Removal of Nitrogen From Secondary Wastewater Effluent Through No 3-N Reduction Using Sulfur Dioxide (SO2)

Javid Ghorashian
V. Dean Adams
Dennis B. George

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EFFLUENT THROUGH NO$_3$-N REDUCTION USING

SULFUR DIOXIDE (SO$_2$)

by

Javid Chorashian
V. Dean Adams
and
Dennis B. George

Report to

International Environmental, Inc.
Salt Lake City, Utah

Submitted by

Utah Water Research Laboratory
Utah State University
Logan, Utah 84322

May 1982
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ACKNOWLEDGMENTS

This publication represents the final report of a project evaluating the removal of nitrogen from secondary wastewater effluent through NO₃-N reduction using sulfur dioxide (SO₂) which was supported by funds provided by International Environmental, Inc. of Salt Lake City, Utah.

The authors express gratitude to all who contributed to the completion of this study. A sincere thanks is also extended to the Utah Water Research Laboratory for providing laboratory equipment and facilities necessary to complete this study and to the capable editorial and secretarial staff for their assistance in preparation and publication of this report.
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ABSTRACT

The overall purpose of this study was to evaluate the ability of sulfur dioxide (SO₂) to remove nitrate-nitrogen (i.e., reduction to a gaseous form) from the secondary wastewater effluent. To accomplish the above task, a jar test procedure was established and the concentration of NO₃-N along with the concentration of NH₃-N present in the secondary wastewater, treated with SO₂, were measured initially and after 10 min, 20 min, 30 min, 40 min, and 24 hr. Then, the percent NO₃-N removal was calculated, comparing the NO₃-N concentrations measured in each treatment with the initial values. The above procedures were conducted for 36 different runs resulting from variation of the parameters which were believed to effect the kinetics of the reaction (i.e., SO₂ concentration, presence of catalysts, temperature, and NO₃-N concentration). Three levels of SO₂ (500, 1000, 2000 mg/l), two levels of NO₃-N (25-30 and 40-45 mg/l), two temperatures (20° and 35°C), and two different catalysts (Fe³⁺ 1 mg/l and Fe⁺ 1 g/l) were used in this study.

Prior to the jar tests, it was necessary to develop techniques to eliminate the SO₂ interferences with analysis of NO₃-N, and NH₃-N. Two approaches were made to accomplish this task. First by air stripping of the SO₂ treated secondary wastewater sample; secondly by diluting the SO₂ treated secondary water to decrease the SO₂ concentration to a level of less than 80 mg/l as SO₂. Satisfactory results were obtained applying both stripping and dilution methods.
The highest NO₃−N removal (44.7%) after 24 hr treatment was obtained where the SO₂ concentration was 1000 mg/l, NO₃−N concentration was 40–45 mg/l, the temperature was 20°C, and powdered iron was used as the catalyst. Elevation of temperature from 20°C to 35°C had almost no effects on the NO₃−N removal between the time period of zero and 40 min. Variation of NO₃−N concentration from low levels (25–30 mg/l) to high levels (40–45 mg/l) had no effect on the NO₃−N removal. Powdered iron (1 g/l) had a significant catalytical role in NO₃−N removal while Fe³⁺ (1 mg/l) had almost no catalytical role. From three different levels of SO₂ concentrations used, no significant effects on the NO₃−N removal were observed, when no catalyst was used or Fe³⁺ was used as catalyst. However, in the cases where powdered iron was used as catalyst, the results show that, the higher the SO₂ concentration the higher the NO₃−N removal.
INTRODUCTION

Statement of Problem

The removal of nitrogen and nitrogen compounds from wastewater is receiving wide attention because the discharge of these contaminants is manifested in the growth of algae and plants. Investigation into the causes of eutrophication have led many workers to conclude that a nutrient such as nitrogen or phosphorus is likely to be the major factor which stimulates the process. Unless steps are taken to control the discharge of these contaminants, overfertilization will continue to increase, especially with the multiple reuse of water. Wastewater treatment facilities in the near future will have to be designed for nitrogen control. The effluent standards in the future will require, directly or indirectly, nitrogen removal.

Methods of removing nitrogen from wastewater can be grouped as either biological or physical-chemical processes. General reviews of these methods are well documented (EPA; 1975, McCarty, 1970; Samples, 1967; Stern, 1966; and Rohlich, 1964).

In most conventional wastewater treatment plants, nitrogen removal is achieved through biological nitrification of ammonia followed by denitrification. The principal effect of the nitrification process is to transform ammonia-nitrogen to nitrate. Oxidation of ammonium can be as high as 98 percent (EPA, 1975). Nitrification can be carried out in conjunction with secondary wastewater treatment or in a tertiary stage in either suspended growth reactors (activated sludge) or attached growth reactors (trickling filters). Biological
Denitrification refers to biological reduction of nitrate-nitrogen to gaseous forms of nitrogen such as N₂O and N₂. Biological denitrification occurs in an anoxic environment in either suspended growth or attached growth reactors.

The biological denitrification process requires a long detention time, pH control, and carbon substrate. Therefore other methods such as chemical reduction of nitrate seem to be attractive alternatives. Chemical processes have the advantages of being easier to control and more adaptable to the fluctuating flows and concentrations inherent to municipal wastewater systems than biological processes.

Sulfur dioxide (SO₂) as an available, well known reducing agent, can be used to reduce nitrate-nitrogen from wastewater effluent to gaseous nitrogen species through a chemical process. SO₂ has a solubility of 11.78 grams/100 ml of water at 20°C and one atmosphere of pressure (Handbook of Chemistry and Physics, 1980). Absorption of SO₂ in water results in the formation of sulfurous acid (H₂SO₃), which has a high tendency to be oxidized. The half oxidation reaction equation for sulfurous acid is as follows (Handbook of Chemistry and Physics, 1980):

\[ H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^- \quad E^0 = -0.2 \text{ volts} \]  

(1)

Conversely, nitrate and nitrite ions can be considered as oxygen carriers or potential contributors of oxygen to an aqueous solution giving rise to a number of reduced nitrogen species. The complete reduction of nitrate can be shown by a half oxidation reaction equation as follows (Handbook of Chemistry and Physics, 1980):

\[ 2 NO_3^- + 12 H^+ + 10 e^- + N_2 + 6 H_2O \quad E^0 = +1.25 \text{ volts} \]  

(2)
The complete chemical reaction can be written by adding half reactions (1) and (2):

\[ 2 \text{NO}_3^- + 5 \text{H}_2\text{SO}_3 \rightarrow \text{N}_2 + 5 \text{SO}_4^{2-} + \text{H}_2\text{O} + 8 \text{H}^+ \quad \ldots \quad (3) \]

It is believed that the above oxidation reduction reaction can be catalyzed by trace metals such as iron and copper. Conversion of nitrate to \( \text{N}_2 \) is ideal, since nitrogen gas has the lowest water solubility and greatest oxidation resistance of all the nitrogenous gases (Frank et al., 1968). No study has been conducted to investigate the potential of \( \text{SO}_2 \) to reduce \( \text{NO}_3^- \) in drinking water or wastewater. Evaluation of this possibility was the primary objective of this study.

**Objectives**

The overall objective of this study is to evaluate the ability of sulfur dioxide to remove nitrate-nitrogen (reduction to gaseous form) from the secondary wastewater effluent. The specific objective of this study can be outlined in the following manner:

1. Development and verification of analytical techniques necessary to accurately and precisely measure the parameters of interest (i.e., \( \text{NO}_3^- \), \( \text{NO}_2^- \), and \( \text{NH}_3^- \)) in the presence of \( \text{SO}_2 \).

2. Evaluate the potential of sulfur dioxide to remove nitrate-nitrogen from secondary wastewater effluent in conjunction with the following factors:
   a) Variation of \( \text{SO}_2 \) concentration
   b) Effects of the presence of catalysts
   c) Effects of temperature
   d) Variation of nitrate concentration
LITERATURE REVIEW

Nitrogen Cycle

Nitrogen occurs in the biosphere in a variety of forms ranging in oxidation state from +5 to -3. Inorganic nitrogen is present primarily as highly oxidized nitrite and nitrate, as reduced ammonia and as molecular nitrogen. A variety of intermediate gaseous oxides of nitrogen are important in atmospheric chemistry but not in natural waters. Naturally occurring organic nitrogen consists primarily of amino and amide (proteinaceous) nitrogen along with some heterocyclic compounds present as cellular constituents, as nonliving particulate matter, as soluble organic compounds, and as inorganic ions in solution (Patrick, 1973). All these forms are interrelated by a series of reactions known collectively as the "Nitrogen Cycle," which portrays the flow of nitrogen from inorganic forms in soil, air and water into living systems and then back again into inorganic forms.

Figure 1 shows a presentation of nitrogen cycle (Sawyer and McCarty, 1978). The atmosphere serves as a reservoir of N₂ gas from which nitrogen is removed naturally by electrical discharge and nitrogen-fixing organisms and artificially by chemical manufacturing. Nitrogen gas is returned to atmosphere by the action of denitrifying organisms. In the fixed state, nitrogen can undergo the various reactions shown. Transformation reactions of importance include fixation, ammonification, assimilation, nitrification, and denitrification (Christensen and Harremoes, 1972).
Figure 1. The nitrogen cycle (Sawyer and McCarty, 1978).
Fixation of nitrogen from $\text{N}_2$ gas to organic nitrogen is accomplished biologically by specialized microorganisms. This reaction requires energy. Biological fixation accounts for most of the natural transformation of nitrogen to compounds which can be used by plant and animal life. Lightning fixation has been estimated to account for approximately 15 percent of the total which occurs naturally (Delwicke, 1970).

Ammonification is the change from organic nitrogen to the ammonium ($\text{NH}_3/\text{NH}_4^+$) form. This occurs to dead animal and plant tissue and to animal fecal matter:

$$\text{Organic N (protein)} + \text{microorganisms} \rightarrow \text{NH}_3/\text{NH}_4^+ \quad \ldots \quad (4)$$

Also nitrogen in urine exists principally as urea. Urea is hydrolyzed by the enzyme urease to ammonium carbonate:

$$\text{H}_2\text{NCONH}_2 + 2 \text{H}_2\text{O} \xrightleftharpoons{\text{Urease}} (\text{NH}_4)_2 \text{CO}_3 \quad \ldots \quad \ldots \quad (5)$$

Assimilation is the use of ammonium or nitrate compounds to form plant protein and other nitrogen-containing compounds:

$$\text{NO}_3^- + \text{CO}_2 + \text{green plants} + \text{sunlight} \rightarrow \text{protein} \quad \ldots \quad (6)$$

and

$$\text{NH}_3/\text{NH}_4^+ + \text{CO}_2 + \text{green plants} + \text{sunlight} \rightarrow \text{protein} \quad \ldots \quad (7)$$

Animals require protein from plants or from other animals. With certain specific exceptions, they are incapable of converting inorganic nitrogen forms into organic forms.

Nitrification is applied to the biological oxidation of ammonium, first to the nitrite, then to the nitrate form. The bacteria responsible for these reactions are termed chemoautotrophic because they use inorganic chemicals as their source of energy. Generally, the
Nitrosomonas genera are involved in conversion of ammonium to nitrite under aerobic conditions as follows:

\[ 2 \text{NH}_4^+ + 3 \text{O}_2 \xrightarrow{\text{bacteria}} 2 \text{NO}_2^- + 4 \text{H}^+ + 2 \text{H}_2\text{O} \quad \ldots \quad (8) \]

The nitrites are oxidized to nitrate generally by *Nitrobacter* according to the following reaction:

\[ 2 \text{NO}_2^- + \text{O}_2 \xrightarrow{\text{bacteria}} 2 \text{NO}_3^- \quad \ldots \quad \ldots \quad \ldots \quad (9) \]

The overall nitrification reaction is as follows:

\[ \text{NH}_4^+ + 2 \text{O}_2 \rightarrow \text{NO}_3^- + 2 \text{N}^+ + \text{H}_2\text{O} \quad \ldots \quad \ldots \quad \ldots \quad (10) \]

When synthesis of nitrifiers is neglected, oxidation of 1 mg/l of ammonia-nitrogen requires about 4.6 mg/l of oxygen.

Denitrification refers to the biological reduction of nitrate, first to nitrite and then nitrogen gas. A broad range of bacteria can accomplish denitrification, including *Pseudomonas*, *Micrococcus*, *Achromobacter*, and *Bacillus*. In simplified form, the reaction steps are as follows:

\[ \text{NO}_3^- + 0.33 \text{CH}_3\text{OH} \rightarrow \text{NO}_2^- + 0.33 \text{CO}_2 + 0.67 \text{H}_2\text{O} \quad \ldots \quad \ldots \quad (11) \]

(organic carbon source)

and

\[ \text{NO}_2^- + 0.5 \text{CH}_3\text{OH} \rightarrow 0.5 \text{N}_2 + 0.5 \text{H}_2\text{O} + \text{OH}^- + 0.5 \text{CO}_2 \quad \ldots \quad (12) \]

(organic carbon source)

Here methanol is used as the example organic carbon source. Many natural and synthetic organic compounds can serve as the carbon source for denitrification. Bacteria gain their energy through oxidation of organic matter to carbon dioxide and water. Either oxygen or nitrate may be used for the oxidation, but the use of oxygen results in the release of more energy when both oxygen and nitrate are
present, bacteria preferentially use oxygen. Therefore, use of nitrite for denitrification can only occur under anoxic conditions, an important consideration when attempting to remove nitrate from wastewater.

Source of Nitrogen

Nitrogen enters the aquatic environment from either natural or man-caused sources. Natural sources of nitrogenous substances include precipitation, dustfall, nonurban runoff, and biological fixation (EPA, 1975). Amounts from all may be increased in some way by man. It may be quite difficult to determine quantities which might be expected under completely natural conditions. For example, in order to find levels of nitrogenous substances in precipitation, it is necessary to take samples far from urban or agricultural areas.

The quantities of nitrogen in nonurban runoff from nonfertilized land may be expected to vary greatly, depending on the erosive characteristics of the soil. One study found that runoff from forested land in Washington contained 0.13 mg/l of nitrate-nitrogen and 0.20 mg/l of total nitrogen (Sylvester, 1963).

Biological fixation may add nitrogen to both soil and surface water environment. Certain photosynthetic blue-green algae, such as the species of Nostoc, Anabaena, Gleotrichia, and Calothrix, are common nitrogen fixers (Martin and Goff, 1972).

Sources deriving from human activities include runoff from urban area, municipal wastewaters, drainage from agricultural
lands and feedlots, industrial wastes, and septic tank leachate (Metcalf and Eddy, 1979).

Nitrogen concentration in raw municipal wastewaters are well documented (EPA, 1973). Values generally range from 15 to 50 mg/l, of which approximately 60 percent is ammonia-nitrogen, 40 percent is organic, and a small amount (1 percent) is nitrite- and nitrate-nitrogen.

Urban runoff can contribute significant quantities of nitrogen to receiving waters during and after periods of precipitation. Average concentrations which have been reported are 2.7 mg/l total nitrogen in Cincinnati (Weibel, Anderson, and Woodward, 1971), 2.1 mg/l total nitrogen in Washington, D. C. (American Public Works Association, 1969), 2.5 mg/l total nitrogen in Ann Arbor Michigan (Burn, Krawezyk, and Harlow, 1968), and .85 mg/l organic nitrogen in Tulsa, Oklahoma (Avco Economic Systems Corporation, 1970).

Feedlot runoff constitutes a source of nitrogen which has become significant as a result of the increased number of concentrated, centralized feedlots (EPA, 1975). Ammonium is a major constituent of feedlot waste as a result of urea hydrolysis. Ammonia-nitrogen concentration may reach 300 mg/l, and organic nitrogen concentration of up to 600 mg/l have been reported (Kaufman, 1974).

Nitrogen discharged into individual septic tank systems can also create pollution problems. It has been estimated that up to 25 percent of the national population utilizes individual systems, contributing up to 0.23 million metric tons of nitrogen annually (EPA, 1975).
The use of artificial fertilizers has increased the nitrogen concentration which can be expected in nonurban runoff. In rural Ohio, runoff from a 1.45 acre field planted in winter wheat contained an average of 9 mg/l total nitrogen (Weibel, 1966). On a 75-acre site in North Carolina which consisted of grassed pasture, wooded pasture, cornfield, and orchard, the mean nitrogen concentration in the runoff was 1.2 mg/l (EPA, 1971).

The nitrogen content of industrial wastes varies dramatically from one industry to the next. Among those industries whose wastewater nitrogen contents may be quite high are meat processing plants, milk processing plants, petroleum refineries, ice plants, fertilizer manufacturers, certain synthetic fiber plants, and industries using ammonia for scouring and cleaning operations (Martin and Goff, 1972).

Problems Associated with Nitrogen Discharge

Although biostimulation of receiving waters has generated the most concern in recent years, other less well publicized impacts can be of major importance in particular situations. These impacts include toxicity to fish life, reduction of chlorine disinfection efficiency, an increase in the dissolved oxygen depletion in receiving waters, adverse public health effects - principally in groundwater, and a reduction in the suitability for reuse (EPA, 1975).

Eutrophication, excessive plant growth, and/or algae "blooms" resulting from over-fertilization of river, and lakes is a major problem in the field of water pollution. Four basic factors are
required for algal growth: nitrogen, phosphorus, carbon dioxide, and light energy (EPA, 1975). The absence of any one will limit growth. Light and carbon dioxide are essentially impossible to control. Both nitrogen and phosphorus are present in waste discharges and hence subject to control. The questions which must usually be answered when faced with a eutrophication problem are: is nitrogen or phosphorus (or neither) the limiting nutrient, and if either one is can the amount entering the receiving water be significantly reduced by removing that nutrient from the waste stream?

Ammonia in the molecular form (NH₃) can adversely affect fish life in receiving waters. An increase in pH may cause a increase in toxicity as the ammonium ion (NH₄⁺) is transformed to ammonia in accordance with the following equation

\[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} \]  \hspace{0.5cm} (13)

Factors which may increase ammonia toxicity at a given pH are: greater concentrations of dissolved oxygen and carbon dioxide, elevated temperatures, and bicarbonate alkalinity (EPA, 1973). Reported levels at which acute toxicity to trout is detectable have ranged from 0.01 mg/l to over 2.0 mg/l of molecular ammonia-nitrogen (EPA, 1975; EPA, 1973; and Brown, Cladwell/Dewante, and Stowell, 1972).

In the disinfection processes, when chlorine, in the form of chlorine gas or hypochlorite salt, is added to wastewater containing ammonium, chloramines, which are less effective disinfectants are formed. The major reactions are as follows:

\[ \text{NH}_4^+ + \text{HOCI} \rightarrow \text{NH}_2\text{Cl} (\text{monochloramine}) + \text{H}_2\text{O} + \text{H}^+ \]  \hspace{0.5cm} (14)
\[ \text{NH}_2\text{Cl} + \text{HOCI} \rightarrow \text{NHCl}_2 \text{ (dichloramine)} + \text{H}_2\text{O} \quad \ldots \quad (15) \]
\[ \text{NHCl}_2 + \text{HOCI} \rightarrow \text{NCl}_3 \text{ (nitrogen trichloride)} + \text{H}_2\text{O} \quad \ldots \quad (16) \]

If the effluent ammonia-nitrogen concentration were 20 mg/l, about 200 mg/l of chlorine would be required to complete the reactions with ammonium and organic compounds (EPA, 1975).

Biological oxidation of ammonium to nitrite and then to nitrate in receiving waters adds to the oxygen demand imparted on the stream by carbonaceous materials. If either conventional biological treatment or physical-chemical treatment is utilized to provide 90 percent BOD\(_5\) removal, an effluent will be discharged which still contains over 100 mg/l of oxygen demand (EPA, 1975). This high level of oxygen demand may cause significant oxygen depletion in the receiving water if insufficient dilution is available. The Potomac Estuary in the United States (EPA, 1970), and the Thames Estuary in Great Britain (Effects of Pollution Discharge on the Thames Estuary, 1964), are examples of estuaries which are greatly affected by nitrification.

The nitrogen problem with regard to the public health hazard is associated with the nitrate form and is limited principally to groundwater where high concentration can occur. When water high in nitrate is used for preparing infant formulas, nitrate is reduced to nitrite in the stomach after ingestion. The nitrites react with hemoglobin in the blood to form methemoglobin, which is incapable of carrying oxygen. The result is suffocation accompanied by a bluish tinge to the skin, which accounts for the use of the term "blue babies" in conjunction with methemoglobinemia (EPA, 1975). In suspect areas water should be analyzed for both nitrite and nitrate since
either form will cause methemoglobinemia. Since 1945, about 2,000 cases of methemoglobinemia have been reported in the U. S. and Europe, with a mortality rate of 7 to 8 percent (Kaufman, 1974).

**Nitrogen Removal Processes (General)**

Many processes have been explored for the removal of nitrogen from water and wastewater. Those applied to wastewater are reported in Table 1. The four principal methods found feasible are biological nitrification, followed by denitrification, air stripping of ammonia at high pH, removal of nitrate or ammonia by ion exchange, and breakpoint chlorination. These four methods will be discussed in depth in this review. Other removal processes that have been proposed will not be discussed in depth. These include electrochemical treatment, electrodialysis, reverse osmosis, distillation, algae harvesting, and land application.

**Biological nitrification-denitrification**

Probably the most common method of removing nitrogen from wastewater is the biological nitrification of ammonia followed by biological denitrification process. The process basically consists of oxidizing all the ammonia to nitrates (nitrification) and then reducing the nitrates to nitrogen gas (denitrification) which is released to the atmosphere.

Nitrification alone will remove ammonia-nitrogen, but the resulting nitrite- and nitrate-nitrogen normally will not be removed and can serve as nutrients for undesirable algal growths in streams and lakes. However, nitrification can help to eliminate the problems of ammonia toxicity to fish and will minimize excessive oxygen
Table 1. Effect of various treatment processes on nitrogen compounds (Metcalf and Eddy, 1979).

