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REMOVAL OF THIOCYANATE FROM INDUSTRIAL EFFLUENTS BY BIOLOGICAL AND PHOTOCHEMICAL PROCESSES

By

WEI LI

B. Eng. in Environmental Engineering

Wuhan Institute of Urban Construction

A thesis submitted to

the Faculty of Graduate Studies and Research

in partial fulfillment of the requirements for the degree of

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ABSTRACT

Thiocyanate present in industrial waste effluents is a precursor to many toxic compounds that could have adverse effect on the environment when such streams are discharged into the waterways. Although several methods are available for thiocyanate remediation, technical and economic concerns related to these methods have prompted investigation of other processes. Two such processes are the biological process and the photolytic process, which are the subjects of this research.

In the biological process, thiocyanate oxidation and ammonia nitrification were studied in two separate Aerated Biological Filters (ABF), each operating at two different temperature levels - one at room temperature of about 24 °C and the other at about 8 °C, with the low temperature experiments carried out in a well-maintained cold room. Results indicate that, comparatively, nitrification process is more sensitive than thiocyanate oxidation to variations in hydraulic loading, recycle ratio, temperature, and alkalinity. Biological reaction kinetics including average thiocyanate removal rates and hydraulic loadings were estimated. The results indicate that thiocyanate oxidation and ammonia nitrification can indeed be achieved in an ABF operating at temperatures as low as 8 °C - a finding that is relevant to the Canadian climatic conditions in which wastewater temperatures are significantly low.

In the photochemical process, both Direct Photolysis and Advanced Photo-oxidation Process (APP) using UV/H₂O₂ were capable of oxidizing the thiocyanate to a variety of oxidation products. However complete oxidation of thiocyanate could not be achieved by direct photolysis. In contrast, APP worked well. The results indicate that the course of the reaction is very dependent on the pH of the solution being irradiated.

Without pH adjustment the solution rapidly became acidic, and under such conditions, thiocyanate was primarily converted to cyanide with little cyanate being formed. However, with pH control (pH maintained above 10), thiocyanate was mainly converted to cyanate, with very little cyanide generation. Cyanate formed can be oxidized primarily to ammonia, nitrite and nitrate under sufficient UV dose and H_2O_2 . A reaction scheme was postulated for the photochemical degradation of thiocyanate, and based on the model, the kinetic parameters were evaluated.

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Chapter 1 Introduction

1.1 General

Thiocyanate (SCN^-) is a linear, electronegative polyatomic ion. It is a typical pseudohalogen ion that is closely related to the halogens (Halogens form insoluble ionic salts with silver, mercury, lead (II), copper and zinc). Thiocyanate exists in aqueous solution primarily as the SCN^- ion, because the dissociation constant of HSCN is quite high (1.4×10^{-1} , $\text{pK}_a = 0.85$). HSCN is essentially fully dissociated when the pH value is above 2 (Hung et al., 1997; IEC Ltd., 1980).

Due to some of its unique properties, thiocyanate is used in many industrial processes such as dyeing, photofinishing, herbicide & insecticide production, acrylic fiber production, metal separation, and electroplating, (Hung et al., 1997) and most importantly in gold mining industry. Cyanidation process is widely used to extract gold from ores, which results in the formation of thiocyanate through the reaction of free cyanide with various sulfur-containing species. The formation of thiocyanate has a negative influence on gold recovery as it increases the cyanide consumption.

Because of the wide use and appearance of thiocyanate in industries, the environmental impact of thiocyanate containing wastewaters has become a major concern. As a precursor to the toxic cyanide, thiocyanate removal may be required prior to effluent discharge into water streams.

Thiocyanate is less toxic (1/1000) than cyanide. For cyanide the limit of discharging in aquatic-biota waters is 50 ppb ($\mu\text{g/L}$). In North America, with respect to toxicity and environmental issues, the presence of thiocyanate in treated effluents has not been regulated yet (Mudder and Botz, 2000), but according to the available data from

Canadian gold mills, the average thiocyanate concentration in the discharged gold mill wastewater is 1 ppm (mg/L). It is non-acutely toxic to fish all year using the standard 96 hour bioassay test (Scott, 1993).

Compared to cyanide remediation, degradation of thiocyanate has not been studied to any great extent and detailed research is required on the different treatment methods, especially in the chemical and biological areas. Also very little is known about the photochemical methods of thiocyanate destruction. Information is required on:

- the biological pathways of thiocyanate oxidation, influence of alkalinity, reaction rates, etc.

- the combination of thiocyanate destruction and subsequent nitrification, influences of temperature, reaction rates, etc.

- the new technology for efficient thiocyanate removal such as advanced photo-oxidation processes (UV/H₂O₂), the possible reaction schemes, kinetics, etc.

1.2 Objectives

Following a literature study of the properties of the thiocyanate and other related chemicals and an evaluation of the currently used remediation technologies, the biological process and the photochemical process were chosen for further study. In the case of the biological process, the primary objective was to delineate the influence of the operating parameters on the course of the reaction, as well as to establish the feasibility of the biological process at low temperatures that would be relevant to the Canadian climatic conditions.

On the photochemical process, the objective was to investigate both the Direct Photolysis and the Advanced Photo-oxidation Process using hydrogen peroxide as the

oxidant. A batch reactor was employed to study the effect of the operating conditions on the efficiency of destruction of the thiocyanate.

1.3 *Organization of Thesis*

The thesis consists of seven chapters.

Chapter 1 introduces the basic information about thiocyanate, its application and treatment.

Chapter 2 introduces the characteristics of thiocyanates and their detection methods; the characteristics of cyanides; the environmental impact of thiocyanate and related chemicals, regulations, and guidelines; data on typical wastewater composition of gold mills; past and current thiocyanate removal technologies.

Chapter 3 consists of the biological experiments, including the process scheme, experimental procedures, and analytical methods.

Chapter 4 describes the results obtained in the biological experiments and a discussion of the results.

Chapter 5 gives details of the photochemical experiments, including the process scheme, experimental procedures, and analytical methods.

Chapter 6 describes the results obtained in the photochemical experiments, and a discussion of the results.

Chapter 7 presents the conclusions and recommendations.

Chapter 2 Thiocyanates: Chemistry, Environmental Impact and Treatment Methods

2.1 Chemistry of Thiocyanates

2.1.1 Thiocyanic Acid

Thiocyanic acid, HSCN, formula weight 59.09, exists as a colorless volatile liquid when the temperature is above 5°C, decomposing rapidly at ambient temperature. The density of the anhydrous acid at 0°C is 1.14, and at 20°C is 1.15. Aqueous solutions of 12.7% have a density of 1.04 at 12.7°C. Thiocyanic acid is a strong acid, approaching hydrochloric acid in strength. The ionization constant is 1.4×10^{-1} , at pH values above 2.0, HSCN is essentially fully dissociated (Karchmer, 1970).

Thiocyanic acid is moderately toxic but is dangerous when heated, because of the formation of highly toxic hydrogen cyanide vapors. Aqueous solutions up to 5% are stable. Stronger solutions decompose into hydrogen cyanide and xanthane hydride.

The acid can be decomposed by hydrogen sulfide to carbon disulfide and ammonia. It reacts with oxidizing agents such as potassium permanganate and hydrogen peroxide to yield hydrogen cyanide and sulfuric acid. The hydrogen peroxide reaction is accelerated by the presence of nickel and cobalt.

Thiocyanic acid is obtained by distillation, under reduced pressure, from an aqueous solution of thiocyanate and dilute sulfuric or phosphoric acid. Aqueous and nonaqueous solutions are prepared by dissolving ammonium thiocyanate in the appropriate solvents such as acetone and methyl ethyl ketone and passing the solution through a column containing a dry cation exchange resin in the acid form. Isobutylethyl ketone is also used to extract thiocyanic acid from a 0.1 M sulfuric acid solution of

sodium thiocyanate. Re-extraction into water gives a pure thiocyanic acid solution (Karchmer, 1970; IEC Ltd., 1980).

2.1.2 Characteristics of Thiocyanates

The thiocyanates, also known as sulfocyanides or rhodanates, are compounds of the general formula MCNS or M(CNS)₂, where M can be mono or divalent metal ion. Small amounts of thiocyanates are found in some plants and animal body fluids. They are readily formed from cyanides by the addition of sulfur. Thiocyanate is a halogenoid or pseudohalogen ion, a group of anions that are closely related to the halogens. (IEC Ltd., 1980)

Figure 2-1. Structure of Thiocyanate Ion

The hydric acids, with the exception of hydrocyanic acid, are highly dissociated. They form water insoluble salts with silver, mercury, lead (II), copper and zinc, polyhalogenoid complexes, and characteristic double and complex salts such as K₂[Hg(SCN)₄]. Based on electrical conductivity data, the electromotive series for halogen halogenoid ions is F⁻, ONC⁻, OCN⁻, Cl⁻, N₃⁻, Br⁻, CN⁻, SCN⁻, SCSN₃⁻, I⁻, SeCN⁻, and TeCN⁻. However, iodine oxidizes aziododithiocarbonate, and it appears that the order should be reversed for these two anions. In applying analytical methods for the determination of thiocyanate in the presence of halides or other halogenoids, the possibility of interference should be considered. The formation constants for thiocyanate complexes are considerably lower than those for the corresponding cyanide complexes with the exception of gold (I) and mercury (II). Consequently, if both cyanide and

thiocyanate are present in solution the cyanide complexes will exist in solution in preference to the respective thiocyanate complexes. In the absence of competing cyanide ions, the thiocyanate complexes will be present, but will be more dissociated than the corresponding cyanide complexes.

Thiocyanates have a low acute toxicity. Prolonged exposure may produce skin eruptions, running nose, cramps, nausea, vomiting, occasional dizziness, and disturbances of the nervous system. Thiocyanates are dangerous when heated or if in contact with acids. Under these conditions, highly toxic cyanides may be produced (Karchmer, 1970).

2.1.2.1 Alkali and Ammonium Thiocyanates

Alkali and ammonium thiocyanates are most discussed species because of their relative commercial importance, their similarity and their chemical simplicity. Ammonium thiocyanate is one of the principal technical products of the thiocyanate family. It is formed by reacting aqueous ammonia under pressure with carbon disulfide at 110°C. Potassium thiocyanate, the major alkali salt, is prepared by melting potassium cyanide and sulfur or a mixture of potassium ferrocyanide, potash, and sulfur. The ammonium and alkali thiocyanates are used in the dyeing of textiles, as agricultural chemicals, and in the paint and photographic processing industries. They are also used extensively as analytical reagents (Karchmer, 1970).

Physical Properties:

The alkali and ammonium thiocyanates are very water-soluble and moderately soluble in several organic solvents. Table 2-1 shows the major physical properties of the ammonium and alkali thiocyanates (Karchmer, 1970).

Table 2-1. Physical Properties of Ammonium and Alkali Thiocyanates

Formula	NH ₄ SCN	KSCN	NaSCN
Formula weight	76.12	97.17	81.08
Crystalline form	Monoclinic Rhombic above 92°C	Monoclinic	Rhombic
Melting point	149.6°C	172.3°C	287°C
Decomposition T.	170°C	500°C	300°C
Refractive index	1.685	1.660	1.625
Specific gravity	1.305	1.886	---
Heat of formation (Kcal/mole)	---	47.4	40.36
Solubility in water (g/100g)	122 (0°C) 170 (20°C)	177(0°C) 217(20°C)	110(0°C) 225(20°C)

Chemical Properties:

The valency information of thiocyanate-related compounds is presented in Table 2-2.

Table 2-2. Oxidation States of Thiocyanate-related Compounds (Botz et al. 2000)

Compound	Formula	Element oxidation state			
		C	N	S	O
Cyanide	CN ⁻	+2	-3	-	-
Thiocyanate	SCN ⁻	+4	-3	-2	-
Cyanate	OCN ⁻	+4	-3	-	-2
Thiosulfate	S ₂ O ₃ ⁻²	-	-	+2	-2
Sulfite	SO ₃ ⁻²	-	-	+4	-2
Sulfate	SO ₄ ⁻²	-	-	+6	-2

Thiocyanate can be oxidized chemically by such agents as hydrogen peroxide or potassium permanganate to form cyanide and sulphuric acid. Oxidation with nitric acid

(1 molar) results in the formation of hydrogen cyanide, sulphuric acid, sulphur dicyanide, and nitrous acids as final products (Karchmer, 1970).

Under alkaline conditions, permanganate oxidation tends to favor formation of cyanate rather than cyanide. Chlorination or bromination would result in the formation of the corresponding cyanogen halide, CNCl or CNBr. Cyanogen chloride is nearly as toxic as cyanide.

The use of hypobromite (and presumably hypochlorite) as an oxidizing agent results in the formation of cyanate. Cyanate is of approximately equivalent toxicity to thiocyanate, and both are considerably less toxic than cyanide.

The electrolysis of a thiocyanate solution will produce hydrogen cyanide and sulfate as follows:

Nascent hydrogen in acid solution will convert thiocyanate into hydrogen sulfide and methylamine.

Passing hydrogen through dry and fused alkali thiocyanate will give hydrogen sulfide and hydrogen cyanide.

When dilute solutions of thiocyanates and sulfuric acid are heated, the thiocyanic acid may be collected under reduced pressure.

Ammonium thiocyanate solutions attack zinc, copper, iron, and some chromium alloys, but have little effect on aluminum. The dry salt, if heated to its melting point, will partially isomerize to thiourea:

On further heating (190 – 200 °C), hydrogen sulfide, ammonia, and carbon disulfide are evolved, and guanidine thiocyanate is found in the residue. Additional heating will produce melam thiocyanate, melem and, finally, melon.

The alkali thiocyanates when fused with finely divided iron, in the absence of air, will yield the alkali cyanide and iron sulfide:

The alkali and ammonium thiocyanates form double salts and complex compounds with many heavy metals. The formation of a large number of metallic complexes, many of which exhibit characteristic colors in aqueous solutions and organic solvents, is of importance to analytical chemistry. These metallic complexes can be extracted or used for masking undesirable metallic constituents in analytical systems (Karchmer, 1970).

2.1.2.2 Other Metal Thiocyanates

The metal thiocyanates are very important because of their unique behavior. The chromophoric properties of the iron (III), cobalt, uranium (VI), niobium (V), molybdenum (V), tungsten (V), and rhenium (VI) complexes are used for their colorimetric determination. Other elements that give colored thiocyanates are bismuth, titanium, vanadium, tantalum, rhodium, ruthenium, osmium, indium, nickel, and copper.

Most thiocyanate color complexes fade in aqueous acid medium. The addition of acetone increases color stability and color intensity. An increase in color stability and concentration of the colored complex can be achieved by extraction into an organic solvent. The thiocyanate-metal complexes used in spectrophotometric procedures are generally extracted by ethers and esters (Karchmer, 1970).

2.1.3 Methods of Detection

2.1.3.1 Ferric Thiocyanate Complex

The formation of the red iron (III) thiocyanate complex is the best-known test for both iron and thiocyanate. The details are discussed in the section of chemical analyses.

2.1.3.2 Cobalt Salts

Cobalt (II) in the presence of acetone reacts with thiocyanate to form a series of blue cobalt thiocyanate complexes. Under the test conditions, halides, especially iodide, give only a slight greenish color. As little as six micrograms of thiocyanate can be detected in the presence of 1000 times the amount of iodide, bromide, chloride, thiosulfate, and acetate. Thiosulfate and acetate, when evaporated with cobalt salts, give a green color which is not extracted into acetone. Nitrites interfere, since they give the red nitrosyl thiocyanate by reaction with thiocyanates (Karchmer, 1970).

2.1.3.3 Benzidine Blue Test

Soluble thiocyanates are converted to cyanide by a number of oxidizing agents. The formation of benzidine blue by reacting copper salts with benzidine in the presence of cyanide is the basis for the test. When permanganate is used for the oxidation, the reaction is as follows:

Chlorides, bromides, and iodides interfere. Cyanide, if initially present, is removed by making the solution slightly acidic and boiling in a fume hood (Karchmer, 1970).

2.1.3.4 Catalysis of Iodine-Azide Reaction

Both soluble and insoluble thiocyanates can be detected by evolution of nitrogen resulting from the addition of the thiocyanate to an iodide-azide solution. Special precautions must be taken in the presence of sulfides and thiosulfates to eliminate interference (Karchmer, 1970).

2.2 Chemistry of Cyanides

Cyanide is a singly-charged anion containing unimolar amounts of carbon and nitrogen atoms triply-bonded together: CN^- . It is a strong ligand, capable of complexing at low concentrations with virtually any heavy metal. Cyanide is considered very toxic because it may hinder the transport of heavy metals through the tissues of plants and animals, degrading their health and endangering their survival. Cyanide also reacts with the hemoglobin in the blood of animals, displacing oxygen, and preventing its circulation to critical tissues, essentially suffocating the animal. The mean lethal dose to the human adult is between 50 and 200 mg (Young and Jordan, 1996). U.S. EPA standards for drinking and aquatic-biota waters regarding total cyanide are 200 and 50 ppb, respectively (total cyanide refers to free and metal-complexed cyanides).

