen are suspected of being formed and partly released by bacterial media

like activated sludge, during re-condensation of peptides and sugars, and as a result of degradation of proteins and sugars present in fresh organic matter (Dignac et al., 1999; Parkin et al., 1980).

Many advanced oxidation processes have been used to enhance the biodegradability of the recalcitrant organic compounds contained in the wastewater. Ferrate (IronVI), with its oxidizing, disinfecting, antifouling, and coagulant powers, is a promising technology that may be used to convert these compounds to more oxidized and readily biodegradable intermediates (Sharma, 2002; White et al., 1998; Bielski et al., 1987; Zhu et al., 2005). The redox potential of ferrate is higher than ozone under acidic conditions and is the highest of all the oxidant disinfectants used for water and wastewater treatment (Jiang. et al, 2002). Several halogen and oxygen-based oxidants are widely used, but each one of them has limitations with respect to the production of by-products. During oxidation, ferrate also generates ferric ions which at high pH, remove metal ions present as a result of hydroxide precipitation. Bartzatt and Nagel (1991) found that ferrate has the ability to oxidize hydroxyl groups to carbonyl groups as well as *nitrosamines* in solution. Studies in the use of ferrate as an oxidant have shown that it can remove organic pollutants and effectively treat nitrogen and sulfur-containing contaminants in water and wastewater effluents by oxidizing them into harmless products (Lee. et al., 2003). The extent of organic compounds oxidation strongly depends on the ferrate dose. Organic matter present in domestic secondary effluent was oxidized with ferrate at a dose of less than 10 mg/L (as Fe) (Jiang. et al., 2002). Total Organic Carbon (TOC) and Biodegradable Oxygen Demand (BOD) from a secondary effluent were removed by 95% and 93%,

respectively, by ferrate treatment (Jiang. et al., 2002). Because of the strong evidence in the literature of the ability of ferrate to removed organic matter, it was selected as the oxidant of choice for the removal of recalcitrant nitrogen in effluent wastewater.

1.1. Objectives

The objectives of this research are to:

- Determine an optimum dose of ferrate and pH for the removal of refractory TKN from effluent wastewater, and
- Evaluate the biodegradability of the ferrate-treated effluent under anoxic conditions.

1.2. Thesis Organization

In addition to the introduction chapter, this thesis contains four chapters. A review of technical literature is presented in Chapter 2. Chapter 3 describes the materials and methodologies used to determine an optimum dose of ferrate for the removal of refractory nitrogen and the biodegradability under anoxic conditions of an effluent wastewater before chlorination and after its treatment with ferrate. Chapter 4 presents the results and discussion of this research. The engineering relevance of this research and its findings are presented in Chapter 5, along with recommendations for application of future study.

2. LITERATURE REVIEW

2.1. Introduction

As water pollution increases and the standards of drinking water supply and wastewater discharge become more stringent, a new technology or chemical reagent that can treat the water and wastewater more efficiently is needed. Such chemical reagents should be able to degrade and oxidize organic and inorganic matter, disinfect microorganisms, and remove colloidal/suspended particles as well as heavy metals (Jiang et al., 2002). Special concerns about refractory forms of nitrogen that even with sequential biological systems are not removed completely from wastewater discharges has motivated this research. Ferrate, a strong oxidant, was used for the treatment of these nitrogen forms with the objective of producing nitrogen compounds that can be removed by subsequent biological processes.

2.2. Biological Nitrogen Removal

Processes that employ biological means for the removal of nitrogen either in the ammonia-ammonium or nitrate form are used in conventional treatment plants. Biological nitrification and denitrification are the most widely used method for the reduction of nitrogen (Reynolds and Richard, 1996).

2.2.1. Nitrification

Biological nitrification is the conversion of ammonia (NH_3) to nitrate (NO_3^-) under aerobic conditions. Certain bacteria are capable of oxidizing reduced nitrogen compounds, such as ammonia, to supply energy for cellular functions (Cooper et al, 2000). This is done in a two-step process with the use of oxygen and two types of bacteria, *nitrosomonas* and *nitrobacters* known as nitrifiers. First the ammonia is oxidized by oxygen to nitrite in the presence of *nitrosomonas*. Since this form of nitrogen is unstable, nitrite is then converted to nitrate in the presence of *nitrobacter* (Equation 2.1).

$$NH_3 + O_2 + CO_2 \rightarrow \text{cell mass} + HNO_3 + H_2O \qquad (2.1)$$

2.2.2. Denitrification

Biological denitrification is an integral part of the biological nitrogen removal. Biological denitrification is used more frequently in wastewater treatment where there is a concern about eutrophication and groundwater contamination due to elevated nitrate concentration when effluent is used as reclaimed water. The biological reduction of nitrate to nitrite and finally to nitrogen gas is called denitrification. Proper conditions must be maintained in the system during this process that allows the denitrifiers to break down the organic substances and use nitrate as one of their electron acceptors (Cooper et al, 2000). Equation 2.2 shows the unbalance reaction that occurs during the denitrification process.

$$HNO_3 + C_{10}H_{19}O_3N- \rightarrow \text{cell mass} + CO_2 + N_2 \qquad (2.2)$$

The oxygen for this process is obtained from chemical forms (nitrate, nitrite, sulfate, etc) as the final electron acceptor rather than molecular oxygen. Denitrification takes place under anaerobic or anoxic conditions characterized by the complete absence or low levels of dissolved oxygen. Certain forms of microorganisms, called heterotrophic denitrifiers develop under these conditions and are the driving force for biological denitrification. The presence of dissolved oxygen can inhibit the process because of the preference of microorganisms for oxygen over nitrate. A high concentration of nitrites also inhibits denitrification. The reduction of COD in the primary and secondary clarifier of a wastewater treatment facility plays an important part in the denitrification process; the less remaining demand for oxygen consumption, the greater the reduction of nitrate by denitrification (Nowak et al., 1996).

During the denitrification process, heterotrophic bacteria need a carbon source for food to survive, while breaking down nitrate to obtain oxygen (Schreff et al., 1998; Jiang et al., 2002; and Ruiz et al., 2006). Frequently an external source of carbon is required. The most common form of carbon is methanol. Methanol theoretically produces carbon dioxide and water without cellular growth and subsequent accumulation of solids during its metabolism in the system (Savage et al, 1973). Equation 2.3 shows the stoichiometric reaction of methanol during denitrification.

$$6H^+ + 6\ NO_3^- + 5CH_3OH \rightarrow 5CO_2 + 3N_2 + 13H_2O \qquad (2.3)$$

During denitrification, one equivalent of alkalinity is produced per equivalent of NO_3-N reduced which equates to 3.57 g of alkalinity as $CaCO_3$ per gram of nitrate reduced (Metcalf & Eddy, 2003). The amount of methanol required is approximately three times the weight of the nitrate-nitrogen to be removed (Savage et al, 1973). The kinetics for methanol utilization as a carbon source demonstrate that the solids retention time (SRT) required for a suspended growth process is in the same range for nitrification and denitrification, equaling three to six days.(Metcalf & Eddy, 2003).

2.2.3. Biological Removal of Recalcitrant Organic Compounds

A large percentage of organic compounds present in domestic and industrial wastewater is of natural origin and can be degraded by common bacteria. As new synthetic organic chemicals are created, new problems also are developing with respect to wastewater treatment. Due to their resistance to biodegradation and potential toxicity to the environment, these compounds are called recalcitrant or refractory (Metcalf & Eddy, 2003). Some of the refractory compounds can be biodegraded during extended periods of treatment (days or even weeks), under specific environmental conditions in the presence of bacteria capable of breaking down these compounds. All of these conditions create new demands for the wastewater treatment facility due to the increase in solid residence time, and a higher maintenance cost.

Concern about the environmental effect caused by the presence of recalcitrant compounds in wastewater treatment plants, has created the necessity to understand the fate and transport of these compounds during biological treatment processes. There is a possibility of transport of these compounds to the environment without treatment as a result of adsorption to mixed liquor solids and subsequent release during biosolids disposal (Metcalf & Eddy, 2003).

2.3. Wastewater Treatment Systems

Physical-chemical systems such as ion exchange, volatilization and membrane processes, can remove 80 to 90 percent of the nitrogen from wastewater, but the utilization of such processes are limited due to a high cost of operation (EPA fact sheet 9). Biological nutrient removal is one of the processes most used in wastewater treatment plant. Nitrogen removal can be either an integral part of the biological treatment system or an add-on process (Metcalf & Eddy, 2003). Nitrogen removal that employs a biological process requires the nitrogen to be in either ammonia/ammonium form or nitrate form prior to ultimate nitrogen removal from the waste stream (Reynolds et al., 1996). There are two main types of systems for biological nitrogen removal in wastewater treatment (1) suspended growth biological nitrogen removal processes and (2) attached growth biological nitrogen removal (Metcalf & Eddy, 2003).

2.3.1. Suspended Growth

A variety of activated sludge process configurations is used to accomplish biological nitrogen removal. The selection of the configuration will depend on the

site conditions, existing processes and equipment, and treatment needs (Metcalf & Eddy, 2003). A description of the most used process configuration is presented below.

2.3.1.1. Modified Ludzack-Ettinger (MLE)

The MLE process is one of the most common methods used in wastewater treatment for biological nitrogen removal (BNR). This method is based on an anoxic-aerobic process with recycling of biomass into the anoxic zone, but with an improvement in the process by providing an internal recycle to feed nitrate to the anoxic tank directly from the aerobic zone. A typical internal recycle flow to influent flow ratio ranges from 2 to 4, and retention time in the anoxic zone is 2 to 4 hrs. Dissolved oxygen (DO) on the internal recycle has to be controlled to limit the amount of DO carried from the aerobic to the anoxic zone. This process is used when an effluent total nitrogen concentration of less than 10 mg/L needs to be achieved (Metcalf & Eddy, 2003).

2.3.1.2. Step Feed

The step feed process is also used when a concentration of total nitrogen of less then 10 mg/L is required as in the MLE process. The influent is fed into a series of anoxic-aerobic zones. The process requires a DO control in each recycle stream. Influent flow splitting measurements and control are also necessary to optimize the process. The flow entering the last anoxic zone will determine the concentration of

nitrogen in the effluent, since nitrate produced in the last aerobic tank will not be reduced (Metcalf & Eddy, 2003).

2.3.1.3. Sequencing Batch Reactor (SBR)

A sequencing batch reactor process utilizes a fill-and draw reactor with complete mixing during the batch reaction step (after filling) and where the subsequent steps of aeration and clarification occur in the same tank. This reactor has five steps (1) fill, (2) react (aeration), (3) settle (sedimentation/clarification), (4) draw (decant), and (5) idle (Metcalf & Eddy, 2003). Mixing of mixed liquor with the influent during the filling step provides anoxic condition for the nitrate removal. A nitrate concentration of 5 mg/L can be achieved with this process. The slow mixing and filling without aeration, improves sludge settling. Nitrate removal also occurs during the nonaerated settle and decant period (Reynolds et al., 1996).

2.3.1.4. Bio-Denitro

The bio-denitro is a process with large volume reactors and DO control. This process is also called phased-isolation oxidation ditch technology. The bio-denitro process uses at least two oxidation ditches where the sequence of operating the ditches and the anoxic zones varies. The tanks are provided with bottom mixers. Removal of total nitrogen to less than 5 mg/l is possible with this process (Metcalf & Eddy, 2003).

2.3.1.5. Nitrox

The Nitrox process operates in an oxidation ditch by switching off and on from aerobic to anoxic conditions. The switching of these conditions is controlled by oxidation-reduction potential (ORP). At selected times of the day, the aeration will be turn off and the mixer on. The aeration will turn on when the nitrate is depleted in the wastewater. Typically operation condition for a Nitrox process is to turn off the aerators at least twice at day. The nitrate depletion time takes approximately 3 to 5 hours. Concentration of nitrate-nitrogen in the effluent of this process is in the range of 5 to 8 mg/L. However during the off period of aeration, the wastewater accumulates ammonia resulting in high concentration of ammonium in the effluent (Metcalf & Eddy, 2003).

2.3.1.6. Single-Sludge

A mixed anoxic tank in this process is located after an aerobic nitrification system. The denitrification rate is proportional to the endogenous respiration rate; therefore a long retention time is required to obtain a high percent removal of the nitrogen (Metcalf & Eddy, 2003).

2.3.1.7. Four-Stage Bardenpho

The process uses carbon in the raw wastewater as well as from the endogenous respiration. Although the use of an external carbon source is not required, concentrations of total nitrogen in the effluent of less than 3 mg/L can be

achieved if methanol is added. Although operational costs are reduced because an additional carbon source is not needed, capital cost increases due to the larger size of reactors required. In the first stage, nitrate is denitrified, followed by the oxidation of carbonaceous BOD and nitrification of the ammonia to nitrate in aerobic tanks. A combination of nitrate from the first and second stage of the process is denitrified in the third stage and at the fourth stage, all the ammonia is oxidized to nitrate with stripping of nitrogen gas produced during the previous stages (Reynolds et al., 1996). The Bardenpho process operates with an internal recycle of flow rate from the aerobic to the anoxic basin between 200 and 400% of the influent, and a return activated sludge between 50 to 100% of the incoming flow (Metcalf & Eddy, 2003).

2.3.1.8. Five-Stage Bardenpho

This process is a modification of the four-stage banderpho process. An anaerobic first stage is added to the four-stage Banderpho process. This modification provides anaerobic, anoxic, and aerobic stages for nitrogen, phosphorous and carbon removal. A second anoxic stage is provided for additional denitrification. (Metcalf & Eddy, 2003) The five-stage Banderpho process uses 10 to 20 days of solid retention time, and thus increases carbon oxidation capability. In this process, the fifth aerobic stage serves to reduce the amount of phosphorous in the effluent (Reynolds et al., 1996).

2.3.2. Attached Growth

Attached growth processes utilize inert media, to which bacteria attach and form biofilms. Typically, an exogenous carbon source is added to this process to provide an electron donor that can be oxidized biologically using nitrate or nitrite.

2.3.2.1. Downflow Packed-Bed

Downflow packed-bed is deep denitrifier filters that have been used for post-anoxic nitrate removal. The filter provides suspended solids and nitrogen removal by microbial growth on the filter packing. Sand is usually the packing type for these filters. With proper control of methanol addition, these filters can achieve 1 to 3 mg/L of total nitrogen in the effluent and less than 0.5 mg/L of TSS. The disadvantages of these filters are that during operation headloss gradually increases due to biomass growth, accumulation of suspended solids, and accumulation of nitrogen gas from denitrification.

2.3.2.2. Upflow Packed-Bed

Two main manufactures of this type of reactors exist: Biofor® and Biostyr®; both function by moving wastewater up through the bed, while aeration across the bed is provided. The packing material for these reactors is clay for the Biofor® and synthetic beads for the Biostyr®. Concentration below 5 mg/L of nitrate as nitrogen can be achieved with these reactors under controlled electron donor dose.

2.3.2.3. Fluidized-Bed Reactors

These reactors maintain a fluidized bed of sand or other packing material provided by a sufficient upward flow velocity. The intense mixing provides good mass transfer. Empty-bed liquid retention time is only 10 to 20 minutes with the production of nitrate effluent of 2 to 4 mg/L as nitrogen.

2.3.3. Anammox

Anaerobic ammonia oxidation is a microbially-mediated process. Anammox eliminates nitrogen by combining ammonia and nitrite to produce nitrogen gas process carried out by bacteria in the order of *Planctomycetales* (Rijn et al., 2006). Simultaneous nitrification and denitrification occurs in an anaerobic reactor without carbon addition (Wimin, 2004). Even though Anammox provides advantages in reducing operating costs, a major limitation is the slow growth rate of the bacteria (Rijn et al., 2006).

2.4. Sodium Ferrate

With the need to minimize the effects that nutrients discharged in effluent wastewater are creating in our environment, especially in their refractory forms, ferrate was considered as an alternative treatment. Ferrate can oxidize these compounds to more favorable forms that can be degraded biologically during subsequent wastewater treatment processes. A brief review of ferrate characteristics is provided below.

2.4.1. Chemical Properties

Ferrate (VI) is an ion in a +6 oxidation state. The oxidation of ferric ion by concentrated hypochlorite in a strong basic solution produces Fe (VI). Ferrate can be prepared in relatively pure form, where it presents an intense purple color that can be seen even at low concentrations in aqueous solutions (White et al., 1998). In aqueous solutions Ferrate (VI) is present as the FeO_4^{-2} ion, and its reaction rate depends on the pH and types of compounds present in the aqueous solution (Bielski et al., 1987). Ferrate oxidizing power decreases from acidic to basic conditions in aqueous solutions; it can deteriorate rapidly in an acidic media resulting in the precipitation of ferric oxides and hydroxides (Bielski et al., 1987). Studies on the use of ferrate demonstrate that it can remove organic pollutants and reduce the COD and BOD of secondary wastewater effluent (Lee et al., 2004).

Ferrate is an efficient coagulant as a result of ferric ion production. In addition, ferrate acts as a disinfectant, eliminating the need for chlorine addition at the end of the treatment, and potentially, the concern of chlorinated compounds production (Sharma, 2002). Being an unstable ion at lower pH, any residual ferrate in the aqueous solution will break down into ferric oxides/hydroxides without causing any additional concerns in a distribution system when used for water treatment (White et al., 1998).

2.4.2. Methods of preparation

There are three methods that have been developed to efficiently prepare ferrate; wet oxidation, dry oxidation, and electrolysis. A variety of ferrate

compounds have been prepared using these methods including Na_2FeO_4, K_2FeO_4, Ba_2FeO_4, and Ag_2FeO_4, with potassium ferrate the most commonly used form (Lee et al., 2004).