<table>
<thead>
<tr>
<th>Treatment operations or processes</th>
<th>Nitrogen compound</th>
<th>Removal of total nitrogen entering process, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Organic nitrogen</td>
<td>NH₃-NH₄⁺</td>
</tr>
<tr>
<td>Conventional treatment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Primary</td>
<td></td>
<td>10-20%</td>
</tr>
<tr>
<td>2. Secondary</td>
<td></td>
<td>15-50%</td>
</tr>
<tr>
<td>Biological processes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Bacterial assimilation</td>
<td></td>
<td>No effect</td>
</tr>
<tr>
<td>2. Denitrification</td>
<td></td>
<td>60-70%</td>
</tr>
<tr>
<td>3. Harvesting of algae</td>
<td></td>
<td>No effect</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Partial transformation to NH₃-NH₄⁺</td>
</tr>
<tr>
<td>4. Nitrification</td>
<td></td>
<td>10-50%</td>
</tr>
<tr>
<td>5. Oxidation ponds</td>
<td></td>
<td>Partial transformation by stripping to NO₃⁻</td>
</tr>
<tr>
<td>Chemical processes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Breakpoint chlorination</td>
<td></td>
<td>Uncertain</td>
</tr>
<tr>
<td>2. Chemical coagulation</td>
<td></td>
<td>50-90%</td>
</tr>
<tr>
<td>3. Carbon sorption</td>
<td></td>
<td>30-50%</td>
</tr>
<tr>
<td>4. Selective ion exchange for ammonium</td>
<td></td>
<td>Slight, uncertain</td>
</tr>
<tr>
<td>5. Selective ion exchange for nitrate</td>
<td></td>
<td>Slight</td>
</tr>
<tr>
<td>Physical operations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Ammonia stripping</td>
<td></td>
<td>No effect</td>
</tr>
<tr>
<td>2. Electrodialysis</td>
<td></td>
<td>100% of suspended organic N removed</td>
</tr>
<tr>
<td>3. Filtration</td>
<td></td>
<td>Slight</td>
</tr>
<tr>
<td>4. Reverse osmosis</td>
<td></td>
<td>Slight</td>
</tr>
<tr>
<td>Land application</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Irrigation</td>
<td></td>
<td>NH₃-NH₄⁺</td>
</tr>
<tr>
<td>2. Rapid infiltration</td>
<td></td>
<td>NH₃-NH₄⁺</td>
</tr>
<tr>
<td>3. Overland flow</td>
<td></td>
<td>NH₃-NH₄⁺</td>
</tr>
</tbody>
</table>
demand exerted by ammonia nitrogen in streams. With proper control of wastewater treatment processes, both nitrification and denitrification can occur. True biological denitrification, or nonassimilative removal of nitrogen, is performed only on the oxidized forms of nitrogen. The oxidation of ammonia, or biological nitrification, is thus essential to biological nitrogen removal.

Biological nitrification occurs in two stages. Conversion of ammonia to nitrates is accomplished by *Nitrosomonas*, and to a lesser degree by *Nitrosococcus*, *Nitrosospira*, *Nitrosocystis* and *Nitrosogloes* (Sawyer, 1971). These groups of chemautotrophic bacteria use CO₂ as a source of carbon for cell material and obtain energy for the process by oxidizing inorganic substrates.

Simple chemical description of the two phases are:

\[ \text{NH}_4^+ + 1.5 \text{O}_2 \rightarrow \text{NO}_2^- + 2 \text{H}^+ + \text{H}_2\text{O} \quad (17) \]
\[ \text{NO}_2^- + 0.5 \text{O}_2 \rightarrow \text{NO}_3^- \quad (18) \]

Biological denitrification is an anaerobic process wherein the nitrite ion is the hydrogen ion acceptor in the electron transport system. The nitrate ion permits the microbial cell to maintain aerobic metabolism in the absence of free oxygen. In the process, nitrates are reduced to nitrogen gas and carbon compounds are oxidized. This reaction is represented by the following equation:

\[ 4 \text{NO}_3^- + 4 \text{H}^+ + 5 \text{CH}_2\text{O} \rightarrow 5 \text{CO}_2 + 2 \text{N}_2 + 7 \text{H}_2\text{O} \quad (19) \]

Most of the denitrifying organisms are aerobes commonly found in the wastewater treatment plant. These include species of *Pseudomonas*, *Achromobacter*, *Bacillus*, and *Micrococcus*. Because the
growth of these microorganisms is not dependent on the reduction of nitrate, the presence of a large denitrifying population does not in itself indicate that conditions are suitable for denitrification.

A three-stage biological system is considered necessary (especially in northern climates). The first stage removes carbonaceous BOD₅ to levels of about 50 mg/l. The second stage accomplishes nitrification and should be designed to employ plug flow as closely as possible (Sawyer, 1971). The third stage accomplishes denitrification. A source of carbonaceous biochemical oxygen demand (BOD) must be added to reduce the nitrates to nitrogen gas.

In situations where nitrogen removal is required and the nitrification-denitrification route is preferred, it will be mandatory to accomplish nitrification in a separate biological system where the reciprocal growth rate can be kept less than the mean cell residence time at all times (Sawyer, 1971). This will mean that a large part of the normal BOD will have to be removed before the wastewater enters the nitrification unit. Sawyer believes that a BOD₅ of 40 to 50 mg/l can be tolerated in the feed stream to the nitrification unit. Consequently, either high-rate activated sludge or trickling filter systems should be acceptable for the first stage of treatment.

Nitrification in biological treatment requires at least 0.5 mg/l of dissolved oxygen (DO), hydraulic detention time in activated sludge units of at least 8 hours, and a low loading factor in terms of BOD₅/day (0.10-0.16 Kg BOD₅/m³.d) (Downing and Knowles, 1966; Downing, 1964; Downing and Bagley, 1961). Other researchers have
stated values that in some cases are drastically different from the previous ones. For example, high levels of nitrification are possible at hydraulic detention times of only 0.48 to 2 hours (Wuhrmann, 1962), while in another case a detention time of 3 hours is necessary (Bringmann, 1960). Wuhrmann found appreciable nitrification at oxygen concentrations as low as 1 mg/l.

It is generally believed that the trickling filter can bring about nitrification comparable to that of conventional activated sludge processes. Nitrification and carbonaceous oxidation take place in trickling filters. From the studies reported on the BOD removal characteristics, the process variables such as depth of filter, size and type of media, and hydraulic loading greatly influence the degree of nitrification obtainable in the trickling filter process (Reeves, 1972). Other factors that influence nitrification include the liquid temperature, carbonaceous matter in the wastewater, and presence of inhibitors.

It has been shown that ammonia-nitrogen concentrations of less than 60 mg/l did not inhibit nitrification (Sawyer, 1971). Sawyer found that pH affected the rate of nitrification (optimum pH was found to be 8.4). Temperature also affected the rate of nitrification. The nitrification rate increased as the temperature was varied from 5° to 30°C. The time required for nitrification was directly proportional to the amount of nitrifiers present in the system. Instantaneous increases or decreases in BOD5 concentration between 5 and 110 mg/l did not affect the rate of nitrification.
There is less information available about the denitrification process. There are three basic requirements for denitrification to proceed: 1) an organic carbon source that can be utilized by the denitrifying organisms, 2) a DO concentration of less than 0.5 mg/l, and 3) a pH of about 6.5 (Baumann, 1971). The interdependence of these factors makes denitrification difficult to control. Denitrification, however, does occur naturally in wastewater treatment plants. The resulting release of nitrogen bubbles is the primary cause of floating sludge in final settling tanks (Reeves, 1972). In early studies it was thought that the final settling tank of an activated sludge system could be used for denitrification. Although denitrification did take place in these tanks, the operational problems in obtaining good solids removal from the final clarifiers and in maintaining a high quality effluent were almost insurmountable (Reeves, 1972). Consequently, it is better to add separate denitrification units to treat a high quality, highly nitrified effluent from a normally operated secondary treatment process. This denitrification process can occur in three possible designs: anaerobic activated sludge, an aerobic filter, or an anaerobic lagoon. When treating a highly clarified and purified effluent with either of these systems, a supplemental organic carbon source must be added to the wastewater stream prior to denitrification. Methanol has been found to be the most economical source of organic carbon. Almost any soluble material, such as sugar or acetic acid, can be used (Sawyer, 1971). The dose of this added carbon source must be regulated very closely to prevent odors from developing through conversion of sulfates to hydrogen.
sulfide. Only enough organic material should be added to react with the nitrite and nitrate and DO remaining in the wastewater effluent.

In some cases, it may be possible to bypass part of the raw wastewater to the denitrification unit to serve as an organic carbon source (Reeves, 1972). With raw wastewater it has been shown that about 20 percent bypass is satisfactory. However, because of the detrimental effect on effluent quality, this is not an attractive alternative when treating municipal wastes. This approach could potentially be best used when treating primarily soluble industrial wastewater (Reeves, 1972).

Detention times in the denitrification units generally range from 2 to 8 hours for both the anaerobic activated sludge and anaerobic filter systems (Baumann, 1971). Anaerobic lagoons are usually designed for 10 to 20 days detention time, which makes the required volume from 30 to 60 times that required for anaerobic activated sludge or filter systems (Baumann, 1971). There are also problems with odors being evolved from this process. Short-circuiting may occur, and oxygen transfer at the surface increases the required dosage of supplemental organic carbon.

**Air stripping**

Ammonia stripping is a modification of the aeration process used for the removal of gases from water. Ammonium ions in wastewater exist in equilibrium with ammonia and hydrogen ions:

\[
\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + H^+ 
\] (20)
When the pH of wastewater is increased above 7.0 the equilibrium is displaced to the right. At a pH above 10, over 85 percent of the ammonia present may be liberated as a gas by agitating the wastewater in the presence of air (EPA, 1975; Sawyer and McCarty, 1978). When the pH is between 10.0 and 11.0 the excess hydroxyl ions converts the ammonium ion to ammonium hydroxide (Farrell, 1969).

\[ \text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_4\text{OH} \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O} \]  

(21)

Bubbling air through the ammonium hydroxide solution will remove ammonia. This is generally accomplished in a packed tray tower equipped with an air blower.

The most advanced and well-known ammonia stripping process was being operated at the South Tahoe (California) advanced wastewater treatment plant (Reeves, 1972). This unit was shut down because of freezing problems during winter period. Because of the high pH, scale forms readily on the closely packed media in the tower and must be removed frequently by acid washing or mechanical scrubbing. In cold weather, ice forms on the tower packing, reducing the effectiveness of ammonia removal and creating the possibility of damage to the structure.

Air stripping of ammonia is attractive because about 60 percent of nitrogen in secondary treated wastewater is in the ammonia form. Furthermore, microbial denitrification and ammonia stripping have comparable costs (Culp and Slechta, 1966). Results of their study (Culp and Slechta, 1966) indicate that it is possible to achieve 95 percent removal of ammonia-nitrogen at a pH of about 11.5 using 3,000 cubic meters of air/cubic meter (400 cubic feet of air/gallon) of wastewater.
A digital computer model for the design of ammonia stripping and cooling towers has been presented (Roesler, 1971). Two major problems may develop in ammonia stripping: 1) absorption of carbon dioxide from the air and subsequent precipitation of carbonates, and 2) the biological oxidation of ammonia to nitrates in the aerobic towers (Roesler, 1971). These problems make the ammonia stripping method all but impractical (McKinney, 1971). McKinney stated that ammonia released in the air is readily soluble in water and will be quickly returned to the water environment with no real gain.

In one study on air stripping towers packed with Rasching rings, it was found that the optimum pH for stripping ammonia was 11.0 (Kuhn, 1956). The loading that yielded the best results was 1.46 to 1.54 m$^3$/min (52 to 55 cfm) of air and 0.63 l/sec (0.10 gpm) of wastewater effluent. Kuhn also stated that the best air:liquid ratio was 205 m$^3$/min/l/sec (453 cfm/gpm). Ammonia-nitrogen removal as high as 90 percent can be obtained by passing wastewater through a closely packed aeration tower (Baumann, 1971). To obtain this percent removal wastewater pH values must be greater than 9.0 and air flow rates of about 2.2 to 3.7 m$^3$/l (300 to 500 ft$^3$/gal). This process has been used successfully for stripping ammonia-nitrogen from highly concentrated industrial waste streams. However, as ammonia-nitrogen concentration approaches the low levels of domestic wastewater, the attractiveness of the process decreases considerably.

**Ion exchange**

Ion exchange is a unit process in which ions of a given species are displaced from an insoluble exchange material by ions of different
species from solution. Ion exchange materials, both natural and synthetic, are absorbants which carry charged ionic groups. To maintain electroneutrality, each ionic site must have associated with it an ion of opposite charge (counter-ion). When all counter-ions have been replaced, the ion exchange material is exhausted. Regeneration is obtained by contacting the exchanger with a concentrated solution of the original counter-ion. Ion exchangers are classified by the charge of the exchangable ion (Eliassen, 1965). Thus, acid or cationic resins will exchange cations such as Ca\(^{2+}\) or Mg\(^{2+}\), and base or anionic resins will exchange OH\(^-\) or Cl\(^-\) anions.

The nitrate ion can be removed by contact with an anion exchange resin and the ammonium ion removed by contact with a cation exchange resin. The chemistry of the ion exchange process may be represented as shown in the anion exchange equation below (Eliassen, 1965):

\[
\text{NO}_3^- + R - \text{Cl} \leftrightarrow \text{Cl}^- + R - \text{NO}_3^-
\]

A cation exchange with the ammonium ion would be similar using a cation exchange resin.

Application of the anion exchange process for nitrogen and phosphorus removal involves two problems which affect the economy of the operation (Eliassen and Tchobanoglous, 1968). These problems are associated with the chemical composition of the wastewater and the ultimate disposal of contaminants. Sulfates and other anions may utilize the resin capacity before adequate removal of nitrogen compounds can take place.
Ammonia-nitrogen removal has been achieved by selective ion exchange of ammonium ions with clinoptilolite, a natural zeolite (Baumann, 1971). Clinoptilolite is available in several large natural deposits in the western U.S., so the process appears to have economic potential. One disadvantage, however, is the complexity of the process.

Commonly available synthetic cation exchange resins also can be used to remove ammonia-nitrogen. However, problems of fouling the resin with dissolved organic material and high volumes of regenerated wastewater make the feasibility of this process questionable. With the clinoptilolite process, the high concentrations of ammonia in the regeneration system may permit the recovery of ammonia-nitrogen for use as fertilizer (Reeves, 1972).

In 1971 it was found that the use of natural ion-exchange materials such as clinoptilolite showed favorable efficiencies for removal of ammonia from secondary effluents during large pilot-plant demonstrations (Barth, 1971). Data, however, were limited to the variation of exchange capacity of various lots of the natural material, on the effects of trace materials such as magnesium, on the attrition over long periods of time. A disadvantage is the necessity of clarifying the effluent before application to the columns.

Synthetic ion-exchange resins have been investigated for the removal of nitrate ions from secondary effluents (Barth, 1971). Barth stated that limited success has been achieved because resins with a high selectivity have not been developed, regeneration of
selective resins is usually inefficient, and, as in the case of clinoptilolite, a concentrated, nitrogen-rich brine must be disposed of. It has also been shown that strongly basic anion exchangers, regenerated with common salt, performed satisfactorily in the removal of nitrate (Reeves, 1972).

**Breakpoint chlorination**

One of the approaches for the removal of nitrogen is breakpoint chlorination (or superchlorination). This is accomplished by the addition of chlorine to the waste stream in an amount sufficient to oxidize ammonia-nitrogen gas. After sufficient chlorine has been added to oxidize the organic matter and other readily oxidizable substances present, a stepwise reaction of chlorine with ammonium takes place. The overall theoretical reaction is as follows (EPA, 1975):

\[
3 \text{Cl}_2 + 2 \text{NH}_4^+ \rightarrow \text{N}_2 + 6 \text{HCl} + 2\text{H}^+ \quad \ldots \ldots \quad (23)
\]

This process has been applied for many years to drinking water supplies.

High chlorine requirements for breakpoint chlorination were reported (Farrell 1968). Up to 10 mg of chlorine was required for 1.0 mg of ammonia-nitrogen. Each milligram of nitrite-nitrogen will exert a chlorine demand of 5.06 mg (McCarty and St. Amat, 1969). In addition, the ammonia that is formed will react to form chloramines, which may or may not be detrimental.

Barth (1971) has demonstrated that essentially all the ammonia can be oxidized to nitrogen gas. Side products such as nitrate and nitrogen trichloride can be produced but appropriate pH control can
limit their concentration to satisfactory levels. The pH is generally controlled by lime or caustic additions. This process significantly increases the TDS (Total Dissolved Solid) content of an effluent. This may limit the application of this process for the removal of the bulk of the ammonia, but consideration can be given to use of breakpoint chlorination as a polishing operation.

Other processes

There are other methods of nitrogen removal not so widely known as those previously described. These include electrochemical treatment, demineralization (electrodialysis, reverse osmosis, and distillation), algae harvesting, and land application.

In the electrochemical process, wastewater is mixed with seawater and passed into a single cell containing carbon electrodes. Because of the relative densities of the seawater and the wastewater, the former accumulates in the anode area at the bottom of the cell and the latter at the cathode area near the top of the cell (Foyn, 1962). The current raises the pH at the cathode, thus precipitating the ammonia as MgNH₄PO₄ along with Mg(OH)₂. Hydrogen bubbles generated at the cathode lift the sludge to the surface where it is skimmed and disposed of. Chlorine developed at the anode of the cell provides for disinfection of the effluent. The remaining seawater-wastewater mixture is then discharged to the ocean.

Electrodialysis is a unit process that uses an induced electric current to separate the cationic and anionic components of a solution by means of selective membranes that permit ions to pass through the material from the diluted solution on one side to the concentrated
solution on the other. Electrodialysis is useful for partial demineralization of low mineralized waters, which preferably do not exceed 2,000 mg/l of TDS (Cohen, 1969). Because municipal wastewater generally does not usually exceed 1,000 mg/l, this process is applicable for the treatment of municipal wastes. Problems associated with the electrodialysis process for wastewater renovation include chemical precipitation and membrane clogging (Eliassen and Tchobanoglous, 1968).

Reverse osmosis involves the forced passage of water through semipermeable membranes against the natural osmotic pressures of up to 53 kg/sp m (750 psi) in order to accomplish separation of water and ions. Problems that have arisen in the application of reverse osmosis for desalination include concentration polarization, membrane fouling, and the passage of certain ions through the membrane (Eliassen and Tchobanoglous, 1968). In one study using reverse osmosis for the removal of nitrates from irrigation return water, it has been found that a portion of the nitrate ions will pass through the membrane; thereby limiting its usefulness in the application (Reeves, 1972).

Distillation is classified as a vapor-liquid transfer operation and involves the driving off of water vapor from wastewater by heating in a retort or still, followed by condensation of the water vapor. In practice, distillation is accomplished using a variety of different processes including flash distillation, differential distillation, and stream distillation. Because of the high cost of this process it is not anticipated that it will find wide application in the removal of nitrogen (Eliassen and Tchobanoglous, 1968).
Algae harvesting can also be used for nitrogen removal. In areas where land is available and the cost is low, aerobic lagoons may be used to convert ammonia-nitrogen (as well as phosphorus) into algal cells. These cells are then collected and removed from the wastewater. In general, except for the simplicity of this process, it does not offer a highly attractive method of nitrogen removal for two reasons. First, algal cells are only about 10 percent nitrogen by weight, and a tremendous amount of material must be formed to effect significant nitrogen removals. Second, the algae cannot be removed easily from the lagoon effluent. In one report only about 40 to 60 percent net removal of nitrogen can be expected with this process (Baumann, 1971).

As water percolates through soil, various constituents are removed, indicating that the soil system may be used as a treatment process for the removal of certain impurities. It has been found that the two most important factors that control the movement of nitrogen through soils are physical adsorption and biological action (Reeves, 1972). Physical adsorption seems to be the principal mechanism in the removal of nitrogen in the form of ammonium ion. If nitrogen is in the form of nitrate, it seems that it will travel unimpeded through the soil system.

There are other methods of nitrogen removal in the literature which either are minor, have been unsuccessful, or are a part of the previously mentioned processes. These include using activated carbon, anaerobic activated sludge, filtering, anaerobic filters, and the addition of ferrous sulfate and a copper catalyst.
Removal of Nitrogen Through Nitrate Reduction by \( \text{SO}_2 \)

Sulfur dioxide (\( \text{SO}_2 \)) reduces nitrite- and nitrate-nitrogen to the gaseous species of nitrogen (i.e., \( \text{N}_2 \), \( \text{N}_2\text{O} \), and \( \text{N}_2\text{O}_4 \)). It is important to consider the chemistry of the process.

Theoretically, the reductibility of nitrite and nitrate can be shown by their oxidation reduction potential. In the same manner the ability of sulfurous acid to reduce, can also be shown by its oxidation reduction potential. The applicable oxidation reduction potentials, in acid solution are listed in Table 2 (Handbook of Chemistry and Physics 1980).