Figure 2-2. Structure of Cyanide Ion

With respect to free cyanide in aqueous systems, equilibrium is rapidly established between molecular cyanide and cyanide ion. This equilibrium is dependent primarily upon pH and, to a lesser degree, temperature. For example, at 10°C and pH 6.0, more than 99% of the cyanide present exists as HCN. The proportion of HCN decreases to 92% at pH 8.5 and 10°C. At 4°C and pH 8.5, the proportion of HCN is 94%. Hence, under typical environmental conditions, most of the free cyanide would be present as HCN (Young and Jordan, 1996).

2.2.1 Categories of Cyanides

Based on the strength of metal cyanide bonds, cyanides are generally classified as these species:

Free cyanide: the most reactive and toxic forms of cyanide: cyanide anion (CN⁻) and hydrogen cyanide (HCN).

Weak-acid dissociables (WADs): cyanide complexes with metals such as cadmium, copper, nickel and zinc.

Thiocyanate (SCN⁻): it is a WAD, but it is often considered in its own category.

Strong-acid dissociables (SADs): cyanide-complexes with metals such as cobalt, gold, iron and silver (Young and Jordan, 1996).

2.2.2 Cyanide's Classes in Hazardous Waste by U.S. EPA and Toxicity

2.2.2.1 Classes

According to RCRA mandate, the U.S. EPA has classified and listed hazardous wastes were given numbers for identification and were broken down into classes as follows:

F class – non-specific sources

K class – specific sources

P and U class – commercial chemical products, intermediates, and residues

D class – hazardous wastes determined by characteristics alone

Cyanide in its various forms is listed numerous times as an F, P, and D hazardous waste, EPA promulgates in the Code of Federal Regulations that cyanide wastes are prohibited from land disposal (Young and Jordan, 1996).

2.2.2.2 Toxicity

Cyanide is taken up through the skin and mucous membranes (e.g. in the mouth, stomach and intestines). Cyanide is highly toxic because it inhibits the oxidative processes of the cells. It affects virtually all body tissues, attaching itself to ubiquitous metalloenzymes and rendering them inactive. Its principal toxicity is probably due to inactivation of cytochrome oxidase (cytochrome aa3) and, thus, cellular respiration, even in the presence of adequate oxygen stores. Consequently, the most oxygen-dependent tissues, such as brain, heart and liver are most profoundly affected by acute cyanide poisoning. The symptoms of acute poisoning from hydrogen cyanide or the cyanides are rapid heartbeat, headache, drowsiness, nausea, and staggering; followed by coma, convulsions, and death. Death may occur rapidly after swallowing as little as 300 milligrams of the salts or inhaling as little as 100 milligrams of hydrogen cyanide. Exposure to concentrations of 200-500 parts of hydrogen cyanide per 1,000,000 parts of air for 30 minutes is also usually fatal. Lengthy exposure to small amounts of cyanide compounds can result in loss of appetite, headache, weakness, nausea, dizziness and irritation of the upper respiratory tract and eyes. In sublethal doses, the cyanide is rapidly detoxified by the human body through combination with sulfur to form nontoxic sulfocyanides, and recovery is usually complete within a few hours, with no permanent after-effects (Young and Jordan, 1996).

Because the poison acts with extreme rapidity, recovery from poisoning depends upon the promptness with which antidotes are administered. Fatalities may be prevented by the administration of such antidotes as amyl nitrite, sodium nitrite, and 25 percent sodium thiosulfate solution.

Sources of cyanide can be from drinking water, touching soil, or eating foods containing cyanide. Other sources can include smoking cigarettes and breathing smoke-filled air during fires (Young and Jordan, 1996).

2.2.3 Physical Properties of Some Cyanides

- *Hydrogen Cyanide (HCN)*
 - **Appearance:** colorless liquid/gas
 - **Melting point:** -13.4°C
 - **Boiling point:** 25.6°C
 - **Vapour pressure:** 53.1 kPa at 10.2°C.
 - **Miscellaneous:** smells like almond

- *Cyanogen Chloride (CNCl)*
 - **Appearance:** colorless gas
 - **Miscellaneous:** react with water to produce toxic and corrosive fumes

- *Potassium Cyanide (KCN)*
 - **Appearance:** white granular powder
 - **Melting point:** 634.5°C
 - **Miscellaneous:** contact with acid releases hydrogen cyanide

- *Sodium Cyanide (NaCN)*
 - **Appearance:** white powder with chunks
 - **Melting point:** 563.7°C
 - **Miscellaneous:** produces a violent reaction with magnesium, nitrites, nitrates, and nitric acid

- *Calcium Cyanide (Ca(CN)₂)*
 - **Appearance:** white, colorless powder
 - **Miscellaneous:** bitter almond odor; releases hydrogen cyanide

- *Copper Cyanide (CuCN)*
 - **Appearance:** colourless gas
 - **Miscellaneous:** insoluble in water, reacts violently with magnesium

- *Cyanogen ((CN)₂)*
 - **Appearance:** white solid
 - **Miscellaneous:** very toxic to the eye

2.2.4 Forms and Occurrences of Cyanide in the Aquatic Environment

Cyanides comprise a diverse group of organic and inorganic compounds. The form of cyanide in water is dependent primarily on pH, but is also influenced to a lesser degree by temperature, dissolved oxygen, salinity and the presence of other ions, complexing agents and sunlight. Cyanide compounds may be grouped according to their physical and chemical properties as free, simple, complex and organic cyanides. Cyanide ion refers to the single, free anion (CN⁻), excluding all other cyanide species. Molecular HCN (hydrocyanic acid, hydrogen cyanide) refers to cyanide in the form of an uncharged, undissociated molecule. Free cyanide refers to the summation of molecular HCN and the cyanide ion in aqueous solution, irrespective of their sources in water. Simple cyanides are those compounds that dissociate directly in water to yield a cation and the cyanide ion, with no soluble intermediates. Complex cyanide may dissociate in water to a cation and an anion composed of two or more different chemical forms, one of which is cyanide. The anion is termed a complex ion and may be subject to further dissociation, possibly releasing free cyanide ions (Lien et al., 1990).

Organic compounds containing the group CN are termed nitriles or cyanides, depending upon the nomenclature used. Cyanates are compounds containing the -OCN

group: aqueous solutions hydrolyze to ammonia and the corresponding bicarbonate. Cyanates are relatively stable at pH 7 in aerobic water at 20°C for up to 10 days, decomposition may accelerate at lower pH. Thiocyanates, compounds containing the SCN group, are more stable than cyanates, and form complexes with numerous elements. Alkali and alkaline earth thiocyanates are usually readily soluble, and appear to be stable in aqueous solutions (Lien et al., 1990).

The term "total cyanide" has been used in the literature to convey different ideas. From an operational viewpoint, total cyanide comprises all cyanide and some cyanate species or groups determinable by a particular, selected analytical method. Total cyanide also refers to the summation of the CN group in all the different forms of cyanide that exist in aqueous solution. Terms such as "total cyanide", "oxidized cyanide", "cyanide amenable to chlorination" and "cyanide amenable to ozonation" reflect the corresponding methods of analysis (Lien et al., 1990; Young and Jordan, 1996).

With respect to free cyanide in aqueous systems, equilibrium is rapidly established between molecular cyanide and cyanide ion. This equilibrium is dependent primarily upon pH and, to a lesser degree, temperature.

Simple cyanides, such as alkali cyanides, readily dissociate in water to yield the cyanide ion, which then enters into equilibrium with HCN. It has been observed that there are 28 elements that may form complex cyanide compounds, and there are more than 68 oxidation states of these elements capable of forming complex cyanides. Hence, there exists the possibility of a multitude of complex metalocyanides that may occur in aqueous systems, each possessing unique physical and chemical properties. Little

information is available on the predominant chemical species of complex cyanides present in the Canadian aquatic environment (Young and Jordan, 1996).

Some complex metallocyanides may dissociate in water, generating complex cyanide ions that may further dissociate, releasing free cyanide ion. In general, many complex ions are more stable than their parent compounds, and hence, subsequent dissociation to cyanide ions may be relatively minor. Depending upon the chemical species, some complex cyanide ions may, however, readily dissociate. The degree of dissociation to form cyanide ion is, in general, dependent upon pH and light intensity. Iron-cyanide complex ions may dissociate to cyanide ions in the presence of sunlight below about pH 8 (Lien et al., 1990).

Most of the information regarding the fate of cyanides in the aquatic environment has been derived from studies on the treatment of complex industrial wastes containing cyanides in the milligram per liter range, usually in association with other substances. Concentrations in wastewater were found to be lowered by such processes as chemical oxidation, irradiation, biodegradation, volatilization, photolysis, dissociation and precipitation. It is, however, difficult and often misleading to extrapolate such information to natural conditions. From the limited information available under natural conditions, it cannot be assumed that cyanides have a short residence time in the aquatic environment (Lien et al., 1990).

Hydrogen cyanide is volatile, having a vapour pressure of 53.1 kPa at 10.2°C. Volatilization is expected to be a significant removal process for free cyanide from concentrated solutions. Chemical oxidation is a commonly used treatment technique; reliable data on the chemical oxidation of free cyanide in dilute solutions are not

available. Cyanide ion is not strongly adsorbed and retained in soils. Numerous microorganisms have been identified which are capable of degrading free cyanide, and cyanides may be removed from waste streams by biological treatment.

Little information is available on the fate of complex cyanides in natural waters. The role of precipitation and sorption in the removal of complex cyanides from the water column has not been adequately examined. Numerous metallocyanide complex ions are stable in aqueous solution in the absence of ultraviolet and visible light; in the presence of sunlight, however, photodecomposition of some complexes, with the resultant release of cyanide ions, may occur (Lien et al., 1990; Young and Jordan, 1996).

2.3 Environmental Impact of Thiocyanate and Related Chemicals

Thiocyanate is toxic to human beings and other animals due to its chemical properties. Untreated thiocyanate containing wastewater will pollute the receiving waters and will harm aquatic life.

The effects of thiocyanate on human beings usually include eye irritation and skin irritation if contacted; gastrointestinal irritation with nausea, vomiting and diarrhea if swallowed. Metabolism may release cyanide, which may result in headache, dizziness, weakness, collapse, unconsciousness and possible death. On inhalation, it may cause respiratory tract irritation. It may be metabolized to cyanide and result in symptoms similar to cyanide poisoning which include tachypnea, hyperpnea, and dyspnea followed rapidly by respiratory depression. Pulmonary edema may also occur (Fisher Scientific, 2001).

Thiocyanate in aqueous solution will liberate very toxic gas (HCN) when it contacts with acids or it is heated. Free cyanide is one of the most lethal materials both in aqueous state and gaseous state, 50 to 200 ppm concentration being the lethal dosage for human beings (Young and Jordan, 1996).

The oxidation products of thiocyanate in solutions usually are cyanate, ammonia, nitrite, and nitrate, which are also toxic. Cyanate is as toxic as thiocyanate. Chronic exposure to ammonia causes throat irritation, headache, hoarseness, cough, hemoptysis, nausea, nervousness, and loss of appetite. Acute exposure to ammonia causes laryngeal edema with asphyxia, pulmonary edema, and bronchopneumonia. It has corrosive effect on the mouth, esophagus, and stomach if swallowed (Fisher Scientific, 2001). Nitrite is

harmful to humans. It can react with amides or amines to form N-titroso compounds, some of which are potential carcinogens. Nitrate is also harmful, because it can cause methomoglobinaemia by oxidizing iron (II) (the oxygen carries in haemoglobin in the blood) to iron (III).

Ammonia and nitrate are nutrients which can stimulate the growth of algae in waters. Excess amounts of those in the discharged wastes will cause eutrophication and thus result in low dissolved oxygen level and unpleasant odor which is harmful to aquatic animals.

2.3.1 Regulations and Guidelines for Effluent and Water Quality

As stated earlier, there is no regulation of the thiocyanate concentration in treated effluents in North America at present. However, considering the limits of cyanide concentration discharged to aquatic-biota waters of 50 ppb ($\mu\text{g/L}$), it would be prudent to control the thiocyanate concentration in effluents. Data from Canadian gold millings (Scott, 1993) show the average SCN concentration in the treated effluents from gold milling is usually less than 1 ppm, and the maximum is not greater than 5 ppm. Hence the target for any new process to be developed should at least match that goal. The regulations of relevant compounds, especially nitrogen-containing chemicals such as ammonia, nitrite, and nitrate, are also given in this section.

2.3.1.1 Guidelines for Industrial Effluent Quality

As the composition of industrial wastewater varies, effluent quality standards have to be established according to the specific condition and requirement.

For ammonia and nitrate, almost all industries have discharge regulations. The most known industries include petroleum refining, pulp & paper, fertilizer, automobile, and organic chemicals, etc.

So far there are no guidelines for the ammonia concentration in treated effluents in mining industry, though ammonia is present widely in mining wastewater. Usually ammonia and nitrate are produced because of the extensive use of explosives in the mining activity. Generally the concentrations of ammonia in mining effluents range between 10 and 50 ppm and sometimes reach as high as 300 ppm.

2.3.1.2 Guidelines for Drinking Water

The guidelines for drinking water are quite strict in Canada. The limit of nitrite nitrogen is 1 mg/L. The limit of nitrate nitrogen is 10 mg/L. For ammonia, there is no specific limit established as such, but normally very little ammonia (0.2 mg/L) is formed in drinking water.

2.3.1.3 Guidelines for the Protection of Aquatic Life

The un-ionized ammonia is much more toxic than ionized ammonia. There is a limit of 0.03 mg/L of un-ionized ammonia and 1.0 mg/L of ionized ammonia in treated effluents discharged in natural waters in Canada. The limit of nitrate is 30 mg/L.

2.3.2 Thiocyanates in Gold Milling Effluents

Over 90% of the gold mined in Canada is extracted from the ore using the cyanidation process. The process consists of leaching gold from the ore as a gold-cyanide complex with gold being precipitated upon the addition of zinc dust (Simovic and Snodgrass, 1985).

Thiocyanate is always present in the waste effluents, and often in high concentrations when treating sulphidic gold ores, due to the reaction between cyanide and sulphides. The formation of thiocyanate is common during the process of beneficiation. It is considered a nuisance side reaction with adverse impacts on the effectiveness of gold recovery and the consumption of cyanide (Scott, 1993).

Tables 2-3 and 2-4 describe the cyanide and thiocyanate concentrations in various gold milling streams and effluents.

Table 2-3. Characteristics of Gold Mining Waste Streams

WASTE STREAM	CONSTITUENT (mg/L except pH)								
	TOTAL CN ⁻	FREE CN ⁻	SCN ⁻	Zn	Cu	Ni	Fe	As	pH
Barren Bleed	68.7	-	35.1	10.7	7.3	2.1	1.9	-	11.7
	562	230	-	42.5	210	125	6	6	-
Primary Flotation	-	1.4	-	0.001	0.3	1	0.1	0.2	-
Thickener Overflow	-	1.5	-	0	0.05	0	0	3.1	-
Cyanide Tailings	18.2	-	11.5	1.5	3.2	1	1.3	-	10.3
	77	27	-	0.02	35	95	2	4	-
Tailings Pond Effluent	6.9	-	9.1	0.3	2.2	0.8	1.2	-	9.1

(Lien, et al., 1990)

Table 2-4. Molar Ratios of SCN to CN in Gold Milling Effluents

	Filter Tailings		Tailings Pond Effluent	
	Mean	Range	Mean	Range
Total CN (m mole/L)	2.84	1.04-5.77	0.44	0.01-1.8
Total SCN (m mole/L)	0.87	0.28-2.07	0.53	0.09-1.10
Ratio SCN:CN (IEC Ltd., 1980)	0.47	0.34-0.90	2.54	0.68-7.82

2.4 Methods for Thiocyanate Degradation

There are many methods for thiocyanate degradation and they fall into three main categories: chemical methods, photochemical methods and biological methods.

2.4.1 Chemical Degradation of Thiocyanate

The traditional and most widely employed chemical oxidation methods are based upon hydrogen peroxide, or sulfur dioxide or sodium sulfite (i.e., the INCO process). These methods do not completely destroy thiocyanate (10-20% removal). Ozone oxidation of thiocyanate is another method that is most widely used (Mudder and Botz, 2000).

Other oxidants such as Caro's acid, nitric acid, chromate, permanganate, ferric ion, and iodine, have also been used.