2.4.2.1. Wet Oxidation

Ferrate is synthesized by the oxidation of ferric ions by a highly concentrated solution of hypochlorite dissolved in a strong basic solution (NaOH). To date, wet oxidation is the most common method used in laboratories. After the production of sodium ferrate, the solution is mixed with strong potassium hydroxide to crystallize and separate the ferrate ions from the solution. Although the application of this method has reported conversion of ferric ions to ferrous with yields of 70% under optimal conditions, it presents disadvantages due to the requirement of chemicals with a high grade of purity, making it a costly process. Equations 2.4 and 2.5 present the reactions that take place during potassium ferrate preparation.

$$2Fe(OH)_3 + 3NaClO + 4NaOH \rightarrow 2Na_2FeO_4 + 3NaCl + 5H_2O \qquad (2.4)$$

$$2Na_2FeO_4 + 4KOH \rightarrow 2K_2FeO_4 \downarrow + 4NaOH \qquad (2.5)$$

2.4.2.2. Dry Oxidation

Under high temperatures and pressures Iron oxides can be treated with a strong oxidant (Na_2O) to produce ferrate. The preparation of ferrate under these

conditions is considered dangerous and difficult to control. A variation of the method using galvanized wastes mixed with ferric oxides has been reported by Jiang and Lloyd (2002) with the formation of sodium ferrate as a result of the reaction describe in Equation 2.6.

$$Fe_2O_3 + 3Na_2O_2 \rightarrow 2Na_2FeO_4 + Na_2O \qquad (2.6)$$

2.4.2.3. Electrolytic Method

The principle behind this method is the anodizing of a pure iron metal electrode in a concentrated alkaline solution under a known current density, composition of the anode material, and type of electrolyte. The production of ferrate with this method is represented in Equations 2.7 and 2.8 (Lee et al., 2003; Jiang et al, 2003).

$$\text{Anode :} \quad Fe + 8OH^- \rightarrow FeO_4^{-2} + 4H_2O + 6e^- \qquad (2.7)$$

$$\text{Cathode :} \quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2.8)$$

2.4.3. Use of Ferrate in Water and Wastewater treatment

The use of ferrate in water and wastewater treatment has recently gained much attention. The dual function of the ferrate as an oxidant and coagulant presents advantages of lower cost and less sludge production in a single dose (Jiang, et al.,

2002). In addition to being an oxidant and coagulant, ferrate is an effective disinfectant that studies have shown can kill bacteria and virus (White et al, 1998).

2.4.3.1. Oxidizing Agent

Fe (VI) is a strong oxidant agent. The redox potential of ferrate is higher than ozone under acidic conditions and is the highest of all the oxidant disinfectants used for water and wastewater treatment (Jiang. et al, 2002). Several halogen and oxygen-based oxidants are widely used, but each one of them has limitations with respect to the production of by products. During oxidation, ferrate also generates a base (OH^-) in aqueous solution, removing metal ions present as a result of hydroxide precipitation. Bartzatt and Nagel (1991) found that ferrate has the ability to oxidize hydroxyl groups to carbonyl groups as well as *nitrosamines* in solution. Studies in the use of ferrate as an oxidant have shown that it can remove organic pollutants and effectively treat nitrogen and sulfur-containing contaminants in water and wastewater effluents by oxidizing them into harmless products (Lee. et al., 2003). The extent of organic compounds oxidation strongly depends on the ferrate dose. Organic matter present in domestic secondary effluent was oxidized with ferrate at a dose of less than 10 mg/L (as Fe). Total Organic Carbon (TOC) and Biodegradable Oxygen Demand (BOD) from a secondary effluent were removed by 95% and 93%, respectively, by ferrate treatment (Jiang. et al., 2002).

Studies done by Sharma et al (1998) on the oxidation of ammonia by ferrate demonstrated that it produces nitrogen-containing products, although reaction rates

were slow. The use of excess ferrate dose demonstrated that it can more rapidly oxidize nitrite to nitrate.

2.4.3.2. Coagulation

During oxidation of organic matter and microorganisms in water, ferrate (VI) will be reduced to ferric (III), generating a coagulant that has proven to reduce turbidity of water and decrease the concentration of natural organic matter (Jiang et al., 2002; Lee et al., 2004). One of the benefits of the use of ferrate for water and wastewater treatment is that lower doses of ferrate are needed when compared with other coagulant agents and thus the sludge generation is reduced (White et al., 1998). Another advantage of ferrate is that it can destabilize colloidal particles within 1 minute (Jiang et al., 2002).

2.4.3.3. Disinfectant

Since the discovery of chlorinated by-products (CBP) and their negative health effects, great efforts have been made to minimize the CBP formation after disinfection with chlorine or other halogens. Ferrate in addition to its oxidant and coagulant powers, acts as disinfect that does not react with organic matter to form carcinogenic trihalomethanes (THM). Since the first observation of the abilities of the ferrate to kill and inactivate bacteria and viruses, many studies have also proven that it can retard the growth of biofilms, and serves as an anti-fouling agent. Researchers have shown that for a low dose of ferrate (10 mg/L as Fe), approximately

two logs of inactivation of total bacteria were observed (Lee et al, 2004; White et al, 1998).

2.5. Summary

The literature demonstrates that nitrogen in wastewater effluent creates adverse environmental impact. While there are many proven techniques to removed significant amounts of nitrogen, there often remains recalcitrant nitrogen that may continue to present environmental risk. An approach that effectively and economically removes this nitrogen is needed.

3. MATERIALS AND METHODS

The presence of nitrogen in water and its different forms are of great interest to wastewater treatment plant operators and others who desire to protect and preserve the environment. Ferrate was used as a strong oxidant to treat refractory forms of organic nitrogen present in these effluents and potentially transform them into more oxidized ones that can be removed by biological means to biomass and water.

3.1. Treatment with Sodium Ferrate

3.1.1. Ferrate Preparation

The procedure to prepare sodium ferrate used in this research was based on the wet oxidation method. Lee (2004); Thompson (1951); and White and Franklin (1998) describe this method as one of the first steps in the preparation of potassium ferrate. The method requires the oxidation of ferric ions with concentrated hypochlorite under alkaline solution (NaOH) to produce sodium ferrate. Calcium hypochlorite was used as a source of chlorine, 50% by weight solution of sodium hydroxide as the alkaline medium, and ferric chloride as the source of iron. The reaction of the oxidation of the ferric ion occurs as describe in Equation 2.4.

A jacketed beaker of 100-ml capacity was used as a reaction vessel for the preparation of ferrate. The beaker was connected to a water bath circulator with a temperature control system (Isotemp 3006-Fisher range –20 to 200^{o}C) and a Corning

stir plate with a speed of 100 to 1000 rpm purchased from Fisher was used to maintain constant mixing during the preparation of ferrate. Figure 3-1 shows a bench-scale unit used during this research for the ferrate preparation.

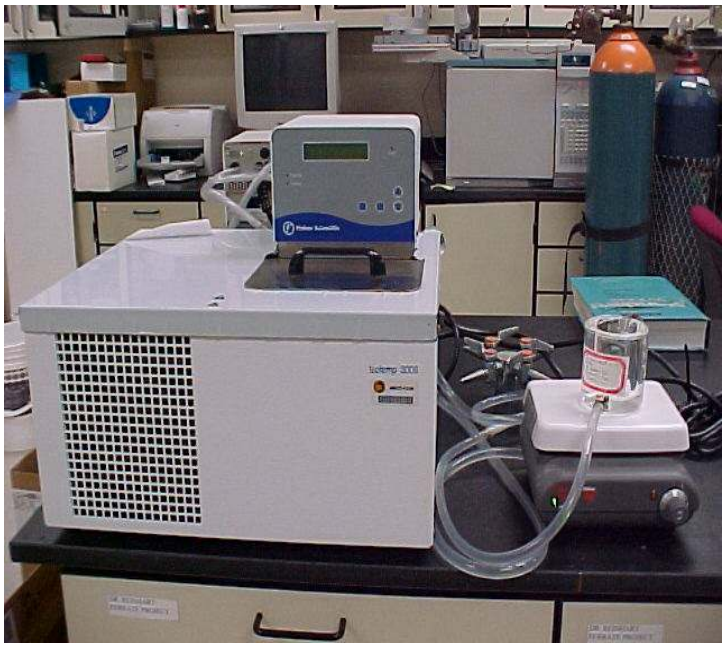


Figure 3-1. Bench-Scale Unit used for the Ferrate Preparation

A CHEM2000 ISS-UV-VIS spectrometer from Ocean Optics (Dunedin, Fl) was used for the determination of the ferrate concentration during its preparation (Figure 3-2). The wavelength range for the instrument is 200-850 nm. The spectrometer has a deuterium tungsten halogen light source, cuvette holder for a 1-cm square cuvette, and a light source/sample holder, which connects to the spectrometer via fiber optic.

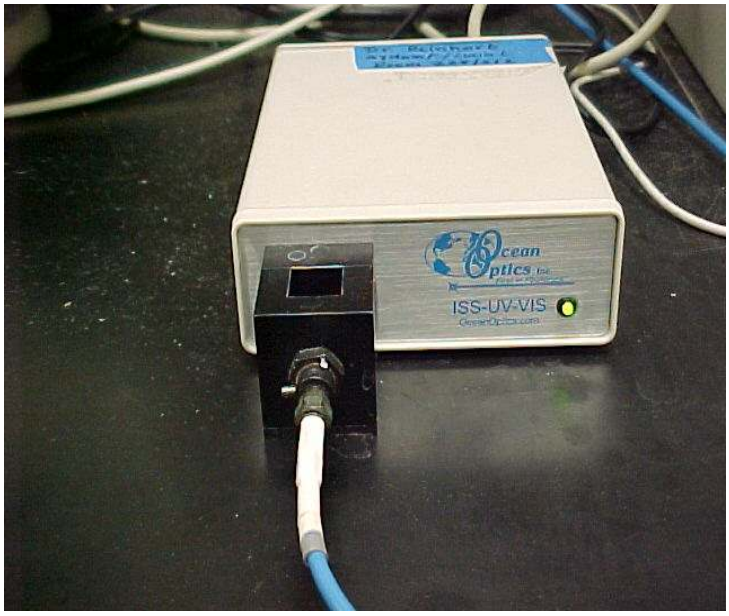


Figure 3-2. Ocean Optics Spectrometer used for the Sodium-Ferrate Preparation.

A solution of calcium hypochlorite (70% available chlorine) and sodium hydroxide (50% by wt) was pre-mixed for one hour in a jacketed beaker containing a stir bar at the speed of 700 rpm. At the end of this period, of ferric chloride (40% by wt) was added slowly to the pre-mixed solution. The speed of mixing was increased to 800 rpm after the addition of ferric chloride. The formation of ferrate ions is easily observed by the presence of a dark purple color. Figure 3-3 shows a typical sodium ferrate solution. All the chemicals used for the ferrate preparation were commercial grade.

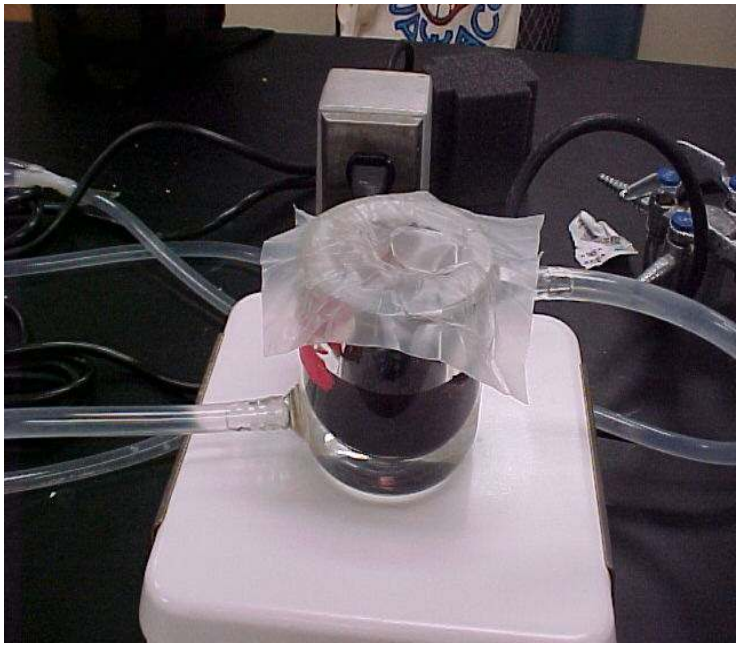


Figure 3-3. Preparation of Sodium Ferrate in a Bench-Scale.

To determine the concentration of ferrate a spectroscopic technique was used. This technique uses absorbance readings of a ferrate solution at a wavelength where ferrate shows its maximum spectra (510 nm). To obtain the absorbance readings, the ferrate needed to be diluted. A borate/sodium buffer (pH 9) was selected due to ferrate stability at high pH. The buffer solution was prepared using sodium tetraborate decahydrate and sodium hydrogen phosphate anhydrous diluted in 1 liter of distilled water. Three drops of ferrate were added and dissolved in a beaker containing 50 ml of a borate/sodium buffer solution previously weighted. The mass of ferrate added to the buffer was then calculated by the difference between the initial weight of the buffer solution and the final weight after ferrate addition. This solution was then stirred and poured into a 1-ml cuvette to measure its absorbance. The concentration of the ion ferrate was than calculated using its weight, density and

extension coefficient and applying Beer's Law. Equations 3.2 to 3.4 show the calculations following to determine the ferrate concentration (Rios, 2004).

$$\mathbf{A = \varepsilon\, l\, c} \qquad (3.2)$$

Where,

A = Absorbance (at 510 nm)

ε = Extinction coefficient (1150 $M^{-1}cm^{-1}$)

l = Cell path length (1 cm)

c = Concentration (M)

Knowing the ferrate concentration and the percent by weight of the ferric chloride solution initially used for the preparation of ferrate, the conversion yield in terms of iron can be calculated using Equation 3.3.

$$Yield = \frac{(P * S * 1000 * \varepsilon * l)}{(MW_{FeCl3} * V * A)} * 100\% \qquad (3.3)$$

Where,

P = Percent of ferric chloride by weight (0.4)

S = Weight of ferrate sample (g)

MW_{FeCl3}= 162.5 g/mole

V = Volume of buffer solution (50 ml)

The concentration of the ferrate ion is calculated using Equation 3.4.

$$[FeO_4]^{-2} = \frac{S_{FeCl3} * P * MW_{FeO4}}{MW_{FeCl3} * T} * yield * \rho \quad (3.4)$$

Where,

$[FeO_4]^{-2}$ =Ferrate concentration (g/L)

MW_{FeO4-2}: = 119.85 g/mol

MW_{FeCl3}: = 162.35 g/mol

Yield = Percentage conversion

ρ = Density of the ferrate solution (1.28 g/ml)

T = Total weight of the solution (g)

P = Percent of ferric chloride by weight (0.4)

S_{FeCl3} = Weight of Ferric Chloride

3.1.2. Ferrate Treatment

Effluent wastewater was collected at a sampling point between final clarification and chlorination from the Eastern Water Reclamation Facility of Orlando, Florida. This facility has a current treatment capacity of 19.4 MGD and uses a five-stage Bardenpho® Advance Nutrient Removal treatment with fermentation, first anoxic tank, aeration basin, second anoxic tank, re-aeration basin, final clarification, filtration and chlorination.

Samples of the effluent were collected in the morning hours of the day (9 to 10 am) prior to each experiment in a 5-gallon carboy. The sample was maintained

under refrigeration at 4°C until its use. The samples were collected, treated and analyzed same day of the collection. Ferrate was prepared immediately prior to use.

Doses between 10 and 50 mg/L of ferrate under unbuffered conditions were used to treat the effluent wastewater. When adding ferrate to treated wastewater, the wastewater pH increased to above 9.5 under unbuffered conditions, allowing any ammonia-nitrogen present in the samples to be converted to free ammonia and potentially stripped. Ammonia concentrations in treated wastewater effluent are typically relatively low, thus ammonia stripping is not expected to be an issue. During ferrate addition, the sample was stirred using a magnetic stirrer plate, until completely mixed conditions were observed. Stirring was then stopped, and the pH of the treated sample was adjusted using 6N hydrochloric acid. Aliquots of the treated samples were collected and prepared for analysis. In order to establish whether nitrogen was removed by oxidation or coagulation, total and soluble TKN were measured. Experiments using ferric chloride ($FeCl_3$) were also run to compare with the benefits of ferrate. All the experiments described were conducted at room temperature (~23°C).

3.1.2.1. Preliminary Treatment

Beakers of 1-liter capacity were used as reaction vessels for the ferrate treated sample. Ferrate was added in doses of 1, 2.5, 5, 7.5, 10, 20, 25, 35, 50 and 100 mg/L as FeO_4^{-2}, mixed at 500 rpm for 1 hour using stir plates. For doses lower than 10 mg/L, the ferrate reacted and was reduced to ferric ions within five minutes of mixing time and within ten minutes for the dose of 10 mg/L. For samples with doses of 35

and 50 mg/L, ferrate was stable for more than three hours. The decomposition of the ferrate was determined visually, by the change in color of the solution from the dark purple of ferrate (VI) to the orange of ferric (III). The pH of each treated sample was determined. The pH of the treated sample increased from 7.5 to 12.89 for the highest dose used (100 mg/L as FeO_4^{-2}). After ferrate fully decomposed, the solids formed during this treatment were allowed to settle for 30 minutes, and the supernatant was collected and prepared for analysis. COD (total), TSS (total), TKN (total), and pH were analyzed in the supernatant. Results of these preliminary tests are presented in Appendix A.

3.1.2.2. Variation of pH

From the data collected during the preliminary experiments, only four doses were selected to continue with the research, 10, 25, 35 and 50 mg/L as FeO_4^{-2}. Eight beakers containing 1-liter of sample, two for each dose, were prepared. Ferrate was added at 10, 25, 35 and 50 mg/L as FeO_4^{-2} and mixed for 30 minutes at 500 rpm. During ferrate addition, the pH of the solution was adjusted to 7 using an auto-titrator with a 6N hydrochloric acid solution. After pH adjustment, portions of the samples without settling were analyzed for COD and TKN. In addition a 100-ml aliquot of the sample was taken to determine the TSS produced during treatment. The remaining volume was passed through a 0.45-micron filter to determine the soluble portion of COD, TKN, nitrate-nitrogen, and nitrite-nitrogen. This procedure was repeated for pH values of 7, 9 and 10 to determine the influence of pH on treatment.

3.1.2.3. Mixing Time

During previous treatment trials, mixing times were observed. Initially the mixing time was 1 hour and then later reduced to 30 minutes, since ferrate at the lowest dose (10 mg/L as FeO_4^{-2}) was observed to react completely within 10 minutes. Subsequent experiments were run using a 10 minute mixing time. This period of time is also considered realistic for the application in a wastewater treatment plant at large scale. The speed of mixing was based only on the need to create a homogeneous solution. A speed of 500 rpm was used.

3.2. Biodegradability of a Ferrate Treated Sample

After the optimum dose of sodium ferrate was determined, three bench-scale anoxic reactors, one as a control (untreated wastewater) and two as duplicates containing treated wastewater, were set up to determine what fraction of the remaining recalcitrant TKN could be removed biologically. Doses of 10 and 25 mg/L of ferrate as FeO_4^{-2} were selected for these experiments.

3.2.1. Reactor Design

Three 5-liters glass Kimax brand aspirator bottles, were used as the main body of the reactors. Tubing and ball valves were placed on the bottom parts of the bottles to facilitate sampling of the reactors. These connections were also placed on the top for injection of nitrogen gas. To seal all tubing connections, aquarium silicone was used. After several hours, the silicone dried and the reactors were filled with tap

water to test for leaks. The stopper was also covered with silicone to seal the connection for the injection of nitrogen gas through the top of system. Figure 3-4 shows a set up of the anoxic reactors.