A complete chemical reaction can be achieved by adding the \( \text{H}_2\text{SO}_3 \) oxidation half reaction to any of the nitrite or nitrate reduction half reaction. The \( E^\circ \) of cell for the complete reaction is the sum of the two half cell reaction potentials. From Table 2, one can conclude that a positive value for \( E^\circ \) can be obtained for all formulations involving nitrate. The positive value for \( E^\circ \) translates into a negative free energy for reaction, and hence the thermodynamic conditions would be favorable for the reduction of nitrate by sulfurous acid. For example the reaction for the reduction of nitrate by sulfurous acid to produce nitrogen gas is:

\[ 5 \text{H}_2\text{SO}_3 + 2 \text{NO}_3^- + 5 \text{SO}_4^{2-} + 8 \text{H}^+ + \text{N}_2 + \text{H}_2\text{O} \quad \ldots \ldots \ldots \ldots \quad (24) \]

In this reaction the \( E^\circ \) of cell would be the sum of the half cell reaction potentials, equal to \( E^\circ = +1.04 \text{ volts} \), which is a positive value. It is also possible that other products might form, including \( \text{N}_2\text{O}_4, \text{NO}, \text{H}_2\text{N}_2\text{O}_2, \text{NH}_3\text{OH}^+, \text{N}_2\text{H}_5^- \), and \( \text{NH}_4 \). However, since free nitrogen
Table 2. Oxidation reduction potentials in acid solution  
(modified from Handbook of Chemistry and Physics, 1980).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( E_{\text{OX}}^0 ) (volts)</th>
<th>( E_{\text{RED}}^0 ) (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{SO}_3 + \text{H}_2\text{O} = \text{SO}_4^{2-} + 4 \text{H}^+ + 2 \text{e}^- )</td>
<td>-0.20</td>
<td></td>
</tr>
<tr>
<td>( 2 \text{NO}_2^- + 3 \text{H}_2\text{O} + 4 \text{e}^- = \text{N}_2\text{O} + 6 \text{OH}^- )</td>
<td>+0.15</td>
<td></td>
</tr>
<tr>
<td>( \text{NO}_3^- + \text{H}_2\text{O} + 2 \text{e}^- = \text{NO}_2^- + 2 \text{OH}^- )</td>
<td>+0.01</td>
<td></td>
</tr>
<tr>
<td>( \text{NO}_3^- + \text{H}_2\text{O} + 2 \text{e}^- = \text{NH}_3\text{OH}^+ + 2 \text{H}_2\text{O} )</td>
<td>+0.73</td>
<td></td>
</tr>
<tr>
<td>( 2 \text{NO}_3^- + 4 \text{H}^+ + 2 \text{e}^- = \text{N}_2\text{O}_4 + 2 \text{H}_2\text{O} )</td>
<td>+0.81</td>
<td></td>
</tr>
<tr>
<td>( 2 \text{NO}_3^- + 17 \text{H}^+ + 14 \text{e}^- = \text{N}_2\text{H}_5^+ + 6 \text{H}_2\text{O} )</td>
<td>+0.84</td>
<td></td>
</tr>
<tr>
<td>( \text{NO}_3^- + 10 \text{H}^+ + 8 \text{e}^- = \text{NH}_4^+ + 3 \text{H}_2\text{O} )</td>
<td>+0.87</td>
<td></td>
</tr>
<tr>
<td>( 2 \text{NO}_3^- + 10 \text{H}^+ + 8 \text{e}^- = \text{H}_2\text{N}_2\text{O}_2 + 4 \text{H}_2\text{O} )</td>
<td>+0.87</td>
<td></td>
</tr>
<tr>
<td>( \text{NO}_3^- + 3 \text{H}^+ + 2 \text{e}^- = \text{HNO}_2 \text{H}_2\text{O} )</td>
<td>+0.94</td>
<td></td>
</tr>
<tr>
<td>( \text{NO}_3^- + 4 \text{H}^+ + 3 \text{e}^- = \text{NO} + 2 \text{H}_2\text{O} )</td>
<td>+0.96</td>
<td></td>
</tr>
<tr>
<td>( 2 \text{NO}_3^- + 10 \text{H}^+ + 8 \text{e}^- = \text{N}_2\text{O} + 5 \text{H}_2\text{O} )</td>
<td>+1.11</td>
<td></td>
</tr>
<tr>
<td>( \text{NO}_3^- + 6 \text{H}^+ + 5 \text{e}^- = \text{N}_2 \text{H}_2 + 3 \text{H}_2\text{O} )</td>
<td>+1.24</td>
<td></td>
</tr>
</tbody>
</table>
is the stable of the products, it would be the desired end product. Because the thermodynamic data indicates that the reaction is possible, this does not necessarily mean that the desired reaction will take place within a practical period of time. Thus, the evaluation of factors that could affect the kinetics or rate of reaction (such as temperature or catalyst) needs to be accomplished.

Theoretically, it is believed that some trace metals such as iron can act as a catalyst to carry oxygen from NO₃ to SO₂ according to the following reactions:

\[
2 \text{H}_2\text{O} + 2 \text{Fe}^{+++} + \text{SO}_2 + 2 \text{Fe}^{++} + \text{SO}_4^- + 4 \text{H}^+ \quad \ldots \quad (25)
\]

and

\[
2 \text{H}^+ + 2 \text{Fe}^{++} + \text{NO}_3^- + \text{NO}_2^- + 2 \text{Fe}^{+++} + \text{H}_2\text{O} \quad \ldots \quad (26)
\]

The net result is that, \text{SO}_2 changes to \text{SO}_4^- and \text{NO}_3^- changes to lower oxide of nitrogen with no net change in the iron. No attempt has been made to reduce nitrate presence in the wastewater effluent by \text{SO}_2 and very few studies have been made to investigate the potential of \text{SO}_2 to reduce nitrate in aqueous solution. It has been shown that sulfur dioxide can reduce nitrate to various products, including hydroxylamine (Zeegers, 1951). The most pertinent article claimed that a 10 percent \text{NH}_3 solution saturated with \text{SO}_2 until faintly ammoniacal would reduce oxidizing anions and completely eliminate nitrite ion as \text{N}_2 (Soibelman and Bresler, 1940). No reduction was observed when 50 mg/l \text{NO}_3-N treated with 150 mg/l \text{SO}_2, in presence of \text{Fe}^{+++} and \text{Cu}^{++} as catalysts 85°F (29.4°C) during a 48 hour period (Frank et al., 1968).
In order to get a clear view of this method and its applicability for wastewater effluent, an investigation into the chemical process should be conducted. This investigation should lead to acquiring more information concerning the kinetics of the chemical reactions. It should take into account parameters which can affect these kinetics such as temperature, type of catalysts, and levels of NO₃-N and SO₂ concentrations.
MATERIALS AND METHODS

Development of Analytical Techniques

In order to evaluate potential removal of nitrogen from wastewater when treated with sulfur dioxide, it was necessary to verify or develop analytical techniques to accurately and precisely measure the parameters of interest (i.e., ammonia-, nitrate-, and nitrate-nitrogen) in the presence of SO₂.

The analytical technique chosen to determine ammonia-nitrogen presence in the wastewater effluent was the Phenate method, nitrate and nitrate-nitrogen were measured by the Cadmium-Reduction method using Technicon AutoAnalyzer (Model AA2). Details of these methods are outlined in the Standard Methods For the Examination of Water and Wastewater (APHA, 1975). Figure 2 shows the AutoAnalyzer (Model AA2) used in analysis of NO₃-N and NO₂-N.

Figure 2. AutoAnalyzer Model AA2 used in analysis of NO₃-N and NO₂-N
Preliminary analytical data showed that the presence of SO₂ in concentration levels of 80 mg/l and above in the solution interferes with analysis of ammonia-, nitrate- and nitrite-nitrogen in both the Phenate and Cadmium-Reduction methods. Thus, in order to eliminate the interferences of SO₂, it was necessary to either remove or bring the SO₂ concentration down to less than 80 mg/l. The method used to remove SO₂ was to bubble air through the solution treated with SO₂, and strip the SO₂. Another method chosen to eliminate the SO₂ interferences was to dilute the solution to bring the SO₂ level down.

**Bubbling method**

The secondary clarifier effluent from Hyrum Municipal Wastewater Treatment Plant, located to the northwest of Hyrum City, Utah (an oxidation ditch plant) was used as the secondary wastewater sample throughout this study. Figure 3 shows the plan view of this plant. The sample site is indicated by X.

In order to investigate the bubbling procedure's potential to remove SO₂ from secondary wastewater effluent, a one-liter sample of secondary effluent was treated with about 500 mg/l sulfurous acid (Reynolds and Adams, 1979) in a two-liter beaker (the concentration of sulfurous acid is reported as SO₂, i.e. [SO₂] = 0.8 [H₂SO₃]). Then the solution was bubbled with air. The air flow was adjusted to the 17.5 standard cubic feet per hour (SCfh) per liter of solution using an air flow meter. The samples were taken after 5, 10, 20, 30, 45, and 60 minutes to be analyzed for SO₂ concentration and pH. The analytical technique used to measure SO₂ was the Titrimetric (Iodine)
Figure 3. Plan view of Hyrum Treatment Plant. The sample site is indicated by X.
method (APHA, 1975). Figure 4 shows the apparatus used in the bubbling procedure. An acid trap filled with 10 percent HCl was placed before the bubbling beaker in order to absorb the impurities of the air coming through the air pump. The above experiment was conducted in 5 replicates.

In order to study the effects of pH in the bubbling procedure, the above experiment was repeated in 3 replicates during which the pH was adjusted to 2, by one normal HCl and 3 replicates where the pH was adjusted to 2.5, by one normal HCl prior to the bubbling. The results of this experiment were used to determine the optimum bubbling period, and the appropriate pH.

It was necessary to study the effects of the bubbling procedure on the elimination of SO₂ interferences with the analysis of

Figure 4. Bubbling apparatus.
ammonia-, nitrite-, and nitrate-nitrogen. This was accomplished by bubbling a one-liter sample of secondary wastewater with known ammonia-, nitrite-, and nitrate-nitrogen concentrations, treated with sulfurous acid (500 mg/l as \( \text{SO}_2 \)). The concentration of these species were then measured, and the initial results were compared with them. This experiment was run five times with 3 replicates for analysis of each species in each run. As was previously described, the concentration of \( \text{SO}_2 \) at the end of the bubbling period should be below 80 mg/l in order to eliminate the \( \text{SO}_2 \) interferences.

**Diluting method**

The diluting method is simply based on diluting the secondary wastewater, treated with \( \text{SO}_2 \), with distilled water to the degree where \( \text{SO}_2 \) concentration was 80 mg/l or lower. Diluting the solution brings the concentrations of all species down, including the species of interest. Thus, the method is applicable where the concentration of the interest species are initially at such levels that they could remain within the detectable range by methods aforementioned, after making the appropriate dilution. Investigation into this method was carried out by measuring the ammonia-, nitrite-, and nitrate-nitrogen presence in secondary wastewater sample before and after treatment with sulfurous acid (500 mg/l as \( \text{SO}_2 \)) and after making the appropriate dilutions. The nitrate-nitrogen concentration in the secondary effluent from Hyrum plant was found to be about 20 mg/l (low level) during this study, and the concentration of nitrite-nitrogen was about 25 g/l. Thus 1:25 dilution was chosen in order to bring the nitrate- and nitrite-nitrogen concentrations down to the detectable range by
AutoAnalyzer (0.04 to 2.00 mg/l for nitrate-nitrogen and 2 to 100 μg/l for nitrite-nitrogen). This dilution ratio was desirable, since it brings the SO₂ concentration down to within a safe level. The ammonia concentration in the secondary effluent from Hyrum plant was about 500 μg/l (NH₃-N). 1:10 dilution was chosen in this analysis of ammonia-nitrogen in order to eliminate the SO₂ interferences and keep the ammonia level in the detectable range using the Phenate method. This part of the experiment was repeated 5 times with 2 replicates for the analysis of each species.

Nitrate Removal by SO₂

Table 3 shows the matrix which was set up to investigate the potential of SO₂ to reduce nitrate- and nitrite-nitrogen. This matrix was set up in accordance with the variation of the parameters affecting the kinetics of the nitrate reduction, such as temperature, catalyst, nitrate level, and SO₂ concentration. This matrix presents 36 different conditions resulting from the combinations of the varying parameters \([3(\text{SO}_2 \text{ levels}) \times 2(\text{N}_03\text{-N levels}) \times 2(\text{temperature}) \times 3(\text{catalysts}) = 36]\).

Table 3. Matrix set up to show the variation of parameters affecting the removal kinetics.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ (mg/l)</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>2000</td>
</tr>
<tr>
<td>NO₃-N (mg/l)</td>
<td>25-30</td>
</tr>
<tr>
<td></td>
<td>40-45</td>
</tr>
<tr>
<td>Temperature</td>
<td>20°C</td>
</tr>
<tr>
<td></td>
<td>35°C</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Fe (1 g/l)</td>
</tr>
<tr>
<td></td>
<td>Fe⁺³ (1 mg/l)</td>
</tr>
<tr>
<td></td>
<td>NONE</td>
</tr>
</tbody>
</table>
Three levels of SO₂ concentration (500, 1000, and 2000 mg/l) were chosen arbitrarily. The indicated levels of nitrate concentrations were chosen in accordance with the typical minimum and maximum levels reported to be present in the secondary wastewater effluent (Metcalf and Eddy, 1979). Temperatures of 20°C and 35°C were chosen to study the effects of temperature on the reaction kinetics. Catalysts were chosen according to availability and economical considerations. Powdered iron was used as a source of metallic iron (100 mesh), and ferric chloride (FeCl₃) was used as a source of Fe³⁺.

Typical experimental run

The jar test was to study the potential of SO₂ to remove nitrogen under the different conditions previously described. Figure 5 shows the jar test apparatus used in this experiment. As previously mentioned, secondary wastewater effluent from Hyrum Municipal Wastewater Treatment Plant was used as the nitrogen source. The nitrate-nitrogen level in this effluent was normally low (25-30 mg/l) during the experiment, so additional nitrate (under the form of sodium nitrate) was added where needed. The experiment proceeded at room temperature (20°C) except where elevated temperature was needed (35°C). A water bath was used to keep the temperature constant. Figure 6 shows the jar test apparatus and water bath used when the effects of elevated temperature was evaluated.

A typical experimental run can be outlined as follows:

1. Preparation of the appropriate wastewater samples for determination of the pH, concentration of ammonia-, nitrate-, and nitrite-nitrogen, initially present in the secondary wastewater effluent.
Figure 5. Jar test apparatus.

Figure 6. Jar test apparatus and water bath used where the elevated temperature was needed.
2. Setting up 5 one-liter beakers.

3. Placement of 500 ml of secondary treated wastewater effluent in each beaker.

4. Addition of the appropriate amount of sulfurous acid, sodium nitrate, and catalysts, as needed and described in each condition (one beaker was maintained as a control).

5. Stirring of each solution using jar test apparatus (stirring speed was 20 rpm).

6. Cessation of the stirring process in the first beaker, after 10 min., and preparation of the solution for determination of residual SO₂, the pH, ammonia-, nitrate-, and nitrite-nitrogen presence in the solution. Pretreatment was needed to eliminate the SO₂ interferences using methods already described (i.e., bubbling and diluting methods).

7. Repetition of step 6 for second beaker after 20 min. Stirring period. The stirring period for third beaker was 40 min, and for fourth beaker was 24 hours. Fifth beaker was kept as control with all chemicals added (except sulfurous acid) and stirred for 40 min.

The above procedure was followed for each of the 36 different conditions mentioned in Table 3. The obtained results were used to calculate the percent removal of each species comparing the results obtained during each experiment with the initial values.

The statistical analysis chosen for testing the data obtained from this part of the study was sequential analysis. "Rummage" a computer program developed for data analysis was used for this reason (Bryce, 1978). Sequential analysis is a kind of multilinear
regression analysis. The model chosen for this analysis was as follows:

\[ Y = N(I) + S(J) + T(K) + C(L) + A(M) + NS + NT + NC + NT + NA + ST + SC + SA + TC + TA + CA + E \]

in which

- \( Y \) = dependent variable, percent nitrate removal
- \( N(I) \) = independent variable, different levels of NO\(_3\)-N
- \( S(J) \) = independent variable, different levels of SO\(_2\)
- \( T(K) \) = independent variable, different temperatures
- \( C(L) \) = independent variable, different catalysts
- \( A(M) \) = independent variable, time
- \( E \) = error

and NS, NT, NC, NT, NA, ST, SC, SA, TC, TA, and CA stand for the interactions between N, S, T, C, and A.
RESULTS AND DISCUSSION

Development of Analytical Techniques

Bubbling method

As previously mentioned bubbling method was conducted to eliminate the SO\textsubscript{2} interferences with analysis of ammonia-, nitrate-, and nitrite-nitrogen. Figures 7 through 11 show the plot of the results obtained through the bubbling procedure with an unadjusted pH. The results obtained from five runs all indicate the SO\textsubscript{2} concentration can be lowered from an initial level of 500 mg/l to around 250 mg/l during a 60 minute bubbling period without any pH adjustment. Meanwhile the pH rises almost linearly from values of about 2.6 to about 4.6 during a 60 minute bubbling period.

Figures 12 through 14 show the plot of the results obtained through air stripping of SO\textsubscript{2} from the solution at a level of 2.5. Figures 15 through 17 present the plot of the data obtained when air bubbled through a sample after the pH was adjusted to 2.0. All six runs (three replicates for each pH) show that the SO\textsubscript{2} concentration can be brought down to values less than 50 mg/l during the 60 minute bubbling period if the pH of the secondary wastewater is brought down to 2.0-2.5 prior to the bubbling. The pH also rises almost linearly during the air stripping of SO\textsubscript{2} but the rate of increase is lowered as compared to that of the unadjusted pH.

The rate of SO\textsubscript{2} removal from the solution decreases as the SO\textsubscript{2} concentration present in the solution decreases. It can also be concluded that the rate of SO\textsubscript{2} removal increases with decreasing pH.
Figure 7. Run #1, the plot of the SO2 concentration and pH through the bubbling of the secondary wastewater treated with 500 mg/l SO2 (unadjusted pH).

Figure 8. Run #2, the plot of the SO2 concentration and pH through the bubbling of the secondary wastewater treated with 500 mg/l SO2 (unadjusted pH).
Figure 9. Run #3, the plot of the SO$_2$ concentration and pH through the bubbling of the secondary wastewater treated with 500 mg/l SO$_2$ (unadjusted pH).

Figure 10. Run #4, the plot of the SO$_2$ concentration and pH through the bubbling of the secondary wastewater treated with 500 mg/l SO$_2$ (unadjusted pH).
Figure 11. Run #5, the plot of the $SO_2$ concentration and pH through the bubbling of the secondary wastewater treated with 500 mg/l $SO_2$ (unadjusted pH).
Figure 12. Run #1, the plot of the SO₂ concentration and pH through the bubbling of the secondary wastewater treated with 500 mg/l SO₂ (pH adjusted to 2.5).

Figure 13. Run #2, the plot of the SO₂ concentration and pH through the bubbling of the secondary wastewater treated with 500 mg/l SO₂ (pH adjusted to 2.5).
Figure 14. Run #3, the plot of the SO₂ concentration and pH through the bubbling of the secondary wastewater treated with 500 mg/l SO₂ (pH adjusted to 2.5).
Figure 15. Run #1, the plot of the SO$_2$ concentration and pH through the bubbling of the secondary wastewater treated with 500 mg/l SO$_2$ (pH adjusted to 2.0).

Figure 16. Run #2, the plot of the SO$_2$ concentration and pH through the bubbling of the secondary wastewater treated with 500 mg/l SO$_2$ (pH adjusted to 2.0).
Figure 17. Run #3, the plot of the SO₂ concentration and pH through the bubbling of the secondary wastewater treated with 500 mg/l SO₂ (pH adjusted to 2.0).
It was observed that the difference between the initial and final pH values in the case where pH is not adjusted is much higher than in the two other cases where the pH was adjusted.

As stated previously, the objective of this part of the experiment was to develop a method to eliminate the SO2 interferences in the analytical techniques. Since decreasing the SO2 concentration down to 80 mg/l or less was desired, bubbling of the solution at a low pH (2.0-2.5) seemed to be a satisfactory method in removing the SO2 from the solution.

The second part of the bubbling test was conducted to determine the effects of bubbling on the analytical techniques chosen for ammonia-nitrite, and nitrate-nitrogen. Tables 4 and 5 show the results obtained from the second part of the bubbling procedure. These tables present the differences in the NH3-N, NO2-N, and NO3-N concentrations before and after treatment with SO2 and bubbling (at pH = 2) reported as the percentage of the initial values, noted as average percent error. Results obtained for NO3-N show that these percent errors are very small (i.e., the initial values of NO3-N are so close to that of the SO2 treated and bubbled) that air stripping of SO2 at low pH can be safely used to eliminate SO2 interferences for NO3-N analysis through the cadmium reduction method using Autoanalyzer.

Nitrite-nitrogen levels in Hyrum's secondary wastewater were very low at the time of the experiment (25-75 µg/l). In this low range, the AutoAnalyzer is subjected to a great margin of error after having made the appropriate dilution for analytical reasons (1:25). Thus for secondary wastewaters with higher levels of NO2-N, more investigation would need to be done regarding SO2 interference elimination.
Table 4. NO$_2$-N and NO$_3$-N concentrations before and after treatment with SO$_2$ and bubbling for 60 minutes at pH = 2. Average % error is the percent difference between two concentrations.

<table>
<thead>
<tr>
<th>Run</th>
<th>NO$_2$-N concentration (µg/l) Before SO$_2$ &amp; bubbling</th>
<th>Average % Error</th>
<th>NO$_3$-N concentration (mg/l) Before SO$_2$ &amp; bubbling</th>
<th>Average % Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>25.0</td>
<td></td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>0.0</td>
<td>13.3</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td></td>
<td>12.5</td>
<td>12.5</td>
</tr>
<tr>
<td>2</td>
<td>75.0</td>
<td>-11.1</td>
<td>14.5</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td>75.0</td>
<td></td>
<td>14.0</td>
<td>15.0</td>
</tr>
<tr>
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</table>
Table 5. Absorption and NH₃-N concentrations before and after treatment with SO₂ and bubbling for 60 min. at pH=2. Average % error is the percent difference between two concentrations.

<table>
<thead>
<tr>
<th>Run</th>
<th>Absorption</th>
<th>NH₃-N concentration (μg/l)</th>
<th>Average % Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before SO₂ &amp; bubbling</td>
<td>After SO₂ &amp; bubbling</td>
<td>Before SO₂ &amp; bubbling</td>
</tr>
<tr>
<td>1</td>
<td>.115</td>
<td>.168</td>
<td>159</td>
</tr>
<tr>
<td></td>
<td>.119</td>
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<td>.166</td>
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<td>.159</td>
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<td></td>
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<td>.159</td>
<td>121</td>
</tr>
<tr>
<td>3</td>
<td>.078</td>
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<td>110</td>
</tr>
<tr>
<td></td>
<td>.081</td>
<td>.175</td>
<td>109</td>
</tr>
<tr>
<td>4</td>
<td>.086</td>
<td>.150</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>.091</td>
<td>.147</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>.088</td>
<td>.149</td>
<td>126</td>
</tr>
<tr>
<td>5</td>
<td>.112</td>
<td>.171</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>.111</td>
<td>.171</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>.112</td>
<td>.168</td>
<td>145</td>
</tr>
</tbody>
</table>
The results obtained for NH$_3$-N (Table 5) show that the NH$_3$-N concentration rises by 50 to 150 percent during the 60 minute bubbling period at low pH. A number of attempts were made to find the fact or facts which cause this increase in the NH$_3$-N concentration. These were accomplished through a series of experiments concerning the testing of the reagents used for pH adjustments (1 N HCl and 1 N NaOH), bubbling with an inert gas like Helium instead of air, and even replacing the materials such as glassware, connections, and stoppers. The results, however, remained the same and the NH$_3$-N concentration increased when a secondary wastewater sample treated with SO$_2$ was bubbled with air. In a closed system (bubbling the solution in the beaker closed to the atmosphere) better results were obtained. It was concluded that bubbling the solution in a closed system prevented the ammonia present in the atmosphere to transfer to the solution thereby increasing the NH$_3$-N concentration. Figure 18 shows the apparatus developed to bubble the solution in the closed system.

Table 6 shows the NH$_3$-N concentration initially and after treatment with SO$_2$ (500 mg/l), and bubbling for 60 minutes in a closed system. These results show that the bubbling method (in the closed system) can be applied safely whenever the elimination of SO$_2$ interferences is needed in determining the NH$_3$-N species concentration.