There are also methods based on alkaline chlorination and chlorine dioxide. Both of these methods are capable of completely destroying cyanide, thiocyanate, and other sulfur containing species at initial concentration of over 1000 mg/L. The use of chlorine, which is also a kind of pollutant, is a drawback (Karchmer, 1970; IEC Ltd., 1980).

In the following sections, the more important methods - alkaline chlorination method, ozone method, and hydrogen peroxide method are discussed in detail.

2.4.1.1 Alkaline Chlorination Method

As the name suggests, elevated pH level with the addition of a strong base is a requirement in the process. Chlorine can react with both cyanide and thiocyanate. The process is usually conducted in a series of complete-mix reactors operated at a pH of about 11.0 to avoid the accumulation of cyanogen chloride (CNCl), which forms during the first step of alkaline chlorination as follows:

The intermediate cyanogen chloride is toxic but is rapidly hydrolyzed to cyanate at the high pH according to the following reaction:

The first stage of the process requires about 15 minutes. The second stage of the process involves hydrolysis of the cyanate to ammonia and carbonate according to the following reaction:

The hydrolysis above requires about 1 to 1.5 hours, although reaction periods of more time are sometimes necessary. If excess oxidant is added, the ammonia can be converted to nitrogen gas through a modification of the process known as “breakpoint” chlorination according to the following reaction:

If ammonia removal is not needed in the previous step, alkaline chlorination would be restricted to the oxidation and destruction of cyanide and thiocyanate as follows:

Based on Equations 2-10 and 2-11, the theoretical quantity of chlorine needed to oxidize cyanide and thiocyanate is 2.7 kg per kg and 4.9 kg per kg, respectively. The quantity of lime ($\text{Ca}(\text{OH})_2$) needed for cyanide and thiocyanate destruction is 2.2 kg per kg and 5.0 kg per kg, respectively (Mudder and Botz, 2000).

2.4.1.2 Ozone Method

Ozone is capable of oxidizing both thiocyanate and cyanide. However, little information has been published regarding the reaction of thiocyanate with ozone. It is known that the reaction occurs in two steps, the oxidation of thiocyanate to cyanide and then further oxidation to cyanate (Soto et al., 1994).

Thiocyanate is oxidized by ozone in the pH range of 2 to 12 giving cyanide as an intermediary product. Ozone oxidizes free cyanide in the ionic form CN^{-} but the acid form HCN is not attacked by ozone. Copper cyanide complexes are oxidized by ozone in the pH range of 4 to 12 (Soto et al., 1994; Jenson and Tuan, 1993).

2.4.1.3 Hydrogen Peroxide Method

Hydrogen peroxide can oxidize both thiocyanate and cyanide. In general, thiocyanate is oxidized by hydrogen peroxide forming cyanide, and if excess hydrogen peroxide exists, it continues to oxidize cyanide to ammonia then to nitrate (Christy and Egeberg, 2000; Figlar and Stanbury, 2000).

The whole oxidation will be effected in two steps, steps 1: thiocyanate to cyanide; step 2: cyanide to nitrate.

Thiocyanate to Cyanide:

According to Christy and Egeberg (2000), the oxidation of thiocyanate by hydrogen peroxide proceeds through an intermediate hypothiocyanite (OSCN^-) which undergoes a series of fast reactions leading to end products, which are dependent on the pH of the medium. When the pH is in the range of 4 - 12, the hypothiocyanite is further oxidized to sulphate, ammonia and bicarbonate. The reactions are as follows:

At low pHs, the hypothiocyanite intermediate undergoes fast reactions leading to end products cyanide and sulphate. Cyanide reacts further with OSCN^- and forms sulphur dicyanide S(CN)_2 .

Based on the experiments of Christy and Egeberg (2000), the reaction rate decreases with increasing pH, the reaction rate is first order with respect to hydrogen peroxide concentration. The reaction rate is also first order with respect to thiocyanate concentration.

The overall reaction in acidic media is as follows:

In addition, cyanide can be oxidized by hydrogen peroxide to cyanate, then subsequently to ammonia, nitrite and nitrate. The details will be discussed in the following section.

Cyanide to Nitrate:

Hydrogen peroxide is used to chemically oxidize cyanide (Lien, et al., 1990). Hydrogen peroxide is an oxidant stronger than oxygen but weaker than ozone. It is often considered better because it is relatively cheap, water soluble, and easy to handle and store. The Degussa process has been examined in several research efforts, especially comparing it to other processes. Results of these studies show that hydrogen peroxide reacts with cyanides to produce cyanate and when added in excess, forms nitrite and carbonate and eventually nitrate:

Additionally, the cyanate can also hydrolyze according to the following reaction:

The Degussa process is successful at oxidizing most WADs but has little or no effect on thiocyanate and SADs. Even so, it has been incorporated into numerous mining operations in Canada and the U.S. as a primary cyanide destruction process as well as a stand-by process for emergency situations (Lien, et al., 1990).

Other chemicals can be added to increase reaction rates and the efficiency of hydrogen peroxide: cupric ion, formaldehyde/kastone reagent, and sulfuric acid. Cupric cations act as catalysts for reactions above but can be consumed by precipitating ferroxhexacyanide anions. Formaldehyde (HOCH) reacts with cyanide in the presence of

DuPont's proprietary Kastone reagent to form glycolnitrile (HOCH_2CN) which, in turn, hydrolyses to glycolic acid amide ($\text{HOCH}_2\text{CONH}_2$) in the presence of hydrogen peroxide (Boucabeille et al., 1994).

When sulfuric acid and hydrogen peroxide are mixed, a highly exothermic reaction occurs, forming persulfuric or Caro's acid, H_2SO_5 . Caro's acid readily decomposes to oxygen and sulfuric acid and therefore must be made on site at the time of use. It reacts with cyanide to produce cyanate. It reacts with thiocyanate and WADs similarly but does not react with SADs (Lien, et al., 1990).

Mine tailings pond wastewater is treated by hydrogen peroxide that will decompose copper, nickel, and zinc cyanides complexes with the formation of hydroxide sludge. During this treatment procedure, pH adjustment of wastewater is not needed. The effluent cyanide concentration of 2 – 3 ppm appears to be the lower limit at a practical H_2O_2 dosage. But this method has an obvious disadvantage – the formation of ammonia, so a subsequent treatment will probably be required to reduce the ammonia concentration to acceptable levels. Another obvious disadvantage is its cost. This method is expensive. The reagent cost for a H_2O_2 dosage of 2.5 times stoichiometric, which produces an effluent cyanides concentration of 2 – 3 ppm, would be about US\$ 5/1,000 gal of tailings pond wastewater treated. A dosage of 10 times stoichiometric is required to produce an effluent cyanide concentration of about 1 ppm with a reagent cost of about US\$ 20/1,000 gal (Lien, et al., 1990). Tables 2-5 and 2-6 describe the performance of the H_2O_2 treatment method.

Table 2-5. Effects of H₂O₂ Dosage and Retention Time on CN Decomposition (Lien, et al., 1990)

H ₂ O ₂ dosage ² (mL/L)	Retention time (h)	Final pH	Effluent CN (ppm)
1	72	9.5	27
	262	9.2	22
2.5	4	10	95
	70	9.4	3.1
	264	9.1	2.8
5	4	9.8	21
	70	9.5	3.6
	264	9.2	2.4
10	2	9.7	9
	4	9.6	3.5
	21.5	9.7	1
	73	9.6	1

¹ Head solution contained about 280 ppm CN. Initial pH was 10.5

² The H₂O₂ dosage ranged from 1 to 10 times stoichiometric.

Table 2-6. Effect of Cupric Ion Addition on Cyanide Decomposition at pH 10.5 (Lien, et al., 1990)

H ₂ O ₂ dosage ³ (mL/L)	Cupric ion (g/L)	Final pH	Effluent CN (ppm)
1	0	10.5	62
1	0.187	10.5	117
1	0.373	10.5	158
1	1	10.5	152

¹ Head solution contained about 280 ppm CN.

² Solutions were agitated for 2 h.

³ H₂O₂ was added first followed immediately by CuCl₂ 2H₂O. NaOH added throughout the test to maintain pH.

The data in Table 2-7 show tailings pond effluent contaminant concentrations and the concentrations after hydrogen peroxide treatment.

Table 2-7. Solution Analyses after H₂O₂ Treatment (Lien, et al., 1990)

Element	Concentration (ppm)		
	Feed	Effluent	NDWS
Cyanide	280	3	0.2
Arsenic	0.2	<0.05	0.05
Copper	4.5	<1	1
Iron	16	<0.015	0.3
Selenium	5	4	0.01
Silver	3.2	1	0.05
Zinc	157	<1	5

NDWS: National Drinking Water
Standards of US

The contaminant concentration variations before and after H₂O₂ Treatment (2.5 mL/L dosage) are shown. The effluent concentrations of arsenic, copper, iron and zinc met NDWS; the effluent levels of selenium and silver were well above the standards (Lien, et al., 1990).

2.4.2 Photochemical Degradation of Thiocyanate

Photolysis can enhance redox reactions by providing energy from electromagnetic radiation to catalyze electron transfer processes. Usually Ultraviolet (UV) radiation possesses the energy which can promote electrons from the ground state to the excited state. Many substances can absorb UV at specific wavelength and change states or forms (Phillips, 1983). Thiocyanate is one of them. Figure 2-3 gives the molar extinction coefficient as a function of wavelength determined at Carleton University.

Figure 2-3. Molar Extinction Coefficients of NaSCN from 190 to 400 nm

From Figure 2-3, it can be concluded that beyond the UV wavelength of 260 nm, there is very little absorbance; when UV wavelength is less than 260nm, the absorbance becomes much higher.

Usually photolysis is divided into two major categories, Direct Photolysis and Advanced Photolysis. Process in which the substance is treated only by UV radiation is called Direct Photolysis. When UV and an oxidant are used together, the process is called Advanced Photolysis. Study of treatment of thiocyanate in a UV reactor by both these processes is one of the objectives of this study.

2.4.2.1 Direct Photolysis

Natural degradation of thiocyanate by sunlight was not found, because the minimum wavelength of sunlight reaching the surface of the earth is approximately 290 nm, which is not short enough to induce any significant dissociation of thiocyanate.

IEC Ltd. (1980) reported on experiments on the flash photolysis of thiocyanate in ethanol and water. Light sources of 253.7 nm and 229 nm were used to determine quantum yields.

pH dramatically affects quantum yield. Below pH 7.0, quantum yields of 0.8 to 0.85 are obtained at 254 nm, while above pH 7.8, quantum yields are reduced to about 0.5. The photolysis produces cyanide and sulphur. Sulphate was formed when oxygen is available. The presence of cyanide in unspecified concentrations could entirely suppress the photolysis (IEC Ltd., 1980). The reactions are as follows:

A rapid back reaction is also postulated:

The speed and efficiency of the back reaction indicates that the dissociation products have separated with little excess energy. The energy of dissociation was found to be 106 Kcal which is 6.5 Kcal less than the energy supplied by 254 nm light. With the 229 nm light the excess was 12.5 Kcal. This means that at wave lengths longer than about 285 nm, the energy of the incident UV light will be insufficient to induce significant dissociation.

The data explain why sunlight reaching the surface of the earth cannot decompose thiocyanate. In addition, the penetration of light into surface waters decreases rapidly with depth and turbidity, further limiting the possibility of photochemical decomposition of thiocyanate.

Conn (IEC Ltd., 1980) did some experiments and he found the irradiation of 500 ppm of SCN with 300 nm UV light for 2 hours produced only 1.1 ppm of cyanide at pH 7.8. A similar concentration of SCN left exposed to sunlight in a closed glass vessel produced 0.85 ppm of cyanide. As UV light does not penetrate the glass, it would appear that only a small part of the 1.1 ppm of cyanide at pH 7.8 was produced by photodecomposition, with the bulk of the cyanide presumably released by spontaneous decomposition of thiocyanate to cyanide.

2.4.2.2 Advanced Photo-oxidation of Thiocyanate

Homogeneous photolysis with hydrogen peroxide and ozone has been investigated and shown to remediate free cyanide WADs, and SADs to concentrations below 0.1 ppm. In this study, UV/H₂O₂ method was used to oxidize thiocyanate.

Hydrogen peroxide is a clear, colorless liquid which is completely miscible with water. Its aqueous solution is acidic. Table 2-8 lists some physical constants of the commercially available grades (Yang, 1998).

Table 2-8. Physical Properties of Commercial Hydrogen Peroxide Solutions

Property	H ₂ O ₂ Strength (wt %)		
	35	50	70
Density at 20.0 °C, g/mL	1.1312	1.1953	1.2886
Viscosity at 20.0 °C (mPa s)	1.11	1.17	1.23
Freezing point (°C)	-33.0	-52.2	-40.3
Boiling point (°C)	107.9	113.8	125.5

Hydrogen peroxide is a strong oxidizing agent and can be reduced to water. Numerous reducing agents can react with it. It can be reduced by sulphate, thiosulphate, ferrous ion, etc. Hydrogen peroxide also oxidizes thiocyanate to cyanide, then to

ammonia and nitrate. But in the presence of UV irradiation, the following reaction becomes more important:

The hydroxyl radical ($OH^\bullet$) produced is a powerful oxidant. Some properties of aqueous hydroxyl radical are listed in Table 2-9 (Liu, 1999).

Table 2-9. Properties of Aqueous Hydroxyl Radical

Property	Value
Absorption wavelength (max.)	230 nm
Molar Extinction coefficient	$530 \text{ M}^{-1} \text{ cm}^{-1}$
pK _a	11.9
E°	1.77 V
Diffusion coefficient	$2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
ΔG_f°	$13 \text{ kJ} \cdot \text{mol}^{-1}$
ΔH_f°	$-7 \text{ kJ} \cdot \text{mol}^{-1}$
S_{298}°	$96 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$

Hydroxyl radicals are devoid of charge and have a high affinity for electrons, they can quickly strip virtually any chemical of its electrons including cyanide, thiocyanate, WADs and SADs, then causing their oxidation:

Cyanate produced above will hydrolyze or will continuously react with excess hydroxyl radicals to produce bicarbonate and either nitrogen gas, nitrite or nitrate:

Reactions 2-30 – 2-35 are primary reactions when thiocyanate is oxidized by homogeneous photolysis of hydrogen peroxide. Because hydrogen peroxide decomposes to hydroxyl radicals very rapidly under UV irradiation, direct reactions between thiocyanate and H_2O_2 do not occur.

In the advanced photo-oxidation process with UV/ H_2O_2 , increasing UV intensities, hydrogen peroxide concentrations, and solution temperatures enhance the reaction rates (Young and Jordan, 1996).

2.4.3 Biological Degradation of Thiocyanate and Subsequent Nitrification

2.4.3.1 Biological Degradation of Thiocyanate

Biological degradation of thiocyanate has been widely investigated and used. A number of organisms capable of degrading thiocyanate have been identified and isolated. Such as (IEC Ltd., 1980; Dubey and Holmes, 1995):

- *Thiobacillus thiocyanoxidans*
- *Thiobacillus denitrificans*
- *Pseudomonas stutzeri*
- *Thiobacillus thioparus*
- *Thiobacillus thiocyanoxidans*
- *Thiobacillus*

The metabolic pathways of thiocyanate degradation are poorly understood. There are several suggested degradation pathways that have been studied and reported.

Thiocyanate degradation by Autotrophs:

Pathway A:

Thiobacillus thioparus has been reported to use thiocyanate as both a carbon and nitrogen source. A consortium of *Bacillus* and *Pseudomonas* species have also been found to use the thiocyanate autotrophically (Irwin et al., 1996).

The biochemical pathway involved in this autotrophic growth is unknown. A possible pathway is that thiocyanate is hydrolyzed to produce cyanate and sulfide. The cyanate then is further hydrolyzed to form ammonia and carbon dioxide via the enzyme cyanase. The sulfide produced is oxidized to sulfate, which has been suggested to be the only energy-yielding step that allows autotrophic growth (Irwin et al., 1996).

Pathway B:

Thiobacillus thioparus, which is a chemolithoautotrophic sulfur bacterium, can also degrade thiocyanate through a second pathway. Thiocyanate hydrolase, a newly found enzyme from *Thiobacillus thioparus* catalyzes the conversion of thiocyanate to carbonyl sulfide and ammonia. (Karavaiko et al., 2000; Brazeau and Ouyang, 2002)

Carbonyl sulfide can be reduced by nitrogenase to carbon monoxide in *Azotobacter vinelandii*. Carbon monoxide can be oxidized to carbon dioxide by methane monooxygenase in *Methylococcus capsulatus*, by carbon monoxide oxygenase in *Pseudomonas aeruginosa*, and by carbon monoxide dehydrogenase in many microbes. Figure 2-4 describes the whole procedure and relevant products (Brazeau and Ouyang, 2002).

further to carbon dioxide and ammonia by cyanase. Figure 2-5 describes the whole procedure and relevant products (Brazeau and Ouyang, 2002).