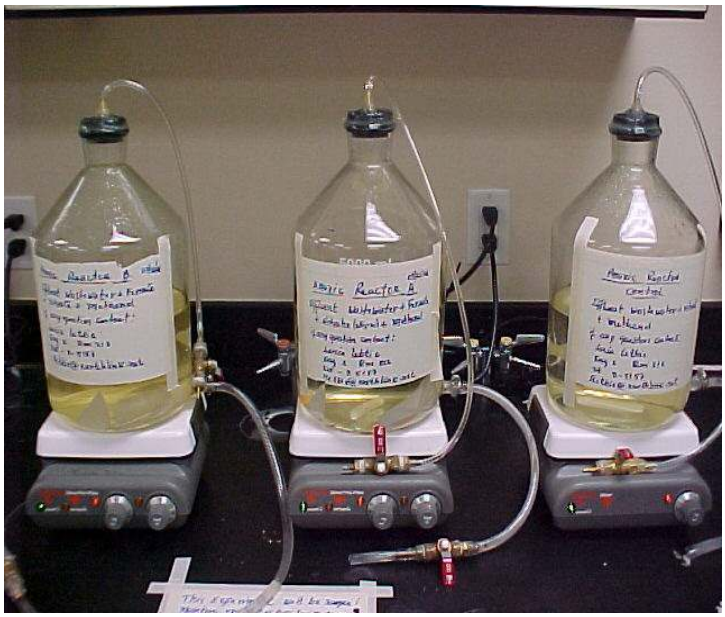


Figure 3-4. Bench-Scale Anoxic Reactors

3.2.2. Sample Preparation

Twelve liters of effluent wastewater were treated with ferrate, with pH adjusted between 7 and 8 using a 12N sulfuric acid solution. Ferrate may have residual chlorine after its production; this was eliminated by the addition of sodium thiosulfate after the 10 minutes reaction time of ferrate with the sample. Eleven liters of the treated sample were used for the anoxic reactors without filtration and one liter was used to analyze the removal of TKN of the sample after ferrate treatment.

3.2.3. Set up and monitoring of the Anoxic Reactors

Each reactor was filled with 5.5 liters of sample; two of them with treated samples as duplicates, and one with untreated effluent wastewater as a control. The reactors were then spiked with 20 mg/L of nitrate-nitrogen to simulate the effluent coming from a nitrification system. Nitrate was added in excess to make sure adequate electron acceptor was presented to remove TKN. Methanol was selected as the carbon source for the reaction at a ratio of. 1.5:1 methanol: nitrate by weight. Pieces of plastic dishes were added to each reactor to support biofilms to accelerate treatment. The plastic dishes were chosen due to their inert properties. A stir bar also was added. Each reactor was placed on top of a stir plate and mixed at a very low and constant speed (100 rpm) to maintain sample homogeneity. After 10 minutes of mixing the solution, 700 ml of sample were drawn from each reactor and labeled as Time Zero, to be analyzed to determine initial conditions. The reactors were then sealed using the stoppers previously prepared. An additional layer of silicone was added to seal the stoppers at the mouth of the bottles. Once the silicone was solidified, the top valve was opened and the bottom one was connected to a nitrogen gas tank. Nitrogen gas was bubbled through the system entering from the bottom and exiting from the top, at a low pressure for a period of five minutes to displace the oxygen present in the head space of the reactors.

The reactors were sampled every 24 hours to test for nitrate; the reduction in the concentration gave an indication that biological activity was occurring. Every 48 hours, a sample was drawn from each reactor to measure pH, DO, nitrate, nitrite, Heterotrophic Plate Counts (HPC), COD (total and soluble), and TKN (total and

soluble). Since 500 ml of the sample were used for the TKN analysis, a total of 700 ml was needed to measure all these constituents, limiting the reactor operation to a maximum of 12 days. This process was repeated for the two selected doses of ferrate, 10 and 25 mg/L as $FeO4^{-2}$. During the entire experiment the reactors were constantly mixed at a very low speed to allow contact with the bacterial population. The pH of the sample during the entire experiment was stable at 8.2 and the DO less than 1mg/L.

3.3. Analytical Methods

All the analytical methods were based on the Standard Methods for the Examination of the Water and Wastewater (APHA 1995).

3.3.1. Total Kjeldhal Nitrogen

The macro-kjeldahl method was applied to determine the amount of TKN present in the samples. TKN determines the sum of ammonia nitrogen plus organic nitrogen in the sample. This method is based on the conversion of amino nitrogen of organic materials into ammonium, in the presence of sulfuric acid, potassium sulfate, and cupric sulfate. The ammonium is distilled from the sample under alkaline conditions (pH 9.5) and absorbed by a boric acid solution containing red methyl and blue methylene indicators. The presence of ammonia is identified visually by the change in color of the boric acid solution from a violet-magenta to a green color. The more intense the green color the higher concentration of ammonia in the sample. The

concentration of the ammonia is than determined by titration with a standard mineral acid (0.02N H_2SO_4 solution).

Due to the low concentration of organic nitrogen in the samples, 1 to 2 mg/L-N, 500 ml of sample was required for each determination of total and soluble TKN. Soluble TKN was determined for a volume of sample passed through a 0.45-micron filter using a vacuum filtration system.

3.3.2. Chemical Oxidation Demand

A slightly modified version of the closed reflux tritimetric method 5220 C of the standard method (APHA 1995) was used for the total and soluble COD determination. Two ml of sample (total and soluble), two ml of potassium dichromate and four ml of sulfuric acid reagent were put into 10-ml volume vials with caps. The vials were capped, shaken vigorously and put into a heater at 150^{o}C for two hours. After this period of time, the vials were allowed to cool to room temperature and titrated against a 0.03-M ammonium ferrous sulfate (FAS) solution (4.9 g of ferrous ammonium sulfate and 20 ml of sulfuric acid diluted to 1 L). Ferroin was used as the indicator solution. A duplicate of each sample (total and soluble), a blank, and a standard (500 mg/L KHP) were tested following the same procedure as the samples. The concentration of the titrant solution (FAS) was calculated every time this constituent was analyzed. For each analysis, soluble COD was determine for samples passed through a 0.45-micron filter.

3.3.3. Total Suspended Solids

The total suspended solids of all samples were measured following 2540 D method of the standard method (APHA 1995). The sample was mixed until a homogeneous solution was observed; an aliquot of this sample was filtered using standard glass-fiber filters (Whatman grade 934AH filters). The residue retained on the filter was dried to a constant weight at 103-105^{o}C. The increase of weight on the filter divided by the volume of the sample filtered represents the total suspended solids.

3.3.4. Nitrite-Nitrogen

To measure the nitrite-nitrogen concentration in the samples, a Hach colorimetric method was used. The samples were initially treated to reduce interference produced by the presence of high concentrations of iron after ferrate treatment. The pH of the samples was increased to 11 to allow ferric hydroxide to precipitate. The samples were passed through a 0.45-micron filter. A 10-ml aliquot of the filtered sample was used for the analysis. Nitriver 3 Hach pillows for a 10-ml sample and a nitrite-nitrogen range of 0 to 0.3 mg/L NO_2-N was used for the test. After a twenty-minute reaction time a reddish purple azo dye was produced. The sample was placed in a 10-ml cuvette and the absorbance was read in a DR/4000 Hach spectrophotometer at 507 nm. Three standards, duplicates for each sample, and one spike were prepared using the same procedure as the samples. All the readings were taken in absorbance mode. A standard curve was created and the concentration of the nitrite-nitrogen was determined using linear regression of data.

3.3.5. Nitrate-Nitrogen

Due to the high concentration of iron in the samples, it was not possible to measure nitrate-nitrogen by the ion chromatograph method. Instead, an Accumet nitrate-selective probe was used for the determination of the nitrate concentration. The known addition method was applied. The samples were filtered using a 0.45-micron filter to eliminate organic matter present in the sample, because presence of organic matter can affect the membrane of the probe and its work time.

3.3.6. Heterotrophic Plate Count

The HPC method or formerly known as standard plate count, was used to measured bacteria growth in the anoxic reactors. A homogeneous sample was taken from the anoxic reactors in conjunction with the daily samples to analyze the other parameters. The samples were analyzed same day following standard method procedure for the spread plate method.

3.3.7. Variation of pH

As a result of ferrate addition, the sample pH increased above 10. To adjust the pH back to 7, 9, or increase to 11 a 719 S Titrino-Metrohm auto-titrator purchased from Fisher was used (Figure 3-5). The auto-titrator provides a total volume of the titrant used to meet a pre-set end point. The pH values are displayed constantly on the front screen of the apparatus. An acid or basic (6N HCL or 6N NaOH) solution was used to adjust the pH.

Figure 3-5. Auto-titrator 719 Titrino, Metrohm

4. RESULTS AND DISCUSSION

4.1. Sodium Ferrate Treatment

Effluent wastewater collected at a sampling point between final clarification and chlorination from the Eastern Water Reclamation Facility of Orlando, Florida was treated with different doses of ferrate (1 to 50 mg/L as FeO_4^{-2}) under unbuffered conditions. Preliminary tests were done to determine the impact of ferrate at low and high doses. The following results are based on these preliminary treatments where the sample was treated with ferrate, its pH adjusted to 7 after treatment and solids formed during treatment, allowed to settle. The supernatant of these treated samples were prepared for analysis. Raw data and additional preliminary results are presented in Appendix C. Table 4-1 summarizes the effect of ferrate treatment.

Table 4-1. Summary of Results of Ferrate Treatment of Treated Wastewater

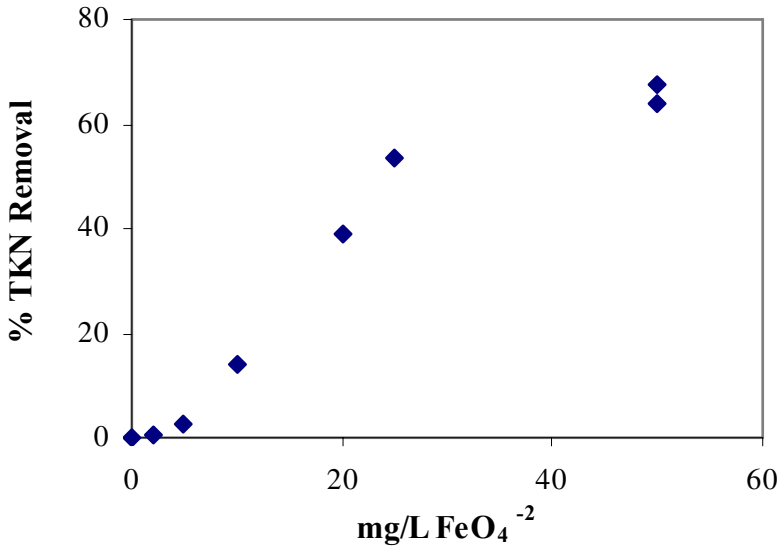
Ferrate Doses	Concentration in mg/L			
mg/L FeO_4^{-2}	NH_3-N	TOrg-N	TKN	TCOD
0	0.3	1.49	1.75	29.3
0	0.0	1.31	1.31	27.4
10	0.0	1.12	1.12	22.6
20	0.0	0.79	0.79	21.8
25	0.0	0.61	0.61	22.3
50	0.0	0.42	0.42	22.0

Duplicates of each dose were prepared and analyzed. Different concentrations of nicotinic acid solution were also prepared and tested as standards to confirm the ability of the macro-kjeldahl method to measure organic nitrogen at low concentrations and the results are presented in Table 4-2.

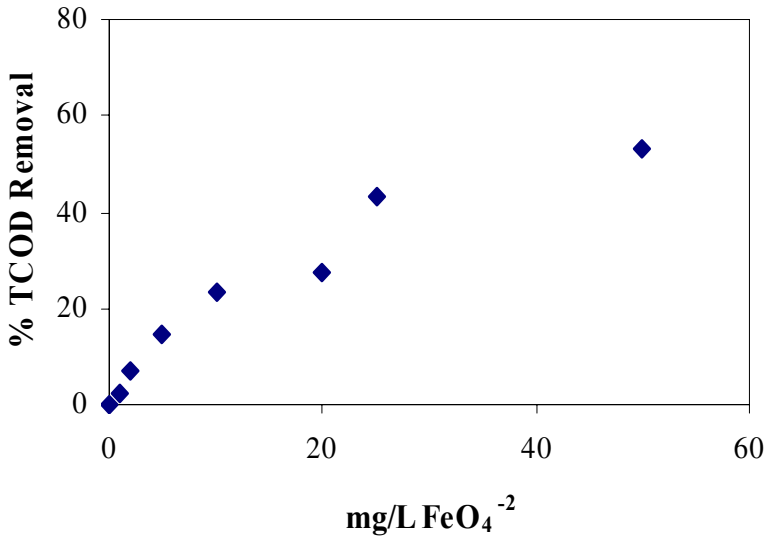
Table 4-2. Determination of Nicotinic Acid Concentration using Macro-Kjeldahl Method.

Nicotinic Acid mg/L as N	NH_3-H mg/L as N	Organic Nitrogen mg/L as N	TKN mg/L as N
0.2	0.1	0.2	0.28
0.2	0.0	0.2	0.20
0.25	0.0	0.25	0.25
0.25	0.0	0.25	0.25
0.5	0.0	0.5	0.5
0.5	0.0	0.5	0.5
1.0	0.0	1.01	1.01
1.0	0.0	1.01	1.01

Figures 4-1 and 4-2 present results of effluent wastewater treated with 1 to 50 mg/L FeO_4^{-2} of ferrate. The treated sample pH was adjusted to 7 before analysis. Figure 4-1 presents results of TKN and TCOD reduction after ferrate treatment. As a result of the treatment, TKN removal as high as 70% and COD removal greater than 55% was observed. Twelve to over 200 mg/L of TSS were produced after ferrate treatment for doses between 10 and 50 mg/L as FeO_4^{-2}, as presented in Figure 4-2. As can be seen the concentration of solids increase as the ferrate dose increases, this can be due to the increase in the amount of Fe introduced into the sample by each dose.



(a) Percent Removal of TKN



(b) Percent Removal of Total COD

Figure 4-1. Percentage Removal of TKN and TCOD by Sodium Ferrate From an Effluent Wastewater. (a). Percent Removal of TKN, (b). Percent Removal of TCOD

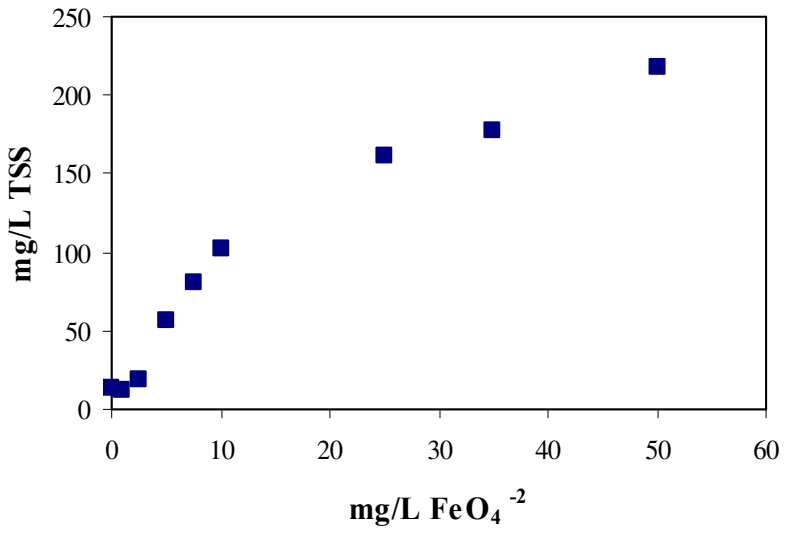


Figure 4-2. TSS Production Due to Ferrate Treatment at pH 7

Additional experiments were performed to compare the coagulant capabilities of ferrate as compared to ferric chloride to examine whether the TKN removed from the treated samples was due to coagulation/flocculation or oxidization by ferrate. As shown in Figure 4-3, ferrate consistently provides greater removal of TKN than $FeCl_3$. Figure 4-4 shows a range of 0.3 to 0.6 mg/L difference between unfiltered and filtered TKN for treated samples; indicating that over 30% of the TKN is found in particulate form, and apparently ferrate does not impact these particulates.

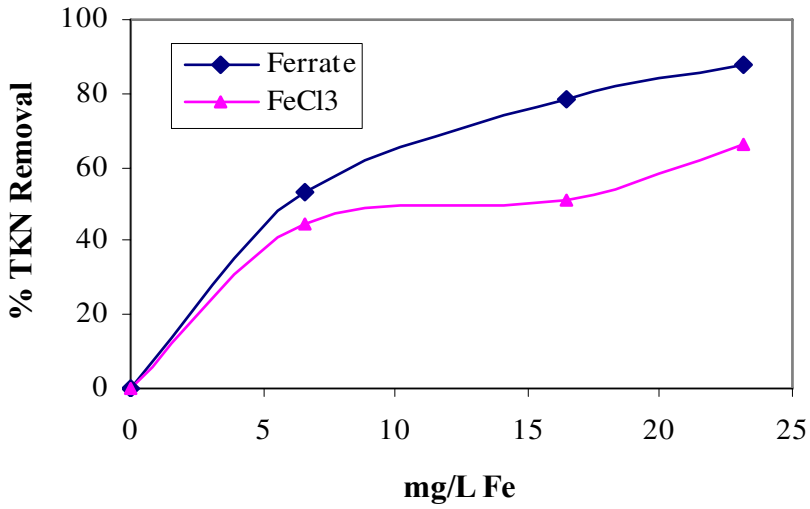


Figure 4-3. Treatment Efficiency Resulting From Two Sources of Fe; Ferrate and $FeCl_3$ at pH 7

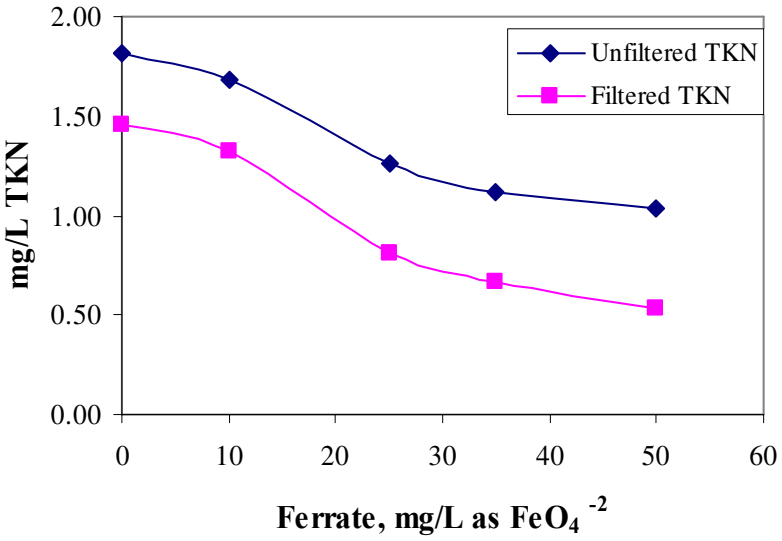


Figure 4-4. Filtered and Unfiltered TKN Resulting From Ferrate Treatment at pH 7

4.1.1. Variation of pH

During ferrate addition (doses of 10 to 50 mg/L FeO_4^{-2}) to an effluent wastewater, the sample pH was adjusted to maintain a constant value for all doses applied. pH values of 7, 9, 10, and 11 were used. A mixing time of 10 minutes for the reaction was maintained for all samples. From Figure 4-5 it can be seen that at pH 11 the percentage removal of TKN is doubled compared with the removal at pH 7. These results demonstrate that the oxidizing power of ferrate will be greater at high pH; this may be a result of the combined benefits that ferrate presents as an oxidant and coagulant.