**Diluting method**

The diluting method was developed to eliminate the SO$_2$ interferences with analysis of ammonia-, nitrate-, and nitrite-nitrogen. Tables 7 and 8 show the results obtained for this part of the experiment. Again, the difference between NH$_3$-N, NO$_2$-N, and NO$_3$-N concentrations
Figure 18. Apparatus developed for bubbling the SO$_2$ treated solution in a closed system.
Table 6. Absorption and NH$_3$-N concentrations before and after treatment with SO$_2$ and bubbling for 60 minutes at pH=2 in a closed system. Average % error is the percent difference between two conc. concentrations.

<table>
<thead>
<tr>
<th>Run</th>
<th>Absorption</th>
<th>NH$_3$-N concentration (µg/l)</th>
<th>Average % Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>After SO$_2$ &amp; bubbling</td>
<td>Before bubbling</td>
</tr>
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<td>1</td>
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<td></td>
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<td>.132</td>
<td>181</td>
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Table 7. NO$_2$-N and NO$_3$-N concentration before and after treatment with SO$_2$ and diluting.
Average % is the percent difference between two concentrations.

<table>
<thead>
<tr>
<th>Run</th>
<th>NO$_2$-N concentration (µg/l) Before diluting</th>
<th>After SO$_2$ &amp; diluting</th>
<th>Average % Error</th>
<th>NO$_3$-N concentration (mg/l) Before diluting</th>
<th>After SO$_2$ &amp; diluting</th>
<th>Average % Error</th>
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<td>12.0</td>
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<td>0.0</td>
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<td>25.0</td>
<td>0.0</td>
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<td>12.5</td>
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Table 8. Absorption and NH₃-N concentrations before and after treatment with SO₂ and diluting. Average % error is the percent difference between two concentrations.

<table>
<thead>
<tr>
<th>Run</th>
<th>Absorption Before diluting</th>
<th>Absorption After SO₂ &amp; diluting</th>
<th>NH₃-N concentration (µg/l) Before diluting</th>
<th>NH₃-N concentration (µg/l) After SO₂ &amp; diluting</th>
<th>Average % Error</th>
</tr>
</thead>
<tbody>
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<tr>
<td></td>
<td>0.128</td>
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<td>0.130</td>
<td>197</td>
<td>198</td>
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<tr>
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<tr>
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<td>0.128</td>
<td>0.125</td>
<td>193</td>
<td>188</td>
<td>-2.2</td>
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<td>0.125</td>
<td>193</td>
<td>188</td>
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<td></td>
<td>0.128</td>
<td>0.127</td>
<td>193</td>
<td>192</td>
<td></td>
</tr>
</tbody>
</table>
before and after treatment with \( \text{SO}_2 \) and diluting are reported as the percentage of the initial value noted as percent error. The values of percent errors calculated for each species are quite low as indicated in five different runs for each species. This method can be used safely, and eliminates the \( \text{SO}_2 \) interferences completely in the determination of \( \text{NH}_3\text{-N}, \text{NO}_2\text{-N}, \text{NO}_3\text{-N} \). It should be noted that this method is applicable where the \( \text{NH}_3\text{-N}, \text{NO}_2\text{-N}, \text{NO}_3\text{-N} \) concentrations present in wastewater effluent are high enough that they can remain within detectable range after having made the appropriate dilution.

In general, it was concluded that the diluting method rather than the bubbling method is the safer method in eliminating \( \text{SO}_2 \) interferences when determining \( \text{NO}_3\text{-N}, \text{NO}_2\text{-N}, \text{and NH}_3\text{-N} \). Since the diluting method is restricted to the samples where \( \text{NH}_3\text{-N}, \text{NO}_2\text{-N}, \text{and NO}_3\text{-N} \) concentrations are high enough to remain in a detectable range after diluting, the bubbling method in a closed system can be applied whenever the \( \text{NH}_3\text{-N}, \text{NO}_3\text{-N}, \text{and NO}_3\text{-N} \) concentrations are not high enough to apply diluting method, and/or diluting the solution is undesirable.

**Nitrate Removal by \( \text{SO}_2 \)**

As stated previously, this part of the experiment was conducted to investigate the potential of the \( \text{SO}_2 \) (in the form of sulfurous acid) to reduce \( \text{NO}_3\text{-N} \) present in the secondary wastewater effluent to gaseous form of nitrogen (i.e., \( \text{N}_2 \) and \( \text{N}_2\text{O} \)). Table 3 presents the 36 different conditions resulting from combinations of the variation
of SO₂ levels, NO₃-N levels, temperature, and different catalysts, in which this part of the study was carried out.

Most of the attention was focused on NO₃-N species and not to NO₂-N because of three reasons; first, the objective of this part of the study was primarily to investigate the reduction of nitrate-nitrogen present in the secondary wastewater using SO₂; secondly the concentration of nitrite-nitrogen present in the secondary wastewater sample was very low (less than 25 µg/l); and third because of some difficulties with the AutoAnalyzer recorder, NO₂-N was not measured in some cases during the experiment. However in the cases where the NO₂-N concentrations were analyzed, the results show that the NO₂-N concentration decreased to zero in all cases (see Appendix A).

In the cases where powdered iron was used as a catalyst, it was observed that the solution became cloudy after about 10 minutes of treatment with SO₂. The intensity of the cloudiness and the time of its appearance were dependent on the SO₂ levels. The higher SO₂ concentration, the sooner and more intense the cloudiness. This cloudiness disappeared after a 30 to 45 minute treatment, depending on the SO₂ concentration, leaving a black precipitate at the bottom of the beaker. A smell of H₂S was noticed when this black precipitation treated with HCl (1 N). A sample of this black precipitate was taken for elemental analysis on the electron microscope. Figure 19 shows the results obtained for elemental analysis of the black precipitate. The results show that the black precipitate mostly consists of two elements: Fe (iron) and S (sulfur). Unfortunately it was impossible to determine the components in which these two
Figure 19. Micrograph for element analysis from the black precipitation left from treatment of the secondary wastewater with SO₂ in precone of powdered iron.
elements exist. Since the color of the precipitate, however, was black the precipitate may have been "Fe S" (Iron sulfide). It is also observed that a smell of H₂S (hydrogen sulfide) was noticed when the black precipitation was treated with HCl (hydrochloric acid).

In cases where iron was used as a catalyst and the solution was bubbled with air at the end of the treatment for analytical reasons (to eliminate the SO₂ interferences with the analytical techniques), the solution turned a light brownish color after about 5-10 minutes bubbling. The intensity and the time for the color change was dependent upon the SO₂ levels. The higher the SO₂ concentration the faster and more intense the appearances of the brownish color. However, this brownish color disappeared upon the continuation of the bubbling. SO₂ concentration declined to zero upon the disappearance of the brownish color from the solution.

Table 9 shows a portion of the statistical analysis conducted on the data obtained from this part of the research. This table indicates to what degree the variation of the parameters (nitrate levels, SO₂ levels, temperature, catalysts, and time) and their combinations of two are affecting the removal of the NO₃-N from the solution. The confidence interval for these tests was 95 percent. The hypothesis in each test was that the variation of one or combination of two parameters have no effects on the NO₃-N removal. Thus the high F ratio is the indication of the rejection of the hypothesis (i.e., the higher F ratio stands for a higher contribution of variation of the parameter in the removal of NO₃-N from the solution. For example the variation of temperature with a F-ratio equal to 27.64 has the highest effect on
Table 9. The results of the F ratio tests from the statistical analysis of data obtained from experiment.

<table>
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<tr>
<th>SOURCE</th>
<th>DEGREE OF FREEDOM</th>
<th>F RATIO</th>
<th>SIGNIFICANT LEVEL</th>
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<tr>
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<td>CAT(C)</td>
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<td></td>
</tr>
<tr>
<td>TIME(A)</td>
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</tbody>
</table>
the removal of NO₃-N and the variation of the combination of nitrate and SO₂ (NS) with a F ratio equal to 0.03 has no effects on the removal of NO₃-N from the solution. The column indicating the significant level shows the portion of the area under the probability curve for each test (the total area is equal to 1). Its values indicate to what degree the hypothesis can be accepted. Thus they have a reciprocal relation with the F-ratios. Therefore the lower significant levels are indications of higher F-ratios. Table 9 also shows that the NO₃-N removal was affected by variations of all the parameters involved except for the two levels of nitrate (F ratio equal to 4.84) which has almost no effects on the removal. The F ratios for the variation of the combination of two parameters indicate that most of them have no effects on NO₃-N removal except for "SC" (i.e., the combination of SO₂ and catalysts with F ratio equal to 6.18) and "TA" (i.e., the combination of temperature and time with F ratio 17.29). The complete computer output for this statistical analysis can be found in Appendix B.

Figures 20 through 55 present the plot of the NH₃-N, NO₃-N concentrations, and percentage removal of the NO₃-N vs time. Each of these figures presents the results of one run under different conditions resulting from combinations of the varying parameters shown in Table 3. Values at time zero are the concentrations of NH₃-N, and NO₃-N initially present in the secondary wastewater. The percent removal of NO₃-N at each time is the percentage of decrease in NO₃-N concentration compared to the initial value as the treatment proceeds.
Figure 20. (a) The plot of the NO$_3$-N, and NH$_3$-N concentrations vs. time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs. time throughout the experiment.
Figure 21. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs. time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs. time throughout the experiment.

CONDITION: $\text{SO}_2 = 1000 \text{ mg/l as } \text{SO}_2$, Temperature = 20$^\circ$C
NO$_3$-N = 25-30 mg/l Catalyst = None
Figure 22. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs. time throughout the experiment. (b) The plot of the percent NO$_3$-N removal vs. time throughout the experiment.

CONDITION:  
SO$_2$ = 2000 mg/l as SO$_2$  
NO$_3$-N = 25-30 mg/l  
Temperature = 20°C  
Catalyst = None
Figure 23. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs. time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs. time throughout the experiment.

CONDITION: SO$_2$ = 500 mg/l as SO$_2$    Temperature = 20°C
NO$_3$-N = 25-30 mg/l    Catalyst = Fe$^0$ (1 g/l)
CONDITION: $\text{SO}_2 = 1000$ mg/l as $\text{SO}_2$  
$\text{NO}_3\text{-N} = 25-30$ mg/l 
Temperature = 20° C  
Catalyst = Fe$^0$ (1 g/l)

Figure 24. (a) The plot of the $\text{NO}_3\text{-N}$ and $\text{NH}_3\text{-N}$ concentrations vs. time throughout the experiment. 
(b) The plot of the percent $\text{NO}_3\text{-N}$ removal vs. time throughout the experiment.
Figure 25. (a) The plot of the NO3-N and NH3-N concentrations vs. time throughout the experiment.
(b) The plot of the percent NO3-N removal vs. time throughout the experiment.

CONDITION: SO2 = 2000 mg/l as SO2  Temperature = 20°C
NO3-N = 25-30 mg/l  Catalyst = Fe° (1 g/l)
Figure 26. (a) The plot of the NO₃⁻-N and NH₃⁻-N concentrations vs. time throughout the experiment.
(b) The plot of the percent NO₃⁻-N removal vs. time throughout the experiment.

CONDITION:

SO₂ = 500 mg/l as SO₂  
NO₃⁻-N = 25-30 mg/l  
Temperature = 20°C  
Catalyst = Fe⁺³ (1 mg/l)
Figure 27. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs. time throughout the experiment.  
(b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.
Figure 28. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs. time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs. time throughout the experiment.

**Condition:**
- SO$_2$ = 2000 mg/l as SO$_2$
- NO$_3$-N = 25-30 mg/l
- Temperature = 20°C
- Catalyst = Fe$^{+3}$ (1 mg/l)
Figure 29. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs. time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.

CONDITION: SO$_2$ = 500 mg/l as SO$_2$  Temperature = 20°C
NO$_3$-N = 40-45 mg/l  Catalyst = None
CONDITION: $SO_2 = 1000$ mg/l as $SO_2$  
Temperature $= 20^\circ C$  
$NO_3-N = 40-45$ mg/l  
Catalyst $= $ None

Figure 30. (a) The plot of the $NO_3-N$ and $NH_3-N$ concentrations vs time throughout the experiment.  
(b) The plot of the percent $NO_3-N$ removal vs time throughout the experiment.
Figure 31. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs time throughout the experiment. (b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.

**CONDITION:**
- SO$_2$ = 2000 mg/l as SO$_2$
- Temperature = 20°C
- NO$_3$-N = 40-45 mg/l
- Catalyst = None
CONDITION: \( \text{SO}_2 = 500 \text{ mg/l as } \text{SO}_2 \) \hspace{1cm} \text{Temperature} = 20^\circ \text{C}
\text{NO}_3^-\text{N} = 40-45 \text{ mg/l} \hspace{1cm} \text{Catalyst} = \text{Fe}^0 (1 \text{ g/l})

Figure 32. (a) The plot of the \text{NO}_3^-\text{N} and \text{NH}_3^-\text{N} concentrations vs time throughout the experiment.
(b) The plot of the percent \text{NO}_3^-\text{N} removal vs time throughout the experiment.
Figure 33. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.

CONDITION: SO$_2$ = 1000 mg/l as SO$_2$  Temperature = 20°C
NO$_3$-N = 40-45 mg/l  Catalyst = Fe$^0$ (1 g/l)
Figure 34. (a) The plot of the NO₃-N and NH₃-N concentrations vs time throughout the experiment.
(b) The plot of the percent NO₃-N removal vs time throughout the experiment.

CONDITION: SO₂ = 2000 mg/l as SO₂  Temperature = 20°C
NO₃-N = 40-45 mg/l  Catalyst = Fe⁰ (1 g/l)
CONDITION: $SO_2 = 500 \text{ mg/l as } SO_2$  \hspace{1cm} \text{Temperature} = 20^\circ C$

$NO_3-N = 40-45 \text{ mg/l}$  \hspace{1cm} $Catalyst = Fe^{+3}$ (1 mg/l)

Figure 35. (a) The plot of the $NO_3-N$ and $NH_3-N$ concentrations vs time throughout the experiment.

(b) The plot of the percent $NH_3-N$ removal vs time throughout the experiment.
RUN #17

Figure 36. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.

CONDITION:  
SO$_2$ = 1000 mg/l as SO$_2$  
Temperature = 20°C  
NO$_3$-N = 40-45 mg/l  
Catalyst = Fe$^+$ (1 mg/l)
Figure 37. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.

CONDITION:  
SO$_2$ = 2000 mg/l as SO$_2$  
Temperature = 20°C  
NO$_3$-N = 40-45 mg/l  
Catalyst = Fe$^+3$ (1 mg/l)
As concluded from the statistical analysis, the variation of the temperature has the greatest effect on the removal of NO$_3$-N. The comparison of Figures 20 to 37 with Figures 38 to 55 presenting the results of two tests conducted under the same conditions, except two different temperatures (20°C and 35°C) indicates that the elevation of the temperature had practically no effect on the rate of the NO$_3$-N removal between time periods from zero to 40 minutes treatment. However, the effects of the temperature appeared after 40 minutes into the test. Almost in every case elevation of temperature had adverse effect on the NO$_3$-N removal after the 40 minute treatment period. Plots clearly show that the NO$_3$-N concentration increases between the 40 minutes and the 24 hour period of treatment. It is also clear that NH$_3$-N concentration increases in this period of time in conjunction with NO$_3$-N. Due to a long period of treatment (40 minutes to 24 hours) and lack of enough information, it is difficult to determine when and how this increase started between 40 minutes and 24 hour period. The variation of the NO$_3$-N levels and different catalysts (at 35°C) had no effects on the increase of NO$_3$-N and NH$_3$-N concentrations. However, in some cases it was shown that SO$_2$ levels had some effects on the rate of increase. In Figures 32, 38, and 41 where SO$_2$ concentration was 500 mg/l there was no increase on the NO$_3$-N concentration after the 40 minute treatment. In order to get a clearer view of the adverse temperature effect on the NO$_3$-N removal, more study needs to be conducted concerning the variation of temperature, the amount of catalysts used, the SO$_2$ levels, and other factors that might affect the kinetics of the processes.
Run #19

(a) The plot of the NO\textsubscript{3}-N and NH\textsubscript{3}-N concentrations vs time throughout the experiment.

(b) The plot of the percent NO\textsubscript{3}-N removal vs time throughout the experiment.

**CONDITION:**
- SO\textsubscript{2} = 500 mg/l as SO\textsubscript{2}
- Temperature = 35°C
- NO\textsubscript{3}-N = 25-30 mg/l
- Catalyst = None

*Figure 38.*
CONDITION: $SO_2 = 1000$ mg/l as $S_2O_3$  Temperature = $35^\circ C$
$NO_3-N = 25-30$ mg/l  Catalyst = None

Figure 39. (a) The plot of the $NO_3-N$ and $NH_3-N$ concentrations vs time throughout the experiment.
(b) The plot of the percent $NO_3-N$ removal vs time throughout the experiment.
RUN #21

(a) The plot of the NO₃-N and NH₃-N concentrations vs time throughout the experiment.

(b) The plot of the percent NO₃-N removal vs time throughout the experiment.

CONDITION: SO₂ = 2000 mg/l as SO₂  Temperature = 35°C
NO₃-N = 25-30 mg/l  Catalyst = None
Figure 41. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.

CONDITION: SO$_2$ = 500 mg/l as SO$_2$ Temperature = 35°C
NO$_3$-N = 25-30 mg/l Catalyst = Fe$^0$ (1 g/l)
Figure 42. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.

CONDITION: SO$_2$ = 1000 mg/l as SO$_2$  
NO$_3$-N = 25-30 mg/l  
Temperature = 35°C  
Catalyst = Fe$^0$ (1 g/l)
CONDITION:  
\[ \text{SO}_2 = 2000 \text{ mg/l as } \text{SO}_2 \]  
\[ \text{NO}_3^- - \text{N} = 25-30 \text{ mg/l} \]  
\[ \text{Catalyst} = \text{Fe}^0 (1 \text{ g/l}) \]  

Figure 43.  
(a) The plot of the NO\textsubscript{3}-N and NH\textsubscript{3}-N concentrations vs time throughout the experiment.  
(b) The plot of the percent NO\textsubscript{3}-N removal vs time throughout the experiment.
Figure 44. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs. time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.

CONDITION:  
SO$_2$ = 500 mg/l as SO$_2$  \( \text{Temperature} = 35^\circ\text{C} \)  
NO$_3$-N = 25-30 mg/l  \( \text{Catalyst} = \text{Fe}^{3+} \) (1 mg/l)
RUN #26

(a) The plot of the NO₃-N and NH₃-N concentrations vs time throughout the experiment.

(b) The plot of the percent NO₃-N removal vs time throughout the experiment.

CONDITION: SO₂ = 1000 mg/l as SO₂  
NO₃-N = 25-30 mg/l  
Catalyst = Fe³⁺ (1 mg/l)

Temperature = 35°C
RUN #27

(a) The plot of the NO₃-N and NH₃-N concentrations vs time throughout the experiment.

(b) The plot of the percent NO₃-N removal vs time throughout the experiment.

CONDITION: SO₂ = 2000 mg/l as SO₂  Temperature = 35°C
NO₃-N = 25-30 mg/l  Catalyst = Fe³⁺ (1 mg/l)

Figure 46.
Figure 47. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.

CONDITION: SO$_2$ = 500 mg/l as SO$_2$  Temperature: 35°C
NO$_3$-N = 40-45 mg/l  Catalyst = None
RUN #29

(a)

(b)

CONDITION: $SO_2 = 1000$ mg/l as $SO_2$  
Temperature = $35^\circ$C  
$NO_3-N = 40-45$ mg/l  
Catalyst = None

Figure 48. (a) The plot of the $NO_3-N$ and $NH_3-N$ concentrations vs time throughout the experiment.
(b) The plot of the percent $NO_3-N$ removal vs time throughout the experiment.
Figure 49. (a) The plot of the NO₃⁻N and NH₃-N concentrations vs time throughout the experiment.
(b) The plot of the percent NO₃⁻N removal vs time throughout the experiment.

CONDITION:  
SO₂ = 2000 mg/l as SO₂  Temperature = 35°C  
NO₃⁻N = 40-45 mg/l  Catalyst = None
Figures 50. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs time throughout the experiment. (b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.
CONDITION: \( \text{SO}_2 = 1000 \text{ mg/l as SO}_2 \), \( \text{Temperature} = 35^\circ\text{C} \)
\( \text{NO}_3^-\text{N} = 40-45 \text{ mg/l} \)
Catalyst = Fe\(^0\) (1 g/l)

Figure 51. (a) The plot of the \( \text{NO}_3^-\text{N} \) and \( \text{NH}_3^-\text{N} \) concentrations vs time throughout the experiment.
(b) The plot of the percent \( \text{NO}_3^-\text{N} \) removal vs time throughout the experiment.
CONDITION: $SO_2 = 2000$ mg/l as $SO_2$  \hspace{1cm} Temperature = 35°C  
$NO_3-N = 40-45$ mg/l  \hspace{1cm} Catalyst = Fe$^0$ (1 g/l)

Figure 52. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs time throughout the experiment.  
(b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.
RUN #34

(a)

![Graph showing NO₃-N and NH₃-N concentrations vs time](graph1)

(b)

![Graph showing %NO₃-N removal vs time](graph2)

CONDITION:  
SO₂ = 500 mg/l as SO₂  
NO₃-N = 40-45 mg/l  
Temperature = 35°C  
Catalyst = Fe⁺³ (1 mg/l)

Figure 53. (a) The plot of the NO₃-N and NH₃-N concentrations vs time throughout the experiment.  
(b) The plot of the percent NO₃-N removal vs time throughout the experiment.
RUN #35

(a)

(b)

CONDITION: $SO_2 = 1000 \text{ mg/l as } SO_2$  
$NO_3-N = 40-45 \text{ mg/l}$  
$Temperature = 35^\circ C$  
$Catalyst = Fe^3+ (1 \text{ mg/l})$

Figure 54. (a) The plot of the $NO_3-N$ and $NH_3-N$ concentrations vs time throughout the experiment.  
(b) The plot of the percent $NO_3-N$ removal vs time throughout the experiment.
Figure 55. (a) The plot of the NO$_3$-N and NH$_3$-N concentrations vs time throughout the experiment.
(b) The plot of the percent NO$_3$-N removal vs time throughout the experiment.

CONDITION: $SO_2 = 2000$ mg/l as $SO_2$  
$NO_3$-N = 40-45 mg/l  
Temperature = 35°C  
Catalyst = Fe$^3+$ (1 mg/l)
The variation of NO$_3$-N concentration from low levels (25-30 mg/l) to high levels (40-45 mg/l) had almost no effects on the NO$_3$-N percent removal throughout the 24-hour treatment (Figures 20 to 55). The results obtained from statistical analysis of data substantiated this conclusion since the F ratio obtained for the variation of NO$_3$-N levels (4.84) has the smallest value compared to that of the other parameters (see Table 9). There is also no indication of any consistent effect on the NH$_3$-N concentration throughout the 24 hour treatment concerning the variation of NO$_3$-N from one level to another.