Figure 2-5. Thiocyanate Degradation Pathway (Heterotrophic)

Thiocyanate degradation in mixed microbial populations:

The exact reaction equations of the thiocyanate degradation by aerobic, mixed microbial populations (both heterotrophic and autotrophic) are as follows (Hung et al, 1997; Chinnaswamy et al., 1992).

(a). Hydrolysis of thiocyanate:

(b). Hydrolysis of cyanate:

(c). Oxidation of sulfide:

(d). Overall reaction:

Cyanate is an intermediate product in the first stage of thiocyanate hydrolysis and is further hydrolyzed to ammonia and bicarbonate.

Primary parameters for thiocyanate degradation:

There are some primary parameters discussed which influence the biological degradation of thiocyanate significantly.

The low temperature of the reclaim solution needing treatment in the winter would likely result in an unacceptable decrease in performance. Usually the solution temperature should be above 10 °C to support adequate biological growth and treatment. Typically the only limiting nutrient in solution is phosphate, which is conveniently added in concentrations ranging from about 1 to 5 ppm using concentrated phosphoric acid. Oxygen is also a basic need, which can be done either by natural or artificial aeration, and the minimum dissolved oxygen needed is about 2.0 mg/L (Henze et al, 1997).

Types of Bioreactor:

Biological degradation of thiocyanate is generally carried out in suspended growth systems and attached growth systems. The choice between attached and suspended growth systems is usually based upon the influent thiocyanate levels.

Usually attached growth systems include aerated biological filter (ABF) and rotating biological contactor (RBC). The ABF is typically constructed of a plastic column, which is filled with either crushed rock or plastic media. Bacteria grow attached on the supporting media. The RBC has rotating discs in the solution with about half of the surface area exposed to the air at any one time. The two attached growth systems are similar in the case of operation and exhibit similar performance. The ABF has no moving

parts, and so is less complicated and requires somewhat less maintenance (Henze et al, 1997; Thorn et al, 1996).

2.4.3.2 Nitrification

This study is about biodegrading thiocyanate to ammonia and nitrifying the ammonia to nitrate in the same biofilter. Information about nitrification process is given in the section (Metcalf & Eddy, 2003; Sawyer et al., 1994).

Aerobic autotrophic bacteria are responsible for nitrification in the activated sludge and biofilm processes. Nitrification is a two-step process involving two groups of bacteria.

The process for the ammonium oxidizing bacteria is:

The process for the nitrite oxidizing bacteria is:

The total nitrification reaction is:

Carbon dioxide is used as the carbon source by the nitrifying bacteria. For oxidation of ammonia, the expression for growth is:

For oxidation of nitrite, the corresponding growth expression is:

Neglecting cell tissue, the amount of alkalinity required to carry out the total nitrification can be estimated by the following equation:

In Equation 2-47, for each gram of ammonia nitrogen converted, 7.14 g of alkalinity as $CaCO_3$ will be required.

Along with obtaining energy, a portion of the ammonium ion is assimilated into cell tissue. The reaction can be represented as follows:

Chapter 3 Biological Experiments

Biological experiments were carried out to investigate the aerobic biodegradation of thiocyanate and subsequent nitrification in aerated biological filters (ABF).

All biological experiments were conducted at the Mining and Mineral Sciences Laboratories (MMSL) of the Minerals and Metals Sector (MMS), Natural Resources Canada (NRCan).

3.1 *Materials*

All chemicals used were ACS grade. Potassium thiocyanate (KSCN) was purchased from Anachemia Canada Inc., Montreal, QC. Other reagents used in the preparation of the synthetic wastewater were magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) and sodium bicarbonate (NaHCO_3). They were also purchased from Anachemia Canada Inc., Montreal, QC.

pH buffer solutions (4, 7, 10) were purchased from Fisher Scientific. Reagents for analyses of SCN, $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NO}_3\text{-N}$ were from Hach Company.

Distilled water was used for all analytical determinations. Tap water was used in all experiments to prepare the synthetic wastewater.

3.2 Equipment

3.2.1 Air Compressor

To keep the biological reactions aerobic in the aerated biological filters, forced aeration was used in the study. As compressed air source, a single-cylinder air compressor (Craftsman®) was used. It has a pressure range from 0 to 200 psi (40 psi @ 7.8 scfm; 90 psi @ 5.5 scfm) and the effluent air pressure can reach as high as 135 psi. In this study, 20-25 psi was used to supply air to both ABFs.

3.2.2 Mass Controller

Two mass controllers were used to adjust the air flowrate going into the 2 columns. The first one was a Matheson® 8200, which had a flowrate range from 0 to 2000 mL/min with a minimum increment of 10 mL/min. The second one was a TYLAN RO-28, which had a flowrate range from 0 to 20 L/min with a minimum increment of 0.2 L/min.

3.2.3 Pump

Masterflex® digital controlling pumps were used for feeding and recycling aqueous solutions. They were supplied by Cole-Parmer Instrument Company, Barrington, U.S. and had a range of flowrate from 15 to 975 mL/min with a minimum increment of 1 mL/min. Masterflex® tubing was used. Calibration was needed whenever the flowrate was changed.

3.2.4 Other Equipment

A 500 L Nalgene® tank was used as feed tank of the synthetic thiocyanate solution for the room temperature column and a 200 L Nalgene® tank was used for the column in the cold room at a temperature of 8.5 °C. 0.45 µm filters were used for sampling to remove biomass present in the sample solution. Analytical instruments used in the experiments included a pH meter from Fisher Scientific, a dissolved oxygen meter 830 from Orion Research, Inc., a Spectrophotometer DR/2010 and a Colorimeter DR890 from Hach Company.

3.3 *Experimental Setup and Operation*

The thiocyanate biodegradation experiments were carried out in two continuous aerated biological filters (ABF). Column A, which was always operated at room temperature (18 to 30 °C, average 24 °C), was set up in February 2002. The second filter, Column B, was set up in August 2002 and initially operated at the room temperature (18 to 30 °C) for 97 days and then moved to the cold room maintained at 8.5 °C. These two columns have been operating continuously ever since they were commissioned.

3.3.1 Experimental Setup

3.3.1.1 PVC Column

The ABF was made up of a 0.91 m (36") high PVC column with an internal diameter of 0.15 m (6"). There were four sampling ports on the column located at heights of 0.20 m (8"), 0.36 m (14"), 0.51 m (20"), and 0.66 m (26"). The effluent port was located at 0.81 m (32") on the column, so the column had an effective height of 0.81 m

(32"). A perforated plate was placed at the column base to evenly distribute the feed solution and air.

Figure 3-1. Schematic Illustration of Biological Experimental Setup

3.3.1.2 ABF Support Media

The support media used in ABF was crushed rock. The crushed rock with sizes ranging from 9.5 mm (3/8") to 12.7 mm (1/2") was 50%. The crushed rock with sizes ranging from 12.7 mm (1/2") to 22.2 mm (7/8") was the remainder. The specific surface area of the mixed rock is difficult to determine, but $45 \text{ m}^2/\text{m}^3$ can be considered a reasonable value, a suggestion in Metcalf & Eddy (2003).

Both in column A and column B, the support media had the same height of 0.79 m (31"), so the effective volume of the support media (V_s) plus void volume (V_v) is as follows.

$$V_s + V_v = \pi \times \frac{d^2}{4} \times h = 1.44 \times 10^{-2} m^3 \quad (3-1)$$

where:

d = internal diameter of the column, 0.15 m (6")

h = effective height of packed support media, 0.79 m (31")

Void volume can be determined by actual measurement, in this case, the void volume in column A (V_{vA}) was $7.25 \times 10^{-3} m^3$ and the void volume in Column B (V_{vB}) was $6.45 \times 10^{-3} m^3$.

According to these values and Equation 3-1, the effective volume of the support media in Column A and B can be calculated as follows:

$$V_{sA} = 1.44 \times 10^{-2} - 7.25 \times 10^{-3} m^3 = 7.15 \times 10^{-3} m^3 \quad (3-2)$$

$$V_{sB} = 1.44 \times 10^{-2} - 6.45 \times 10^{-3} m^3 = 7.95 \times 10^{-3} m^3 \quad (3-3)$$

Once the volumes of the support media were calculated, the effective surface area used in this study was obtained, which is the product of effective volumes and specific surface area of support media.

$$A_{sA} = V_{sA} \times \text{Specific surface area} = 7.15 \times 10^{-3} m^3 \times 45 m^2 / m^3 = 0.32 m^2 \quad (3-4)$$

$$A_{sB} = V_{sB} \times \text{Specific surface area} = 7.95 \times 10^{-3} m^3 \times 45 m^2 / m^3 = 0.36 m^2 \quad (3-5)$$

The effective surface area of the support media in Column A is $0.32 m^2$. The effective surface area of the support media in Column B is $0.36 m^2$.

3.3.1.3 Feed and Recycle

The aerated biological filters were operated in upflow mode, and synthetic wastewater prepared in the feed tank was pumped into the columns from the base. The effluent was removed from the top at height 0.81 m (32"), and was collected in the waste storage tank. A pipet connected with a tube was set on the top of the column with the opening near the effluent port and submerged in the liquid. The appropriate amount of recycling solution was pumped out of the column and reintroduced into the column through a T-joint on the feed line.

Figure 3-2. Photo of Biological Experimental Setup

3.3.1.4 Aeration System

Compressed air was added to the columns from the base through mass controllers, which adjusted the air flowrate and pressure. The air was injected at the same port as the feed and the recycle in order to thoroughly mix the feed, the recycle and air before entering into the column.

3.3.2 Synthetic Thiocyanate Feed Solution

The synthetic feed solution was prepared on a weekly basis by dissolving potassium thiocyanate and other chemicals in tap water. Table 3-1 lists the composition of the synthetic feed solution.

Table 3-1. Composition of Synthetic Feed Solution

Component	Concentration (mg/L)
KSCN	335
KH ₂ PO ₄	4
MgSO ₄ ·7H ₂ O	480
CaCl ₂ ·2H ₂ O	96
FeCl ₃ ·6H ₂ O	10
NaHCO ₃	550
Na ₂ S ₂ O ₃	1

Sodium thiosulfate was used to eliminate the residual chlorine in tap water. Other chemicals in the feed are provided for the growth of the biomass in the columns.

3.3.3 Sampling

Aqueous samples were taken through the sample ports. There are four of them on the column, and one of each on the feed & effluent line. Feed & effluent sampling was done twice a week, while the sampling from the column was taken once a week.

Nalgene HDPE narrow mouth bottles were used to store the liquid samples. Samples were analyzed immediately if possible, otherwise, they were treated to eliminate possible interferences and stored at 4°C for later analyses according to standard methods of chemical analyses. The influent and effluent samples were analyzed twice a week for pH values, thiocyanate, ammonia-nitrogen, nitrite-nitrogen, and nitrate-nitrogen. Alkalinity and sulfate in feed and effluent were analyzed once a week. Dissolved oxygen in the effluent was checked once a week. Cyanate in feed and effluent was checked once a month.

3.3.4 Abiotic Assays

The synthetic thiocyanate solution was prepared every 7 days. No thiocyanate degradation was observed in the feed tank during the 7 day period.

Hung et al. (1997) conducted batch aerobic abiotic assays of thiocyanate and cyanate, and found that thiocyanate was stable for the whole period while cyanate was gradually hydrolyzed at pH values above neutrality. Thiocyanate is unstable in mineral acid solution as hydrolysis or polymerization (high SCN conc.) may take place. (In this study, the pH values of synthetic SCN wastewater were always adjusted to approximately 8 with sodium bicarbonate.)

These experimental results suggest that thiocyanate hydrolysis in the feed tank without biomass function could be ignored. The microbial activity was responsible for the thiocyanate degradation.

3.4 Chemical Analyses

Spectrophotometer DR/2010 and Colorimeter DR890 from HACH were used for chemical analyses in this study. The analytical methods following standard protocols described in the literature are outlined briefly in the section. Details of chemical analyses are given in Appendix E.

3.4.1 Thiocyanate

A colorimetric method was used to measure thiocyanate concentration in the samples. Thiocyanate reacts with ferric ion under acidic conditions to form ferric thiocyanate, which has an intense red color. The intensity of color of the ferric thiocyanate formed is proportional to the concentration of thiocyanate ion in the sample. A spectrophotometer DR/2010 from HACH was used to measure the absorbance of the sample at 460 nm. The concentration of thiocyanate is determined from a standard calibration curve. Usually the detection range of this method is 0.1 to 2.0 mg SCN⁻/L. For higher concentrations, the sample should be diluted (Patnaik, 1997).

3.4.2 Cyanate

Under acidic conditions, cyanate can be converted to an ammonium salt, the concentration of ammonia minus nitrogen before and after acid hydrolysis is measured and the cyanate concentration is equivalent to this difference (Patnaik, 1997).

3.4.3 Ammonia Nitrogen

The Salicylate method was used to measure the ammonia nitrogen in the samples. Ammonia compounds react with chlorine to form monochloramine, which reacts with

salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue-colored compound. The blue color is masked by the yellow color from the excess reagent present to give a final green-colored solution. The intensity of the color is proportional to the concentration of ammonia nitrogen in the sample. A DR890 colorimeter was used to measure the $\text{NH}_3\text{-N}$ concentration. Usually the detection range of this method is 0 to 0.50 mg $\text{NH}_3\text{-N/L}$. For higher concentrations, the sample is diluted (Hach Company, 1999).

3.4.4 Nitrite Nitrogen

Diazotization method was used for the measurement of nitrite nitrogen concentration in the samples. Nitrite in the sample reacts with sulfanilic acid to form an intermediate diazonium salt. The diazonium salt reacts with chromotropic acid to produce a pink colored complex. The intensity of the color is proportional to the concentration of nitrite nitrogen in the sample. A colorimeter DR890 was used to measure the $\text{NO}_2\text{-N}$ concentration. Usually the detection range of this method is 0 to 0.350 mg $\text{NO}_2\text{-N /L}$. For higher concentrations, use a diluted sample (Hach Company, 1999).

3.4.5 Nitrate Nitrogen

The chromotropic acid method was used for the measurement of nitrate nitrogen concentrations. Nitrate in the sample reacts with chromotropic acid under strongly acidic conditions to yield a yellow-colored product. The intensity of the color is proportional to the conc. of nitrate nitrogen in the sample. A colorimeter DR890 was used to measure the $\text{NO}_3\text{-N}$ conc. Usually the detection range of this method is 0 to 30.0 mg $\text{NO}_3\text{-N /L}$. For higher concentrations, use a portion of diluted sample (Hach Company, 1999).

3.4.6 Sulphate

The turbididimetric method was used for the measurement of sulphate concentration in the samples. Sulfate ions in the sample react with barium in the SulfaVer 4 Sulfate Reagent to form insoluble barium sulfate. The SulfaVer 4 also contains a stabilizing agent to hold the precipitate in suspension. The amount of turbidity formed is proportional to the sulfate concentration in the sample. A colorimeter DR890 was used to measure the SO_4 conc. Usually the detection range of this method is 0 to 70.0 mg SO_4/L . For higher concentrations, use a portion of diluted sample (Hach Company, 1999).

3.4.7 Alkalinity

Alkalinity of water is a measure of its acid-neutralizing ability. The titrable bases that contribute to the total alkalinity of a sample are generally the hydroxides, carbonates, and bicarbonates. However, other bases such phosphates, borates, and silicates can also contribute to the total alkalinity.

The alkalinity value depends on the pH end point designated in the titration. The two end points commonly fixed in the determination of alkalinity are the pH 8.3 and pH 4.5. When the alkalinity is determined to pH 8.3, it is termed phenolphthalein alkalinity. In such alkalinity titration, phenolphthalein or metacresol purple may be used as an indicator. On the other hand, the total alkalinity is measured by titrating the sample to pH 4.5 using bromocresol green as the indicator. An acid standard solution, usually 0.02 N H_2SO_4 or HCl, is used in all titrations (Patnaik, 1997).

Chapter 4

Results and Discussion of Biological Experiments

This section presents the results obtained from experiments conducted on thiocyanate biodegradation studies using aerated biological filters (ABF). The ABF columns were operated over a period of several months to evaluate the effect of feed flowrate, temperature, recycle ratio, and alkalinity on thiocyanate degradation.

Column A was operated at room temperature condition (18-30 °C, average 24 °C). The thiocyanate degradation at feed flowrates of 15, 25, 30, 35, 50, 75 mL/min was investigated. At feed flowrate of 15 mL/min, the recycle ratios of 0 and 1 were used. At feed flowrates of 25, 30, 35, and 50 mL/min, the effect of recycle ratios at 0 and 0.5 on SCN degradation was tested. At feed flowrate of 75 mL/min, the effluent was not recycled.