The production of TSS during the treatment of an effluent wastewater sample with ferrate at different pH values is presented in Figure 4-6. Solids production in the sample is proportional to the dose of ferrate added. Peak solids production occurs at pH 11, minimum at pH 9, although highest TKN removal was observed at pH 7. This reinforces the observations that oxidation, not coagulation, is removing TKN.

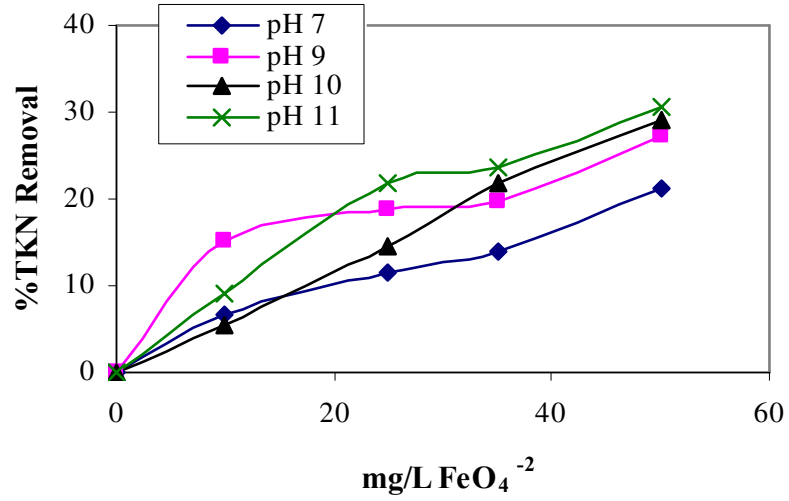


Figure 4-5. Effect of pH in the Removal of TKN with Ferrate

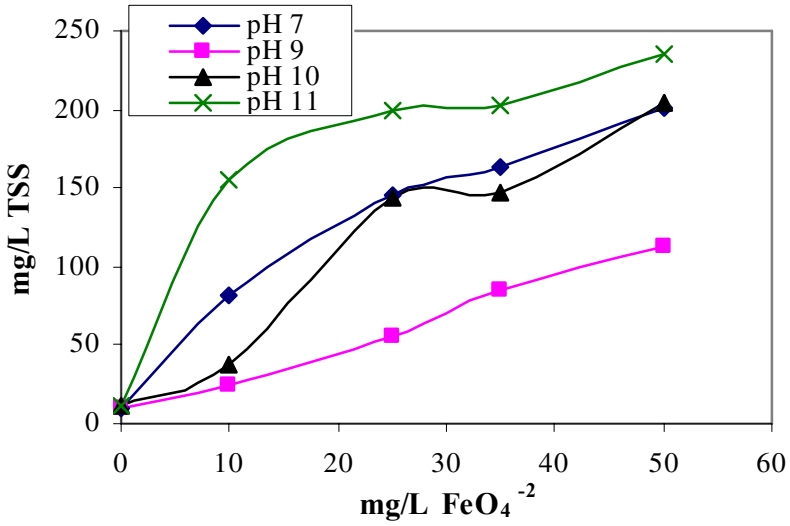


Figure 4-6. Influence of pH on the TSS Production During Treatment With Ferrate

The relationship between mg/L of soluble TKN removed and mg/L of ferrate added is presented in Figure 4-7. This curve was constructed using an average data from four trials of ferrate treatment with pH adjustment to 7. As more ferrate is added, less removal of filtered TKN is obtained. It is possible that at lower doses, ferrate reacts with greater amounts of reactants present in the sample, and as the dose is increased, the remaining TKN is more difficult to oxidize. This can explain the fact that at lower dose, 10 mg/L, a relative high removal (~0.6 mg/L) was observed.

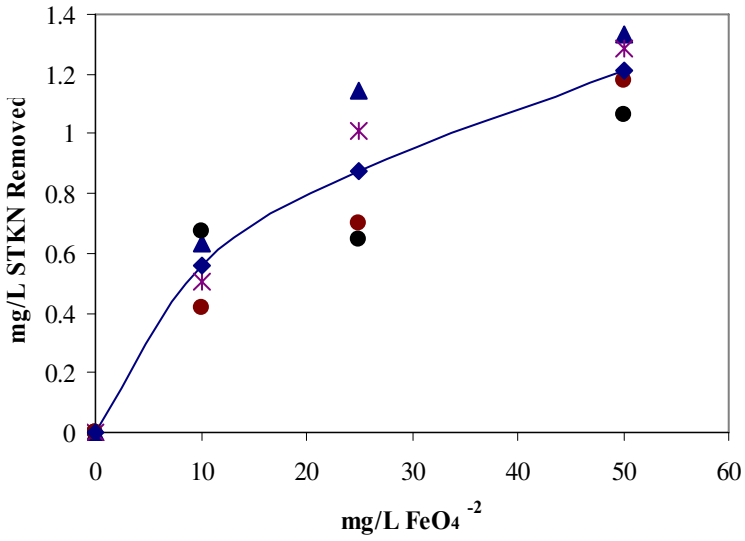


Figure 4-7. Average Removal of STKN from an Effluent Wastewater Treated with Ferrate and pH adjusted to 7.(a) Filtered TKN, (b) Particulate TKN.

The product of oxidation by ferrate is examined in Figure 4-8 where the change in Org-N and NO_2-N vs. the production of NO_3-N from treated samples is

plotted. This figure was constructed using the results obtained from samples treated with ferrate doses of 10, 25, 35, and 50 mg/L FeO_4^{-2} and pH adjusted to 7 after treatment. From this figure it can be seen that approximately 80% of TKN and nitrite is converted to nitrate. The remaining difference is ammonia stripped during ferrate treatment.

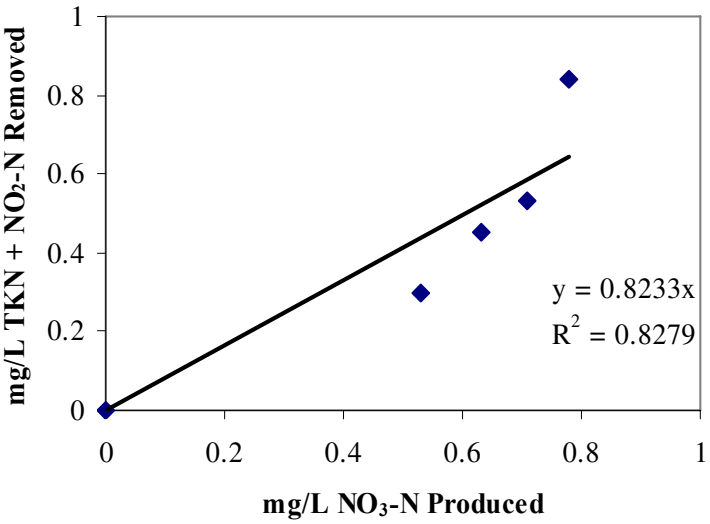


Figure 4-8. Change in TKN and Nitrite-Nitrogen With Respect to Nitrate Production During Treatment of Effluent Wastewater With Ferrate at pH 7

4.1.2. Optimum dose and conditions

After the variations of dose, pH and mixing times for the treatment of the effluent with ferrate, and based on the results of the analysis in the removal of TKN, a dose of 25 mg/L was selected as the optimum dose. The pH and mixing conditions were selected as pH 7 and 10 minutes respectively.

4.2. Biodegradability of the Sample Treated with Sodium Ferrate

The biodegradability of the effluent wastewater after its treatment with ferrate under anoxic conditions was tested. Although 25 mg/L FeO4-2 was selected optimum dose, a lower dose was also evaluated to look the combine effectiveness of oxidation and biological degradation. Two doses of ferrate were selected to run these experiments, 10 and 25 mg/L FeO_4^{-2}. The pH of the samples after treatment was adjusted to 7 and any chlorine residual eliminated. The idea of this pre-treatment was to promote satisfactory conditions for the development of heterotrophic bacteria within the system and the subsequent reduction of TKN. The use of methanol as a carbon source for a denitrification system has been investigated with findings that it will not increase the turbidity in the wastewater and the final products are CO_2 and water (Savage et al., 1973). Following are results obtained from this research. The names assigned to each reactor are based on their content; treated A and B refers to duplicates of effluent wastewater treated with ferrate at doses of 10 or 25 mg/L FeO_4^{-2}; and control refers to the untreated effluent. The reactors were spiked, sealed and run under identical conditions.

4.2.1. Treatment with 10 mg/L of Ferrate

For the reactors with samples treated with 10 mg/L FeO_4^{-2}, the results in the removal of nitrogen by ferrate treatment and biodegradability of its constituents are presented in Table 4-3. Removal of TKN is masked by an increase of bacteria during the biological process. Since bacteria population would be removed by filtration or clarification in a full-scale treatment, we will focus only on the soluble TKN (STKN),

Organic nitrogen, and COD (Figures 4-9 to 4-15). The figures related to the total results are presented in Appendix B.

From Table 4-3 we can see that initially 18% of STKN was removed by ferrate treatment, and after 10 days of biological treatment, the removal of STKN increased by only 31% for a total maximum removal of 43%. Approximately 44% of the ammonia-nitrogen present in the sample was consumed; we considered that it was consumed by bacterial assimilation during this process. From the reactors with the treated sample, only a 25% of COD reduction was observed. Results presented in Table 4-4 for the control reactor, indicated that only 12% of the STKN, and a 34% of soluble organic nitrogen was removed during this process.

Table 4-3. Results from an Effluent Treated with 10 mg/L FeO_4^{-2}

Constituents	Initial Concent. mg/L	Conc. After Ferrate Treatment mg/L	% Removal by Ferrate Treatment	Conc. After Biological Treatment mg/L*	% Removal by Biological Treatment	% Total Removal
STKN	1.96	1.60	18	1.11	31	43
SOrg-N	1.46	1.26	14	0.92	27	37
NH_3-N	0.50	0.34	32	0.19	44	62
NO_3-N	1.18	1.53	-	11.21	-	-
NO_2-N	0.36	0.21	42	0.76	-	-
SCOD	47	41	13	35	14	25

* The values of concentrations after biological treatment are based on sample spiked with 20 mg/L nitrate-nitrogen and methanol as carbon source.

Table 4-4. Results for an Untreated Effluent (Control Reactor)

Constituents	Initial Concent. mg/L	Conc. After Biological Treatment mg/L *	% Total Removal
STKN	2.13	1.88	12
SOrg-N	1.65	1.10	34
NH_3-N	0.31	0.78	-
NO_3-N	1.18	8.97	-
NO_2-N	0.36	1.66	-
SCOD	47	40	15

* The values of concentrations after biological treatment are based on sample spiked with 20 mg/L nitrate-nitrogen and methanol

From Figure 4-9 we can observe that ammonia concentrations in the reactors were consumed. The behavior virtually is the same for all three reactors until approximately 150 hours, after which period of time the ammonia concentration started to increase in the control reactor. A slow reduction of organic nitrogen was observed in the reactors (Figure 4-10). After the microbial population reached critical mass, in approximately 50 hours, SCOD, STKN and nitrate concentrations started to decrease, as we can observe in Figures 4-11, 4-12, and 4-13. It took more than 100 hours for the methanol added to the system to be consumed, as can be seen in Figure 4-12, to reach the initial SCOD concentration of 49 mg/L; eventually an additional 10 mg/L was removed. Unfortunately after 240 hours of operation, we ran out of sample in the reactors. It is possible that more nitrate could be removed if operation of the system had continued.

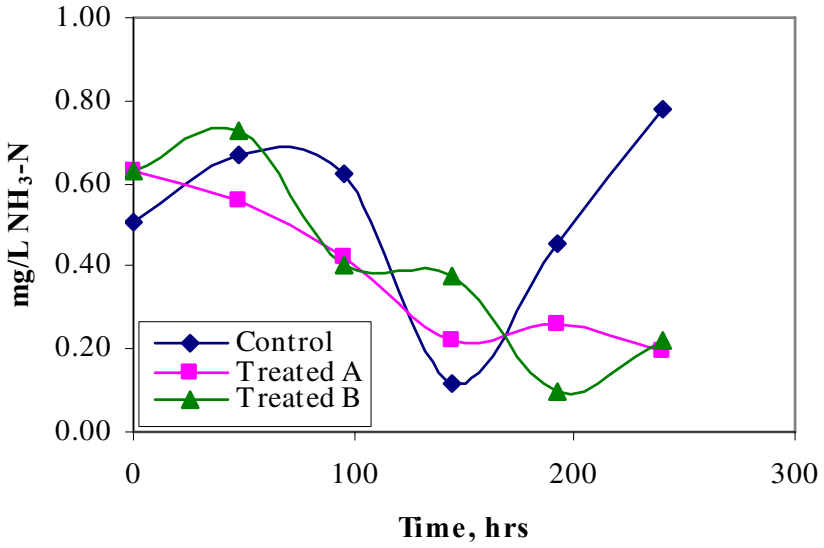


Figure 4-9. Ammonia-Nitrogen Behavior Under Anoxic Conditions of an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}

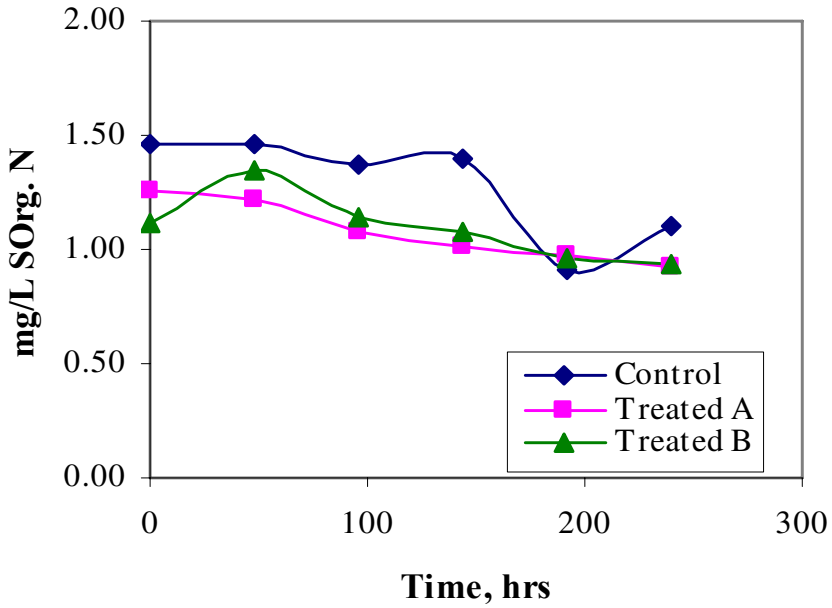


Figure 4-10. Soluble Organic Nitrogen Under Anoxic Conditions from an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}

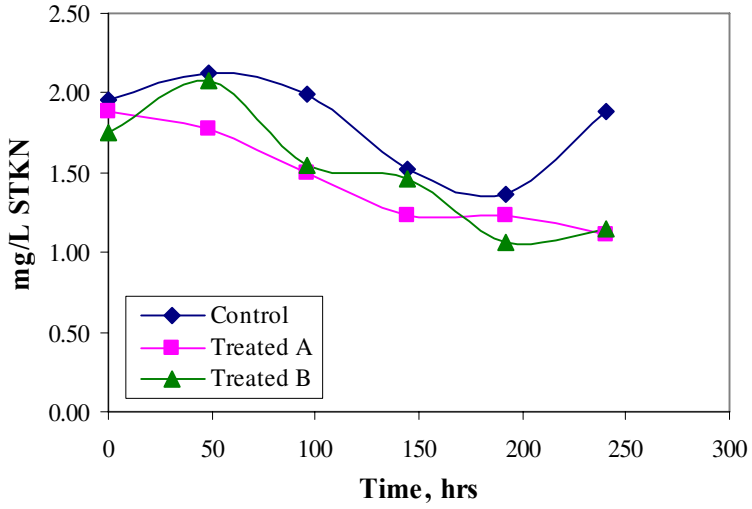


Figure 4-11. STKN Under Anoxic Conditions from an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}.

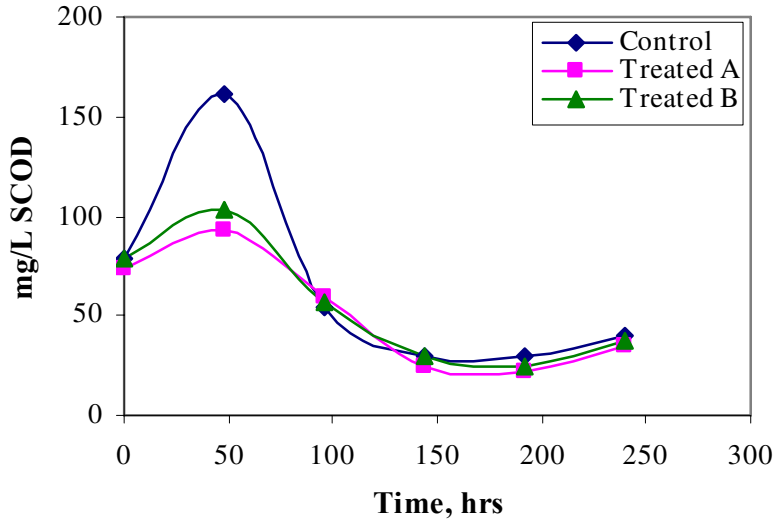


Figure 4-12. Soluble COD Under Anoxic Conditions from an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}.