As was previously indicated two different catalysts (Fe$^0$ 1 g/l, and Fe$^{+3}$ 1 mg/l) were used during the experiment. The variation on the type of catalyst used significantly effect the removal of the NO$_3$-N from the solution (F ratio equal to some values about 14.07). These effects can be easily identified in Figures 20 with 55. The usage of metallic iron (in the form of powdered iron 100 mesh, 1 gr/l) gives better NO$_3$-N removal than the two other cases where Fe$^{+3}$ or no catalysts were used. The best result obtained from this part of the experiment (44.7 percent NO$_3$-N removal after the 24 hour treatment) is the case when metallic iron was used as a catalyst, and the SO$_2$ concentration was 1000 mg/l. No significant differences between the cases where no catalysts were used, and the cases where Fe$^{+3}$ 1 mg/l (under the form of FeCl$_3$) were used, have been observed. This indicated that Fe$^{+3}$ at this concentration had no catalytic role in the NO$_3$-N removal using SO$_2$. There is also no indication that the type of catalyst used had any significant effect on the NH$_3$-N
concentration during the 24 hour treatment. Since the use of the proper catalyst has a very significant role in the oxidation and reduction processes, more investigation needs to be done concerning the type and proper amount of the catalysts which can be successfully used in these processes.

Three levels of \( \text{SO}_2 \) were used throughout this experiment. In the statistical analysis it was shown that the removal of the \( \text{NO}_3^-\text{N} \) from the solution was affected not only by variation of the \( \text{SO}_2 \) concentration alone but also with variation of combinations of \( \text{SO}_2 \) and the type of the catalysts used (Table 9). Thus the discussion on the effects of \( \text{SO}_2 \) concentration can be best done in conjunction with the type of the catalysts which were used. Comparison of the results obtained from this part of the experiment indicated that there were no significant differences in the \( \text{NO}_3^-\text{N} \) removal for different \( \text{SO}_2 \) concentrations when no catalysts were used. The same results were concluded for the cases where \( \text{FeCl}_3 \) was used as a catalyst. No significant difference was observed for different \( \text{SO}_2 \) levels were used. However, in the cases where powdered iron was used as a catalyst it was observed that the higher \( \text{NO}_3^-\text{N} \) removal was obtained at higher \( \text{SO}_2 \) concentrations.

**Engineering Significance**

Based on the results obtained during this study, the highest \( \text{NO}_3^-\text{N} \) removal (44.7 percent) was achieved when the secondary wastewater was treated with \( \text{SO}_2 \) (1000 mg/l) (temperature was 20°C, \( \text{NO}_3^-\text{N} \) concentration was 40–45 mg/l, and powdered iron (100 mesh) was used as a
catalyst). This percent NO$_3$-N removal was obtained after 24 hr contact time. If SO$_2$ reduction of NO$_3$-N process is to be applied to wastewater treatment plants, and NO$_3$-N removal of 44.7 is desired, a hydraulic detention time of 24 hours is needed which requires a large contact basin. The 36.8 percent NO$_3$-N removal was achieved after 40 min. contact time at the same conditions mentioned above, based on the results obtained in this study. The hydraulic detention time of 40 min. is practical in the wastewater treatment plants. The 36.8 percent NO$_3$-N removal compared to those can be achieved by applying other methods such as biological denitrification (80-90 percent NO$_3$-N removal), or selective ion exchange (75-90 percent NO$_3$-N removal) (see Table 1) is very low. In addition, some of the problems associated with application of this method would be 1) the process requires considerable amount of iron (1 g/l) to catalyze the reduction, 2) the contact tank should be protected against the low pH (2-3.5), 3) diffusing of SO$_2$ gas into the wastewater requires considerable amount of energy, and it would be costly, 4) the pH of the effluent (3-4) would need to be raised to $\approx 6.5$ by applying lime, or by air stripping the SO$_2$, probably recycling the released SO$_2$. According to the facts mentioned above, and the results obtained in this study, SO$_2$ reduction of NO$_3$-N does not appear to be an attractive method for removing NO$_3$-N from wastewater. Further studies, however, need to be conducted. Specifically, the use of catalysts other than iron need additional investigation to potentially achieve higher NO$_3$-N removal (greater than 40 percent).
CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The general scope of this research was to investigate the potential of \( \text{SO}_2 \) in the form of sulfurous acid to remove \( \text{NO}_3^- - \text{N} \) (reduction of \( \text{NO}_3^- - \text{N} \) to the gaseous form of nitrogen) from secondary wastewater. This study was divided to two series of laboratory experiments as follows:

A. The first series of laboratory experiments were conducted to verify or develop analytical techniques to accurately and precisely measure the ammonia-, nitrate-, and nitrite-nitrogen in the presence of \( \text{SO}_2 \). From the results obtained in this part of the study, the following conclusions were derived.

1. In order to eliminate the \( \text{SO}_2 \) interferences with analyzing for \( \text{NO}_3^- - \text{N} \), and \( \text{NO}_2^- - \text{N} \) using cadmium-reduction method, and \( \text{NH}_3^- - \text{N} \) when using phenate method; the \( \text{SO}_2 \) concentration must be brought to some level less than 80 mg/l.

2. The \( \text{SO}_2 \) concentration of a \( \text{SO}_2 \) treated wastewater sample can be decreased from 500 mg/l as \( \text{SO}_2 \) to approximately 250 mg/l if bubbled with the air for 60 min. at the rate of 17.5 standard cubic feet per hour per liter without any pH adjustment. However if the pH is adjusted by HCl IN to an approximate value of 2.0-2.5 prior to bubbling, the \( \text{SO}_2 \) concentration can be decreased to approximately 50 mg/l during 60 min. bubbling.
3. The air bubbling method can be appropriately used to remove the SO₂ from the solution and eliminate its interferences with the cadmium-reduction technique for NO₃-N, and NO₂-N in low levels. For NH₃-N the results show that in order to maintain the NH₃-N concentration, the solution must be bubbled in a system closed to the air.

4. Adequately diluting the wastewater sample treated with SO₂ to concentrations of 80 mg/l or less will also eliminate SO₂ interferences affecting the NO₃-N, NO₂-N, and NH₃-N analyses. This method is more reliable than the bubbling method, however, it is restricted to the samples where NH₃-N, NO₃-N, and NO₂-N concentrations are high enough to remain in a detectable range after diluting.

B. The second series of experiments were conducted to study the potential of SO₂ to remove the NO₃-N present in the secondary wastewater in conjunction with the varying parameters, which were believed affecting the kinetics of the process. These parameters were: SO₂ concentration, NO₃-N concentration, temperature, and catalyst. From the results obtained in this part of study, the following conclusions were derived.

1. The highest NO₃-N removal (44.7%) after 24 hr treatment, was obtained when the SO₂ concentration was 1000 mg/l, NO₃-N concentration was 40-45 mg/l, the temperature was 20°C, and powdered iron was used as catalyst.
2. Elevation of the temperature from 20°C to 35°C had almost no effects on the NO₃-N removal between the time period of zero and 40 min. The results, however, showed that the elevation on temperature adversely effects the NO₃-N removal after 40 min. of treatment and caused some increases in the NO₃-N concentration between the time period of 40 min. and 24 hr. The NO₃-N removal was more affected by temperature at higher SO₂ levels. There was no indication of any specific effects on the NH₃-N concentration due to variation of temperature during the 24 hr treatment.

3. Variation of NO₃-N concentration from low levels (25-30 mg/l) to high levels (40-45) had no effects on the NO₃-N removal, and NH₃-N concentration during the 24 hr treatment period.

4. Iron, in the form of the powdered 100 mesh (1 g/l), had a significant catalytical role in the removing of the NO₃-N from the secondary wastewater using SO₂. The results showed that Fe⁺³ (the form of FeCl₃ 1 mg/l) had almost no catalytical role in this process.

5. From three different levels of SO₂ concentrations (500, 1000, 2000 mg/l) used in this experiment, no significant effects on the NO₃-N removal were observed, when no catalyst was used or Fe⁺³ was used as catalyst. However, in the cases where powdered iron was used as catalyst, the results showed that, the better NO₃-N removal were obtained at higher SO₂ levels (i.e., 1000 and 2000 mg/l).
Future Recommendations

Based on evaluation of the concepts presented in this investigation and a review of the literature, the following recommendations for research are made.

1. More study needs to be done concerning the analysis of NO$_2$-N at high levels in the presence of SO$_2$.

2. The effects of the air bubbling procedure on the NH$_3$-N needs more investigation.

3. The adverse effects of temperature on the NO$_3$-N removal needs to be studied.

4. The use of other types of catalysts such as copper and nickel should be investigated.

5. The use of iron as a catalyst in other forms rather than powdered should be verified.
REFERENCES


Stern, G. 1966. Removal of nitrogen from wastewater. Internal Report. Taft Water Research Center. Federal Water Pollution Control Admin., Cincinnati, Ohio. (This document is unavailable. However, much information contained in the report is also found in Nitrogen Removal from Wastewaters. Report No. ORD-17010, FWQA, Cincinnati, Ohio.)


APPENDIXES
CONDITION: \( \text{SO}_2 = 500 \text{ mg/l}, \text{NO}_3-N = 25-30 \text{ mg/l}, \text{Temperature} = 20^\circ \text{C}, \text{Catalyst} = \text{none} \)

Table A-1. Run # 1: Laboratory data obtained for \( \text{NH}_3-N, \text{NO}_2-N, \) and \( \text{NO}_3-N \) concentrations, and their % Removal throughout the treatment of secondary wastewater with \( \text{SO}_2 \) during 24 hr. (The column \( \text{pH} \) presents the \( \text{pH} \) of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SO}_2 ) mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>( \text{NH}_3-N ) ( \mu g/1 )</th>
<th>% Removal</th>
<th>( \text{NO}_2-N ) ( \mu g/1 )</th>
<th>% Removal</th>
<th>( \text{NO}_3-N ) (mg/l)</th>
<th>% Removal</th>
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<td>483</td>
<td>-</td>
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<tr>
<td>10 min.</td>
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<td>5.20</td>
<td>.102</td>
<td>452</td>
<td>6.4</td>
<td></td>
<td></td>
<td>25.75</td>
<td>14.3</td>
</tr>
<tr>
<td>20 min.</td>
<td>256</td>
<td>6.05</td>
<td>.100</td>
<td>442</td>
<td>8.5</td>
<td></td>
<td></td>
<td>27.05</td>
<td>10.0</td>
</tr>
<tr>
<td>40 min.</td>
<td>253</td>
<td>5.91</td>
<td>.106</td>
<td>473</td>
<td>2.1</td>
<td></td>
<td></td>
<td>25.65</td>
<td>14.6</td>
</tr>
<tr>
<td>24 hr.</td>
<td>224</td>
<td>4.92</td>
<td>.102</td>
<td>452</td>
<td>6.4</td>
<td></td>
<td></td>
<td>23.50</td>
<td>21.8</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 1000$ mg/l, $NO_3-N = 25-30$ mg/l, Temperature = $20^\circ C$, Catalyst = none

Table A-2. Run #2: Laboratory data obtained for NH$_3$-N, NO$_2$-N, and NO$_3$-N concentrations, and their % Removal throughout the treatment of secondary wastewater with SO$_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>NH$_3$-N $\mu g$/l</th>
<th>% Removal</th>
<th>NO$_2$-N $\mu g$/l</th>
<th>% Removal</th>
<th>NO$_3$-N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>-</td>
<td>.025</td>
<td>520</td>
<td>-</td>
<td>480</td>
<td>-</td>
<td>76.46</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>-</td>
<td>.023</td>
<td>498</td>
<td>4.2</td>
<td>480</td>
<td>-</td>
<td>23.55</td>
<td>11.0</td>
</tr>
<tr>
<td>10 min.</td>
<td>293</td>
<td>5.11</td>
<td>.022</td>
<td>479</td>
<td>7.9</td>
<td>0</td>
<td>100</td>
<td>21.25</td>
<td>19.7</td>
</tr>
<tr>
<td>20 min.</td>
<td>275</td>
<td>5.25</td>
<td>.022</td>
<td>480</td>
<td>7.7</td>
<td>0</td>
<td>100</td>
<td>22.50</td>
<td>15.0</td>
</tr>
<tr>
<td>40 min.</td>
<td>280</td>
<td>5.18</td>
<td>.023</td>
<td>480</td>
<td>7.7</td>
<td>0</td>
<td>100</td>
<td>19.58</td>
<td>26.0</td>
</tr>
<tr>
<td>24 hr.</td>
<td>280</td>
<td>5.20</td>
<td>.021</td>
<td>469</td>
<td>9.8</td>
<td>0</td>
<td>100</td>
<td>16.04</td>
<td>39.4</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 2000 \text{mg/l}$, $NO_3-N = 25-30 \text{ mg/l}$, $Temperature = 20^\circ C$, Catalyst = none

Table A-3. Run #3: Laboratory data obtained for $NH_3-N$, $NO_2-N$, and $NO_3-N$ concentrations, and their % Removal throughout the treatment of secondary wastewater with $SO_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>$NH_3-N$ $\mu g/l$</th>
<th>% Removal</th>
<th>$NO_2-N$ $\mu g/l$</th>
<th>% Removal</th>
<th>$NO_3-N$ (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.25</td>
<td>.052</td>
<td>689</td>
<td>-</td>
<td></td>
<td></td>
<td>28.8</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.18</td>
<td>.061</td>
<td>866</td>
<td>-25.7</td>
<td></td>
<td></td>
<td>28.8</td>
<td>-</td>
</tr>
<tr>
<td>10 min.</td>
<td>162</td>
<td>5.19</td>
<td>.060</td>
<td>860</td>
<td>-11.3</td>
<td></td>
<td></td>
<td>27.3</td>
<td>5.2</td>
</tr>
<tr>
<td>20 min.</td>
<td>160</td>
<td>5.18</td>
<td>.056</td>
<td>767</td>
<td>-11.4</td>
<td></td>
<td></td>
<td>26.8</td>
<td>6.9</td>
</tr>
<tr>
<td>40 min.</td>
<td>152</td>
<td>4.60</td>
<td>.060</td>
<td>847</td>
<td>-22.9</td>
<td></td>
<td></td>
<td>25.1</td>
<td>12.5</td>
</tr>
<tr>
<td>24 hr.</td>
<td>170</td>
<td>4.98</td>
<td>.060</td>
<td>847</td>
<td>-22.9</td>
<td></td>
<td></td>
<td>25.0</td>
<td>13.2</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 500\, mg/l$, $NO_3-N = 25-30\, mg/l$, Temperature $= 20^\circ C$, Catalyst $= Fe^0\, (1\, g/l)$

Table A-4. Run #4: Laboratory data obtained for $NH_3-N$, $NO_2-N$, and $NO_3-N$ concentrations, and their % Removal throughout the treatment of secondary wastewater with $SO_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$ (mg/l)</th>
<th>pH</th>
<th>Absorption</th>
<th>$NH_3-N$ ($\mu g/l$)</th>
<th>% Removal</th>
<th>$NO_2-N$ ($\mu g/l$)</th>
<th>% Removal</th>
<th>$NO_3-N$ (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.33</td>
<td>.226</td>
<td>867</td>
<td>-</td>
<td>28.4</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>6.83</td>
<td>.235</td>
<td>903</td>
<td>-4.2</td>
<td>28.2</td>
<td>.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 min.</td>
<td>0</td>
<td>5.39</td>
<td>.223</td>
<td>855</td>
<td>1.4</td>
<td>27.0</td>
<td>4.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 min.</td>
<td>0</td>
<td>5.37</td>
<td>.213</td>
<td>815</td>
<td>6.0</td>
<td>26.2</td>
<td>7.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 min.</td>
<td>0</td>
<td>5.32</td>
<td>.219</td>
<td>839</td>
<td>3.3</td>
<td>25.6</td>
<td>9.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 hr.</td>
<td>0</td>
<td>5.85</td>
<td>.208</td>
<td>794</td>
<td>8.4</td>
<td>24.0</td>
<td>15.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


CONDITION: \( \text{SO}_2 = 1000 \text{ mg/l}, \text{NO}_3-N = 25-30 \text{ mg/l}, \text{Temperature} = 20^\circ \text{C}, \text{Catalyst} = \text{Fe}^0 \ (1 \text{ g/l}) \)

Table A-5: Run #5: Laboratory data obtained for \( \text{NH}_3-N, \text{NO}_2-N, \) and \( \text{NO}_3-N \) concentrations, and their % Removal throughout the treatment of secondary wastewater with \( \text{SO}_2 \) during 24 hr. (The column \( \text{pH} \) presents the \( \text{pH} \) of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SO}_2 ) mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>( \text{NH}_3-N ) ( \mu \text{g/l} )</th>
<th>% Removal</th>
<th>( \text{NO}_2-N ) ( \mu \text{g/l} )</th>
<th>% Removal</th>
<th>( \text{NO}_3-N ) (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>6.97</td>
<td>.113</td>
<td>479</td>
<td>-</td>
<td>24.0</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>6.63</td>
<td>.119</td>
<td>504</td>
<td>-5.3</td>
<td>25.2</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 min.</td>
<td>0</td>
<td>5.38</td>
<td>.112</td>
<td>475</td>
<td>.9</td>
<td>23.1</td>
<td>3.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 min.</td>
<td>0</td>
<td>5.27</td>
<td>.106</td>
<td>449</td>
<td>6.2</td>
<td>22.2</td>
<td>7.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 min.</td>
<td>0</td>
<td>5.28</td>
<td>.102</td>
<td>432</td>
<td>9.8</td>
<td>20.7</td>
<td>13.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 hr.</td>
<td>0</td>
<td>6.17</td>
<td>.109</td>
<td>462</td>
<td>3.6</td>
<td>19.2</td>
<td>20.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CONDITION: \( \text{SO}_2 = 2000 \text{mg/l}, \text{NO}_3^{-}-\text{N} = 25-30 \text{ mg/l}, \text{Temperature} = 20^\circ \text{C}, \text{Catalyst} = \text{Fe}^{0} (1 \text{ g/l}) \)

Table A-6. Run #6: Laboratory data obtained for \( \text{NH}_3^{-}-\text{N}, \text{NO}_2^{-}-\text{N}, \) and \( \text{NO}_3^{-}-\text{N} \) concentrations, and their \% Removal throughout the treatment of secondary wastewater with \( \text{SO}_2 \) during 24 hr. (The column \( \text{pH} \) presents the \( \text{pH} \) of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SO}_2 ) mg/l</th>
<th>( \text{pH} )</th>
<th>Absorption</th>
<th>( \text{NH}_3^{-}-\text{N} ) ( \mu \text{g/l} )</th>
<th>% Removal</th>
<th>( \text{NO}_2^{-}-\text{N} ) ( \mu \text{g/l} )</th>
<th>% Removal</th>
<th>( \text{NO}_3^{-}-\text{N} ) (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>6.84</td>
<td>0.247</td>
<td>547</td>
<td>-</td>
<td></td>
<td></td>
<td>25.8</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>6.86</td>
<td>0.225</td>
<td>497</td>
<td>9.1</td>
<td></td>
<td></td>
<td>25.5</td>
<td>1.2</td>
</tr>
<tr>
<td>10 min.</td>
<td>0</td>
<td>4.77</td>
<td>0.210</td>
<td>463</td>
<td>15.4</td>
<td></td>
<td></td>
<td>21.9</td>
<td>15.1</td>
</tr>
<tr>
<td>20 min.</td>
<td>0</td>
<td>4.66</td>
<td>0.198</td>
<td>435</td>
<td>20.5</td>
<td></td>
<td></td>
<td>21.3</td>
<td>17.4</td>
</tr>
<tr>
<td>40 min.</td>
<td>0</td>
<td>4.62</td>
<td>0.190</td>
<td>417</td>
<td>23.8</td>
<td></td>
<td></td>
<td>19.2</td>
<td>25.6</td>
</tr>
<tr>
<td>24 hr.</td>
<td>0</td>
<td>6.7</td>
<td>0.200</td>
<td>440</td>
<td>19.7</td>
<td></td>
<td></td>
<td>16.8</td>
<td>34.9</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 500 \text{ mg/l}$, $NO_3-N = 25-30 \text{ mg/l}$, Temperature $= 20^\circ\text{C}$, Catalyst $= \text{FeCl}_3 (1 \text{ mg/l})$

Table A-7. Run #7: Laboratory data obtained for $NH_3-N$, $NO_2-N$, and $NO_3-N$ concentrations, and their % Removal throughout the treatment of secondary wastewater with $SO_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$</th>
<th>pH</th>
<th>Absorption</th>
<th>$NH_3-N$</th>
<th>% Removal</th>
<th>$NO_2-N$</th>
<th>% Removal</th>
<th>$NO_3-N$</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.23</td>
<td>0.139</td>
<td>516</td>
<td>-</td>
<td>30.0</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.17</td>
<td>0.135</td>
<td>500</td>
<td>3.1</td>
<td>30.2</td>
<td>-0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 min.</td>
<td>220</td>
<td>5.21</td>
<td>0.140</td>
<td>520</td>
<td>-0.8</td>
<td>29.3</td>
<td>2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 min.</td>
<td>214</td>
<td>5.03</td>
<td>0.164</td>
<td>617</td>
<td>-19.5</td>
<td>28.7</td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 min.</td>
<td>206</td>
<td>5.21</td>
<td>0.135</td>
<td>500</td>
<td>3.1</td>
<td>27.8</td>
<td>7.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 hr.</td>
<td>212</td>
<td>5.01</td>
<td>0.150</td>
<td>575</td>
<td>-10.3</td>
<td>27.8</td>
<td>7.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 1000\text{mg/l}$, $NO_3-N = 25-30\text{ mg/l}$, Temperature = $20^\circ\text{C}$, Catalyst = $\text{FeCl}_3 (1\text{ mg/l})$