Column B was operated in the temperature control room maintained at 8.5 °C. Feed flowrates including 15, 20, and 30 mL/min were used to investigate thiocyanate biodegradation. At feed flowrate of 15 mL/min, recycle ratios of 1 and 2 were used. At feed flowrate of 20 mL/min, recycle ratios of 0, 1 and 1.5 were used. At feed flowrate of 30 mL/min, recycle ratios of 0, 0.5, 1 and 1.5 were used.

The synthetic feed solution to the two columns had a SCN concentration of 200 mg/L and a pH value ranging from 7.8 to 8.0.

4.1 Inoculation and Growth

Microorganism seed for Column A was obtained from an on-going project at MMSL on application of suspended growth bioreactor for SCN degradation. The initial seed for MMSL project itself was obtained from the wastewater treatment plant operating at the Nickel Plate Mine in British Columbia.

Thirty liters of effluent was collected from the on-going project at MMSL and used as a seed solution for the ABF. Seed solution was mixed with synthetic thiocyanate solution (as described in Table 3-1), and then the mixed solution was pumped into Column A at a flowrate 94 of mL/min. The ABF effluent removed from the top of the column was directed into the feed tank. The flowrate 94 mL/min was maintained for 10 days (March 1-March 10, 2002), and was increased to 192 mL/min for another 10 days (March 11-March 20, 2002).

Initially the SCN concentration in the feed was 1000 mg/L. On March 11, 2002, mixed solution was diluted by replacing a half with tap water. For the next 20 days (March 21 to April 11, 2002), flowrate was lowered to 46 mL/min in order to speed up the colonization of the filter media by the desired microorganisms. Every 3 days, 75 L of solution containing 150 mg/L of thiocyanate was prepared to replace 75% volume of old solution.

Since March 1, 2002, the first day of inoculation, biomass in column A had accumulated for 41 days until April 11, 2002. Yellow-colored microorganisms could be seen growing in Column A. Complete thiocyanate degradation was observed - the SCN concentration of 111.60 mg/L in the influent was reduced to <1 mg/L in the effluent after 39 days (April 9). However most of the nitrogen in the feed was only converted to nitrite.

This observation is typical during initial start-up phase of the bioreactor, because nitrite to nitrate oxidizing bacteria growth rates are much lower than those of SCN oxidizing bacteria and ammonia to nitrite oxidizing bacteria (Dietor, et al., 1997).

March 25, 2002

August 8, 2002

Figure 4-1. Biomass Buildup in Column A

Nitrite was also building up in the column due to complete recycle of effluent to the feed tank. On April 12, 2002, the feed pattern to the ABF was changed to control the nitrite accumulation. All old SCN feed solution was dumped. Every 3 days 200 L of 200 mg/L thiocyanate solution was made and fed into column A. The effluent from the top of the column was discharged into the waste tank rather than to the feed tank. The feed flowrate was adjusted to 35 mL/min, and a 10 mL/min recycle was added by pumping the solution out from the top of Column A and reintroducing it into the column from the base (April 12-24, 2002). On April 25, 2002, the feed flowrate was changed to 15mL/min with recycle flowrate of 10mL/min (April 25-May 10, 2002).

On May 10, 2002 (28 days after April 12), the results showed all thiocyanate was oxidized and subsequent nitrification was also complete. The SCN, NH₃-N, NO₃-N, and NO₂-N concentrations in the effluent were <1, <1, 29.8, and 3.4 mg/L, respectively.

In total it took 69 days for Column A to achieve complete SCN oxidation and subsequent nitrification.

Effluent from Column A was used as a seed solution to inoculate Column B during July 25-September 9, 2002 (46 days).

August 8, 2002

November 15, 2002

Figure 4-2. Biomass Buildup in Column B

4.2 ABF Performance at Room Temperature

The results from experiments indicated that both thiocyanate oxidation and ammonia nitrification occurred in the ABF. Nitrification is found to be more sensitive to environmental factors than thiocyanate oxidation. Temperature, recycle ratio, feed flowrate and alkalinity can significantly influence the nitrification process.

In this study, Column A was operated in a flow-through mode with/without effluent recycle at room temperature (18-30 °C, average 24 °C). Experimental results presented in Table 4-1 summarize the performance of Column A under different flowrates and recycle ratios at room temperature.

Table 4-1. Performance of Column A at Room Temperature (average 24 °C)

Feed Flowrate (mL/min)	Recycle Ratio	SCN		NH ₃ -N		NO ₂ -N		NO ₃ -N	
		η (%)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)
15	0, 1	99.5	<1	<2	<2	<0.1	<1	<0.5	29.8
25	0, 0.5	99.5	<1	<2	<2	<0.1	<1	<0.5	25.6
35	0	99.5	<1	<2	4.0	<0.1	7.9	<0.5	18.8
35	0.5	99.5	<1	<2	<2	<0.1	<1	<0.5	25.3
50	0	99.5	<1	<2	20	<0.1	6.8	<0.5	4.4
50	0.5	99.5	<1	<2	6.0	<0.1	7.3	<0.5	10.7
75	0	99.5	<1	<2	21.8	<0.1	6.1	<0.5	3.5

Note: η – SCN removal efficiency

Thiocyanate concentration in the influent was approximately 200 mg/L

Other concentrations were typical values obtained under steady conditions

Column A was operated at feed flowrates of 15, 25, 35, 50, and 75 mL/min with initial SCN concentration of approximately 200 mg/L at room temperature (average 24 °C). Recycle ratios were changed to investigate the performance of the ABF at each feed flowrate.

As can be seen in Table 4-1, when the feed flowrates were 15 mL/min (HRT of 8.1 h) and 25 mL/min (HRT of 4.83 h), thiocyanate oxidation and subsequent nitrification were complete despite variations of recycle ratios (0, 0.5, or 1). The SCN concentrations in the effluent decreased to below 1 mg/L. The NH₃-N, NO₂-N and NO₃-N concentrations in the effluent were <2 mg/L, <1 mg/L and 25-30 mg/L respectively. In this period, the variations of recycle ratios did not seem to have an impact on the ABF performance.

At the feed flowrate of 35 mL/min (HRT of 3.7 h) with a recycle ratio of 0, SCN oxidation was complete but only partial nitrification was achieved. The SCN conc. in the effluent decreased to below 1 mg/L. The NH₃-N, NO₂-N and NO₃-N concentrations in the effluent were 4 mg/L, 7.9 mg/L and 18.8 mg/L respectively. After the recycle ratio was raised to 0.5 at the same feed flowrate of 35 mL/min, nitrification in the ABF was improved. The NO₃-N concentration in the effluent was up to 25.3 mg/L. The NH₃-N and NO₂-N concentrations in the effluent were <2 mg/L, <1 mg/L respectively. SCN concentration in the effluent was still less than 1 mg/L. In this case (feed flowrate of 35 mL/min), increasing recycle ratio improved the nitrification process.

At the feed flowrate of 50 mL/min (HRT of 2.6 h) with a recycle ratio of 0, SCN oxidation was complete but only partial nitrification was achieved. The SCN concentrations in the effluent decreased to below 1 mg/L. The NH₃-N, NO₂-N and

NO₃-N concentrations in the effluent were 20 mg/L, 6.8 mg/L and 4.4 mg/L respectively. After the recycle ratio was raised to 0.5 at the same feed flowrate of 50 mL/min, nitrification in the ABF was improved but still incomplete. The NH₃-N, NO₂-N and NO₃-N concentrations in the effluent were 6 mg/L, 7.3 mg/L, 10.7 mg/L respectively. SCN concentration in the effluent was still less than 1 mg/L. In this case (feed flowrate of 50 mL/min), increasing recycle ratio improved the nitrification process but did not influence thiocyanate oxidation in the ABF.

At the feed flowrate of 75 mL/min (HRT of 1.7 h, the maximum flowrate used) with a recycle ratio of 0, SCN oxidation was complete. The flowrate of 75 mL/min significantly reduced ammonia nitrification. The SCN concentrations in the effluent decreased to below 1 mg/L. The NH₃-N, NO₂-N and NO₃-N concentrations in the effluent were 21.8 mg/L, 6.1 mg/L and 3.5 mg/L respectively.

As can be seen in Figures 4-3 – 4-7, Column A at room temperature (18-30 °C, average 24 °C) has run continuously since May 10, 2002 (Day 0). The thiocyanate concentration in the feed was approximately 200 mg/L, but the feed rates, the recycle ratio, the alkalinity were changed a number of times during the experimental period.

Figures 4-3 – 4-7 show SCN oxidation is less sensitive than ammonia nitrification to variations of feed flowrates, recycle ratios, and dissolved oxygen. Complete thiocyanate degradation occurred in Column A during the entire experimental period except for two days when the air compressor was not functioning due to power outages. Figures 4-3 – 4-7 also show nitrification in the column was not stable. Variations of feed flowrate, operating temperature, and recycle ratio influenced nitrification. Once nitrification was inhibited, it took a long period (20-30 days) to return to normal.

Figure 4-3. SCN and its Products Conc. in the Influent and Effluent of Column A (May 10 - Nov. 25, 2002)

Figure 4-4. SCN Conc. in the Influent and Effluent of Column A (May 10 - Nov. 25, 2002)

Figure 4-5. Ammonia Nitrogen Conc. in the Influent and Effluent of Column A (May 10 - Nov. 25, 2002)

Figure 4-6. Nitrate Nitrogen Conc. in the Influent and Effluent of Column A (May 10 - Nov. 25, 2002)

Figure 4-7. Nitrite Nitrogen Conc. in the Influent and Effluent of Column A (May 10 - Nov. 25, 2002)

A mass balance on nitrogen was performed for the ABF. The thiocyanate feed is the only source of influent nitrogen. In the effluent, the concentrations of SCN, NH₃-N, NO₂-N, and NO₃-N were measured after the removal of microorganisms from the samples with 0.45 µm filters. The results indicated that there was a nitrogen deficit in the effluent to the extent of 8-15 mg/L of nitrogen. A plausible explanation for this discrepancy in the nitrogen balance is as follows.

In the biological process, there are several steps in which the uptake or loss of nitrogen occurs. Firstly, some nitrogen (5-10% of the nitrogen in SCN) gets incorporated into microorganisms in the column. Secondly, some nitrogen is consumed in the growth of algae in the column that seems to accumulate especially in the areas having high concentrations of dissolved oxygen and high light intensity. (for Column A, in the area near the top and towards the ceiling lights). Thirdly, according to Grady et al. (1999), denitrification occurs any time the oxygen concentration is low, the nitrate concentration is high, and organic matter is present as an electron donor.

Figure 4-8. Black Areas of Column A

In Column A, when large amount of microorganisms accumulated, some area near the bottom became black because of low DO as seen in Figure 4-8. Decaying algae

could also be an energy source (electron donor) for the denitrification process. Hence denitrification occurred in the column converting some nitrate to nitrogen gas, which has escaped and remained unaccounted for in the nitrogen mass balance.

4.3 ABF Performance at 8.5 °C

Biological processes are sensitive to temperature, especially the nitrification process. In this study, Column B was initially operated at the room temperature (average 24 °C) for 97 days, and then it was moved and operated in a cold room maintained at 8.5 °C. Experimental results presented in Table 4-2 show the performance of Column B under different flowrates and recycle ratios at 8.5 °C.

Table 4-2. Performance of Column B at 8.5 °C

Feed Flowrate (mL/min)	Recycle Ratio	SCN		NH ₃ -N		NO ₂ -N		NO ₃ -N	
		η(%)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)
15	1	99.5	<1	<2	8.0	<0.1	<1	<0.5	31.4
15	2	99.5	<1	<2	<2	<0.1	<1	<0.5	33.1
20	0, 1, 1.5	99.5	<1	<2	10.0	<0.1	<1	<0.5	26.8
30	0, 0.5	99.5	<1	<2	21.6	<0.1	<1	<0.5	16.8
30	1, 1.5	99.5	<1	<2	28.6	<0.1	<1	<0.5	14.5

Note: η – thiocyanate removal efficiency

Thiocyanate concentration in the influent was approximately 200 mg/L

Column B was operated at feed flowrates of 15, 20, and 30 mL/min with initial SCN concentration of approximately 200 mg/L at 8.5 °C. Recycle ratios were changed to investigate the performance of the ABF at each feed flowrate.

As can be seen in Table 4-2, at the feed flowrate of 15 mL/min (HRT of 7.7 h) with a recycle ratio of 1, thiocyanate oxidation was complete but only partial nitrification was achieved. The SCN concentration in the effluent decreased to below 1 mg/L. The $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations in the effluent were 8 mg/L, <1 mg/L and 31.4 mg/L respectively. After the recycle ratio was raised to 2 at the same feed flowrate of 15 mL/min, nitrification in the ABF improved. The $\text{NO}_3\text{-N}$ concentration in the effluent was up to 33.1 mg/L. The $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ concentrations in the effluent were <2 mg/L, <1 mg/L respectively. SCN concentration in the effluent was still less than 1 mg/L. In this case (feed flowrate of 15 mL/min), increasing recycle ratio improved the nitrification process but did not influence thiocyanate oxidation in the ABF.

At the feed flowrate of 20 mL/min (HRT of 5.8 h), thiocyanate oxidation was complete but only partial nitrification was achieved. Recycle ratios of 0, 1, and 1.5 were used to investigate if nitrification was improved by higher recycle ratios. Experimental results indicated that variations of recycle ratios did not seem to have an impact on both SCN oxidation and nitrification at the feed flowrate of 20 mL/min at 8.5 °C. The SCN concentration in the effluent decreased to below 1 mg/L. The $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations in the effluent were 10 mg/L, <1 mg/L and 26.8 mg/L respectively.

At the feed flowrate of 30 mL/min (HRT of 3.8 h), thiocyanate oxidation was complete but not the subsequent nitrification. Recycle ratios of 0, 0.5, 1, and 1.5 were used to investigate if nitrification could be improved by higher recycle ratios. Experimental results indicated that variations of recycle ratios did not seem to have an impact on both SCN oxidation and nitrification at the feed flowrate of 30 mL/min. The SCN concentration in the effluent decreased to below 1 mg/L. The $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and

NO₃-N concentrations in the effluent were 22.6-28.6 mg/L, <1 mg/L and 14.5-16.8 mg/L respectively. Experimental results show thiocyanate oxidation is less sensitive than ammonia nitrification to variations of feed flowrate and the recycle ratio.

The results of the low temperature studies clearly show that ABFs are capable of achieving SCN oxidation and subsequent nitrification at temperature as low as 8.5 °C. This result is important for countries like Canada and Russia, where for most of the year, wastewater has to be treated under low temperature conditions.

Nitrogen mass balance was calculated in the experimental period. It is considered that the only nitrogen source in the feed is from thiocyanate. In the effluent, the concentrations of SCN, NH₃-N, NO₂-N, and NO₃-N were measured after microorganisms in the samples were removed by 0.45 µm filters. As before, the results show there was a deficit of 8-10 mg/L of nitrogen in the effluent (compared to the influent).

The explanations for this discrepancy in the nitrogen balance are the same as those discussed earlier about the column at the room temperature: microorganism growth, algae growth, and denitrification. The nitrogen deficit in the effluent of Column B at 8.5 °C was less because of the lower algae accumulation in the column and lower hydraulic loadings (lights in the cold room were always turned off during the operation).

4.4 Concentration Profile along the Column

Samples were taken once a week from four sampling ports on the column located at heights of 0.20 m (sample port 1), 0.36 m (sample port 2), 0.51 m (sample port 3), and 0.66 m (sample port 4) in order to understand the reaction occurring along the column. These samples and those from influent (before mixing with recycle) and effluent described how the concentrations of thiocyanate, ammonia, nitrite, and nitrate changed along the column.

Figure 4-9 presents the concentration profile of SCN and its degradation products from four sampling ports on Column A when complete thiocyanate oxidation to ammonia and subsequent nitrification occurred at room temperature (average 24 °C).

As can be seen, almost all SCN oxidation to ammonia occurred in the section between the base and sampling port 1. Some nitrification of ammonia also occurred in the same section. In this section, SCN concentration decreased from 201 mg/L (Influent) to 1.33 mg/L (port 1). $\text{NH}_3\text{-N}$ concentration increased from 3 mg/L to 17 mg/L. $\text{NO}_2\text{-N}$ concentration changed from 0.1 to 3 mg/L. $\text{NO}_3\text{-N}$ concentration increased from 0.4 mg/L to 27.6 mg/L. From Sampling port 1 to effluent port, the thiocyanate concentration changed marginally - from 1.33 mg/L to <1 mg/L. Nitrification occurred to some extent. $\text{NH}_3\text{-N}$ concentration decreased from 17 mg/L to 7 mg/L and $\text{NO}_3\text{-N}$ concentration increased from 27.6 to 36.6 mg/L. $\text{NO}_2\text{-N}$ concentration was down to 1.4 mg/L.