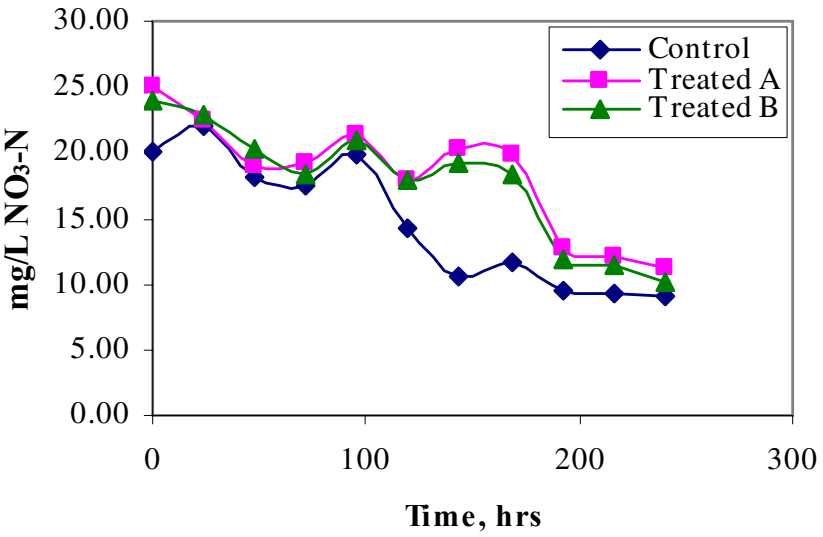


Figure 4-13. Nitrate-Nitrogen Under Anoxic Condition from an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}.

Small increases of nitrite-nitrogen concentration were observed during the process for the treated sample, but greater increases for the control sample (Figure 4-14). Accumulation of nitrite during denitrification process can be due to high light intensities, sub-optimal pH values, oxygen repression, or carbon limitation (Rijn et al., 2006). Heterotrophic bacteria growth is presented in Figure 4-15. Approximately a three-log increase was observed in the reactors during biological treatment. This demonstrates that ferrate can removed pollutants without affecting biological treatments.

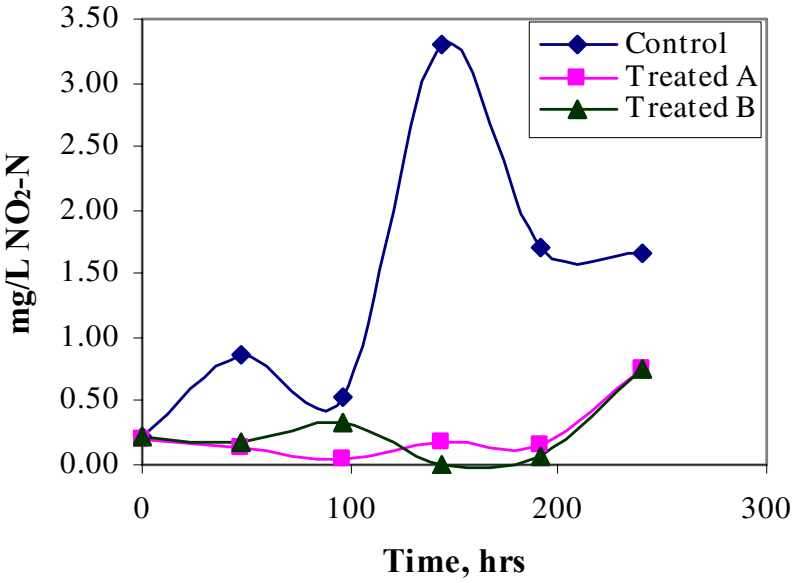


Figure 4-14. Nitrite-Nitrogen Behavior Under Anoxic Conditions for an Effluent Wastewater Treated with Ferrate at 10 mg/L asFeO_4^{-2}.

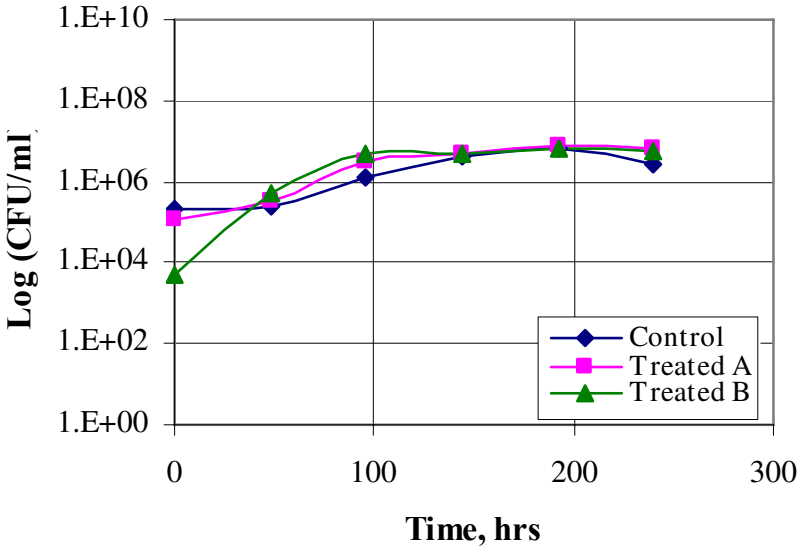


Figure 4-15. Heterotrophic Bacteria Growth under Anoxic Conditions for an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}.

4.2.2. Treatment with 25 mg/L of Ferrate

For reactors with samples treated with 25 mg/L FeO_4^{-2} the behavior of its constituents are presented in Figures 4-16 to 4-21. Table 4-5 and 4-6 present results of the soluble concentration of each constituent of the treated and control samples. Figures related to the total results are presented in Appendix B. The frequency in the collection of samples for analysis was reduced to every two days. Only nitrate-nitrogen was measured daily. This change in the sample collection allowed for the extension of the residence time of the sample in the reactors to 12 days. The reduction in the nitrate concentration gave an indication that biological activity was occurring. From Table 4-5 we can see that initially 9% of the STKN was removed by ferrate treatment, and 70% of the remaining amount was removed biologically in the anoxic reactors. More than 70% of the recalcitrant TKN present in the raw sample was removed as a result of both oxidation treatments, first by ferrate and then biologically. In comparison with the control reactor (Table 4-6), we can see that only 48% of STKN as a total was removed by the biological process. SCOD percent removal for the treated samples was 72% compared with only a total of 23% for the control reactors.

Table 4-5. Results from an Effluent Wastewater Treated with 25 mg/L FeO_4^{-2}

Soluble Constituents	Initial Concent. mg/L	Conc. After Ferrate Treatment mg/L	% Removal by Ferrate Treatment	Conc. After Biological Treatment mg/L*	% Removal by Biological Treatment	% Total Removal
SKN	1.32	1.26	9	0.39	70	71
SOrg-N	0.90	0.88	2	0.39	56	57
NH_3-N	0.42	0.38	-	0.00	100	100
NO_3-N	1.82	2.69	-	5.17	-	-
NO_2-N	0.03	0.01	-	0.86	-	-
SCOD	52	47	10	15	68	72

* The values of concentrations after biological treatment are based on sample spiked with 20 mg/L nitrate-nitrogen and methanol

Table 4-6. Removal of Soluble Constituents from an Untreated Effluent Wastewater (Control Reactor)

Soluble Constituents	Initial Concent. mg/L	Conc. After Biological Treatment mg/L*	% Total Removal
SKN	1.32	0.68	48
SOrg-N	0.90	0.42	53
NH_3-N	0.42	0.26	38
NO_3-N	1.82	2.27	-
NO_2-N	0.03	7.06	-
SCOD	52	40	23

* The values of concentrations after biological treatment are based on sample spiked with 20 mg/L nitrate-nitrogen and methanol

Due to assimilation by bacteria, complete removal of ammonia-nitrogen during the process was observed, as can be seen in Figure 4-16. Initially this concentration was low after ferrate treatment due to stripping and/or oxidation. After 200 hours of operation, the control reactor presented an increase in the ammonia concentration.

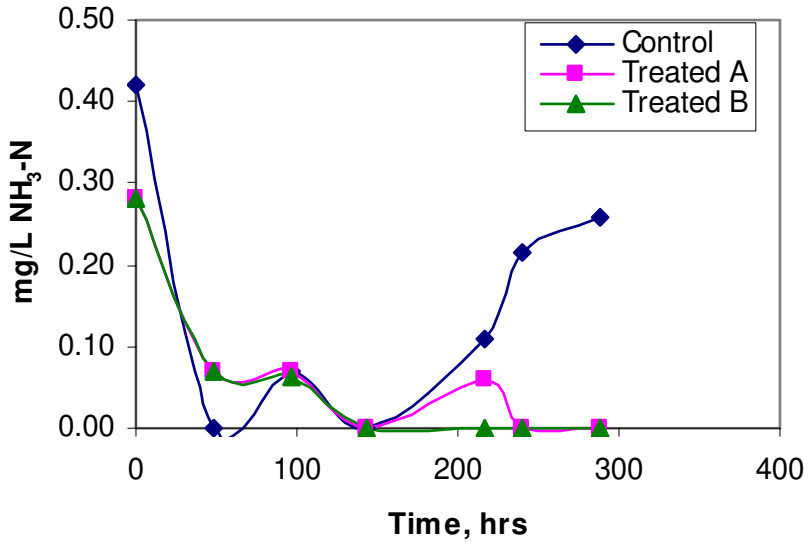


Figure 4-16. Ammonia-Nitrogen Behavior Under Anoxic Conditions for an Effluent Wastewater Treated with 25 mg/L of Ferrate as FeO_4^{-2}

From Figure 4-17 we can observe that the soluble organic-nitrogen reduction in the reactors was similar, and took approximately 200 hours for the concentration to start to decrease. Figure 4-18 presents concentration of SKN for the reactors, and as we can see they follow a similar trend of reduction.

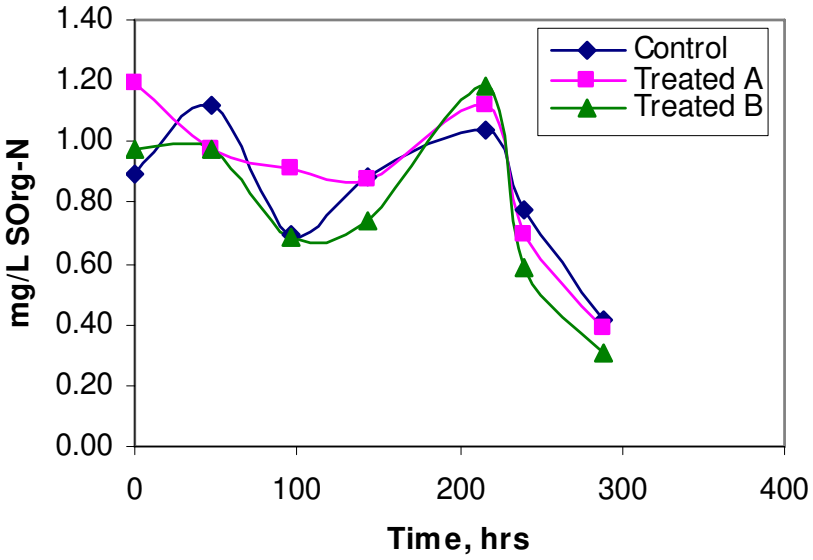


Figure 4-17. Soluble Organic Nitrogen Under Anoxic Conditions from an Effluent Wastewater Treated with 25 mg/L of Ferrate as FeO_4^{-2}

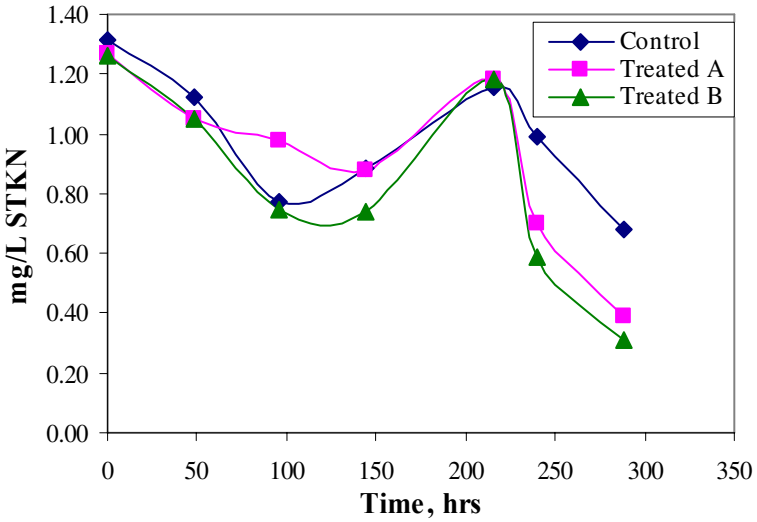


Figure 4-18. STKN Under Anoxic Conditions from an Effluent Wastewater Treated with 25 mg/L of Ferrate as FeO_4^{-2}.

As we can see in Figure 4-19, it took approximately 100 hours for the control reactor to consume the COD added to the system at time zero; and to reach the initial SCOD concentration of 52 mg/L. And for the reactors containing the treated sample, it took almost 200 hours to consume the same amount. During this process accumulation of nitrite was also observed in the control reactor as in the previous trial (Figure 4-20). A nitrite accumulation started at the same time that the nitrate concentration started to decrease. Figure 4-21 shows the behavior of nitrate in the biological reactors. After 100 hours the concentration of nitrate in the control reactor decreased rapidly compared to the treated reactors. This phenomenon could be because at that time, the control reactor had consumed the additional carbon source added to the system and after this period it became limiting.

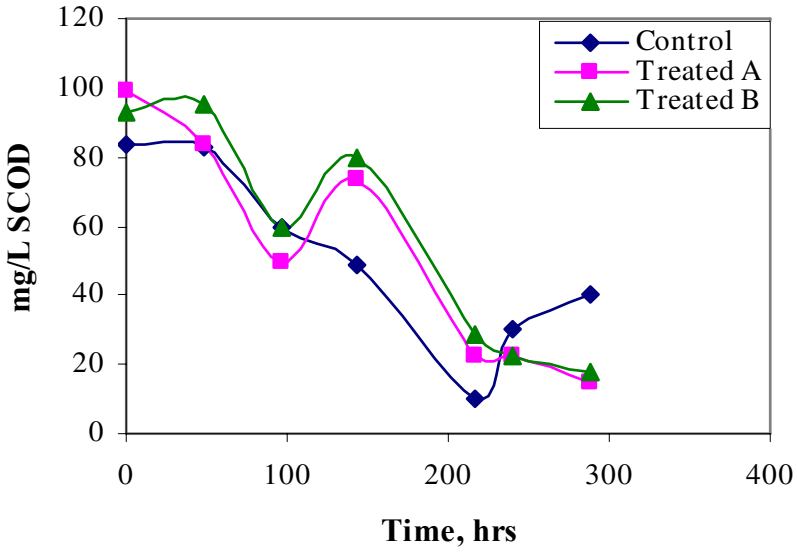


Figure 4-19. Soluble COD Under Anoxic Conditions from an Effluent Wastewater Treated with 25 mg/L of Ferrate as FeO_4^{-2}

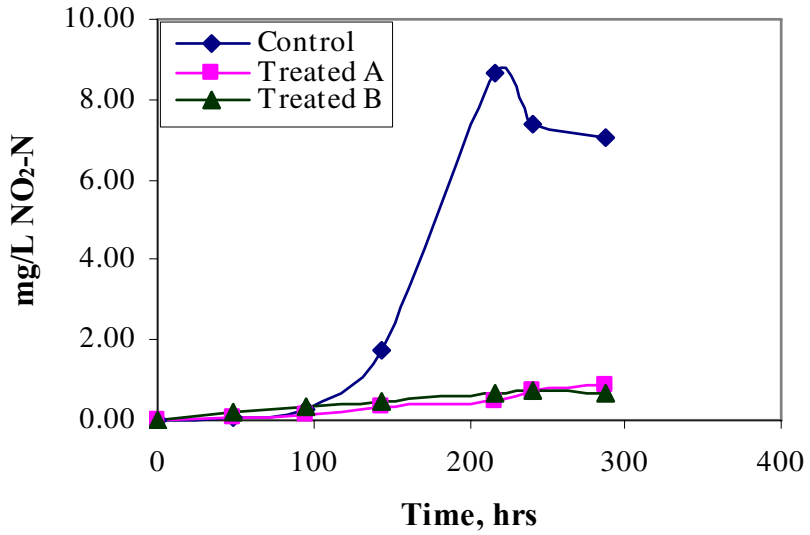


Figure 4-20. Nitrite-Nitrogen under Anoxic Conditions for an Effluent Wastewater Treated with 25 mg/L of Ferrate as FeO_4^{-2}

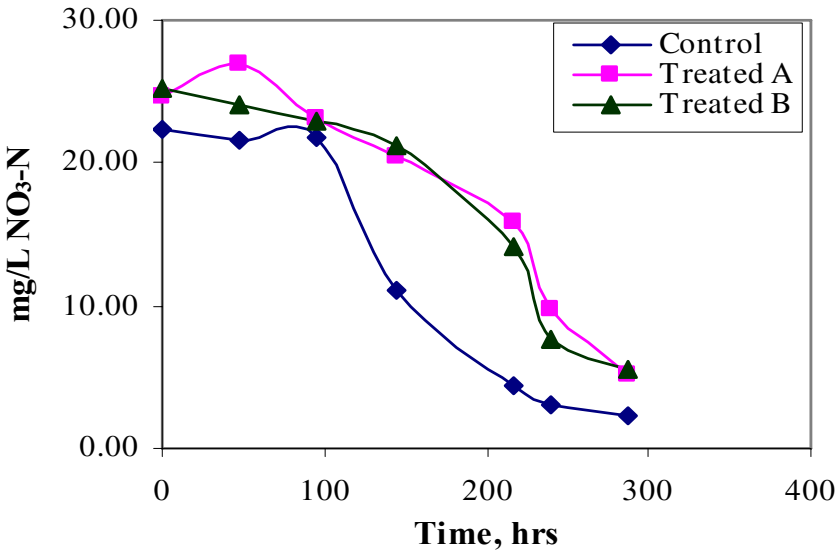


Figure 4-21. Nitrate-Nitrogen under Anoxic Conditions from an Effluent Wastewater Treated with 25 mg/L of Ferrate as FeO_4^{-2}.

Heterotrophic bacteria growth is presented in Figure 4-22. The semi-log figure indicates that approximately three-log of bacteria growth was observed in the reactors. A similar activity was observed in the previous experiment, for the reactors containing sample treated with 10mg/L of ferrate.

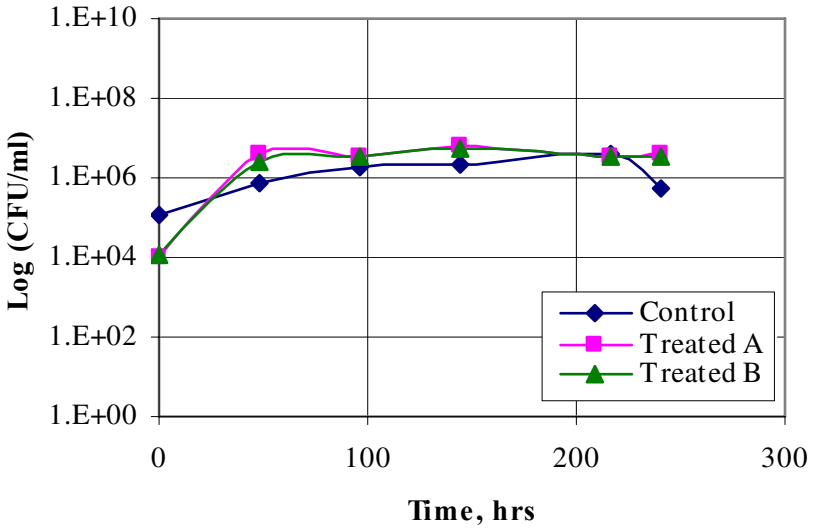


Figure 4-22. Heterotrophic Bacteria Growth under Anoxic Conditions for an Effluent Wastewater Treaded with 25 mg/L of Ferrate as FeO_4^{-2}.