Table A-8: Run #8: Laboratory data obtained for $NH_3-N$, $NO_2-N$, and $NO_3-N$ concentrations, and their % Removal throughout the treatment of secondary wastewater with $SO_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>$NH_3-N$ $\mu g/l$</th>
<th>% Removal</th>
<th>$NO_2-N$ $\mu g/l$</th>
<th>% Removal</th>
<th>$NO_3-N$ (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.23</td>
<td>0.131</td>
<td>484</td>
<td>-</td>
<td></td>
<td></td>
<td>30.8</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.17</td>
<td>0.135</td>
<td>500</td>
<td>-3.4</td>
<td></td>
<td></td>
<td>30.6</td>
<td>0.7</td>
</tr>
<tr>
<td>10 min.</td>
<td>160</td>
<td>5.25</td>
<td>0.139</td>
<td>516</td>
<td>-6.6</td>
<td></td>
<td></td>
<td>29.4</td>
<td>4.6</td>
</tr>
<tr>
<td>20 min.</td>
<td>176</td>
<td>4.61</td>
<td>0.140</td>
<td>520</td>
<td>-7.5</td>
<td></td>
<td></td>
<td>28.6</td>
<td>7.7</td>
</tr>
<tr>
<td>40 min.</td>
<td>160</td>
<td>4.77</td>
<td>0.140</td>
<td>520</td>
<td>-7.5</td>
<td></td>
<td></td>
<td>27.2</td>
<td>11.7</td>
</tr>
<tr>
<td>24 hr.</td>
<td>168</td>
<td>4.87</td>
<td>0.142</td>
<td>528</td>
<td>-9.15</td>
<td></td>
<td></td>
<td>27.4</td>
<td>11.0</td>
</tr>
</tbody>
</table>
CONDITION: \( \text{SO}_2 = 2000 \text{ mg/l}, \text{NO}_3^{-}-\text{N} = 25-30 \text{ mg/l}, \text{Temperature} = 20^\circ\text{C}, \text{Catalyst} = \text{FeCl}_3 \) (1 mg/l)

Table A-9. Run #9: Laboratory data obtained for \( \text{NH}_3^{-}-\text{N}, \text{NO}_2^{-}-\text{N}, \) and \( \text{NO}_3^{-}-\text{N} \) concentrations, and their \% Removal throughout the treatment of secondary wastewater with \( \text{SO}_2 \) during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SO}_2 ) mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>( \text{NH}_3^{-}-\text{N} ) ( \mu \text{g/l} )</th>
<th>% Removal</th>
<th>( \text{NO}_2^{-}-\text{N} ) ( \mu \text{g/l} )</th>
<th>% Removal</th>
<th>( \text{NO}_3^{-}-\text{N} ) (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.12</td>
<td>.056</td>
<td>768</td>
<td>-</td>
<td>30.2</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.11</td>
<td>.054</td>
<td>728</td>
<td>5.1</td>
<td>29.8</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 min.</td>
<td>115</td>
<td>5.22</td>
<td>.053</td>
<td>754</td>
<td>1.8</td>
<td>28.3</td>
<td>6.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 min.</td>
<td>112</td>
<td>5.21</td>
<td>.056</td>
<td>768</td>
<td>0</td>
<td>27.1</td>
<td>10.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 min.</td>
<td>116</td>
<td>5.25</td>
<td>.053</td>
<td>709</td>
<td>7.7</td>
<td>76.4</td>
<td>12.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 hr.</td>
<td>120</td>
<td>5.69</td>
<td>.060</td>
<td>847</td>
<td>-10.3</td>
<td>26.2</td>
<td>13.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**CONDITION:** \( \text{SO}_2 = 500 \text{ mg/l}, \text{NO}_3-N = 35-40 \text{ mg/l}, \text{Temperature} = 20^\circ\text{C}, \text{Catalyst} = \text{none} \)

Table A-10. Run #10: Laboratory data obtained for \( \text{NH}_3-N, \text{NO}_2-N, \) and \( \text{NO}_3-N \) concentrations, and their % Removal throughout the treatment of secondary wastewater with \( \text{SO}_2 \) during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SO}_2 ) mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>( \text{NH}_3-N ) ( \mu g/l )</th>
<th>% Removal</th>
<th>( \text{NO}_2-N ) ( \mu g/l )</th>
<th>% Removal</th>
<th>( \text{NO}_3-N ) (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.20</td>
<td>0.130</td>
<td>500</td>
<td>-</td>
<td>360</td>
<td>-</td>
<td>40.50</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.32</td>
<td>0.130</td>
<td>500</td>
<td>0</td>
<td>360</td>
<td>-</td>
<td>42.25</td>
<td>-4.3</td>
</tr>
<tr>
<td>10 min.</td>
<td>220</td>
<td>5.00</td>
<td>0.131</td>
<td>504</td>
<td>-0.8</td>
<td>0</td>
<td>100</td>
<td>40.00</td>
<td>1.2</td>
</tr>
<tr>
<td>20 min.</td>
<td>236</td>
<td>5.20</td>
<td>0.129</td>
<td>496</td>
<td>0.8</td>
<td>0</td>
<td>100</td>
<td>39.25</td>
<td>3.1</td>
</tr>
<tr>
<td>40 min.</td>
<td>232</td>
<td>5.21</td>
<td>0.130</td>
<td>500</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>37.50</td>
<td>7.4</td>
</tr>
<tr>
<td>24 hr.</td>
<td>225</td>
<td>5.24</td>
<td>0.132</td>
<td>508</td>
<td>-1.6</td>
<td>0</td>
<td>100</td>
<td>35.50</td>
<td>12.3</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 1000 \text{ mg/l}$, $NO_3^- = 35-40 \text{ mg/l}$, Temperature = $20^\circ C$, Catalyst = none

Table A-11: Run #11: Laboratory data obtained for $NH_3$-$N$, $NO_2$-$N$, and $NO_3$-$N$ concentrations, and their % Removal throughout the treatment of secondary wastewater with $SO_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$ (mg/l)</th>
<th>pH</th>
<th>Absorption</th>
<th>$NH_3$-$N$ (µg/l)</th>
<th>% Removal</th>
<th>$NO_2$-$N$ (µg/l)</th>
<th>% Removal</th>
<th>$NO_3$-$N$ (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.33</td>
<td>0.125</td>
<td>479</td>
<td>-</td>
<td>380</td>
<td>-</td>
<td>41.75</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.30</td>
<td>0.125</td>
<td>479</td>
<td>0</td>
<td>380</td>
<td>-</td>
<td>42.50</td>
<td>-1.8</td>
</tr>
<tr>
<td>10 min.</td>
<td>220</td>
<td>5.23</td>
<td>0.126</td>
<td>483</td>
<td>-0.8</td>
<td>0</td>
<td>100</td>
<td>39.75</td>
<td>4.8</td>
</tr>
<tr>
<td>20 min.</td>
<td>244</td>
<td>4.83</td>
<td>0.125</td>
<td>479</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>39.00</td>
<td>6.6</td>
</tr>
<tr>
<td>40 min.</td>
<td>216</td>
<td>5.40</td>
<td>0.127</td>
<td>487</td>
<td>-1.7</td>
<td>0</td>
<td>100</td>
<td>37.50</td>
<td>10.2</td>
</tr>
<tr>
<td>24 hr.</td>
<td>225</td>
<td>5.17</td>
<td>0.130</td>
<td>500</td>
<td>-4.4</td>
<td>0</td>
<td>100</td>
<td>35.75</td>
<td>14.4</td>
</tr>
</tbody>
</table>
CONDITION: $\text{SO}_2 = 2000\, \text{mg/l}, \text{NO}_3^- - \text{N} = 35-40\, \text{mg/l}$, Temperature $= 20^\circ\text{C}$, Catalyst $=$ none

Table A-12. Run #12: Laboratory data obtained for NH$_3$ - N, NO$_2$ - N, and NO$_3$ - N concentrations, and their % Removal throughout the treatment of secondary wastewater with SO$_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO$_2$ (mg/l)</th>
<th>pH</th>
<th>Absorption</th>
<th>NH$_3$ - N ($\mu$g/l)</th>
<th>% Removal</th>
<th>NO$_2$ - N ($\mu$g/l)</th>
<th>% Removal</th>
<th>NO$_3$ - N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.10</td>
<td>0.144</td>
<td>537</td>
<td>-</td>
<td>95</td>
<td>-</td>
<td>48.00</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.07</td>
<td>0.143</td>
<td>533</td>
<td>0.7</td>
<td>95</td>
<td>-</td>
<td>47.00</td>
<td>2.1</td>
</tr>
<tr>
<td>10 min.</td>
<td>168</td>
<td>4.75</td>
<td>0.127</td>
<td>467</td>
<td>13.0</td>
<td>0</td>
<td>100</td>
<td>44.00</td>
<td>8.3</td>
</tr>
<tr>
<td>20 min.</td>
<td>135</td>
<td>4.66</td>
<td>0.130</td>
<td>480</td>
<td>10.6</td>
<td>0</td>
<td>100</td>
<td>41.50</td>
<td>13.5</td>
</tr>
<tr>
<td>40 min.</td>
<td>245</td>
<td>5.10</td>
<td>0.131</td>
<td>484</td>
<td>9.9</td>
<td>0</td>
<td>100</td>
<td>40.50</td>
<td>15.6</td>
</tr>
<tr>
<td>24 hr.</td>
<td>200</td>
<td>4.86</td>
<td>0.140</td>
<td>520</td>
<td>3.2</td>
<td>0</td>
<td>100</td>
<td>38.50</td>
<td>19.8</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 500$ mg/l, $NO_3-N = 35-40$ mg/l, Temperature $= 20^\circ C$, Catalyst $= Fe^0 (1$ g/l)

Table A-13. Run # 13: Laboratory data obtained for $NH_3-N$, $NO_2-N$, and $NO_3-N$ concentrations, and their % Removal throughout the treatment of secondary wastewater with $SO_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>$NH_3-N$ μg/l</th>
<th>% Removal</th>
<th>$NO_2-N$ μg/l</th>
<th>% Removal</th>
<th>$NO_3-N$ (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.13</td>
<td>0.146</td>
<td>545</td>
<td>-</td>
<td>95</td>
<td>-</td>
<td>47.00</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>6.99</td>
<td>0.142</td>
<td>428</td>
<td>3.1</td>
<td>95</td>
<td>-</td>
<td>46.50</td>
<td>2.1</td>
</tr>
<tr>
<td>10 min.</td>
<td>0</td>
<td>5.24</td>
<td>0.143</td>
<td>533</td>
<td>2.2</td>
<td>0</td>
<td>100</td>
<td>43.00</td>
<td>8.5</td>
</tr>
<tr>
<td>20 min.</td>
<td>0</td>
<td>5.12</td>
<td>0.140</td>
<td>520</td>
<td>4.6</td>
<td>0</td>
<td>100</td>
<td>42.00</td>
<td>10.6</td>
</tr>
<tr>
<td>40 min.</td>
<td>0</td>
<td>5.11</td>
<td>0.138</td>
<td>512</td>
<td>6.1</td>
<td>0</td>
<td>100</td>
<td>41.00</td>
<td>12.8</td>
</tr>
<tr>
<td>24 hr.</td>
<td>0</td>
<td>5.06</td>
<td>0.141</td>
<td>524</td>
<td>3.9</td>
<td>0</td>
<td>100</td>
<td>38.00</td>
<td>19.1</td>
</tr>
</tbody>
</table>
CONDITION: \( \text{SO}_2 = 1000 \text{ mg/l}, \text{NO}_3^- = 35-40 \text{ mg/l}, \text{Temperature} = 20^\circ\text{C}, \text{Catalyst} = \text{Fe}^0 \) (1 g/l)

Table A-14. Run #14: Laboratory data obtained for \( \text{NH}_3^-\text{N} \), \( \text{NO}_2^-\text{N} \), and \( \text{NO}_3^-\text{N} \) concentrations, and their % Removal throughout the treatment of secondary wastewater with \( \text{SO}_2 \) during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SO}_2 ) mg/l</th>
<th>( \text{pH} )</th>
<th>Absorption</th>
<th>( \text{NH}_3^-\text{N} ) ( \mu\text{g/l} )</th>
<th>% Removal</th>
<th>( \text{NO}_2^-\text{N} ) ( \mu\text{g/l} )</th>
<th>% Removal</th>
<th>( \text{NO}_3^-\text{N} ) (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.50</td>
<td>0.126</td>
<td>452</td>
<td>-</td>
<td></td>
<td></td>
<td>45.60</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.55</td>
<td>0.126</td>
<td>452</td>
<td>0</td>
<td></td>
<td></td>
<td>44.40</td>
<td>2.6</td>
</tr>
<tr>
<td>10 min.</td>
<td>0</td>
<td>4.67</td>
<td>0.127</td>
<td>456</td>
<td>-0.9</td>
<td></td>
<td></td>
<td>40.80</td>
<td>10.5</td>
</tr>
<tr>
<td>20 min.</td>
<td>0</td>
<td>4.54</td>
<td>0.125</td>
<td>448</td>
<td>-0.9</td>
<td></td>
<td></td>
<td>40.00</td>
<td>12.3</td>
</tr>
<tr>
<td>40 min.</td>
<td>0</td>
<td>4.51</td>
<td>0.130</td>
<td>468</td>
<td>-3.5</td>
<td></td>
<td></td>
<td>28.80</td>
<td>36.8</td>
</tr>
<tr>
<td>24 hr.</td>
<td>0</td>
<td>6.20</td>
<td>0.135</td>
<td>488</td>
<td>-8.0</td>
<td></td>
<td></td>
<td>25.20</td>
<td>44.7</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 2000\text{mg/l}$, $NO_3-N = 35-40 \text{mg/l}$, Temperature = $20^\circ\text{C}$, Catalyst = Fe$^0$ (1 g/l)

Table A-15. Run # 15: Laboratory data obtained for NH$_3$-N, NO$_2$-N, and NO$_3$-N concentrations, and their % Removal throughout the treatment of secondary wastewater with $SO_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>NH$_3$-N $\mug$/l</th>
<th>% Removal</th>
<th>NO$_2$-N $\mug$/l</th>
<th>% Removal</th>
<th>NO$_3$-N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.48</td>
<td>0.127</td>
<td>456</td>
<td>-</td>
<td></td>
<td></td>
<td>47.2</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.46</td>
<td>0.125</td>
<td>448</td>
<td>1.7</td>
<td></td>
<td></td>
<td>40.8</td>
<td>13.6</td>
</tr>
<tr>
<td>10 min.</td>
<td>0</td>
<td>4.96</td>
<td>0.129</td>
<td>464</td>
<td>-1.7</td>
<td></td>
<td></td>
<td>37.6</td>
<td>20.3</td>
</tr>
<tr>
<td>20 min.</td>
<td>0</td>
<td>4.80</td>
<td>0.130</td>
<td>468</td>
<td>-2.6</td>
<td></td>
<td></td>
<td>37.2</td>
<td>21.2</td>
</tr>
<tr>
<td>40 min.</td>
<td>0</td>
<td>4.62</td>
<td>0.133</td>
<td>480</td>
<td>-5.3</td>
<td></td>
<td></td>
<td>36.0</td>
<td>23.7</td>
</tr>
<tr>
<td>24 hr.</td>
<td>0</td>
<td>5.42</td>
<td>0.141</td>
<td>512</td>
<td>-12.3</td>
<td></td>
<td></td>
<td>34.8</td>
<td>26.3</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 500 \text{ mg/l}$, $NO_3-N = 35-40 \text{ mg/l}$, Temperature = $20^\circ C$, Catalyst = $FeCl_3$ (1 mg/l)

Table A-16. Run #16: Laboratory data obtained for $NH_3-N$, $NO_2-N$, and $NO_3-N$ concentrations, and their % Removal throughout the treatment of secondary wastewater with $SO_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>$NH_3-N$ $\mu$g/l</th>
<th>% Removal</th>
<th>$NO_2-N$ $\mu$g/l</th>
<th>% Removal</th>
<th>$NO_3-N$ (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>6.51</td>
<td>0.160</td>
<td>591</td>
<td>-</td>
<td>90</td>
<td>-</td>
<td>45.50</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>5.50</td>
<td>0.162</td>
<td>599</td>
<td>-1.4</td>
<td>85</td>
<td>-</td>
<td>44.00</td>
<td>3.3</td>
</tr>
<tr>
<td>10 min.</td>
<td>158</td>
<td>4.70</td>
<td>0.155</td>
<td>571</td>
<td>3.4</td>
<td>0</td>
<td>100</td>
<td>43.00</td>
<td>5.5</td>
</tr>
<tr>
<td>20 min.</td>
<td>180</td>
<td>4.69</td>
<td>0.160</td>
<td>591</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>42.00</td>
<td>7.7</td>
</tr>
<tr>
<td>40 min.</td>
<td>150</td>
<td>5.06</td>
<td>0.158</td>
<td>583</td>
<td>1.4</td>
<td>0</td>
<td>100</td>
<td>40.00</td>
<td>12.1</td>
</tr>
<tr>
<td>24 hr.</td>
<td>188</td>
<td>4.81</td>
<td>0.168</td>
<td>623</td>
<td>-5.4</td>
<td>0</td>
<td>100</td>
<td>38.00</td>
<td>16.5</td>
</tr>
</tbody>
</table>
CONDITION: \( \text{SO}_2 = 1000 \text{ mg/l}, \text{NO}_3^-\text{N} = 35-40 \text{ mg/l}, \) Temperature = 20°C, Catalyst = \( \text{FeCl}_3 \) (1 mg/l)

Table A-17. Run # 17: Laboratory data obtained for \( \text{NH}_3^-\text{N}, \text{NO}_2^-\text{N}, \) and \( \text{NO}_3^-\text{N} \) concentrations, and their % Removal throughout the treatment of secondary wastewater with \( \text{SO}_2 \) during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SO}_2 ) mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>( \text{NH}_3^-\text{N} ) μg/l</th>
<th>% Removal</th>
<th>( \text{NO}_2^-\text{N} ) μg/l</th>
<th>% Removal</th>
<th>( \text{NO}_3^-\text{N} ) (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.00</td>
<td>0.160</td>
<td>591</td>
<td>-</td>
<td>85</td>
<td>-</td>
<td>46.00</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>6.41</td>
<td>0.161</td>
<td>595</td>
<td>-0.7</td>
<td>85</td>
<td>-</td>
<td>44.50</td>
<td>3.3</td>
</tr>
<tr>
<td>10 min.</td>
<td>130</td>
<td>4.76</td>
<td>0.152</td>
<td>560</td>
<td>5.2</td>
<td>0</td>
<td>100</td>
<td>41.50</td>
<td>9.8</td>
</tr>
<tr>
<td>20 min.</td>
<td>170</td>
<td>4.89</td>
<td>0.155</td>
<td>571</td>
<td>3.4</td>
<td>0</td>
<td>100</td>
<td>41.00</td>
<td>10.9</td>
</tr>
<tr>
<td>40 min.</td>
<td>156</td>
<td>4.78</td>
<td>0.153</td>
<td>563</td>
<td>4.7</td>
<td>0</td>
<td>100</td>
<td>43.00</td>
<td>6.5</td>
</tr>
<tr>
<td>24 hr.</td>
<td>178</td>
<td>4.76</td>
<td>0.165</td>
<td>611</td>
<td>-3.4</td>
<td>0</td>
<td>100</td>
<td>38.00</td>
<td>17.4</td>
</tr>
</tbody>
</table>
**CONDITION:** \( \text{SO}_2 = 2000 \text{mg/l}, \text{NO}_3^- - \text{N} = 35-40 \text{ mg/l}, \text{Temperature} = 20^\circ \text{C}, \text{Catalyst} = \text{FeCl}_3 (1 \text{ mg/l}) \)

Table A-18. Run #18: Laboratory data obtained for NH\(_3\)-N, NO\(_2\)-N, and NO\(_3\)-N concentrations, and their % Removal throughout the treatment of secondary wastewater with SO\(_2\) during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO(_2) mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>NH(_3)-N (\mu\text{g/l})</th>
<th>% Removal</th>
<th>NO(_2)-N (\mu\text{g/l})</th>
<th>% Removal</th>
<th>NO(_3)-N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>6.35</td>
<td>0.152</td>
<td>560</td>
<td>-</td>
<td>85</td>
<td>-</td>
<td>45.00</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>6.67</td>
<td>0.150</td>
<td>552</td>
<td>1.4</td>
<td>85</td>
<td>-</td>
<td>43.00</td>
<td>4.4</td>
</tr>
<tr>
<td>10 min.</td>
<td>68</td>
<td>4.84</td>
<td>0.151</td>
<td>556</td>
<td>0.7</td>
<td>0</td>
<td>100</td>
<td>40.50</td>
<td>10.0</td>
</tr>
<tr>
<td>20 min.</td>
<td>150</td>
<td>4.75</td>
<td>0.152</td>
<td>560</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>40.00</td>
<td>11.1</td>
</tr>
<tr>
<td>40 min.</td>
<td>140</td>
<td>5.26</td>
<td>0.154</td>
<td>567</td>
<td>-1.3</td>
<td>0</td>
<td>100</td>
<td>39.00</td>
<td>13.3</td>
</tr>
<tr>
<td>24 hr.</td>
<td>142</td>
<td>4.34</td>
<td>0.157</td>
<td>579</td>
<td>-3.4</td>
<td>0</td>
<td>100</td>
<td>38.00</td>
<td>15.6</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 500$ mg/l, $NO_3-N = 25-30$ mg/l, Temperature $= 35^\circ C$, Catalyst = none

Table A-19. Run # 19: Laboratory data obtained for NH$_3$-N, NO$_2$-N, and NO$_3$-N concentrations, and their % Removal throughout the treatment of secondary wastewater with $SO_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>NH$_3$-N $\mu$g/l</th>
<th>% Removal</th>
<th>NO$_2$-N $\mu$g/l</th>
<th>% Removal</th>
<th>NO$_3$-N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>-</td>
<td>0.112</td>
<td>495</td>
<td>-</td>
<td></td>
<td></td>
<td>29.0</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>-</td>
<td>0.113</td>
<td>500</td>
<td>-1.0</td>
<td></td>
<td></td>
<td>29.0</td>
<td>0</td>
</tr>
<tr>
<td>10 min.</td>
<td>244</td>
<td>5.40</td>
<td>0.112</td>
<td>495</td>
<td>0</td>
<td></td>
<td></td>
<td>27.0</td>
<td>6.9</td>
</tr>
<tr>
<td>20 min.</td>
<td>248</td>
<td>5.42</td>
<td>0.110</td>
<td>486</td>
<td>1.8</td>
<td></td>
<td></td>
<td>27.3</td>
<td>5.9</td>
</tr>
<tr>
<td>40 min.</td>
<td>243</td>
<td>5.41</td>
<td>0.108</td>
<td>476</td>
<td>3.8</td>
<td></td>
<td></td>
<td>25.6</td>
<td>11.7</td>
</tr>
<tr>
<td>24 hr.</td>
<td>248</td>
<td>5.38</td>
<td>0.107</td>
<td>471</td>
<td>4.8</td>
<td></td>
<td></td>
<td>24.9</td>
<td>14.1</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 1000 \text{ mg/l}$, $NO_3^- - N = 25-30 \text{ mg/l}$, Temperature $= 35^\circ C$, Catalyst $= $ none