Figure 4-9. Concentration Profile along Column A at Room Temperature: I
(Feed flowrate 25 mL/min with a recycle ratio of 0.5; Thiocyanate concentration: approximately 200 mg/L in influent, and less than 1 mg/L in effluent)

Figure 4-10. Concentration Profile along Column A at Room Temperature: II
(Feed flowrate 50 mL/min with a recycle ratio of 0.5; Thiocyanate concentration: approximately 200 mg/L in influent, and less than 1 mg/L in effluent)

Figure 4-10 presents the concentration profile of SCN and its degradation products from four sampling ports on Column A when thiocyanate oxidation to ammonia was complete but subsequent nitrification occurred only partially at room temperature (average 24 °C).

As can be seen, most of thiocyanate oxidation to ammonia occurred in the section between the base and sampling port 1. Nitrification of ammonia occurred at a low rate. In this section, SCN concentration decreased from 197.8 mg/L to 46.9 mg/L. $\text{NH}_3\text{-N}$ concentration increased from 0.2 mg/L to 15.3 mg/L. $\text{NO}_2\text{-N}$ concentration changed from 0.1 to 10.3 mg/L. $\text{NO}_3\text{-N}$ concentration increased marginally from 0.1 mg/L to 3.3 mg/L. From Sampling port 1 to effluent port, the thiocyanate concentration continuously dropped – from 46.9 mg/L to <1 mg/L. Nitrification occurred to some extent. $\text{NH}_3\text{-N}$ concentration decreased from 15.3 mg/L to 6 mg/L and $\text{NO}_3\text{-N}$ concentration increased from 3.3 mg/L to 17.3 mg/L. $\text{NO}_2\text{-N}$ concentration changed marginally from 10.3 mg/L to 10.7 mg/L.

The ABF at 8.5 °C has similar concentration profiles along the column at lower feed flowrates.

4.5 Thiocyanate Biodegradation Kinetics

The results from the experiments indicated that both thiocyanate oxidation and ammonia nitrification took place in the aerated biological filters (ABF).

Complete thiocyanate degradation occurred in Column A during the entire experimental period except for two days when the air compressor was not functioning due to power outage. Nitrification in the column was not stable, and variations of hydraulic loading, alkalinity, recycle ratio influenced nitrification. Kinetics of SCN oxidation and nitrification are evaluated under four conditions as follows.

Kinetics for Complete SCN Oxidation and Nitrification at Room Temp.

For the aerated biological filter at room temperature, the maximum feed flowrate, at which complete thiocyanate degradation and nitrification could be achieved, was 35 mL/min. The recycle ratio was 0.5. In this case, the total hydraulic loading for the trickling filter can be calculated as follows.

$$\begin{aligned} \text{Hydraulic Loading} &= \frac{(1+R) \times F}{A_{SA}} = \frac{(1+0.5) \times 35 \text{ mL/min}}{0.32 \text{ m}^2} \\ &= 0.236 \text{ m}^3 / \text{m}^2 / \text{d} \end{aligned} \quad (4-1)$$

where,

R = recycle ratio, 0.5 in this case

A_{SA} = effective surface area of support media in Column A, 0.32 m^2 .

Once the hydraulic loading is known, the thiocyanate removal rate can be calculated as the SCN concentration in the feed is also known. (approximately 200 mg/L)

$$\begin{aligned} \text{SCN Removal Rate} &= \frac{200 \text{ mg/L}}{1+0.5} \times 0.236 \text{ m}^3 / \text{m}^2 / \text{d} \\ &= 31.5 \text{ g/m}^2 / \text{d} \end{aligned} \quad (4-2)$$

The amount of 200 mg/L thiocyanate synthetic solution, that can be completely oxidized by Column A at room temperature, was 0.05 m³/d.

Kinetics for Complete SCN Oxidation and Partial Nitrification at Room Temp.

For the aerated biological filter at room temperature, at a feed flowrate of 75 mL/min (maximum) without recycle, thiocyanate oxidation to ammonia was complete but only partial nitrification occurred. In this case, hydraulic loading was 0.338 m³/m²/d and SCN removal rate was 67.6 g/m²/d. The amount of 200 mg/L thiocyanate synthetic solution, that can be oxidized by Column A at room temperature, was 0.11 m³/d.

Kinetics for Complete SCN Oxidation and Nitrification at 8.5 °C

For the aerated biological filter at 8.5 °C, at a feed flowrate of 15 mL/min (maximum) with a recycle ratio of 2, both thiocyanate oxidation and subsequent nitrification were complete. In this case, hydraulic loading was 0.18 m³/m²/d and SCN removal rate was 12.0 g/m²/d. The amount of 200 mg/L thiocyanate synthetic solution, that can be completely oxidized by Column B at 8.5 °C, was 0.02 m³/d.

Kinetics for Complete SCN Oxidation and Partial Nitrification at 8.5 °C

For aerated biological filters at 8.5 °C, when feed flowrate was set at 30 mL/min (maximum) without recycle, thiocyanate oxidation was complete but nitrification was not. In this case, hydraulic loading was 0.12 m³/m²/d and SCN removal rate was 24.0 g/m²/d. The amount of 200 mg/L thiocyanate synthetic solution, that can be oxidized by Column B at 8.5 °C, was 0.04 m³/d.

Comparison and discussion

Table 4-3 presents data on the kinetics of biological thiocyanate oxidation under 4 different conditions.

Table 4-3. Loadings and Removal Rates under Different Conditions

Column	Temp. (°C)	Flowrate (mL/min)	Recycle Ratio	Hydraulic Loading (m ³ /m ² .d)	Reaction Type	SCN Removal Rate (g/m ² .d)	NH ₃ -N Removal Rate (g/m ² .d)
A	24*	35	0.5	0.24	1	31.50	7.59
A	24*	75	0	0.34	2	67.60	8.96 (NH ₄ ⁺ →NO ₂ ⁻ +NO ₃ ⁻) ^{&}
B	8.5	15	2	0.18	1	12.00	2.89
B	8.5	30	0	0.12	2	24.00	3.14 (NH ₄ ⁺ →NO ₃ ⁻) [#]

Note:

* - Room Temperature (18-30 °C, average 24 °C)

& - Ammonia oxidation to nitrite plus nitrate

- Ammonia oxidation to nitrate only

Type 1: Both SCN oxidation and subsequent nitrification were complete

Type 2: SCN oxidation was complete but subsequent nitrification was not

Evangelho et al. (2001) reported that a hydraulic load of 4.5 m³/m²/d was used in a continuous pilot-scale trickling filter treating SCN-containing gold milling effluent with initial thiocyanate concentration of approximately 30 mg/L (only thiocyanate oxidation, nitrification not considered). Polypropylene Pall ring with a mean diameter of 0.016 m and 341 m²/m³ specific surface area was used as the support media in the experiments.

Compared to the hydraulic load value of 4.5 m³/m²/d in his case, the hydraulic loading rates in Table 4-3 are low. However, because high influent thiocyanate

concentration of 200 mg/L was used, the thiocyanate removal rates are still high. At room temperature, when thiocyanate oxidation and subsequent nitrification were complete, the SCN removal rate was 31.5 g/m².d. Even at the low temperature of 8.5 °C, the SCN removal rate for complete thiocyanate oxidation and subsequent nitrification was still 12.0 g/m².d.

4.6 Parametric Studies

This section presents experimental results on the effects of temperature, dissolved oxygen, recycle ratio, and alkalinity.

4.6.1 Effect of Temperature

Microbial processes are sensitive to temperature. Thiocyanate oxidation and subsequent nitrification in the ABF were affected by the operating temperature. In this study, Column B was initially operated at the room temperature (18-30 °C, average 24 °C) for 97 days, and then it was operated in the cold room maintained at 8.5 °C. Table 4-4 shows the performance of Column B under different operating temperature.

Table 4-4. Effect of Temperature on the Performance of Column B

Temp. (°C)	Reaction Type	Feed Flow rate (mL/min)	Recycle Ratio	SCN		NH ₃ -N		NO ₂ -N		NO ₃ -N	
				η (%)	Eff. (mg/L)	Inf. (mg/L)	Eff. (mg/L)	Inf. (mg/L)	Eff. (mg/L)	Inf. (mg/L)	Eff. (mg/L)
24°C*	I	25	0.5	99.5	<1	<2	<2	<0.1	<1	<0.5	28.3
8.5°C	I	15	2	99.5	<1	<2	<2	<0.1	<1	<0.5	33.1
24°C*	II	50	0.5	99.5	<1	<2	20.0	<0.1	<1	<0.5	12.2
8.5°C	II	30	0.5	99.5	<1	<2	21.6	<0.1	<1	<0.5	16.8

Note: * – Room Temperature (18-30 °C, average 24 °C)

η – thiocyanate removal efficiency

Type I – Complete Thiocyanate oxidation and nitrification

Type II – Complete Thiocyanate oxidation but partial nitrification

Thiocyanate conc. in the influent was approximately 200 mg/L

Other conc. were typical values obtained under steady conditions in each run

As can be seen in Table 4-4, both thiocyanate oxidation and subsequent nitrification (Type I) were complete at a maximum feed flowrate of 25 mL/min with a recycle ratio of

0.5 at average room temperature of 24 °C. The SCN concentrations in the effluent decreased to below 1 mg/L. The NH₃-N, NO₂-N and NO₃-N concentrations in the effluent were <2 mg/L, <1 mg/L and 28.3 mg/L respectively. When operating temperature was down to 8.5 °C, both thiocyanate oxidation and subsequent nitrification were complete at a maximum feed flowrate of 15 mL/min with a recycle ratio of 2. The SCN concentrations in the effluent decreased to below 1 mg/L. The NH₃-N, NO₂-N and NO₃-N concentrations in the effluent were <2 mg/L, <1 mg/L and 33.1 mg/L respectively. In this case, when the temperature was changed from 24 °C to 8.5 °C, the SCN removal rate of Column B dropped 40% from 20.0 g/m²/d to 12.0 g/m²/d.

Thiocyanate oxidation was complete but subsequent nitrification was incomplete (Type II) at a maximum feed flowrate of 50 mL/min with a recycle ratio of 0.5 at average room temperature of 24 °C. The SCN concentrations in the effluent decreased to below 1 mg/L. The NH₃-N, NO₂-N and NO₃-N concentrations in the effluent were 20 mg/L, <1 mg/L and 12.2 mg/L respectively. When operating temperature was down to 8.5 °C, the same reactions occurred at a maximum feed flowrate of 30 mL/min with a recycle ratio of 0.5. The SCN concentrations in the effluent decreased to below 1 mg/L. The NH₃-N, NO₂-N and NO₃-N concentrations in the effluent were 21.6 mg/L, <1 mg/L and 16.8 mg/L respectively. In this case, when temperature was changed from 24 °C to 8.5 °C, the SCN removal rate of Column B dropped 40% from 40.0 g/m²/d to 24.0 g/m²/d.

These data show that the performance of the ABF for the biodegradation of thiocyanate decreased when the operating temperature was lower.

4.6.2 Effect of Process Upsets

Air was pumped into the ABF from the base in order to maintain aerobic conditions in the column. The air flowrate was adjusted from 1000 mL/min to 2000 mL/min depending on the condition of the column. The DO values in the top of the column varied from 5 to 6 mg/L. The DO concentration decreased in the lower section of the column. When the hydraulic loading was increased, the biomass near bottom of the column became black and then the black area extended upwards. This situation could be corrected by increasing the air flowrate or the recycle ratio.

Table 4-5 and Figure 4-11 show the importance of DO for thiocyanate oxidation and subsequent nitrification in the ABF.

On Aug. 13, 2002, a 10 hour power outage occurred. On Aug 16, 2002, the air compressor was shut down for several hours. (Conc. in the influent and effluent were not checked on the same day). On Aug. 30, 2002, the air compressor was shut down for 10 hours again. The first time, no air and no solution went into column A. The second and third time, feed and recycle pumps were working, but no air went into column A.

As can be seen in Table 4-5, prior to process upset on Aug. 13, 2002, Column A worked well, the thiocyanate was degraded completely to the final product nitrate. On Aug. 13, 2002, samples were taken after 10 hours of no air in the column. The results indicated that the thiocyanate degradation processes in the column occurred only under the aerobic condition.

Table 4-5. Effect of Air Supply on the Performance of Column A

Date	SCN		NH3-N		NO2-N		NO3-N	
	Inf. (mg/L)	Eff. (mg/L)	Inf. (mg/L)	Eff. (mg/L)	Inf. (mg/L)	Eff. (mg/L)	Inf. (mg/L)	Eff. (mg/L)
Aug. 12, 2002	202.3	<1	1.0	<0.1	0.1	1.2	0.2	29.8
Aug. 13, 2002	207.9	198.2	1.0	5.0	<0.1	<0.1	<0.1	0.7
Aug. 15, 2002	203.2	<1	2.0	22.2	0.2	0.2	0.6	24.5

Note: Concentrations of Aug. 13, 2002 measured after 10 h power outage

Figure 4-11. Effect of Air Supply on the Performance of Column A

Data also showed that only 48 hours after the return of air supply (Aug. 15), oxidation of thiocyanate to ammonia resumed, but nitrification did not.

After the third upset on Aug. 30.2002, it took 38 days before nitrification returned to normal. But only 2-3 days were required to resume complete thiocyanate oxidation. It is concluded that nitrification is more sensitive than thiocyanate oxidation to the DO concentration in the column.

4.6.3 Effect of Recycle Ratio

The recycle ratio was changed in order to determine how it influenced the effluent quality of the ABF. At the feed flowrate studied, recycle ratios of 0, 0.5, and 1 were studied. Performance of Column B in the cold room at 8.5 °C was evaluated at even higher recycle ratios of 1.5 and 2.0

Based on the data from the experiments, it can be affirmed that recycle ratio did not influence thiocyanate oxidation to ammonia (Table 4-1, 4-2). If thiocyanate can be converted to ammonia completely at certain feed flowrate, no matter what recycle ratios were used (0, 0.5, 1), it did not change the thiocyanate removal efficiencies.

Recycle ratios influenced nitrification processes in the column. Within proper hydraulic loading range, increasing recycle ratio can improve the extent of nitrification.

The rationales for the above conclusion are as follows: 1) Recycled solution from the top contained high concentration of dissolved oxygen. It was pumped back into column from the base, where DO was low. The process improved the DO distribution in the column, and consequently improved the overall nitrification processes. 2) Active biomass in the recycled solution was pumped back into the column. 3) After recycle and feed solutions were mixed, SCN loading in the influent was lowered.

Figure 4-12 describes the typical phenomena that variation of recycle ratio did improve the nitrification process. But thiocyanate oxidation to ammonia was always complete and was not influenced.

Figure 4-12. Typical Performance Change Caused by Recycle Ratio in Column A
(Period I: Recycle ratio 0, Period II: Recycle ratio 0.5. Feed flowrate 35 mL/min always. SCN conc. in feed approximately 200 mg/L)

As can be seen, from Oct. 16 to Nov. 8, 2002 the feed flowrate to the column was always 35 mL/min. But before Oct. 28 the recycle ratio was 0 and after that it is 0.5. According to the difference, it could be divided into 2 periods (I and II) shown in Figure 4-12.

Period I (35 mL/min Feed, 0 Recycle Ratio) lasted 12 days, results obtained from these days showed that thiocyanate oxidation was complete, SCN in effluent was always <1 mg/L. However, nitrification was not complete, NH₃-N in effluent was around 3 mg/L. NO₂-N was high, around 11 mg/L. NO₃-N varied between 16 and 18 mg/L.

After Oct. 28 the recycle ratio was adjusted to 0.5. Period II (35 mL/min Feed, 0.5 Recycle Ratio) began and lasted 11 days. The results showed that thiocyanate oxidation was satisfactory, and there was no negative influence because of higher hydraulic loading. Nitrification process was significantly improved, $\text{NH}_3\text{-N}$ in the effluent dropped to 1 mg/L, $\text{NO}_2\text{-N}$ went down to 0.5 ppm, and $\text{NO}_3\text{-N}$ increased to 25 ppm gradually.

4.6.4 Effect of Alkalinity

Alkalinity is always an important factor in many biological reactions, and especially in nitrification processes. In this study, thiocyanate oxidation and subsequent nitrification were two biological reactions occurring in the ABF. They both involved bicarbonate.

The thiocyanate oxidation to ammonia is complex and can be represented as follows. Bicarbonate is produced during this process.

The resulting ammonia can be removed by conversion to nitrate by the nitrification process (Kapoor et al., 2002):

In the nitrification process, neglecting cell tissue, the amount of alkalinity required to carry out the total nitrification can be estimated by the following equation:

For each gram of ammonia nitrogen converted, 7.14 g of alkalinity as CaCO_3 will be required (Metcalf & Eddy, 2003). This was the basis of alkalinity dosage to be used in the experiments.