5. CONCLUSIONS AND RECOMENDATIONS

The use of sodium ferrate as a strong oxidant to create a polishing treatment in the removal of recalcitrant TKN was the objective of this research. The removal of recalcitrant nitrogen from an effluent wastewater collected from a local facility was investigated. After ferrate treatment, the biodegradability of these samples was analyzed. To determine the benefits of a ferrate treated sample, a control (untreated effluent) was also analyzed following the same conditions of treatment for the treated samples. For doses of ferrate ranging from 1 to 50 mg/L FeO_4^{-2}, a dose of 25 mg/L was selected as optimum, with pH adjustment to 7 to achieve a 70% reduction in TKN. The TSS production after ferrate treatment was in a range of 12 to 250 mg/L for doses between 10 and 50 mg/L FeO_4^{-2}.

Even though the dose of 25 mg/L FeO_4^{-2} was selected as optimum, a dose of 10 mg/L was also considered to test for the effectiveness of oxidation and biological degradation of TKN. More than 70% of the soluble TKN was removed by chemical and biological oxidation for samples treated with a dose of 25 mg/L FeO_4^{-2}, and less than 50% when treated with 10 mg/L FeO_4^{-2}. For the control samples, a total removal of soluble TKN was as high as 48% and as low as 12%. It is important to acknowledge that the samples used for each set of reactors were collected on different dates and times of the day, which explains the fact that the results for the controls are different.

Sodium ferrate at low doses has been demonstrated to enhance the biodegradability of recalcitrant TKN present in municipal wastewaters. Wastewater treatment facilities require extended retention time plus additional treatment units to accomplish removals of nitrogen to comply with water quality standards. Treatment with sodium ferrate could reduce these retention times, providing a beneficial cost savings of infrastructure, capital and operating cost.

Sodium ferrate was found to be an effective oxidant of recalcitrant TKN. This research was completed with the use of batch reactors simulating a polishing denitrification process. There is a need to investigate the biodegradability of a treated sample under continuous flow conditions simulating a full-scale treatment facility to fully explore the cost effectiveness and efficiency of the process.

APPENDIX A

FERRATE TREATMENT: PRELIMINARY DATA

The data presented here was collected during initial trials to create a methodology and guide to reach the objectives of this research.

Table A-1. Preliminary Results for an Effluent Wastewater before Chlorination Treated with Various Doses of Ferrate

Date	Ferrate mg/L as FeO_4^{-2}	pH	NH_3-N mg/L	TOrganic Nitrogen mg/L	TKN mg/L	TCOD mg/L
6/08/05	0	7.85	5.21	0.34	5.5	
	2	9.14	5.21	0.028	5.2	
	10	10.40	5.37	0	5.4	
	25	11.28	4.7	0	4.1	
	50	12.75	3.25	0	3.2	
	100	13.34	0.17	0	0.2	
9/16/05	0	7.71	0.0	0.84	0.84	24.0
	1	8.48	0.6	0.67	1.23	28.4
	2	8.92	0.6	0.81	1.37	22.1
	5	9.67	0.0	0.73	0.73	20.5
	10	10.10	0.0	0.79	0.79	24.6
09/17/05	0	7.78	0.3	1.75	-	29.3
	10	7.5	-	1.52	-	26.4
	20	7.7	-	1.22	-	21.2
	25	7.6	-	1.01	-	16.6
	50	7.6	-	0.74	-	13.8

During the preliminary tests, we used doses of ferrate between 1 and 100 mg/L as FeO_4^{-2} to treat the effluent wastewater. The results presented in Figure A-1 indicate that for doses between 1 and 10mg/L significant reduction in the soluble TKN concentration between the raw and treated sample did not occur. These analyses were performed without any adjustment of pH of the sample after ferrate treatment. Decision was made after these preliminary tests to continue the research using doses between 10 and 50 mg/L of Ferrate as FeO_4^{-2}.

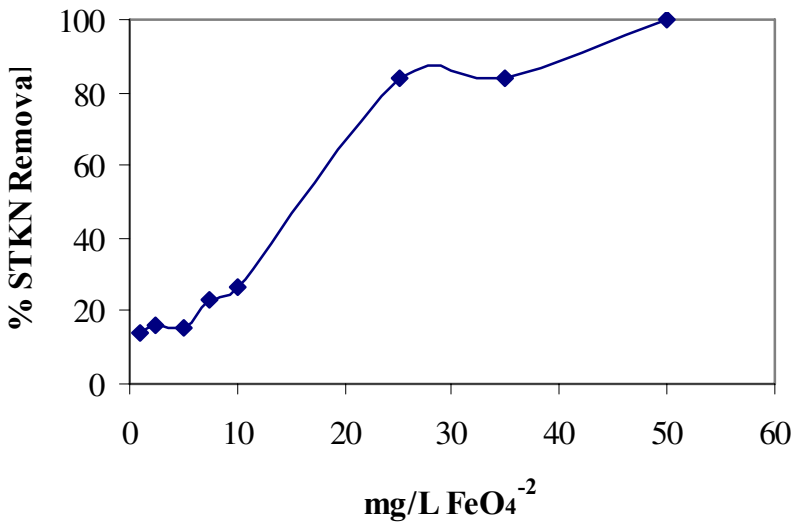


Figure A-1. Percent Removal of TKN of an Effluent Wastewater using Ferrate

A 5 mg/L solution of nicotinic acid as nitrogen was treated with the same doses applied to treat the effluent (10 to 50 mg/L FeO_4^{-2}) to determine the effectiveness of the ferrate to remove or oxidize complex organic nitrogen bonds. Nicotinic acid serves as an organic nitrogen standard referred by the Standard Method of the Water and Wastewater Examination (APHA, 1995), and the results presented in Figure A-2 are indicating that ferrate removed more than 25% of the concentration for dose of 50 mg/L. The pH of the nicotinic acid solution after its treatment with ferrate was adjusted to 7. Since the solution was prepared using distilled water only a soluble part of TKN was analyzed, for this the solution was filtered using a 0.45 micron filter.

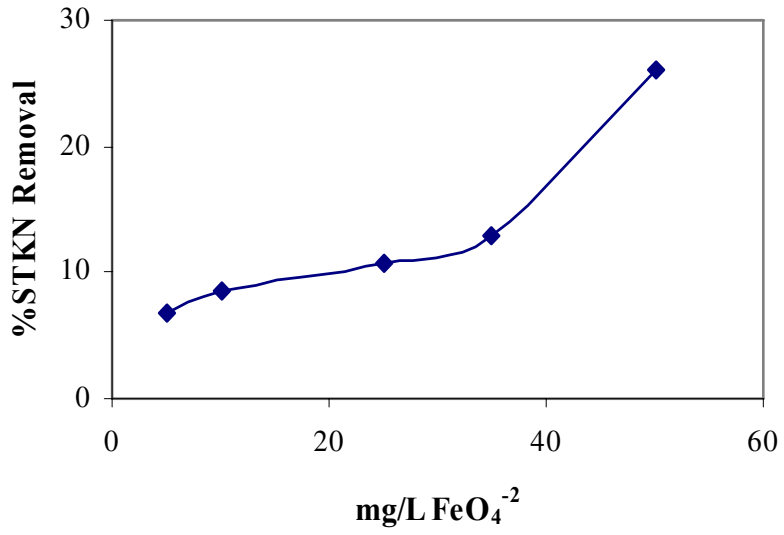


Figure A-2. Percentage Removal of a 5 mg/L as Nitrogen Nicotinic Acid Solution Treated with Ferrate

Table A-2 presents mg/L of Total and soluble TKN from an effluent wastewater after its treatment with ferrate. The samples were treated with ferrate at doses of 10, 25, and 50 mg/L FeO_4^{-2}. The pH of the samples after treatment was adjusted to 7. Table A-3 shows the average of the raw data used to create Figure 4-7 presented in Chapter 4, it presents the average and standard deviation of the results obtained and presented in table A-2.

Table A-2. Removal of TKN from an Effluent Wastewater Treated With Ferrate and pH adjustment to 7(Raw Data for Figure 4-7)

Date	Ferrate mg/L as FeO_4^{-2}	NH_3-N mg/L	TOrg-N mg/L	TKN mg/L	NH_3-N mg/L	SOrg-N mg/L	STKN mg/L
09/17/05	0	0.30	1.49	1.75	0.0	1.31	1.31
	10	0.0	1.52	1.52	0.0	1.12	1.12
	25	0.0	1.01	1.01	0.0	0.61	0.61
	50	0.0	0.74	0.74	0.0	0.42	0.42
09/22/05	0	0.0	1.48	1.48	0.0	1.32	1.32
	10	0.0	1.50	1.50	0.0	1.06	1.06
	25	0.0	1.37	1.37	0.05	0.73	0.78
	50	0.10	1.40	1.40	0.0	0.31	0.31
09/30/05	0	0.11	1.09	1.09	0.08	0.64	0.73
	10	0.03	0.42	0.42	0.03	0.40	0.44
	25	0.06	0.45	0.45	0.06	0.34	0.39
	50	0.0	0.03	0.03	0.0	0.0	0.0
10/07/05	0	0.3	1.82	1.82	0.30	1.20	1.46
	10	0.3	1.68	1.68	0.30	1.06	1.32
	25	0.0	1.26	1.26	0.0	0.81	0.81
	50	0.0	1.04	1.04	0.0	0.67	0.53

Table A-3. Average TKN Removal from an Effluent Wastewater During Ferrate Treatment (Raw Data for Figure 4-7)

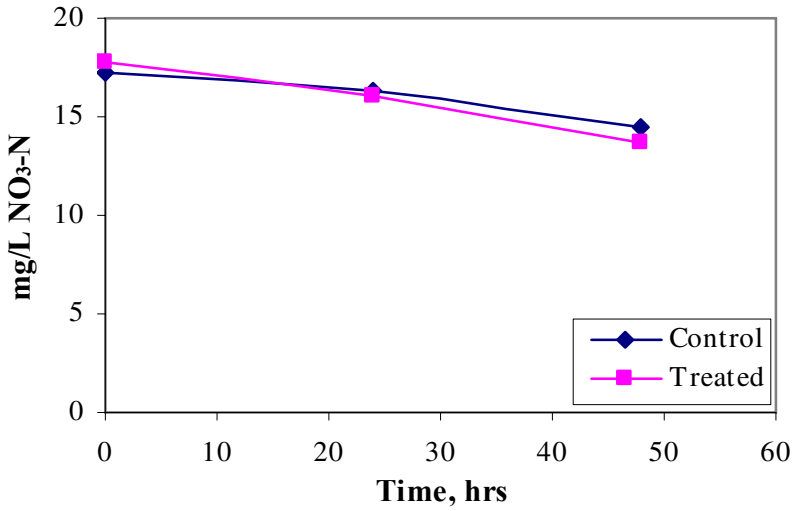
Ferrate Dose mg/L as FeO_4^{-2}	Average mg/L of TKN Removal	Standard Deviation
0	0.000	0.0
10	0.557	0.116
25	0.874	0.242
50	1.214	0.120

APPENDIX B

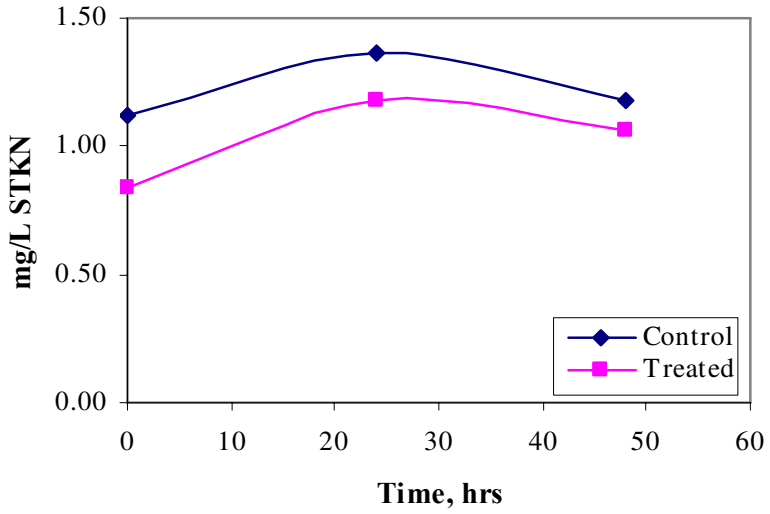
ANOXIC REACTOR: PRELIMINARY DATA

Denitrification is one of the biological processes currently used to reduce nitrogen from a wastewater during treatment. Denitrification defined as the reduction of nitrogen under anoxic or anaerobic conditions. The idea of the biological treatment under these conditions came from the fact of today's facilities are using more and more a combination of aoxic-anoxic-aoxic system. After ferrate addition the samples were treated for pH adjustment and elimination of residual chlorine.

In order to determine the best conditions for the reactors to function under anoxic conditions, different settings for the reactors were initially tried. Figure B-1 presents results of TKN and nitrate-N for two anoxic reactors, one control and one treated with 10 mg/L of ferrate. These reactors were run for only 48 hours. The treated sample was seeded with mixed liquor suspended solids (MLSS) from the same wastewater facility from which the effluent sample was collected, spiked with 30 mg/L of nitrate-nitrogen, and methanol 3:1 methanol: nitrate by weight. The dose of MLSS added to each reactor was based on the percentage of seed necessary to add to a sample during BOD determination. This percentage is referred in the standard method for the BOD test. Even after 48 hours of reaction, the samples in the reactors presented high turbidity and flocs were not easy to settle.



(a)Reduction of Nitrate-Nitrogen



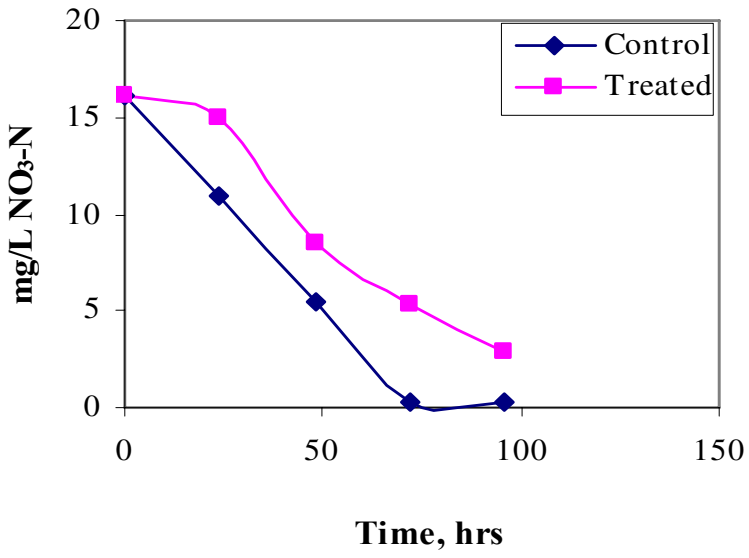
(b)Reduction of Soluble TKN

Figure B-1. STKN and Nitrate-Nitrogen Under Anoxic Conditions from an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}. (a) Reduction of Nitrate-Nitrogen, (b) Reduction of Soluble TKN.

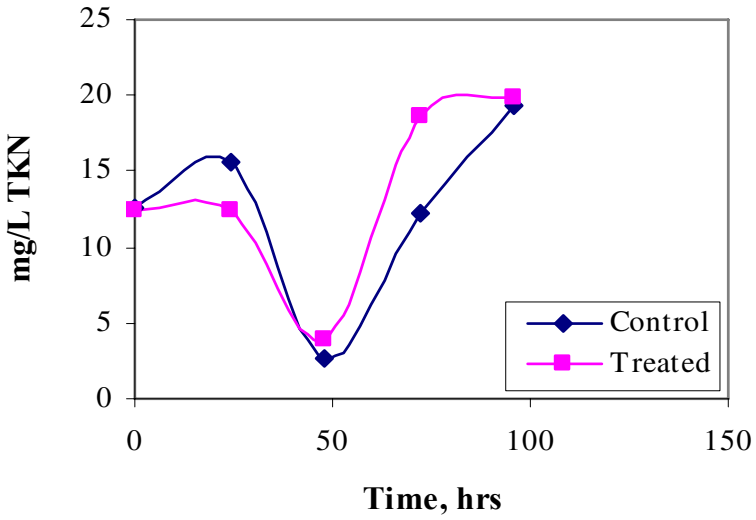
Second Trial

The effluent wastewater was treated with 10 mg/L of ferrate and its pH adjusted to 7 with a 6N HCL solution. Five liters of treated and untreated (without filtration) sample were spiked with 15 mg/L of nitrate-N, seeded with 500 ml of MLSS and methanol on a proportion of 3:1 (methanol: nitrate). The samples were sealed and process on two reactors under anoxic conditions during 96 hours. Figure B-2 presents the results for this trial.

The increment of biomass to the system under limiting concentrations of carbon reduced the nitrate-nitrogen concentrations to over 80% for the treated and over 90% for the untreated or control within 72 hours. The rapid reduction of nitrate can be explained as the assimilation of nitrate by biomass under limitation of carbon source. Even though the results for the reduction of nitrate present promising, there is another situation affecting the TKN concentration. In the figure B-2b, we can observe the impact that the increase on biomass (MLSS) to the system has in the removal of TKN. The effluent resulting from this trial presented a visible high concentration of suspended solids.



(a) Reduction of Nitrate-N



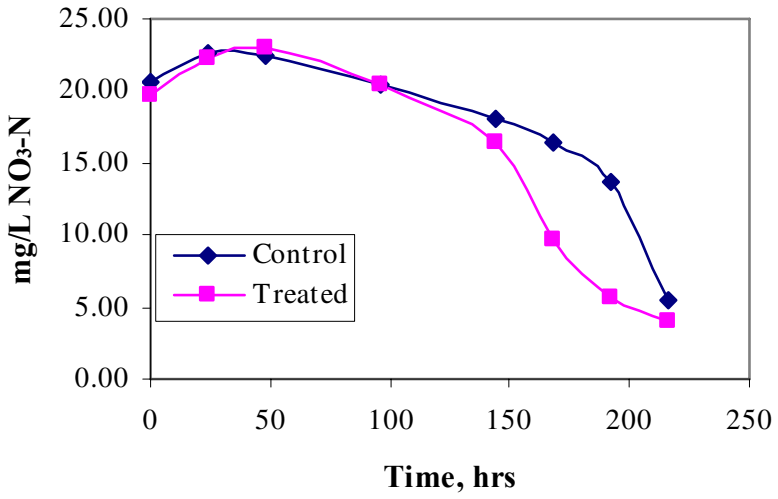
(b) Reduction of TKN

Figure B-2. TKN and Nitrate-Nitrogen Under Anoxic Conditions from an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}. (a) Nitrate-N Reduction, (b) TKN Reduction.