Table A-20. Run # 20: Laboratory data obtained for $NH_3^- - N$, $NO_2^- - N$, and $NO_3^- - N$ concentrations, and their % Removal throughout the treatment of secondary wastewater with $SO_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$ (mg/l)</th>
<th>pH</th>
<th>Absorption</th>
<th>$NH_3^- - N$ (µg/l)</th>
<th>% Removal</th>
<th>$NO_2^- - N$ (µg/l)</th>
<th>% Removal</th>
<th>$NO_3^- - N$ (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.29</td>
<td>0.080</td>
<td>567</td>
<td>-</td>
<td></td>
<td></td>
<td>31.0</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.20</td>
<td>0.080</td>
<td>567</td>
<td>0</td>
<td></td>
<td></td>
<td>30.6</td>
<td>1.3</td>
</tr>
<tr>
<td>10 min.</td>
<td>252</td>
<td>4.77</td>
<td>0.080</td>
<td>567</td>
<td>0</td>
<td></td>
<td></td>
<td>29.8</td>
<td>3.9</td>
</tr>
<tr>
<td>20 min.</td>
<td>236</td>
<td>4.76</td>
<td>0.087</td>
<td>625</td>
<td>-10.3</td>
<td></td>
<td></td>
<td>29.0</td>
<td>6.5</td>
</tr>
<tr>
<td>40 min.</td>
<td>244</td>
<td>4.61</td>
<td>0.080</td>
<td>567</td>
<td>0</td>
<td></td>
<td></td>
<td>27.8</td>
<td>10.3</td>
</tr>
<tr>
<td>24 hr.</td>
<td>255</td>
<td>4.53</td>
<td>0.090</td>
<td>637</td>
<td>-12.4</td>
<td></td>
<td></td>
<td>31.0</td>
<td>0</td>
</tr>
</tbody>
</table>
CONDITION: $\text{SO}_2 = 2000 \text{ mg/l}$, $\text{NO}_3^- = 25-30 \text{ mg/l}$, Temperature = $35^\circ \text{C}$, Catalyst = none

Table A-21. Run # 21: Laboratory data obtained for $\text{NH}_3^-$-$\text{N}$, $\text{NO}_2^-$-$\text{N}$, and $\text{NO}_3^-$-$\text{N}$ concentrations, and their % Removal throughout the treatment of secondary wastewater with $\text{SO}_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{SO}_2$ (mg/l)</th>
<th>pH</th>
<th>Absorption</th>
<th>$\text{NH}_3^-$-$\text{N}$ (μg/l)</th>
<th>% Removal</th>
<th>$\text{NO}_2^-$-$\text{N}$ (μg/l)</th>
<th>% Removal</th>
<th>$\text{NO}_3^-$-$\text{N}$ (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.43</td>
<td>0.121</td>
<td>443</td>
<td>-</td>
<td>115</td>
<td>-</td>
<td>36.6</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.40</td>
<td>0.119</td>
<td>435</td>
<td>1.8</td>
<td>110</td>
<td>-</td>
<td>36.4</td>
<td>0.5</td>
</tr>
<tr>
<td>10 min.</td>
<td>212</td>
<td>4.62</td>
<td>0.121</td>
<td>443</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>35.4</td>
<td>3.3</td>
</tr>
<tr>
<td>20 min.</td>
<td>180</td>
<td>4.65</td>
<td>0.120</td>
<td>440</td>
<td>0.7</td>
<td>0</td>
<td>100</td>
<td>33.4</td>
<td>8.7</td>
</tr>
<tr>
<td>40 min.</td>
<td>230</td>
<td>4.90</td>
<td>0.120</td>
<td>440</td>
<td>0.7</td>
<td>0</td>
<td>100</td>
<td>32.2</td>
<td>12.0</td>
</tr>
<tr>
<td>24 hr.</td>
<td>195</td>
<td>4.49</td>
<td>0.124</td>
<td>456</td>
<td>-2.9</td>
<td>0</td>
<td>100</td>
<td>34.0</td>
<td>7.1</td>
</tr>
</tbody>
</table>
CONDITION: \( \text{SO}_2 = 500 \text{ mg/l}, \text{NO}_3^- - \text{N} = 25-30 \text{ mg/l}, \text{Temperature} = 35^\circ \text{C}, \text{Catalyst} = \text{Fe}^0 (1 \text{ g/l}) \)

Table A-22. Run # 22: Laboratory data obtained for \( \text{NH}_3^- - \text{N} \), \( \text{NO}_2^- - \text{N} \), and \( \text{NO}_3^- - \text{N} \) concentrations, and their % Removal throughout the treatment of secondary wastewater with \( \text{SO}_2 \) during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SO}_2 ) mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>( \text{NH}_3^- - \text{N} ) ( \mu \text{g/l} )</th>
<th>% Removal</th>
<th>( \text{NO}_2^- - \text{N} ) ( \mu \text{g/l} )</th>
<th>% Removal</th>
<th>( \text{NO}_3^- - \text{N} ) (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>6.97</td>
<td>0.214</td>
<td>818</td>
<td>-</td>
<td>27.2</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>-</td>
<td>0.210</td>
<td>802</td>
<td>2.0</td>
<td>27.6</td>
<td>-1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 min.</td>
<td>0</td>
<td>4.34</td>
<td>0.220</td>
<td>843</td>
<td>-3.0</td>
<td>26.4</td>
<td>2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 min.</td>
<td>0</td>
<td>4.30</td>
<td>0.221</td>
<td>847</td>
<td>-3.5</td>
<td>26.4</td>
<td>2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 min.</td>
<td>0</td>
<td>4.31</td>
<td>0.215</td>
<td>823</td>
<td>-0.5</td>
<td>25.4</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 hr.</td>
<td>0</td>
<td>6.21</td>
<td>0.200</td>
<td>762</td>
<td>6.9</td>
<td>25.0</td>
<td>8.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 1000 \, mg/l$, $NO_3-N = 25-30 \, mg/l$, Temperature = $35^\circ C$, Catalyst = Fe$^0$ (1 g/l)

Table A-23. Run # 23: Laboratory data obtained for NH$_3$-N, NO$_2$-N, and NO$_3$-N concentrations, and their % Removal throughout the treatment of secondary wastewater with SO$_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO$_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>NH$_3$-N $\mu g/l$</th>
<th>% Removal</th>
<th>NO$_2$-N $\mu g/l$</th>
<th>% Removal</th>
<th>NO$_3$-N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>6.93</td>
<td>0.109</td>
<td>462</td>
<td>-</td>
<td></td>
<td></td>
<td>25.8</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>6.98</td>
<td>0.110</td>
<td>466</td>
<td>-0.9</td>
<td></td>
<td></td>
<td>25.8</td>
<td>-</td>
</tr>
<tr>
<td>10 min.</td>
<td>0</td>
<td>4.26</td>
<td>0.103</td>
<td>436</td>
<td>5.5</td>
<td></td>
<td></td>
<td>23.1</td>
<td>10.5</td>
</tr>
<tr>
<td>20 min.</td>
<td>0</td>
<td>4.21</td>
<td>0.099</td>
<td>419</td>
<td>9.2</td>
<td></td>
<td></td>
<td>21.9</td>
<td>15.1</td>
</tr>
<tr>
<td>40 min.</td>
<td>0</td>
<td>4.25</td>
<td>0.100</td>
<td>424</td>
<td>8.3</td>
<td></td>
<td></td>
<td>19.8</td>
<td>23.3</td>
</tr>
<tr>
<td>24 hr.</td>
<td>0</td>
<td>6.15</td>
<td>0.128</td>
<td>542</td>
<td>-17.4</td>
<td></td>
<td></td>
<td>22.8</td>
<td>11.6</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 2000\, \text{mg/l}$, $NO_3^- - N = 25-30\, \text{mg/l}$, Temperature = $35^\circ\text{C}$, Catalyst = $Fe^0$ (1 g/l)

Table A-24. Run # 24: Laboratory data obtained for $NH_3^- - N$, $NO_2^- - N$, and $NO_3^- - N$ concentrations, and their % Removal throughout the treatment of secondary wastewater with $SO_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>$NH_3^- - N$ $\mu g/l$</th>
<th>% Removal</th>
<th>$NO_2^- - N$ $\mu g/l$</th>
<th>% Removal</th>
<th>$NO_3^- - N$ (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>6.69</td>
<td>0.231</td>
<td>511</td>
<td>-</td>
<td></td>
<td></td>
<td>22.8</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>6.71</td>
<td>0.227</td>
<td>502</td>
<td>1.8</td>
<td></td>
<td></td>
<td>23.4</td>
<td>-2.6</td>
</tr>
<tr>
<td>10 min.</td>
<td>0</td>
<td>4.77</td>
<td>0.196</td>
<td>431</td>
<td>15.7</td>
<td></td>
<td></td>
<td>20.1</td>
<td>11.8</td>
</tr>
<tr>
<td>20 min.</td>
<td>0</td>
<td>4.71</td>
<td>0.191</td>
<td>419</td>
<td>18.0</td>
<td></td>
<td></td>
<td>18.9</td>
<td>17.1</td>
</tr>
<tr>
<td>40 min.</td>
<td>0</td>
<td>4.68</td>
<td>0.202</td>
<td>444</td>
<td>13.1</td>
<td></td>
<td></td>
<td>17.7</td>
<td>22.4</td>
</tr>
<tr>
<td>24 hr.</td>
<td>0</td>
<td>7.00</td>
<td>0.208</td>
<td>458</td>
<td>10.4</td>
<td></td>
<td></td>
<td>20.1</td>
<td>11.8</td>
</tr>
</tbody>
</table>
CONDITION: \( \text{SO}_2 = 500 \text{ mg/l}, \text{NO}_3^- - \text{N} = 25-30 \text{ mg/l} \), Temperature = 35\(^{\circ}\)C, Catalyst = \( \text{FeCl}_3 \) (1 mg/l)

Table A-25. Run # 25: Laboratory data obtained for \( \text{NH}_3^- - \text{N} \), \( \text{NO}_2^- - \text{N} \), and \( \text{NO}_3^- - \text{N} \) concentrations, and their % Removal throughout the treatment of secondary wastewater with \( \text{SO}_2 \) during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SO}_2 ) (mg/l)</th>
<th>pH</th>
<th>Absorption</th>
<th>( \text{NH}_3^- - \text{N} ) (( \mu \text{g/l} ))</th>
<th>% Removal</th>
<th>( \text{NO}_2^- - \text{N} ) (( \mu \text{g/l} ))</th>
<th>% Removal</th>
<th>( \text{NO}_3^- - \text{N} ) (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.42</td>
<td>0.123</td>
<td>452</td>
<td>-</td>
<td>105</td>
<td>-</td>
<td>26.7</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.65</td>
<td>0.117</td>
<td>427</td>
<td>5.5</td>
<td>105</td>
<td>-</td>
<td>28.6</td>
<td>-7.2</td>
</tr>
<tr>
<td>10 min.</td>
<td>172</td>
<td>5.00</td>
<td>0.131</td>
<td>484</td>
<td>-7.1</td>
<td>0</td>
<td>100</td>
<td>27.8</td>
<td>-4.2</td>
</tr>
<tr>
<td>20 min.</td>
<td>150</td>
<td>4.81</td>
<td>0.123</td>
<td>452</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>27.0</td>
<td>-1.2</td>
</tr>
<tr>
<td>40 min.</td>
<td>165</td>
<td>4.88</td>
<td>0.126</td>
<td>464</td>
<td>-2.7</td>
<td>0</td>
<td>100</td>
<td>26.7</td>
<td>0</td>
</tr>
<tr>
<td>24 hr.</td>
<td>154</td>
<td>4.62</td>
<td>0.134</td>
<td>496</td>
<td>-9.7</td>
<td>0</td>
<td>100</td>
<td>30.7</td>
<td>-15.0</td>
</tr>
</tbody>
</table>
CONDITION: \( \text{SO}_2 = 1000 \text{ mg/l}, \text{NO}_3-N = 25-30 \text{ mg/l}, \text{Temperature} = 35^\circ \text{C}, \text{Catalyst} = \text{FeCl}_3 \) (1 mg/l)

Table A-26. Run # 26: Laboratory data obtained for \( \text{NH}_3-N \), \( \text{NO}_2-N \), and \( \text{NO}_3-N \) concentrations, and their % Removal throughout the treatment of secondary wastewater with \( \text{SO}_2 \) during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SO}_2 ) mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>( \text{NH}_3-N ) ( \mu g/l )</th>
<th>% Removal</th>
<th>( \text{NO}_2-N ) ( \mu g/l )</th>
<th>% Removal</th>
<th>( \text{NO}_3-N ) (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.30</td>
<td>0.081</td>
<td>575</td>
<td>-</td>
<td></td>
<td></td>
<td>30.4</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.15</td>
<td>0.081</td>
<td>575</td>
<td>0</td>
<td></td>
<td></td>
<td>30.8</td>
<td>0</td>
</tr>
<tr>
<td>10 min.</td>
<td>196</td>
<td>4.49</td>
<td>-</td>
<td>605</td>
<td>-5.2</td>
<td></td>
<td></td>
<td>31.0</td>
<td>0</td>
</tr>
<tr>
<td>20 min.</td>
<td>180</td>
<td>4.67</td>
<td>0.090</td>
<td>650</td>
<td>-13.0</td>
<td></td>
<td></td>
<td>29.0</td>
<td>4.6</td>
</tr>
<tr>
<td>40 min.</td>
<td>182</td>
<td>4.89</td>
<td>0.079</td>
<td>558</td>
<td>2.9</td>
<td></td>
<td></td>
<td>28.4</td>
<td>6.6</td>
</tr>
<tr>
<td>24 hr.</td>
<td>200</td>
<td>4.59</td>
<td>0.088</td>
<td>621</td>
<td>-8.0</td>
<td></td>
<td></td>
<td>30.2</td>
<td>0.7</td>
</tr>
</tbody>
</table>
CONDITION: \( \text{SO}_2 = 2000 \text{ mg/l} \), \( \text{NO}_3^{-}-\text{N} = 25-30 \text{ mg/l} \), Temperature = 35\(^{\circ}\)C, Catalyst = \( \text{FeCl}_3 \) (1 mg/l)

Table A-27. Run # 27: Laboratory data obtained for \( \text{NH}_3^{-}-\text{N} \), \( \text{NO}_2^{-}-\text{N} \), and \( \text{NO}_3^{-}-\text{N} \) concentrations, and their % Removal throughout the treatment of secondary wastewater with \( \text{SO}_2 \) during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SO}_2 ) mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>( \text{NH}_3^{-}-\text{N} ) ( \mu\text{g/l} )</th>
<th>% Removal</th>
<th>( \text{NO}_2^{-}-\text{N} ) ( \mu\text{g/l} )</th>
<th>% Removal</th>
<th>( \text{NO}_3^{-}-\text{N} ) (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.44</td>
<td>0.125</td>
<td>459</td>
<td>-</td>
<td>105</td>
<td>-</td>
<td>27.6</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.46</td>
<td>0.122</td>
<td>448</td>
<td>2.4</td>
<td>110</td>
<td>-</td>
<td>27.2</td>
<td>1.6</td>
</tr>
<tr>
<td>10 min.</td>
<td>150</td>
<td>4.60</td>
<td>0.120</td>
<td>440</td>
<td>4.1</td>
<td>0</td>
<td>100</td>
<td>25.8</td>
<td>6.5</td>
</tr>
<tr>
<td>20 min.</td>
<td>90</td>
<td>5.00</td>
<td>0.121</td>
<td>444</td>
<td>3.3</td>
<td>0</td>
<td>100</td>
<td>25.4</td>
<td>8.2</td>
</tr>
<tr>
<td>40 min.</td>
<td>228</td>
<td>4.57</td>
<td>0.122</td>
<td>448</td>
<td>2.4</td>
<td>0</td>
<td>100</td>
<td>24.3</td>
<td>12.0</td>
</tr>
<tr>
<td>24 hr.</td>
<td>160</td>
<td>4.45</td>
<td>0.123</td>
<td>452</td>
<td>1.5</td>
<td>0</td>
<td>100</td>
<td>27.2</td>
<td>1.6</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 500$ mg/l, $NO_3-N = 35-40$ mg/l, Temperature $= 35^\circ C$, Catalyst $= $ none

Table A-28. Run # 28: Laboratory data obtained for NH$_3$-N, NO$_2$-N, and NO$_3$-N concentrations, and their % Removal throughout the treatment of secondary wastewater with SO$_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO$_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>NH$_3$-N $\mu g$/l</th>
<th>% Removal</th>
<th>NO$_2$-N $\mu g$/l</th>
<th>% Removal</th>
<th>NO$_3$-N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.12</td>
<td>0.161</td>
<td>603</td>
<td>-</td>
<td></td>
<td></td>
<td>40.8</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.21</td>
<td>0.152</td>
<td>567</td>
<td>6.0</td>
<td></td>
<td></td>
<td>38.9</td>
<td>4.8</td>
</tr>
<tr>
<td>10 min.</td>
<td>300</td>
<td>4.72</td>
<td>0.157</td>
<td>587</td>
<td>2.7</td>
<td></td>
<td></td>
<td>37.6</td>
<td>7.9</td>
</tr>
<tr>
<td>20 min.</td>
<td>316</td>
<td>4.93</td>
<td>0.152</td>
<td>567</td>
<td>6.0</td>
<td></td>
<td></td>
<td>36.9</td>
<td>9.5</td>
</tr>
<tr>
<td>40 min.</td>
<td>316</td>
<td>9.33</td>
<td>0.155</td>
<td>579</td>
<td>4.0</td>
<td></td>
<td></td>
<td>35.0</td>
<td>14.3</td>
</tr>
<tr>
<td>24 hr.</td>
<td>330</td>
<td>4.89</td>
<td>0.167</td>
<td>626</td>
<td>-4.0</td>
<td></td>
<td></td>
<td>38.9</td>
<td>4.8</td>
</tr>
</tbody>
</table>
CONDITION: $SO_2 = 1000 \text{ mg/l}, NO_3-N = 35-40 \text{ mg/l}, Temperature = 35^\circ C, Catalyst = none$

Table A-29. Run # 29: Laboratory data obtained for NH$_3$-N, NO$_2$-N, and NO$_3$-N concentrations, and their % Removal throughout the treatment of secondary wastewater with SO$_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO$_2$ (mg/l)</th>
<th>pH</th>
<th>Absorption</th>
<th>NH$_3$-N ($\mu$g/l)</th>
<th>% Removal</th>
<th>NO$_2$-N ($\mu$g/l)</th>
<th>% Removal</th>
<th>NO$_3$-N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.20</td>
<td>0.149</td>
<td>554</td>
<td>-</td>
<td>39.2</td>
<td>-</td>
<td>39.2</td>
<td>0</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>9.91</td>
<td>0.150</td>
<td>558</td>
<td>-0.7</td>
<td>39.2</td>
<td>0</td>
<td>39.2</td>
<td>0</td>
</tr>
<tr>
<td>10 min.</td>
<td>208</td>
<td>9.61</td>
<td>0.156</td>
<td>583</td>
<td>-5.1</td>
<td>36.7</td>
<td>6.5</td>
<td>36.7</td>
<td>6.5</td>
</tr>
<tr>
<td>20 min.</td>
<td>240</td>
<td>9.47</td>
<td>0.139</td>
<td>514</td>
<td>7.2</td>
<td>34.1</td>
<td>12.9</td>
<td>34.1</td>
<td>12.9</td>
</tr>
<tr>
<td>40 min.</td>
<td>258</td>
<td>9.54</td>
<td>0.142</td>
<td>526</td>
<td>5.1</td>
<td>32.2</td>
<td>17.7</td>
<td>32.2</td>
<td>17.7</td>
</tr>
<tr>
<td>24 hr.</td>
<td>270</td>
<td>4.92</td>
<td>0.154</td>
<td>575</td>
<td>-3.7</td>
<td>34.8</td>
<td>11.3</td>
<td>34.8</td>
<td>11.3</td>
</tr>
</tbody>
</table>
CONDITION: $\text{SO}_2 = 2000 \text{mg/l}, \text{NO}_3^- - \text{N} = 35-40 \text{ mg/l}, \text{Temperature} = 35^\circ \text{C}, \text{Catalyst} = \text{none}$

Table A-30: Run # 30: Laboratory data obtained for NH$_3$-N, NO$_2$-N, and NO$_3$-N concentrations, and their % Removal throughout the treatment of secondary wastewater with SO$_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO$_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>NH$_3$-N $\mu$g/l</th>
<th>% Removal</th>
<th>NO$_2$-N $\mu$g/l</th>
<th>% Removal</th>
<th>NO$_3$-N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.53</td>
<td>0.121</td>
<td>444</td>
<td>-</td>
<td></td>
<td></td>
<td>42.3</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>4.46</td>
<td>0.116</td>
<td>423</td>
<td>4.7</td>
<td></td>
<td></td>
<td>42.3</td>
<td>0</td>
</tr>
<tr>
<td>10 min.</td>
<td>214</td>
<td>4.60</td>
<td>0.123</td>
<td>452</td>
<td>-1.8</td>
<td></td>
<td></td>
<td>40.3</td>
<td>4.7</td>
</tr>
<tr>
<td>20 min.</td>
<td>190</td>
<td>4.61</td>
<td>0.119</td>
<td>435</td>
<td>2.0</td>
<td></td>
<td></td>
<td>38.5</td>
<td>9.1</td>
</tr>
<tr>
<td>40 min.</td>
<td>200</td>
<td>4.86</td>
<td>0.117</td>
<td>427</td>
<td>3.8</td>
<td></td>
<td></td>
<td>36.5</td>
<td>13.8</td>
</tr>
<tr>
<td>24 hr.</td>
<td>200</td>
<td>4.50</td>
<td>0.124</td>
<td>456</td>
<td>-2.7</td>
<td></td>
<td></td>
<td>40.1</td>
<td>5.2</td>
</tr>
</tbody>
</table>
CONDITION: $\text{SO}_2 = 500 \text{ mg/l}, \text{NO}_3^- = 35-40 \text{ mg/l}, \text{Temperature} = 35^\circ\text{C}, \text{Catalyst} = \text{Fe}^0 (1 \text{ g/l})$