Another reason for investigating the effect of alkalinity was there was a large pH drop in the column when thiocyanate oxidation and subsequent nitrification occurred without the presence of bicarbonate.

It is well known, optimum pH for nitrification is in the pH range of 7.5 to 8.5 (Zhu and Chen, 2002; Yen, 1999). Therefore, the second function of alkalinity of the SCN feed solution is to prevent pH value going down to 7 or lower. Figure 4-13 shows that alkalinity does influence nitrification significantly but does not influence thiocyanate oxidation to ammonia.

Figure 4-13. Effect of Alkalinity on Nitrification in Column A

Feed flowrate 15 mL/min, recycle flowrate 10 mL/min

SCN conc. approximately 200 mg/L in the feed, <1 mg/L in the effluent.

Period I - NaHCO₃ 0g/L in the feed, Period II: NaHCO₃ 0.5 g/L in the feed

As can be seen, there were 2 periods divided by May 8, 2002. In Period I, no sodium bicarbonate was added in the feed. Thiocyanate biodegradation to ammonia was

complete. But nitrification process took place poorly. Ammonia-nitrogen concentrations in effluent were quite high: 27-32 mg/L. Nitrite-nitrogen concentrations ranged between 14 and 24 mg/L. Nitrate-nitrogen concentrations in effluent were just around 5 mg/L. pH values were around 8 in influent and about 6.5 or lower in effluent.

After May 8, 2002, in Period II, 0.5 g/L sodium bicarbonate (equivalent to 298 mg/L of CaCO_3) was added into the feed tank. Thiocyanate oxidation to ammonia was still complete, and no negative influence was found.

Nitrification process was improved significantly by the addition of bicarbonate. Ammonia-nitrogen concentrations in effluent were down to 1 mg/L or lower. Nitrite-nitrogen concentrations in effluent went down to 2.1 mg/L finally. Nitrate-nitrogen concentrations in effluent increased to 39.0 ppm gradually. pH values in influent were around 8 and but the pH values in effluent were up to around 7.5.

The final dosage of sodium bicarbonate added in the feed tank in the experiments was 0.55 g/L (equivalent to 327 mg/L of CaCO_3). Normally the alkalinity left in the effluent ranged between 50 and 100 mg/L as CaCO_3 (average 75 mg/L) when thiocyanate oxidation and subsequent nitrification were complete. In this case, it can be calculated that 1.26 g alkalinity of CaCO_3 was required when 1 g SCN was biodegraded to the final product – nitrate in the aerated biological filter.

Chapter 5 Photochemical Experiments

The second part of this research is to study the photochemical process for the destruction of thiocyanate. Both direct photolysis of the thiocyanate as well as the Advanced Photo-oxidation of thiocyanate were investigated and a number of experiments were conducted in the Environmental Engineering laboratory at Carleton University.

5.1 Materials

All chemicals used were ACS grade and were used without further purification, which included:

Precursors:

Sodium thiocyanate (NaSCN) was provided by Fisher Scientific.

Oxidants:

Hydrogen peroxide (H_2O_2 , 30% w/w in H_2O) provided by Fisher Scientific was used as oxidant in the reactions. It is of analytical grade.

Other Reagents:

Sodium hydroxide and pH buffer solutions (4, 7, 10) were supplied by Fisher Scientific. Other reagents for various analyses were from Fisher Scientific or Hach.

Distilled water was used for all analytical determinations, while tap water was used in all experiments for feed preparation.

5.2 Equipment

A Rayox® advanced oxidation system and other equipment were used, which are as follows:

5.2.1 Rayox® Advanced Oxidation System

The Rayox® Advanced Oxidation system was supplied by Calgon Carbon Oxidation Technologies of Markham, Ontario, Canada, in which all experiments were conducted. This system can be operated either as a batch reactor or as a recycle reactor. The UV reactor and UV lamp are the two primary components of the system.

5.2.1.1 UV Reactor

The UV reactor with control system is mounted on a skid and the front and rear views are shown in Figures 5-1 and 5-2 (The figures do not show the recycle loop, which is on a separate skid and was not used in the experiments). The UV reactor is cylindrical and constructed of stainless steel. Its diameter is 36 cm and the height is 50 cm. It has a capacity of 40 L. A UV lamp is mounted in the center of the quartz tube, and separated from the solution by a quartz sleeve of 4.2 cm in diameter. The mean effective path length between the quartz sleeve and the reactor wall is 15.9 cm. This allows a good fraction of light to be absorbed by the solution (Yang, 1998).

There are many accessories provided with the UV reactor, which include a pH probe, a mixer, a cooling water loop, a quartz sleeve wiper, a UV light shutter and a high-circulation pump. The cooling coil, which is suspended in the reactor chamber, helps control the temperature rise of the contents due to the UV output. Cold tap water can be circulated through the coil and the temperature of the reactor contents monitored at all

times. In a preliminary run, 30 L of water was taken in the reactor and the temperature rise was monitored with and without the cooling. Without cooling, the reactor temperature could rise to approximately 60 °C, whereas with cooling, the reactor temperature can be maintained below 40 °C. All the experimental runs were carried out around this temperature.

Figure 5-1. Front View of the UV Reactor

Figure 5-2. Rear View of the UV Reactor

5.2.1.2 UV Lamp

A 1 kW medium-pressure mercury lamp was used in the advanced oxidation system. Its spectral distribution of emission and output are shown in Figure 5-3.

As shown in the figure, in the wavelength range from 200 to 300 nm, there are two emission peaks. One appears around 220 nm with an output of 1.2 kW of radiation energy and another appears around 260 nm with an output of 1.5 kW of radiation energy.

The light intensity of this lamp in the wavelength range from 200 to 500 nm was $(6.45 \pm 0.16) \times 10^{-4}$ Einstein/s. The light intensity of this lamp in the wavelength range between 200 nm and 300 nm was $(2.93 \pm 0.08) \times 10^{-4}$ Einstein/s.

The UV Dose of the lamp was 2.1 kWh/1000 gal/min (0.556 kWh/m³/min). The rated lifetime of this lamp is 3000 hours (Yang, 1998).

Figure 5-3. Energy Distribution of 1 kW Medium-Pressure Mercury Lamp used in Rayox® Advanced Oxidation System (Yang, 1998)

5.2.2 Other Equipment

Nalgene HDPE tanks were used as the feed tanks for the synthetic thiocyanate solution. A Masterflex peristaltic pump with controller was used to pump the water from the feed tank to the UV reactor.

5.3 *Experimental Procedure*

In this study, both direct photolysis and homogeneous photolysis processes (advanced oxidation processes) were conducted in the same Rayox® Advanced Oxidation System, and the experimental procedures are outlined as follows.

5.3.1 Direct Photolysis Process

In a typical experiment for direct photolysis of thiocyanate, 25 L tap water was put in the feed tank, and the required amount of sodium thiocyanate was dissolved into it. The thiocyanate solution was then pumped into the UV reactor through the fill port. The contents in the reactor are kept well stirred. 50% sodium hydroxide (NaOH) or concentrated sulphuric acid (H_2SO_4) was used for pH adjustment as required.

An initial sample was withdrawn through the sample port and then the UV lamp was turned on with the lamp shutter in the closed position. After 3 min warm-up, at time zero, the lamp shutter was opened and the reaction time was counted. With complete mixing at all times, the solution was irradiated by UV light and samples were taken at scheduled sampling frequency (60 min) and sent for analyses.

5.3.2 Advanced Photo-oxidation Process

In a typical experiment on advanced photo-oxidation of thiocyanate, 25 L tap water was taken in the feed tank and the required amount of sodium thiocyanate was dissolved into it. The solution was stirred for several minutes and then the thiocyanate solution was pumped into the UV reactor through the fill port. Mixer was turned on to keep the solution well-mixed. The pH in the reactor was adjusted by dropwise addition of a 50% solution of sodium hydroxide (NaOH) or concentrated sulphuric acid depending on the specific need.

Figure 5-4. Rayox® Advanced Oxidation System
(Modified from Yang, 1998)

An initial sample was withdrawn through the sample port. The predetermined amount of oxidant (30% w/w hydrogen peroxide) was added into the reactor through the reagent port. Then the UV lamp was turned on with the lamp shutter in the 'closed' position. After a 3 min warm-up, at time zero, the lamp shutter was opened and the reaction time count was started. With complete mixing at all times, the solution was irradiated by UV light and samples were taken at scheduled sampling frequencies (30 or 60 min) and sent for analyses.

5.3.3 Sampling

Aqueous samples were taken through the sample port. Nalgene HDPE narrow mouth bottles were used to store the liquid samples. Samples were analyzed immediately if possible, otherwise, they were treated with sodium sulphate and stored at 4°C for later analyses. Standard methods of chemical analyses were followed. Sodium thiosulfate was used to eliminate the influence of chlorine in the sample. Sodium sulphate or catalase was used to eliminate the residual hydrogen peroxide in the sample.

5.4 Chemical Analyses

Spectrophotometer DR/2010 and Colorimeter DR890 from HACH Company were used for most chemical analyses in this study. The analytical methods of hydrogen peroxide and cyanide are given briefly in this section, which follow the standard protocols described in the literature. Details of chemical analyses are presented in Appendix E. Analytical methods for other chemicals such as thiocyanate, cyanate, ammonia, nitrite, nitrate and sulfate are detailed in the biological section.

5.4.1 Hydrogen Peroxide

Iodometric titration method is applicable to samples containing hydrogen peroxide that are free from turbidity or low in color (Vogel, 1961). In this method, hydrogen peroxide reacts with iodide in acidic solution to form iodine and the iodine produced is titrated by sodium thiosulphate solution with starch as the end point indicator. Thiosulphate ($S_2O_3^{2-}$) is oxidized to tetrathionate ($S_4O_6^{2-}$) by iodine during the titration process (Yang, 1998).

5.4.2 Cyanide

A colorimetric method (Pyridine-Pyrazalone Method) was used to measure the cyanide concentration in the samples. Cyanide is converted to cyanogen chloride (CNCl) by using chloramine-T at pH below 8 without hydrolyzing to cyanate (CNO^-). When adding pyridine-pyrazalone reagent, cyanogen chloride reacts with pyridine to form an intermediate nitrile which subsequently hydrolyzes to glutaconaldehyde. The glutaconaldehyde produced reacts with pyrazalone to give a blue color, its intensity is proportional to the concentration of cyanide in the sample. Usually the detection range of this method is 0 to 0.240 mg CN/L. For higher concentrations, a portion of diluted sample is used (Patnaik, 1997).

Chapter 6

Results and Discussion of Photochemical Experiments

Many preliminary experiments were carried out to understand the general behaviour of the UV reactor system and to establish the range of operating parameters, warm-up time for the UV lamp, stirrer speed etc. This was followed by several experiments both in direct photolysis and advanced photo-oxidation with hydrogen peroxide as the oxidant. This chapter presents the results obtained from those experiments and relevant discussion.

6.1 UV Absorption of Thiocyanate and Hydrogen Peroxide

The UV absorptivity of thiocyanate is described in Figure 6-1. As can be seen, thiocyanate has no significant UV absorption when the wavelength is greater than 260 nm. There is significant absorbance below 260 nm.

Figure 6-1. UV Absorption Spectra of Sodium Thiocyanate

As indicated earlier, the UV lamp used in this study has 2 spectral energy peaks, one at 260 nm and another at 220 nm. As can be seen in Figure 6-1, the UV absorption of sodium thiocyanate is relatively weak at 260 nm and the molar extinction coefficient is $3.92 \times 10^2 \text{ M}^{-1}.\text{cm}^{-1}$. At 220 nm, the absorption is much larger and the molar extinction coefficient of sodium thiocyanate is found to be $3.56 \times 10^3 \text{ M}^{-1}.\text{cm}^{-1}$.

Hydrogen peroxide was used as the oxidant in the advanced photo-oxidation process. Figure 6-2 shows the UV absorption spectra of H_2O_2 . The absorptivity of hydrogen peroxide is very weak when the UV wavelength is greater than 300 nm. As the wavelength decreases, the absorption goes up. The molar extinction coefficient is $76 \text{ M}^{-1}.\text{cm}^{-1}$ at 220 nm (US Peroxide Head Office, 2003).

**Figure 6-2. UV Absorption Spectra of Hydrogen Peroxide
(US Peroxide Head Office, 2003)**

6.2 Direct Photolysis of Thiocyanate

Ultraviolet radiation can provide energy to the electrons in the absorbing compound to make them pass from the ground state to an excited state and are therefore more apt to participate in redox reactions. Photolytic reactions can be induced directly if the absorbing compound is the species being remediated (Young and Jordan, 1996). As described in the previous section, at wavelength less than 220 nm, UV absorption by thiocyanate is significant ($\epsilon = 3.56 \times 10^3 \text{ M}^{-1}.\text{cm}^{-1}$ at 220 nm). Direct photolysis of thiocyanate had not been investigated in the past, and no data were available in the literature.

Young and Jordan (1996) indicated that direct photolysis is applicable to some WADs and SADs (thiocyanate is a WAD) but is not applicable to free cyanides.

Several batch reactions were conducted to study the direct photolysis of thiocyanate under different conditions. The effect of the main parameters, initial pH values and initial thiocyanate concentrations, have been studied in detail.

pH levels of 8 and 10 were chosen for these experiments. The pH value of the thiocyanate solution prepared with tap water was about 7.8. pH 10 was chosen to avoid HCN formation from acidic thiocyanate solution.

6.2.1 Experiments at Initial pH Value 8

A series of batch experiments were conducted by irradiating 25 L of aqueous solution of sodium thiocyanate concentration varying from 1.72 mM (100 ppm) to 13.8 mM (800 ppm) at initial pH 8.

6.2.1.1 pH variations under UV Radiation

When conducting experiments under initial pH 8 conditions, there was no pH adjustment of the prepared SCN solution (dissolving NaSCN in tap water), which had an initial pH value near 8.

As shown in Figure 6-3, after 3 h UV radiation, pH values dropped in all 5 experiments. The drops in pH ranged between 1.2 and 2.4.

Figure 6-3. pH Variations under Different Initial SCN Conc. at Initial pH 8

6.2.1.2 SCN Removal Percentages

Thiocyanate initial concentrations have been varied to compare the removal percentages under different conditions. As shown in Figure 6-4, the overall thiocyanate removal percentages varied from 20% to 40% after a 3 hour irradiation.

Figure 6-4. SCN Removal Percentages under Direct Photolysis at initial pH 8

The thiocyanate removal percentage was about 40% at an initial SCN concentration of 1.72 mM. At the initial SCN concentration of 13.8 mM, the thiocyanate removal percentage dropped to about 20%.

Despite the fact that the UV dosage was identical in all five experiments (same solution volume, same 3h radiation time, same 1 kW UV lamp with light intensity $(2.93 \pm 0.08) \times 10^{-4}$ Einstein/s between 200 nm and 300 nm), SCN removal percentage went down with increase in the initial SCN concentrations. However the absolute amount of thiocyanate ions in the solutions being oxidized had increased from 0.24 mM.h⁻¹

(initial SCN: 1.72 mM) to 0.91 mM.h^{-1} (initial SCN: 13.8 mM). But no linear relationship was found between the absolute amount of oxidized SCN and initial SCN concentrations.

6.2.2 Experiments at Initial pH Value 10

A series of batch experiments were conducted by irradiating 25 L aqueous solution of sodium thiocyanate, concentrations varying from 1.72 mM (100 ppm) to 13.8 mM (800 ppm) at an initial pH 10.

6.2.2.1 pH variations under UV Radiation

When conducting experiments under initial pH 10 conditions, pH adjustment by sodium hydroxide was used to raise the pH of the SCN solution (dissolving NaSCN into tap water) to 10.

As shown in Figure 6-5, after 3 h UV radiation, pH values dropped in all 5 experiments, the drop in pH ranged between 1.28 and 1.61.

Figure 6-5. pH Variations under Different Initial SCN Conc. at Initial pH 10

6.2.2.2 SCN Removal Percentages

Thiocyanate initial concentrations have been varied to compare the removal percentages under different conditions. As shown in Figure 6-6, the overall thiocyanate removal percentages ranged from 13% to 37% after a 3 hour irradiation.

Figure 6-6. SCN Removal Percentages under Direct Photolysis at initial pH 10

The thiocyanate removal percentage was about 37% at an initial SCN concentration of 1.72 mM. At the initial SCN concentration of 13.8 mM, the thiocyanate removal percentage dropped to about 13%.