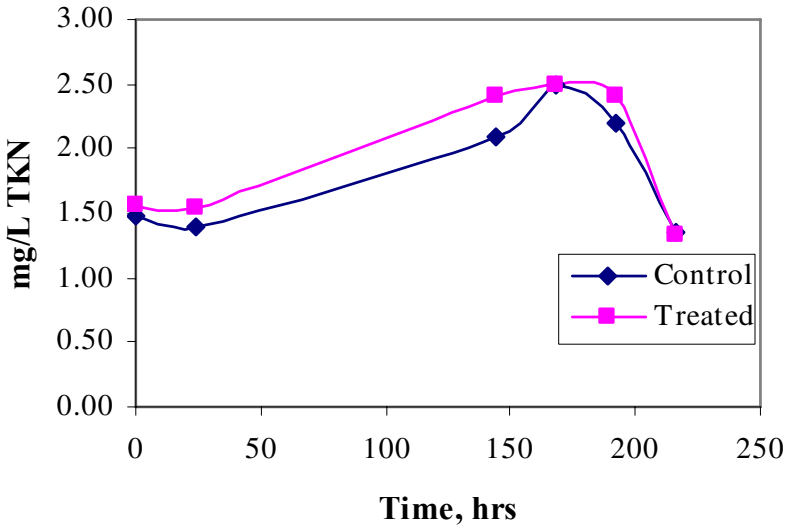
Third Trial

Two reactors were used for this experiment. The effluent wastewater was treated with 10 mg/L of ferrate, spiked with 20 mg/L of nitrate-N, and methanol in a proportion of 3:1 (methanol: nitrate). Seeding with MLSS was eliminated for this trial; to observer the impact of the carbon reduction will create over the system. The results are presented in Figure B-3.

The results present that less than 20% of TKN was removed even though the reduction in nitrate concentration was greater, approximately 80%.



(a) Nitrate-N Reduction



TKN Reduction

Figure B-3. TKN and Nitrate Under Anoxic Conditions from an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}. (a) Nitrate-N Reduction, (b) TKN Reduction.

Fourth Trial

For this trial three reactors were used. The effluent wastewater was treated with 10 mg/L of ferrate, spiked with 20 mg/L of nitrate-N, and methanol in a proportion of 1.5:1 methanol: nitrate by weight was added to each reactor. The results of the soluble concentrations are presented and analyzed in the Tables 4-3 and 4-4 of Chapter 4. The following Figures represent the behavior of the total concentrations of each constituent during the biological treatment.

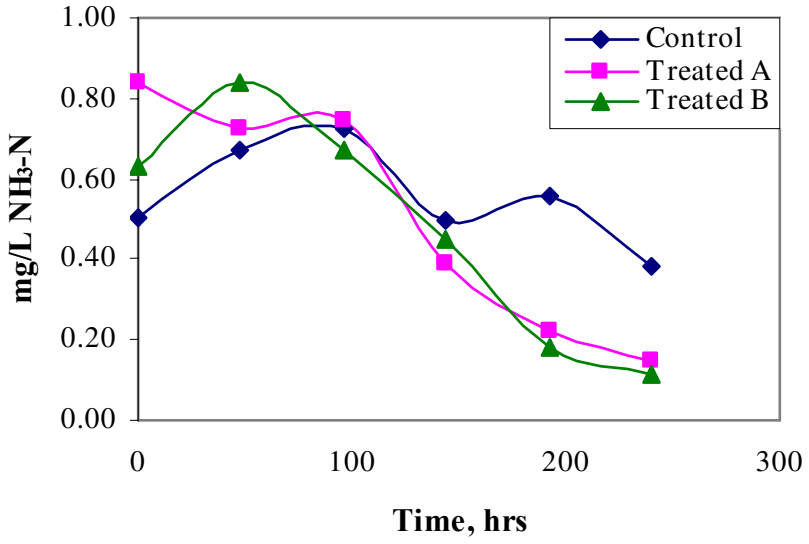


Figure B-4. Ammonia-Nitrogen Behavior Under Anoxic Conditions of an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}

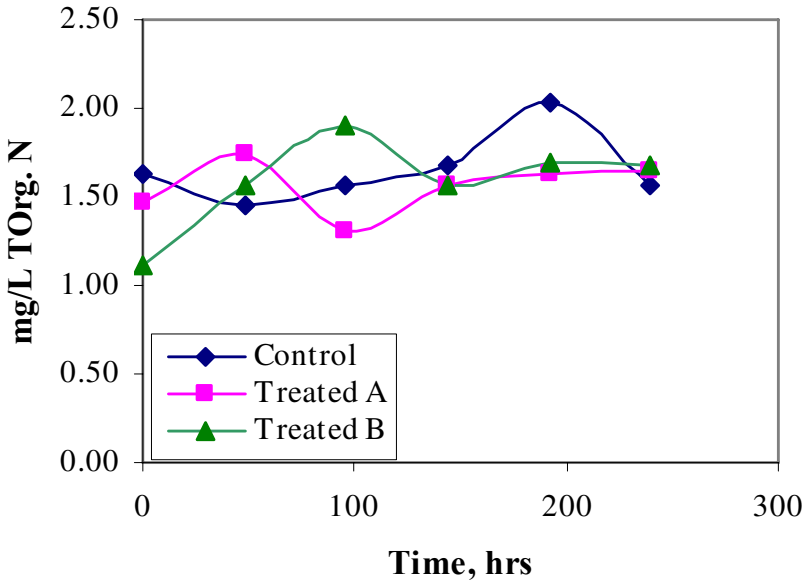


Figure B-5. Total Organic Nitrogen Under Anoxic Condition from an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}.

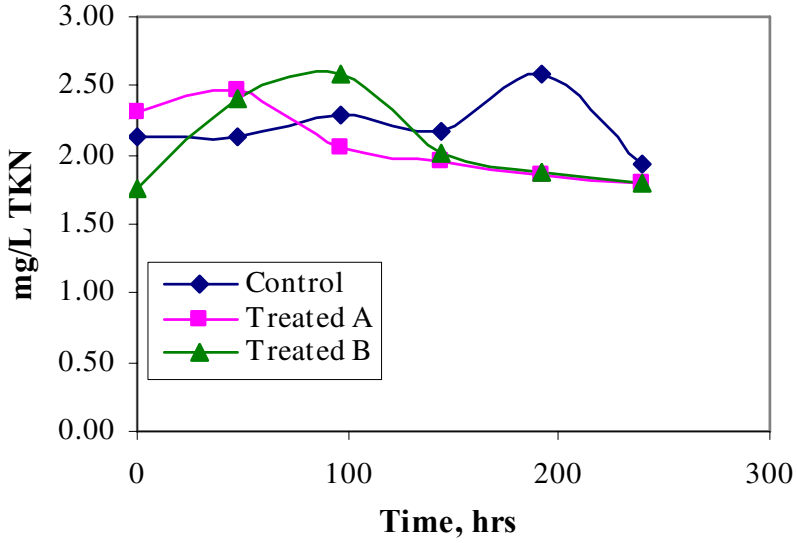


Figure B-6. TKN under Anoxic Conditions from an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}.

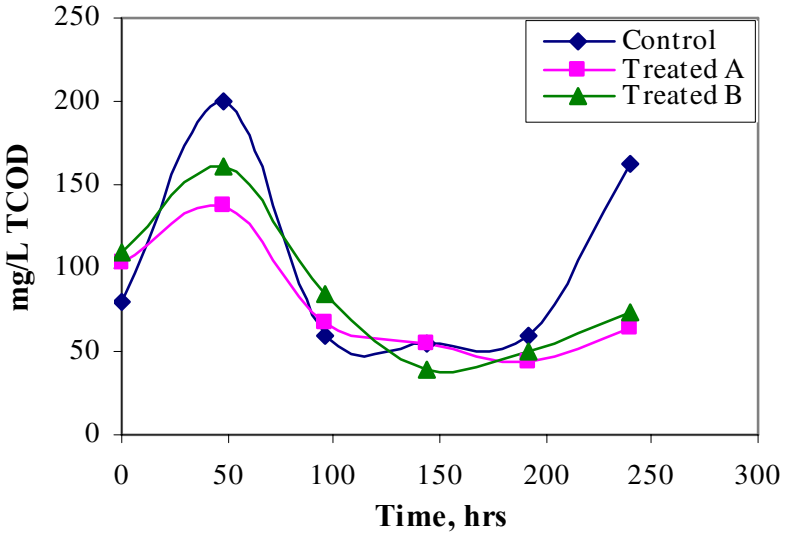


Figure B-7. TCOD Under Anoxic Conditions from an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}.

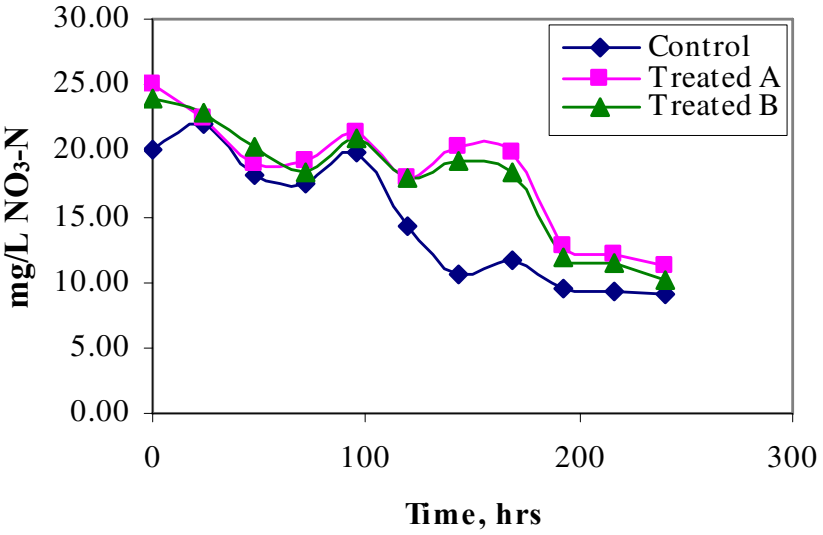


Figure B-8. Nitrate-Nitrogen Under Anoxic Condition from an Effluent Wastewater Treated with 10 mg/L of Ferrate as FeO_4^{-2}.

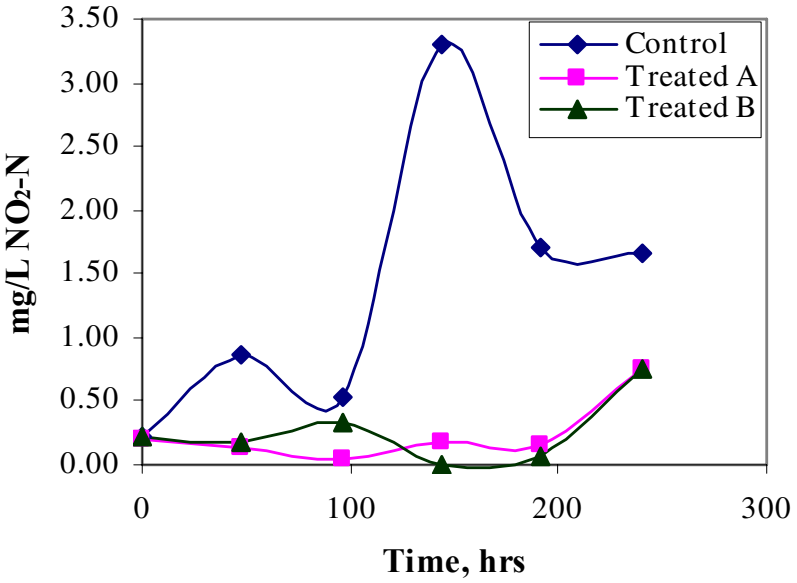


Figure B-9. Nitrite-Nitrogen Behavior Under Anoxic Conditions for an Effluent Wastewater Treated with Ferrate at 10 mg/L asFeO_4^{-2}.

Fifth Trial

For this trial three reactors were used. The effluent wastewater was treated with 25 mg/L of ferrate, spiked with 20 mg/L of nitrate-N, and methanol in a proportion of 1.5:1 methanol: nitrate by weight was added to each reactor. The results of the soluble concentrations are presented and analyzed in the Tables 4-5 and 4-6 of Chapter 4. The following Figures represent the behavior of the total concentration of each constituent during the biological treatment.

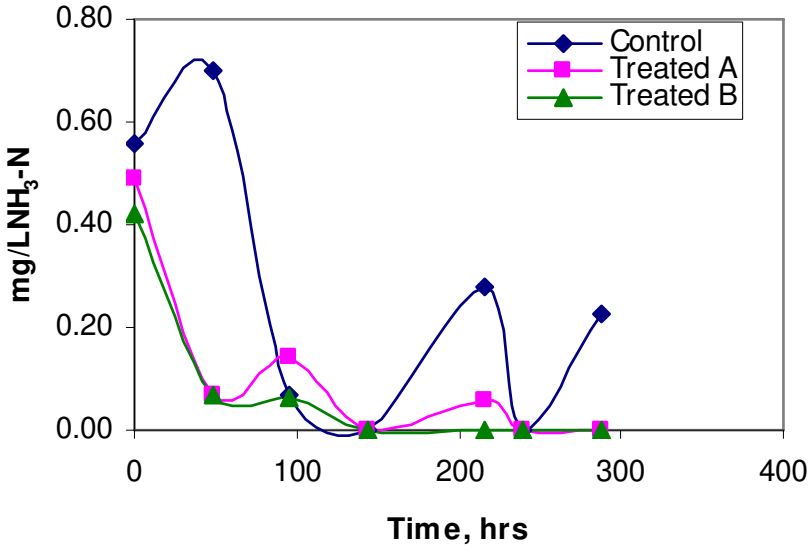


Figure B-10. Ammonia-Nitrogen under Anoxic Conditions from an Effluent Wastewater Treated with 25 mg/L of Ferrate as FeO_4^{-2}

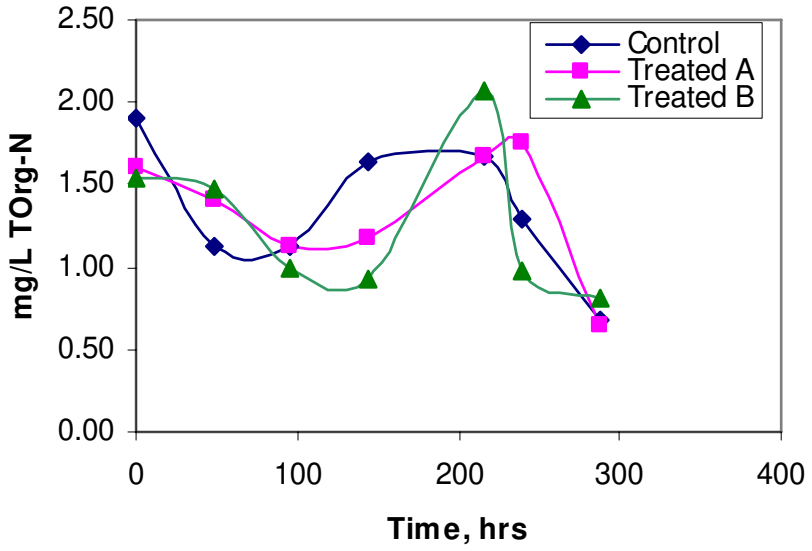


Figure B-11. Total Organic Nitrogen Under Anoxic Conditions from an Effluent Wastewater Treated with 25 mg/L of Ferrate as FeO_4^{-2}.

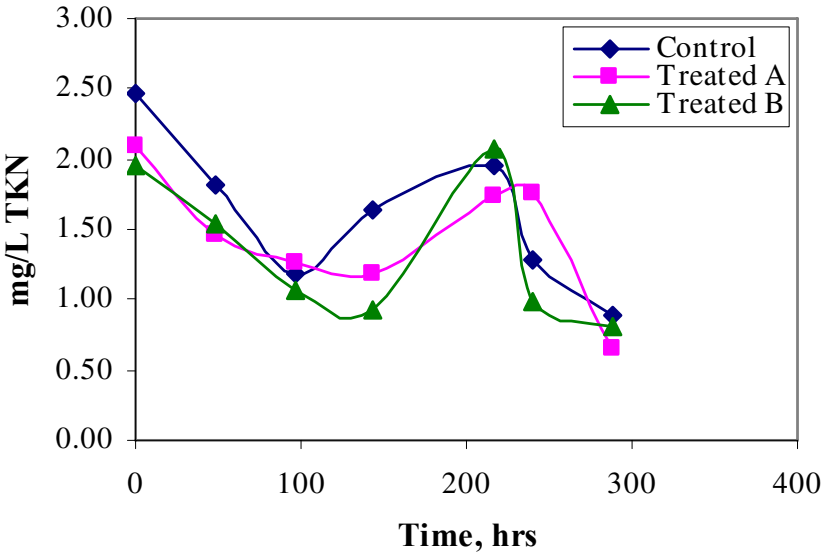


Figure B-12. TKN Under Anoxic Conditions from an Effluent Wastewater Treated with 25 mg/L of Ferrate as FeO_4^{-2}.