Table A-31. Run # 31: Laboratory data obtained for NH$_3$-N, NO$_2$-N, and NO$_3$-N concentrations, and their % Removal throughout the treatment of secondary wastewater with SO$_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO$_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>NH$_3$-N $\mu$g/l</th>
<th>% Removal</th>
<th>NO$_2$-N $\mu$g/l</th>
<th>% Removal</th>
<th>NO$_3$-N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.15</td>
<td>0.076</td>
<td>522</td>
<td>-</td>
<td>200</td>
<td>-</td>
<td>42.0</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.13</td>
<td>0.077</td>
<td>530</td>
<td>-1.5</td>
<td>200</td>
<td>-</td>
<td>41.4</td>
<td>1.4</td>
</tr>
<tr>
<td>10 min.</td>
<td>0</td>
<td>5.03</td>
<td>0.076</td>
<td>522</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>37.9</td>
<td>9.7</td>
</tr>
<tr>
<td>20 min.</td>
<td>0</td>
<td>4.88</td>
<td>0.088</td>
<td>618</td>
<td>-18.4</td>
<td>0</td>
<td>100</td>
<td>39.7</td>
<td>5.6</td>
</tr>
<tr>
<td>40 min.</td>
<td>0</td>
<td>4.99</td>
<td>0.079</td>
<td>546</td>
<td>-4.6</td>
<td>0</td>
<td>100</td>
<td>41.4</td>
<td>1.4</td>
</tr>
<tr>
<td>24 hr.</td>
<td>180</td>
<td>6.44</td>
<td>0.082</td>
<td>570</td>
<td>-9.2</td>
<td>0</td>
<td>100</td>
<td>41.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>
CONDITION: $\text{SO}_2 = 1000$ mg/l, $\text{NO}_3-N = 35-40$ mg/l, Temperature $= 35^\circ C$, Catalyst $= \text{Fe}^0$ (1 g/l)

Table A-32. Run # 32: Laboratory data obtained for NH$_3$-N, NO$_2$-N, and NO$_3$-N concentrations, and their % Removal throughout the treatment of secondary wastewater with SO$_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO$_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>NH$_3$-N µg/l</th>
<th>% Removal</th>
<th>NO$_2$-N µg/l</th>
<th>% Removal</th>
<th>NO$_3$-N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>6.78</td>
<td>0.078</td>
<td>531</td>
<td>-</td>
<td>200</td>
<td>-</td>
<td>41.5</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>6.99</td>
<td>0.075</td>
<td>508</td>
<td>4.3</td>
<td>200</td>
<td>-</td>
<td>39.8</td>
<td>4.1</td>
</tr>
<tr>
<td>10 min.</td>
<td>0</td>
<td>4.94</td>
<td>0.072</td>
<td>484</td>
<td>8.9</td>
<td>0</td>
<td>100</td>
<td>36.9</td>
<td>11.0</td>
</tr>
<tr>
<td>20 min.</td>
<td>0</td>
<td>4.79</td>
<td>0.071</td>
<td>477</td>
<td>10.2</td>
<td>0</td>
<td>100</td>
<td>38.1</td>
<td>8.2</td>
</tr>
<tr>
<td>40 min.</td>
<td>0</td>
<td>4.83</td>
<td>0.070</td>
<td>469</td>
<td>11.7</td>
<td>0</td>
<td>100</td>
<td>38.6</td>
<td>6.8</td>
</tr>
<tr>
<td>24 hr.</td>
<td>0</td>
<td>5.08</td>
<td>0.080</td>
<td>547</td>
<td>-3.0</td>
<td>0</td>
<td>100</td>
<td>39.8</td>
<td>4.1</td>
</tr>
</tbody>
</table>
**CONDITION:** $SO_2 = 2000 \text{ mg/l}$, $NO_3-N = 35-40 \text{ mg/l}$, Temperature = $35^{\circ}C$, Catalyst = $Fe^0 \ (1 \text{ g/l})$

Table A-33. Run # 33: Laboratory data obtained for $NH_3-N$, $NO_2-N$, and $NO_3-N$ concentrations, and their % Removal throughout the treatment of secondary wastewater with $SO_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>$NH_3-N$ μg/l</th>
<th>$%\text{Removal}$</th>
<th>$NO_2-N$ μg/l</th>
<th>$%\text{Removal}$</th>
<th>$NO_3-N$ (mg/l)</th>
<th>$%\text{Removal}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.24</td>
<td>0.072</td>
<td>484</td>
<td>-</td>
<td>200</td>
<td>-</td>
<td>40.0</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>6.99</td>
<td>0.072</td>
<td>484</td>
<td>0</td>
<td>200</td>
<td>-</td>
<td>38.8</td>
<td>5.3</td>
</tr>
<tr>
<td>10 min.</td>
<td>0</td>
<td>4.98</td>
<td>0.065</td>
<td>430</td>
<td>11.2</td>
<td>0</td>
<td>100</td>
<td>34.5</td>
<td>15.8</td>
</tr>
<tr>
<td>20 min.</td>
<td>0</td>
<td>4.80</td>
<td>0.062</td>
<td>406</td>
<td>16.1</td>
<td>0</td>
<td>100</td>
<td>33.4</td>
<td>18.4</td>
</tr>
<tr>
<td>40 min.</td>
<td>0</td>
<td>4.82</td>
<td>0.066</td>
<td>438</td>
<td>9.5</td>
<td>0</td>
<td>100</td>
<td>33.4</td>
<td>18.4</td>
</tr>
<tr>
<td>24 hr.</td>
<td>0</td>
<td>5.21</td>
<td>0.072</td>
<td>484</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>36.7</td>
<td>10.5</td>
</tr>
</tbody>
</table>
**CONDITION:** \( \text{SO}_2 = 500 \text{ mg/l}, \text{NO}_3-N = 35-40 \text{ mg/l}, \text{Temperature} = 35^\circ \text{C}, \text{Catalyst} = \text{FeCl}_3 (1 \text{ mg/l}) \)

Table A-34. Run # 34: Laboratory data obtained for \( \text{NH}_3-N, \text{NO}_2-N, \) and \( \text{NO}_3-N \) concentrations, and their % Removal throughout the treatment of secondary wastewater with \( \text{SO}_2 \) during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{SO}_2 ) mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>( \text{NH}_3-N ) ( \mu \text{g}/l )</th>
<th>% Removal</th>
<th>( \text{NO}_2-N ) ( \mu \text{g}/l )</th>
<th>% Removal</th>
<th>( \text{NO}_3-N ) (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>-</td>
<td>0.150</td>
<td>542</td>
<td>-</td>
<td>240</td>
<td>-</td>
<td>41.4</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>9.87</td>
<td>0.159</td>
<td>577</td>
<td>-6.4</td>
<td>240</td>
<td>-</td>
<td>38.4</td>
<td>7.2</td>
</tr>
<tr>
<td>10 min.</td>
<td>118</td>
<td>4.96</td>
<td>0.157</td>
<td>569</td>
<td>-4.9</td>
<td>0</td>
<td>100</td>
<td>35.4</td>
<td>14.5</td>
</tr>
<tr>
<td>20 min.</td>
<td>104</td>
<td>4.94</td>
<td>0.151</td>
<td>546</td>
<td>-0.6</td>
<td>0</td>
<td>100</td>
<td>33.0</td>
<td>20.3</td>
</tr>
<tr>
<td>40 min.</td>
<td>130</td>
<td>5.07</td>
<td>0.157</td>
<td>569</td>
<td>-4.9</td>
<td>0</td>
<td>100</td>
<td>31.8</td>
<td>23.3</td>
</tr>
<tr>
<td>24 hr.</td>
<td>132</td>
<td>4.41</td>
<td>0.168</td>
<td>612</td>
<td>-12.7</td>
<td>0</td>
<td>100</td>
<td>42.0</td>
<td>-1.4</td>
</tr>
</tbody>
</table>
CONDITION: $\text{SO}_2 = 1000$ mg/l, $\text{NO}_3-N = 35-40$ mg/l, Temperature = 35°C, Catalyst = $\text{FeCl}_3$ (1 mg/l)

Table A-35. Run #35: Laboratory data obtained for NH$_3$-N, NO$_2$-N, and NO$_3$-N concentrations, and their % Removal throughout the treatment of secondary wastewater with SO$_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO$_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>NH$_3$-N µg/l</th>
<th>% Removal</th>
<th>NO$_2$-N µg/l</th>
<th>% Removal</th>
<th>NO$_3$-N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.27</td>
<td>0.155</td>
<td>562</td>
<td>-</td>
<td>280</td>
<td>-</td>
<td>39.0</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.45</td>
<td>0.155</td>
<td>562</td>
<td>0</td>
<td>260</td>
<td>-</td>
<td>37.8</td>
<td>3.1</td>
</tr>
<tr>
<td>10 min.</td>
<td>125</td>
<td>5.00</td>
<td>0.153</td>
<td>554</td>
<td>1.3</td>
<td>0</td>
<td>100</td>
<td>33.6</td>
<td>13.8</td>
</tr>
<tr>
<td>20 min.</td>
<td>90</td>
<td>4.64</td>
<td>0.154</td>
<td>558</td>
<td>0.7</td>
<td>0</td>
<td>100</td>
<td>35.4</td>
<td>9.2</td>
</tr>
<tr>
<td>40 min.</td>
<td>115</td>
<td>5.03</td>
<td>0.151</td>
<td>546</td>
<td>2.8</td>
<td>0</td>
<td>100</td>
<td>31.8</td>
<td>18.5</td>
</tr>
<tr>
<td>24 hr.</td>
<td>120</td>
<td>4.38</td>
<td>0.172</td>
<td>627</td>
<td>-11.7</td>
<td>0</td>
<td>100</td>
<td>43.2</td>
<td>-10.8</td>
</tr>
</tbody>
</table>
Table A-36. Run #36: Laboratory data obtained for NH$_3$-N, NO$_2$-N, and NO$_3$-N concentrations, and their % Removal throughout the treatment of secondary wastewater with SO$_2$ during 24 hr. (The column pH presents the pH of each sample after making the proper dilution for analytical reasons).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO$_2$ mg/l</th>
<th>pH</th>
<th>Absorption</th>
<th>NH$_3$-N $\mu$g/l</th>
<th>% Removal</th>
<th>NO$_2$-N $\mu$g/l</th>
<th>% Removal</th>
<th>NO$_3$-N (mg/l)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>7.15</td>
<td>0.139</td>
<td>500</td>
<td>-</td>
<td>300</td>
<td>-</td>
<td>39.0</td>
<td>-</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>7.22</td>
<td>0.138</td>
<td>492</td>
<td>0.8</td>
<td>300</td>
<td>-</td>
<td>38.4</td>
<td>1.5</td>
</tr>
<tr>
<td>10 min.</td>
<td>65</td>
<td>4.90</td>
<td>0.137</td>
<td>493</td>
<td>1.5</td>
<td>0</td>
<td>100</td>
<td>34.2</td>
<td>12.3</td>
</tr>
<tr>
<td>20 min.</td>
<td>30</td>
<td>4.46</td>
<td>0.135</td>
<td>485</td>
<td>3.1</td>
<td>0</td>
<td>100</td>
<td>34.2</td>
<td>12.3</td>
</tr>
<tr>
<td>40 min.</td>
<td>48</td>
<td>4.77</td>
<td>0.141</td>
<td>508</td>
<td>-1.5</td>
<td>0</td>
<td>100</td>
<td>33.0</td>
<td>15.4</td>
</tr>
<tr>
<td>24 hr.</td>
<td>60</td>
<td>4.64</td>
<td>0.153</td>
<td>554</td>
<td>-10.8</td>
<td>0</td>
<td>100</td>
<td>37.8</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Appendix B
The Computer Output for
Statistical Analysis
-- INUNIT 5
IN UNIT CHANGED TO 5

* MODEL Y=NI+S(J)+T(K)+C(L)+A(M)+NS+NT+NC+NA+ST+SC+SA+TC+TA+CA+E

THE EXPERIMENTAL DESIGN MODEL IS
Y(IJKLM)=NI+S(J)+T(K)+C(L)+A(M)+NS(IJ)+NT(JK)+NC(IL)+
NA(IM)+ST(JK)+SC(JL)+SA(JM)+TC(KL)+TA(KM)+CA(LM)+E

* -- RECO 10 C1 1 C1
RECO VALUES 10.00000 IN C1 INTO 1.00000 PUT INTO C1

* -- RECO 20 C1 2 C1
RECO VALUES 20.00000 IN C1 INTO 2.00000 PUT INTO C1

* -- RECO 40 C1 3 C1
RECO VALUES 40.00000 IN C1 INTO 3.00000 PUT INTO C1

* -- RECO 60 C1 4 C1
RECO VALUES 60.00000 IN C1 INTO 4.00000 PUT INTO C1

* -- RECO 500 C6 1 C6
RECO VALUES 500.00000 IN C6 INTO 1.00000 PUT INTO C6

* -- RECO 1000 C6 2 C6
RECO VALUES 1000.00000 IN C6 INTO 2.00000 PUT INTO C6

* -- RECO 2000 C6 3 C6
RECO VALUES 2000.00000 IN C6 INTO 3.00000 PUT INTO C6

* -- RECO 20 C3 1 C3
RECO VALUES 20.00000 IN C3 INTO 1.00000 PUT INTO C3

* -- RECO 350 C3 2 C3
RECO VALUES 350.00000 IN C3 INTO 2.00000 PUT INTO C3

* -- FIXED N 2 C4 'NITRATE'
THE MAIN EFFECT N IS FIXED WITH SUBSCRIPT I = 1 TO 2 IN COL 4
WITH LABEL = NITRA(N)
-- FIXED S 3 C6 'SO2'
The main effect S is fixed with subscript J = 1 to 3 in col 6
with label = SO2(S)

-- FIXED T 2 C3 'TEMP'
The main effect T is fixed with subscript K = 1 to 2 in col 3
with label = TEMP(T)

-- FIXED C 3 C5 'CAT'
The main effect C is fixed with subscript L = 1 to 3 in col 5
with label = CAT(C)

-- FIXED A 4 C1 'TIME'
The main effect A is fixed with subscript M = 1 to 4 in col 1
with label = TIME(A)

-- ESTI N (L) E (N) .05
-- ESTI S (L) E (N) .05
-- ESTI T (L) E (N) .05
-- ESTI C (L) E (N) .05
-- ESTI A (L) E (N) .05
-- ESTI TA (L) E (N) .05
-- ESTI SC (L) E (N) .05
-- ESTI NC (L) E (N) .05
-- LAST

-- FREAD C1-C6

ENTER FORMAT

The format is
(T5,F2.0,T25,F4.1,T34,F3.0,T40,F1.0,T45,F1.0,T50,F4.0)
NITRA(C4) SO2(C6) TEMP(C3) CAT(C5) TIME(C1) C2

2.00000 2.00000 2.00000 3.00000 4.00000 0.00000
2.00000 3.00000 2.00000 3.00000 1.00000 12.30000
2.00000 3.00000 2.00000 3.00000 2.00000 12.30000
2.00000 3.00000 2.00000 3.00000 3.00000 15.40000
NUMBER OF DATA RECORDS READ = 144  
NUMBER OF DATA RECORDS USED = 144  
SAMPLE SIZE = 144

<table>
<thead>
<tr>
<th>COL</th>
<th>MEAN</th>
<th>VAR.</th>
<th>STD DEV</th>
<th>MIN</th>
<th>MAX</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>11.1846</td>
<td>59.53291</td>
<td>7.71576</td>
<td>0.00000</td>
<td>44.70000</td>
</tr>
</tbody>
</table>

THE MODEL FOR THIS ANALYSIS IS
Y = NITRA(N) + SO2(S) + TEMP(T) + CAT(C) + TIME(A) + NS + NT + NC + NA + ST + SC + SA + TC + TA + CA + E

THE DEPENDENT VARIABLE FOR THIS TABLE IS C2

ADJUSTED HYPOTHESIS TESTS

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>DF</th>
<th>F-RATIO</th>
<th>SIGN. LEVEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>NITRA(N)</td>
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<td>123.117517</td>
<td>4.937912</td>
</tr>
<tr>
<td>ERROR</td>
<td>103</td>
<td>25.449006</td>
<td></td>
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<td>SO2(S)</td>
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<td>282.524740</td>
<td>11.101603</td>
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<tr>
<td>ERROR</td>
<td>103</td>
<td>25.449006</td>
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</tr>
<tr>
<td>TEMP(T)</td>
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<td>103</td>
<td>25.449006</td>
<td></td>
</tr>
<tr>
<td>CAT(C)</td>
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<td>14.066833</td>
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<td>ERROR</td>
<td>103</td>
<td>25.449006</td>
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</tr>
<tr>
<td>TIME(A)</td>
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<td>10.535150</td>
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<td>103</td>
<td>25.449006</td>
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<td>NS</td>
<td>2</td>
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<td>0.028072</td>
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<tr>
<td>ERROR</td>
<td>103</td>
<td>25.449006</td>
<td></td>
</tr>
<tr>
<td>NT</td>
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<td>23.544601</td>
<td>1.003756</td>
</tr>
<tr>
<td>ERROR</td>
<td>103</td>
<td>25.449006</td>
<td></td>
</tr>
<tr>
<td>Code</td>
<td>Value 1</td>
<td>Value 2</td>
<td>Result 1</td>
</tr>
<tr>
<td>------</td>
<td>---------</td>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>NC</td>
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<tr>
<td>ERROR</td>
<td>103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NA</td>
<td>3</td>
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<td>0.900727</td>
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<td>103</td>
<td></td>
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<tr>
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<td>SC</td>
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<td>0.784649</td>
</tr>
<tr>
<td>ERROR</td>
<td>103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TC</td>
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</tr>
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<td></td>
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<tr>
<td>TA</td>
<td>3</td>
<td>439.910804</td>
<td>17.285973</td>
</tr>
<tr>
<td>ERROR</td>
<td>103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA</td>
<td>6</td>
<td>42.392251</td>
<td>1.665772</td>
</tr>
<tr>
<td>ERROR</td>
<td>103</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The dependent variable for this table is C2

Estimated means
Mean square used in Std. Dev. has 103 D.F.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean</th>
<th>Std. Dev. of the mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)</td>
<td>72.00</td>
<td>10.26181</td>
</tr>
<tr>
<td>N(2)</td>
<td>72.00</td>
<td>12.11111</td>
</tr>
</tbody>
</table>

Estimated means
Mean square used in Std. Dev. has 103 D.F.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean</th>
<th>Std. Dev. of the mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)</td>
<td>48.00</td>
<td>8.49375</td>
</tr>
<tr>
<td>S(2)</td>
<td>48.00</td>
<td>11.84354</td>
</tr>
<tr>
<td>S(3)</td>
<td>48.00</td>
<td>13.20208</td>
</tr>
</tbody>
</table>

Estimated means
Mean square used in Std. Dev. has 103 D.F.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean</th>
<th>Std. Dev. of the mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(1)</td>
<td>72.00</td>
<td>13.39653</td>
</tr>
<tr>
<td>T(2)</td>
<td>72.00</td>
<td>8.97639</td>
</tr>
</tbody>
</table>

Estimated means
Mean square used in Std. Dev. has 103 D.F.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean</th>
<th>Std. Dev. of the mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>48.00</td>
<td>10.73333</td>
</tr>
<tr>
<td>C(2)</td>
<td>48.00</td>
<td>14.11563</td>
</tr>
<tr>
<td>C(3)</td>
<td>48.00</td>
<td>8.71042</td>
</tr>
</tbody>
</table>
### ESTIMATED MEANS

**Mean square used in std. dev. has 103 d.f.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean</th>
<th>Std. dev. of the mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(1)</td>
<td>36.00</td>
<td>8.00972</td>
</tr>
<tr>
<td>A(2)</td>
<td>36.00</td>
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<tr>
<td>A(3)</td>
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<td>A(4)</td>
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<td>12.71667</td>
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### ESTIMATED MEANS

**Mean square used in std. dev. has 103 d.f.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean</th>
<th>Std. dev. of the mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA(1,1)</td>
<td>18.00</td>
<td>8.13056</td>
</tr>
<tr>
<td>TA(1,2)</td>
<td>18.00</td>
<td>10.18889</td>
</tr>
<tr>
<td>TA(1,3)</td>
<td>18.00</td>
<td>15.13333</td>
</tr>
<tr>
<td>TA(1,4)</td>
<td>18.00</td>
<td>20.13333</td>
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<td>TA(2,1)</td>
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<td>TA(2,2)</td>
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<tr>
<td>TA(2,3)</td>
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</tr>
<tr>
<td>TA(2,4)</td>
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<td>5.30000</td>
</tr>
</tbody>
</table>

### ESTIMATED MEANS

**Mean square used in std. dev. has 103 d.f.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean</th>
<th>Std. dev. of the mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC(1,1)</td>
<td>16.00</td>
<td>9.98750</td>
</tr>
<tr>
<td>SC(1,2)</td>
<td>16.00</td>
<td>7.93125</td>
</tr>
<tr>
<td>SC(1,3)</td>
<td>16.00</td>
<td>7.56250</td>
</tr>
<tr>
<td>SC(2,1)</td>
<td>16.00</td>
<td>12.28125</td>
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<tr>
<td>SC(2,2)</td>
<td>16.00</td>
<td>14.99687</td>
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<td>SC(2,3)</td>
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<td>8.31250</td>
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<td>SC(3,1)</td>
<td>16.00</td>
<td>9.93125</td>
</tr>
<tr>
<td>SC(3,2)</td>
<td>16.00</td>
<td>19.41875</td>
</tr>
<tr>
<td>SC(3,3)</td>
<td>16.00</td>
<td>10.25625</td>
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<tr>
<td>Sample</td>
<td>Mean</td>
<td>Std. Dev. of Mean</td>
</tr>
<tr>
<td>------------</td>
<td>----------</td>
<td>------------------</td>
</tr>
<tr>
<td>NC(1,1)</td>
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<td>11.67917</td>
</tr>
<tr>
<td>NC(1,2)</td>
<td>24.00</td>
<td>13.31042</td>
</tr>
<tr>
<td>NC(1,3)</td>
<td>24.00</td>
<td>5.79583</td>
</tr>
<tr>
<td>NC(2,1)</td>
<td>24.00</td>
<td>9.78750</td>
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<tr>
<td>NC(2,2)</td>
<td>24.00</td>
<td>14.92083</td>
</tr>
<tr>
<td>NC(2,3)</td>
<td>24.00</td>
<td>11.62800</td>
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</table>
STD. RES. OF C2 VS PRED. VALUE OF C2 VS CAT(C)
<table>
<thead>
<tr>
<th>Time (A)</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.00+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-2.00+</td>
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</tr>
<tr>
<td>-1.00+</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0.00+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.00+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.00+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

STD. RES. OF C2 VS PRED. VALUE OF C2 VS TIME (A)
STD. RES. OF C2 VS NORMAL SCORES