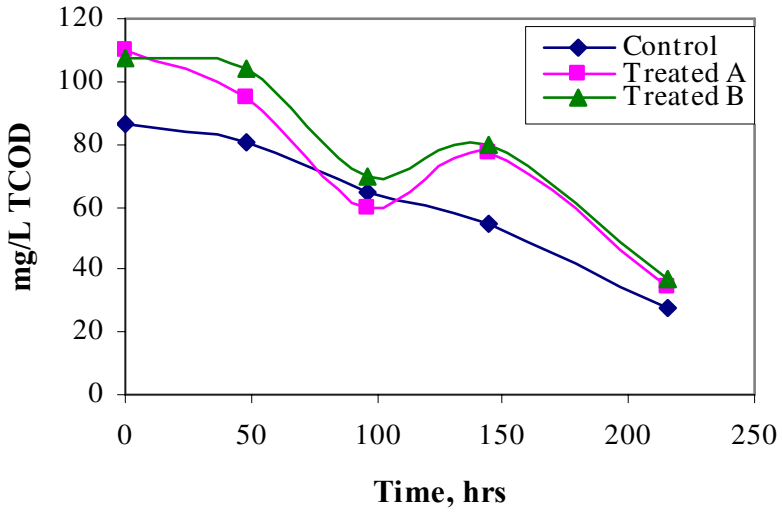


Figure B-13. Total COD under Anoxic Conditions from an Effluent Wastewater Treated with 25 mg/L of Ferrate as FeO_4^{-2}

APPENDIX C

RAW DATA

Table C-1. Results of Ferrate Treatment of an Effluent Wastewater at Various Doses. Raw Data Before and After Treatment

Date	Ferrate Dose mg/L FeO_4^{-2}	NH_3-N mg/L	TOrg-N mg/L	TKN mg/L	NH_3-N mg/L	SOrg-N mg/L	STKN mg/L	Observations
6/7/2005	0	5.21	0.30	5.54				Supernatant,
	2	5.24	0.00	5.24				not filtered
	10	5.38	0.00	5.38				adjusted pH
	25	4.72	0.00	4.72				to 7
	50	3.26	0.00	3.26				
	100	0.17	0.00	0.17				
9/14/2005	0	0.00	0.84	0.84		0.81	0.81	Tested
	1	0.60	0.67	1.23				Without pH
	2	0.60	0.81	1.37				adjustment
	5	0.00	0.73	0.73				
	10	0.00	0.79	0.79				
9/17/2005	0	0.30	1.49	1.75	0.00	1.31	1.31	adjusted to
	10	0.00	1.52	1.52	0.00	1.12	1.12	pH 7
	20	0.00	1.22	1.22	0.00	0.79	0.79	Filtered
	25	0.00	1.01	1.01	0.00	0.61	0.61	samples
	50	0.00	0.74	0.74	0.00	0.42	0.42	
9/22/2005	0	0.00	1.48	1.48	0.00	1.32	1.32	Without pH
	10	0.00	1.50	1.50	0.00	1.06	1.06	adjustment,
	25	0.00	1.37	1.37	0.05	0.73	0.78	
	50	0.10	1.30	1.40	0.00	0.31	0.31	
9/30/2005	0	0.11	0.98	1.09	0.08	0.64	0.73	pH adjusted
	10	0.03	0.39	0.42	0.03	0.40	0.44	to 7
	25	0.06	0.39	0.45	0.06	0.34	0.39	
	50	0.00	0.03	0.03	0.00	0.00	0.00	
10/7/2005	0	0.30	1.57	1.82	0.30	1.20	1.46	pH adjusted
	10	0.30	1.43	1.68	0.30	1.06	1.32	to 7
	25	0.00	1.26	1.26	0.00	0.81	0.81	
	35	0.00	1.12	1.12	0.00	0.67	0.67	
	50	0.00	1.04	1.04	0.00	0.53	0.53	
10/14/2005	0	0.25	1.34	1.60	0.25	1.18	1.43	adjusted
	1				0.25	1.12	1.37	to pH 7
	2.5				0.22	1.12	1.34	
	5				0.22	1.12	1.34	
	7.5				0.22	1.01	1.23	
	10				0.22	0.95	1.18	
	25				0.00	0.25	0.25	
	35				0.00	0.25	0.25	
	50				0.00	0.00	0.00	

Date	Ferrate Dose mg/L FeO_4^{-2}	NH_3-N mg/L	TOrg-N mg/L	TKN mg/L	NH_3-N mg/L	SOrg-N mg/L	STKN mg/L	Observations
10/20/2005	0	0.11	0.95	1.06	0.08	0.76	0.84	adjusted to
	10	0.14	0.64	0.78	0.09	0.68	0.76	pH 7
10/28/2005	0	0.00	1.48	1.48	0.00	0.81	0.81	adjusted to
	1	0.03	1.10	1.13	0.00	0.76	0.76	pH 7
	2.5	0.03	1.07	1.10	0.00	0.73	0.73	
	5	0.03	1.00	1.03	0.03	0.64	0.67	
	7.5	0.03	1.00	1.03	0.00	0.67	0.67	
	10	0.00	0.94	0.94	0.03	0.56	0.59	
	25	0.00	1.00	1.00	0.03	0.62	0.64	
	35	0.00	0.60	0.60	0.00	0.34	0.34	
	50	0.00	0.12	0.12	0.00	0.06	0.06	
12/29/2005	0	0.00	1.34	1.34				adjusted to
	10	0.00	1.29	1.29	0.00	0.78	0.78	pH 7
2/8/2006	0				0.22	1.37	1.60	adjusted to
	10				0.14	1.34	1.48	pH 7
2/22/2006	0				1.01	1.82	2.83	adjusted to
	10				1.20	0.98	2.18	pH 7
3/22/2006	0	0.31	1.51	1.82	0.31	1.34	1.65	adjusted to
	10	0.11	1.62	1.73	0.34	1.26	1.60	pH 7
4/14/2006	0	0.73	1.93	2.66	0.56	1.01	1.57	Adjusted pH
	25	0.67	0.95	1.62	0.51	0.70	1.21	to 7
5/4/2006	0	1.26	3.25	4.51	3.14	0.98	4.12	Adjusted to
	10	1.23	2.97	4.21	2.86	1.21	4.07	pH 7
	25	1.54	2.44	3.99	2.44	1.15	3.59	
	35	1.69	2.19	3.88	2.14	1.29	3.43	
	50	1.63	1.91	3.55	1.80	1.18	2.99	
5/8/2006	0	2.41	1.93	4.34	2.30	1.01	3.30	adjusted to
	10	2.20	2.10	4.30	2.19	0.98	3.17	pH 9
	25	2.08	1.51	3.59	2.02	0.95	2.97	
	35	1.80	1.43	3.22	1.74	0.84	2.58	
	50	1.35	1.32	2.66	1.20	0.76	1.94	
5/23/2006	0	0.45	1.40	1.85	0.08	1.06	1.15	adjusted to
	10	0.25	1.32	1.57	0.25	0.84	1.10	pH 9
	25	0.25	1.25	1.50	0.00	0.79	0.93	
	35	0.06	1.43	1.48	0.03	0.84	0.87	
	50	0.03	1.32	1.34	0.00	0.76	0.78	

Date	Ferrate Dose mg/L FeO_4^{-2}	NH_3-N mg/L	TOrg-N mg/L	TKN mg/L	NH_3-N mg/L	SOrg-N mg/L	STKN mg/L	Observations
5/28/2006	0	0.00	1.54	1.54	0.00	0.90	0.90	adjusted to
	10	0.00	1.46	1.46	0.00	0.90	0.90	pH10
	25	0.00	1.32	1.32	0.00	0.67	0.93	
	35	0.00	1.20	1.20	0.00	0.65	0.65	
	50	0.00	1.09	1.09	0.00	0.59	0.59	
5/28/2006	0	0.00	1.54	1.54	0.00	0.90	0.90	adjusted to
	10	0.00	1.40	1.40	0.00	0.70	0.70	pH11
	25	0.00	1.21	1.21	0.00	0.67	0.67	
	35	0.00	1.18	1.18	0.00	0.56	0.56	
	50	0.00	1.07	1.07	0.00	0.34	0.34	

Data reported after10/28/05 correspond to treatment with ferrate prepared using different formulation.

Table C-2. COD, NO_3-N, and NO_2-N Results of Ferrate Treatment of an Effluent Wastewater at Various Doses. Raw Data Before and After Treatment

Date	Ferrate Dose mg/L FeO_4^{-2}	TCOD mg/L	SCOD mg/L	NO_3-N mg/L	NO_2-N mg/L	Observations
6/7/2005	0	45				Supernatant,
	2	-				not filtered
	10	40				adjusted pH
	25	41				to 7
	50	34				
	100	32				
9/14/2005	0	24	23			Tested
	1	24				Without pH
	2	22				adjustment
	5	20				
	10	-				
9/17/2005	0	29	27			adjusted to
	10		23			pH 7
	20		22			Filtered
	25		22			samples
	50		22			
9/22/2005	0	31	26			Without pH
	10		25			adjustment,
	25		-			
	50		12			
9/30/2005	0	20	15			pH adjusted
	10	20	16			to 7
	25	13	9			
	50	12	5			
10/7/2005	0	50	36			pH adjusted
	10	34	27			to 7
	25	32	24			
	35	29	20			
	50	-	12			
10/14/2005	0	42	37			pH adjusted
	1		36			to 7
	2.5		33			
	5		33			
	7.5		30			
	10		30			
	25		30			
	35		29			
	50		25			

Date	Ferrate Dose mg/L FeO_4^{-2}	TCOD mg/L	SCOD mg/L	NO_3-N mg/L	NO_2-N mg/L	Observations
10/20/2005	0	42	37			adjusted
	10	33	30			pH to 7
10/28/2005	0	41	29			adjusted
	1		27			pH to 7
	2.5		26			
	5		25			
	7.5		25			
	10		24			
	25		23			
	35		20			
	50		19			
12/29/2005	0	64				adjusted
	10		10			pH to 7
2/8/2006	0		46			Adjusted
	10		41			pH to 7
2/22/2006	0					adjusted
	10					pH to 7
3/22/2006	0					adjusted
	10					pH to 7
						Adjusted
4/14/2006	0					pH
	25					to 7
5/4/2006	0	44	30			adjusted
	10	37	30			pH to 7
	25	38	27			
	35	37	27			
	50	36	25			
5/8/2006	0	45	30			adjusted
	10	37	30			pH to 9
	25	38	27			
	35	37	27			
	50	36	25			
5/23/2006	0	42	27			Adjusted
	10	42	32			pH to 9
	25	42	32			
	35	30	29			
	50	-	-			
	35					
	50					

Date	Ferrate Dose mg/L FeO_4^{-2}	TCOD mg/L	SCOD mg/L	NO_3-N mg/L	NO_2-N mg/L	Observations
5/28/2006	0	68	38			Adjusted to
	10	49	34			pH 10
	25	49	43			
	35	-				
	50	-				
5/28/2006	0	68	38			Adjusted to
	10	45	33			pH 11
	25	40	-			
	35	39	38			
	50		30			

Table C-3. TKN Raw Data for Anoxic Reactors

Reactors	Sample ID	NH_3-N	TOrg-N	TKN	NH_3-N	SOrg-N	STKN	Observations
Date		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
12/02/2005	Control	0.056	3.05	3.11				Sample +
	Treated A	0.056	2.41	2.46				MLSS +
96 hrs	Control	0.0	1.68	1.68		2		NO3-N +
	Treated A	0.0	2.38	2.38				Methanol
12/07/2005	Control	2.46	10.08	12.54				Sample +
	Treated A	2.60	9.80	12.40				MLSS +
24 hrs	Control	2.128	13.47	15.60				NO3-N +
	Treated A	2.940	9.50	12.44				Methanol
48 hrs	Control	2.44	0.22	2.66				
	Treated A	3.472	0.36	3.84				
72 hrs	Control	2.46	9.80	12.24				
	Treated A	2.83	15.79	18.62				
96 hrs	Control	3.16	16.16	19.32				
	Treated A	2.07	17.86	19.94				
12/29/2005	Control	0.0	6.44	6.44	0.0	1.12	1.12	Sample +
	Treated A	0.0	6.58	6.58	0.0	0.84	0.84	MLSS +
24 hrs	Control	0.0	4.76	4.76	0.118	1.34	1.46	NO3-N +
	Treated A	0.0	6.30	6.30	0.112	1.06	1.18	Methanol
48 hrs	Control	0.0	3.78	3.78	0.0	1.18	1.18	
	Treated A	0.0	5.74	5.74	0.112	0.95	1.06	
72 hrs	Control							Run out of
	Treated A	0.0	4.62	4.62	0.0	0.67	0.67	sample
2/08/2006	Control				0.22	1.27	1.49	Sample +
	Treated A				0.0	1.57	1.57	NO3-N +
24 hrs	Control				0.24	1.12	1.40	Methanol
	Treated A				0.56	0.98	1.54	
48 hrs	Control							
	Treated A							
96 hrs	Control							
	Treated A							
144 hrs	Control				0.0	2.10	2.10	
	Treated A				0.0	2.40	2.40	
168 hrs	Control				0.0	2.50	2.50	
	Treated A				0.0	2.50	2.50	
192 hrs	Control				0.0	2.19	2.19	
	Treated A				0.0	2.40	2.40	
216 hrs	Control				0.0	1.36	1.36	
	Treated A				0.0	1.32	1.32	

Control: Reactor with untreated effluent
Treated: Reactor with treated effluent

Reactors Date	Sample ID	NH_3-N mg/L	TOrg-N mg/L	TKN mg/L	SNH_3-N mg/L	SOrg-N mg/L	STKN mg/L	Observations
3/22/2006	Control	0.50	1.62	2.13	0.50	1.46	1.96	Sample +
	Treated A	0.84	1.47	2.31	0.63	1.26	1.89	NO_3-N +
	Treated B	0.63	1.12	1.75	0.63	1.12	1.75	Methanol
48 hrs	Control	0.67	1.46	2.13	0.67	1.46	2.13	Treatment
	Treated A	0.73	1.74	2.46	0.56	1.22	1.78	With 10
	Treated B	0.84	1.57	2.41	0.73	1.34	2.07	Mg/L of
96 hrs	Control	0.73	1.57	2.30	0.62	1.37	1.99	ferrate
	Treated A	0.75	1.31	2.05	0.42	1.08	1.50	
	Treated B	0.67	1.90	2.58	0.40	1.14	1.54	
144 hrs	Control	0.50	1.68	2.18	0.12	1.40	1.52	
	Treated A	0.39	1.57	1.96	0.22	1.01	1.23	
	Treated B	0.45	1.57	2.02	0.38	1.08	1.46	
192 hrs	Control	0.56	2.03	2.59	0.45	0.91	1.36	
	Treated A	0.22	1.62	1.85	0.26	0.98	1.24	
	Treated B	0.18	1.70	1.88	0.10	0.97	1.07	
240 hrs	Control	0.38	1.56	1.94	0.78	1.10	1.88	
	Treated A	0.15	1.65	1.80	0.19	0.92	1.11	
	Treated B	0.11	1.68	1.79	0.22	0.93	1.15	
4/14/2006	Control	0.56	1.90	2.46	0.42	0.90	1.32	Sample +
	Treated A	0.49	1.61	2.10	0.28	0.99	1.27	NO_3-N +
	Treated B	0.42	1.54	1.96	0.28	0.98	1.26	Methanol
48 hrs	Control	0.70	1.12	1.82	0.0	1.12	1.12	Treatment
	Treated A	0.07	1.40	1.47	0.07	0.98	1.05	With 25
	Treated B	0.07	1.47	1.54	0.07	0.98	1.05	Mg/L of
96 hrs	Control	0.07	1.12	1.19	0.07	0.70	0.77	ferrate
	Treated A	0.14	1.12	1.26	0.07	0.91	0.98	
	Treated B	0.06	1.00	1.06	0.06	0.68	0.75	
144 hrs	Control	0.0	1.63	1.63	0.0	0.88	0.88	
	Treated A	0.0	1.18	1.18	0.0	0.88	0.88	
	Treated B	0.0	0.93	0.93	0.0	0.74	0.74	
216 hrs	Control	0.28	1.68	1.96	0.11	1.04	1.15	
	Treated A	0.06	1.68	1.74	0.06	1.12	1.18	
	Treated B	0.0	2.07	2.07	0.0	1.18	1.18	
240 hrs	Control	0.0	1.29	1.29	0.22	0.78	0.99	
	Treated A	0.0	1.75	1.75	0.0	0.70	0.70	
	Treated B	0.0	0.98	0.98	0.0	0.59	0.59	
288 hrs	Control	0.22	0.67	0.90	0.26	0.42	0.68	
	Treated A	0.0	0.64	0.64	0.0	0.39	0.39	
	Treated B	0.0	0.81	0.81	0.0	0.31	0.31	

Control: Reactor with untreated effluent
Treated: Reactor with treated effluent

Table C-4. NO_3-N and NO_2-N Raw Data from Anoxic Reactors

Reactors Date	Sample ID	NO_3-N mg/L	NO_2-N mg/L	Observations
12/02/2005	Control	13.56		Sample +
	Treated A	14.31		MLSS +
96 hrs	Control	14.06		NO3-N +
	Treated A	12.84		Methanol
12/07/2005	Control	16.18		Sample +
	Treated A	16.18		MLSS +
24 hrs	Control	10.98		NO3-N +
	Treated A	14.90		Methanol
48 hrs	Control	5.53		
	Treated A	8.47		
72 hrs	Control	0.32		
	Treated A	5.36		
96 hrs	Control	0.25		
	Treated A	2.90		
12/29/2005	Control	17.28		Sample +
	Treated A	17.73		MLSS +
24 hrs	Control	16.26		NO3-N +
	Treated A	16.06		Methanol
48 hrs	Control	14.48		
	Treated A	13.74		
72 hrs	Control			Run out of
	Treated A			sample
2/08/2006	Control	20.60		Sample +
	Treated A	19.78		NO3-N +
24 hrs	Control	22.64		Methanol
	Treated A	22.25		
48 hrs	Control	22.47		
	Treated A	23.07		
96 hrs	Control	20.39		
	Treated A	20.41		
144 hrs	Control	18.11		
	Treated A	16.45		
168 hrs	Control	16.47	0.13	
	Treated A	9.66	0.29	
192 hrs	Control	13.74		
	Treated A	5.68		
216 hrs	Control	5.56		
	Treated A	3.95		

Reactors Date	Sample ID	NO_3-N mg/L	NO_2-N mg/L	Observations
3/22/2006	Control	19.96	0.21	Sample +
	Treated A	25.06	0.21	NO_3-N +
	Treated B	24.04	0.21	Methanol
48 hrs	Control	18.21	0.87	Treatment
	Treated A	19.01	0.14	With 10
	Treated B	20.18	0.18	Mg/L of
96 hrs	Control	19.90	0.53	ferrate
	Treated A	21.37	0.05	
	Treated B	20.87	0.33	
144 hrs	Control	10.54	3.30	
	Treated A	20.22	0.19	
	Treated B	19.29	0.01	
192 hrs	Control	9.56	1.70	
	Treated A	12.64	0.15	
	Treated B	11.81	0.06	
240 hrs	Control	8.97	1.66	
	Treated A	11.21	0.76	
	Treated B	10.11	0.76	
4/14/2006	Control	22.29	0.01	Sample +
	Treated A	24.73	0.01	NO_3-N +
	Treated B	25.17	0.01	Methanol
48 hrs	Control	21.66	0.08	Treatment
	Treated A	26.93	0.08	With 25
	Treated B	24.13	0.23	Mg/L of
96 hrs	Control	21.78	0.27	ferrate
	Treated A	23.05	0.14	
	Treated B	22.96	0.32	
144 hrs	Control	11.12	1.71	
	Treated A	20.40	0.33	
	Treated B	21.29	0.46	
216 hrs	Control	4.44	8.66	
	Treated A	15.82	0.46	
	Treated B	14.14	0.70	
240 hrs	Control	3.07	7.38	
	Treated A	9.75	0.72	
	Treated B	7.64	0.73	
288 hrs	Control	3.27	7.06	
	Treated A	5.17	0.86	
	Treated B	5.50	0.64	

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