Despite the identical UV dosage in all these 5 experiments (same solution volume, same 3h radiation time, same 1 kW UV lamp with light intensity $(2.93 \pm 0.08) \times 10^{-4}$ Einstein/s between 200 nm and 300 nm), SCN removal percentage went down with the increase in initial SCN concentrations. However, the absolute amount of thiocyanate ions oxidized had increased from 0.21 mM.h⁻¹ (initial SCN: 1.72 mM) to 0.60 mM.h⁻¹ (initial SCN: 13.8 mM). But no linear relationship was found between the absolute oxidized

SCN amounts and initial SCN concentrations, the increasing rate of oxidized SCN became slower as initial SCN concentrations went up.

6.2.3 Comparison between Experiments at Initial pH 10 and 8

When initial pH value was 8, after 3 h direct photolysis in Rayox® system, thiocyanate was found to be oxidized and the only related nitrogen product found was cyanide. No cyanate was found. The thiocyanate oxidation rates were quite low from 0.24 mM.h^{-1} to 0.91 mM.h^{-1} . When initial pH value was 10, after 3 h direct photolysis, thiocyanate was found to be oxidized, and the main related nitrogen product was cyanide. Little cyanate was found. The thiocyanate oxidation rates were even lower, ranging from 0.21 mM.h^{-1} to 0.60 mM.h^{-1} .

The pH value of the thiocyanate solutions went down under the UV radiation both under initial pH 8 and initial pH 10 conditions. The sulfur in the thiocyanate has been oxidized to sulfate.

The thiocyanate oxidation rates and percentages were quite low in the direct photolysis at the initial pH values of 8 and 10. The main product was cyanide, which is in fact more toxic than thiocyanate. In view of these, it can be concluded that the direct photolysis would not be a satisfactory method to remove thiocyanate.

6.3 Advanced Photo-oxidation Processes of Thiocyanate with UV/H₂O₂

As shown in the previous section, direct photolysis could only oxidize thiocyanate to cyanide inefficiently and incompletely and is unable to oxidize free cyanides. Chemical oxidation methods such as using Caro's acid (H₂SO₅), hydrogen peroxide (H₂O₂), sulfur dioxide (SO₂), and hypochlorite (OCl⁻) are unable to treat strong metal complexes of cyanides, which are primary products of thiocyanate oxidation. Advanced photo-oxidation processes have been suggested for many contaminant treatments (Young, 1998).

Photolysis can be accomplished with direct or advanced techniques. Advanced oxidation processes depend on the presence of a second material that absorbs the radiation and then transfers the photo-energy to the substance being remediated through activated species. Advanced photolysis consists of two types: 1] Heterogeneous photocatalysis in which a solid semiconductor such as TiO₂ is used. 2] Homogeneous photocatalysis in which dissolved photo-sensitizers such as hydrogen peroxide or ozone are used (Young, 1998).

In this study, homogeneous photolysis with hydrogen peroxide has been used in order to increase reaction efficiencies and lower reaction time. This method using UV/H₂O₂ to produce active free radicals such as hydroxyl radicals that play the role of the oxidative agents is usually called advanced photo-oxidation processes (APPs) (Philippopoulos et al., 2002; Crittenden et al., 1999).

Many preliminary batch reactions were performed to check the reaction properties of the advanced photo-oxidation process of thiocyanate to establish the range of operating

conditions. As main parameters, pH value adjustment, hydrogen peroxide usage, UV radiation dose and methods of addition of reagents were studied in detail.

6.3.1 Photolysis of Hydrogen Peroxide

Hydrogen peroxide decomposed by a zero order reaction when direct photolysis of a H_2O_2 aqueous solution (74 mM) was carried out in the Rayox® system. The rate obtained was 322.92 mM.h^{-1} (Yang, 1998), which is much higher than that of thiocyanate as discussed in previous section (maximum 0.91 mM.h^{-1} or $52.8 \text{ mg.h}^{-1}.\text{L}^{-1}$).

The rapid photolysis of hydrogen peroxide produces highly reactive hydroxyl radicals ($\text{OH}^\bullet$), which attack thiocyanate to initiate a series of fast photochemical reactions (Young and Jordan, 1996; Chiang and Tran, 2002).

6.3.2 Advanced Photo-oxidation of Thiocyanate

The initial thiocyanate concentration $[\text{SCN}]_0 = 3.45 \text{ mM}$ (200 ppm) was used in all advanced photo-oxidation process experiments with $\text{UV}/\text{H}_2\text{O}_2$. The initial pH value of the 25 L thiocyanate solution, prior to H_2O_2 addition, was adjusted to 10. The initial hydrogen peroxide concentrations $[\text{H}_2\text{O}_2]_0 = 3.45 \text{ mM}$ (1:1) and 6.90 mM (2:1) were used. The hydrogen peroxide was added either all at one time or distributed over the course of the experiment. Normally the UV irradiation was carried out for 3 hours, and in some experimental runs, it extended to 6 or 9 hours.

6.3.2.1 Comparison of SCN Removals under Different Conditions

Figure 6-7 describes the thiocyanate removal percentages under $\text{UV}/\text{H}_2\text{O}_2$ advanced oxidation processes. In this experiment, initial SCN concentration was 3.45 mM (200 ppm), 25 L SCN solution was adjusted to pH 10 before adding the

oxidizing agent hydrogen peroxide. 3.45 mM H_2O_2 was added at time 0 in one shot. Then the solution was irradiated in the UV reactor for 3 hours. As stated earlier, the cooling system was turned on. There was no pH control during the whole reaction period. The SCN removal percentage is plotted against the irradiation time as shown as follows:

Figure 6-7. Removal Percentages of Advanced Photo-oxidation of Thiocyanate ($[\text{SCN}]_0 = 3.45 \text{ mM}$, 1:1 molar ratio H_2O_2 put at Time 0 in One shot, initial pH 10)

Comparing the result and that of direct photolysis under the same conditions, it can be seen that the thiocyanate removal percentage has improved from 23.29% to 89.22%.

Experiments were also carried out to investigate the thiocyanate removal by hydrogen peroxide only (Degussa Process). As shown in Figure 6-8, the thiocyanate removal percentages of three processes are compared. The three processes are: thiocyanate removal by H_2O_2 only, thiocyanate removal by UV only, and thiocyanate removal by UV/ H_2O_2 .

As can be seen, the SCN removal percentage was the lowest when the thiocyanate solution was treated by H_2O_2 only. After 3 hours, only 5.10% was oxidized. The SCN

removal percentage was the second highest when the thiocyanate solution was treated by UV only. After 3 hours, 23.39% was oxidized. The highest SCN removal percentage was obtained when the thiocyanate solution was treated by both UV and H_2O_2 . After 3 hours, 89.22% was oxidized. Considering that only a 1:1 molar ratio of hydrogen peroxide was used, the improvement is quite significant.

Figure 6-8. Comparison of SCN Removal Percentages under Different Conditions
(All initial pH values 10; all initial SCN concentrations 3.45 mM, all H_2O_2 dosages 3.45 mM, no pH control)

6.3.2.2 pH Variation in Advanced Photo-oxidation Processes

The pH variations were monitored in the advanced photo-oxidation of thiocyanate experiments. As can be seen in Figure 6-9, pH values dropped with time.

When 1:1 molar ratio hydrogen peroxide was added, the pH value of thiocyanate solution dropped from 10.17 to 5.61 in 1 h. Over the next 4 h, the pH value dropped from

5.61 to 3.61. The drop in pH is usually rapid in the first hour, after which, the drop is much slower.

When 2:1 molar ratio hydrogen peroxide was added, the pH drop was even more significant. The pH value of thiocyanate solution dropped from 9.98 to 3.50 in 1 h. From 1 h to 5 h, the pH value dropped from 3.50 to 3.38. In the first hour the pH value dropped very fast. Further pH drop from 2 h to 5 h was very slow.

In the advanced photo-oxidation of thiocyanate with UV/H₂O₂, the drop in pH was much more significant compared to the value in direct photolysis.

Figure 6-9. pH Variations under Different Conditions in Advanced Photo-oxidation Processes of Thiocyanate

(All initial pH values 10; initial SCN concentrations 3.45 mM; H₂O₂ dosages 3.45 mM and 6.90 mM added at Time 0, no pH control)

6.3.2.3 Processes and Products of Advanced Thiocyanate Oxidation

The goal of this investigation is to convert toxic thiocyanate to products that are either not toxic to the environment or easy to treat with known methods to yield harmless products. Literature review shows nitrate or nitrogen gas is supposed to be the ideal final products of thiocyanate oxidation. Cyanide, cyanate, ammonia, nitrite are the nitrogen intermediates in the SCN oxidation. The SCN oxidation pathways and the rates of formation of these intermediates varied depending on different conditions such as hydrogen peroxide dosages, pH values of treated solutions and the mode of addition of H₂O₂ (Chiang and Tran, 2002; Young, 1998).

Botz et al. (2000) stated that thiocyanate oxidation is through the following pathway. The first step of thiocyanate oxidation is from SCN to CN, in which thiocyanate undergoes the simultaneous chemical oxidation of sulfur and the reduction of carbon to yield free cyanide and sulfate. In the following half-reaction, carbon is reduced from C(IV) to C(II) while sulfur is oxidized from S(-II) to S(VI).

This equation shows the SCN to CN process is a hydrogen ion producing process, and this accounts for the drop in pH in the reaction process. The reaction will take place efficiently at acidic pH, and aqueous hydrogen cyanide is produced instead of free cyanide (Botz et al., 2000).

The second step of thiocyanate oxidation is the conversion of CN to CNO with carbon being oxidized from C(II) to C(IV). This process doesn't take place to a significant extent under acidic conditions. Hydroxyl radicals are the main oxidizing agent and the reaction proceeds as follows (Young and Jordan, 1996).

The third step: the cyanate produced will either hydrolyze to ammonium and bicarbonate or be oxidized by hydroxyl radicals to form nitrite, nitrate or nitrogen gas. Cyanate hydrolysis takes place efficiently under conditions of pH less than 7 at room temperatures, and the reaction equation is as follows.

Cyanate reacting with hydroxyl radicals produces different products under different conditions. Hydroxyl radical concentration seems to influence the directional pathway.

These reactions are as follows.

These reactions are possible thiocyanate oxidation pathways. Experiments were conducted to verify them and to calculate the removal rates.

Products of Advanced Photo-oxidation of thiocyanate without pH control

Figure 6-10 presents the variations of thiocyanate, cyanide, cyanate, and sulfate concentrations in a typical advanced photo-oxidation of thiocyanate process with no pH control.

Figure 6-10. Advanced Oxidation of Thiocyanate without pH control

(Initial pH 10: initial SCN concentration 3.45 mM; H₂O₂ dosage 3.45 mM added at Time 0; no pH control)

As can be seen, during the advanced oxidation of thiocyanate, pH value dropped significantly from 10.17 to 3.61. After 5 hours, 100% of the thiocyanate was removed, and the average rate of removal was 0.70 mM.h⁻¹. Almost all sulfur in the SCN was oxidized to sulfate at the average rate of 0.59 mM.h⁻¹. The main oxidized nitrogen product was cyanide, which accounted for about 97% with an average production rate of 0.74 mM.h⁻¹. Only a little of cyanate was produced - about 0.12 mM after 5 hours. These data confirm the proposed SCN oxidation pathways described earlier: if there is no pH

control, SCN is oxidized to CN with a rapid pH drop. Under acidic conditions, CN to CNO oxidation process is inhibited and becomes slow. SCN can be converted to CN almost completely.

Interestingly, the above process would be of benefit if the objective is the recovery of cyanide rather than removal of thiocyanate by oxidation (usually acidification-volatilization-reneutralization process is used for cyanide recovery). For example, in the Olympias project on gold and silver ores in Greece, thiocyanate concentration in the tailings ranged from 2.5 g/L to 12 g/L. Laboratory and pilot studies were conducted to show that cyanide regeneration from thiocyanate could lower overall cyanide consumption to help reduce operation cost. Meanwhile, no toxic thiocyanate was discharged to the environment (Botz et al., 2000).

Products of Advanced Photo-oxidation of thiocyanate with pH control

Figure 6-11 presents the variations of thiocyanate, cyanide, cyanate, and sulfate concentrations obtained in a typical advanced photo-oxidation experiment with pH control.

As can be seen, the pH of the thiocyanate solution was always kept between 10 and 10.5 during the reaction process. After three hours, nearly 51% of thiocyanate was removed. This value is lower than the result from the experiment without pH control (89%) but still much higher than the result from direct photolysis (24%). The average SCN removal rate in the 3 hours was 0.59 mM.h^{-1} . After 3 hours all sulfur in the thiocyanate was oxidized to sulfate, and the average rate was 0.60 mM.h^{-1} .

After three hours, the cyanide concentration increased from 0 to 0.77 mM with an average formation rate of 0.26 mM.h^{-1} (It is slower than that of experiments without pH

control: 0.74 mM.h^{-1}). After three hours, the cyanate concentration increased from 0 to 1.02 mM . The average rate of formation was 0.34 mM.h^{-1} , which is faster than the average rate of cyanide formation in this experiment (0.26 mM.h^{-1}).

Figure 6-11. Advanced Photo-oxidation of Thiocyanate with pH control
(Initial pH 10; initial SCN concentration 3.45 mM ; H_2O_2 dosage 3.45 mM added at Time 0; solution pH always between 10 to 10.5)

The data presented indicate SCN oxidation pathway with pH control is as follows.

If pH value of the thiocyanate solution was kept between 10 and 10.5, SCN is oxidized to CN, which is subsequently oxidized to CNO.

With pH control, the overall SCN oxidation rate was lower than that without pH control. The oxidation products are cyanide and cyanate (43% of cyanide, 57% of cyanate in moles).

By carrying out a set of experiments, it was found that in order to oxidize thiocyanate to nitrate or nitrogen gas, both the hydrogen peroxide and the UV dosages

should be increased. More importantly it was also found that the mode of addition of hydrogen peroxide needed to be changed from one shot at time 0 to a distributed addition throughout the whole process.

Figure 6-12 describes the experiment after these changes. The experimental conditions are as follows:

The initial pH of solution was 10. The initial SCN concentration was 3.45 mM. In the first 3h, H₂O₂ dosage of 6.90 mM was added in aliquots of (6.90/3) mM at time 0, 60, 120 minutes. The pH was maintained between 10 and 10.5 in the period. In the second 3h, H₂O₂ dosage of 6.90 mM was added in 3 equal batches at time 180, 240, 300 minutes. There was no pH control in the period. In the third 3h, H₂O₂ dosage of 6.90 mM was added in 3 equal batches at time 360, 420, 480 minutes. There was no pH control in the period.

Figure 6-12. 9-hour Advanced Photo-oxidation of Thiocyanate

To discuss the course of the experiment, the run time is divided into three 3-hour periods, referred to as Period I (0 – 180 min), Period II (180 – 360 min), and Period III (360 – 540 min).

As can be seen, the experiment gave much better results. In the first hour, the cyanide concentration increased from 0 to 0.61 mM, then it went down to 0.12 mM after 180 minutes, after which, the cyanide concentration continuously decreased and reached zero at 240 minutes.

At the end of Period I, 77% thiocyanate was removed, and the average SCN removal rate was 0.91 mM.h^{-1} . The primary nitrogen product was cyanate. At the end of Period I, 2.0 mM cyanate was produced, at an average production rate of 0.67 mM.h^{-1} . Among all nitrogen products from SCN oxidation, cyanate accounted for nearly 95%. At the end of Period I, almost all sulfur in the SCN was oxidized to sulfate with an average rate of 0.87 mM.h^{-1} . At the end of Period I, there were negligible amounts of ammonia, nitrite, and nitrate formed.

After 300 minutes, thiocyanate and the cyanide produced were all gone. Cyanate concentration hit its peak at 2.62 mM then went down to 1.62 mM at the end Period II. Oxidation of cyanate produced ammonia, nitrite and nitrate.

In Period II, very little nitrite had accumulated (0.1 mM). Ammonia concentration was up to 0.59 mM with an average generation rate of 0.20 mM.h^{-1} . Nitrate concentration was 0.67 mM at the end of Period II with an average generation rate of 0.22 mM.h^{-1} . All sulfur in the treated solution was oxidized to sulfate, whose concentration was 3.59 mM at the end of Period II.

At the end of Period III, almost all cyanate was oxidized. Its concentration dropped to 0.26 mM with an average oxidation rate of 0.45 mM.h^{-1} in Period III. Nitrite concentration was still very low (0.1 mM). Ammonia concentration was 0.82 mM with an average accumulating rate of 0.08 mM.h^{-1} in Period III.

At the end of Period III, nitrate concentration was 1.55 mM, and the average generation rate was 0.29 mM.h^{-1} in Period III.

The nitrogen material balance across the reactor indicated a deficit of 0.72 mM of nitrogen and it is assigned to nitrogen gas that is released in the process.

The 9-hour experiment shows the preferred thiocyanate oxidation pathway discussed earlier and has the best reaction efficiency. This advanced photo-oxidation technique as developed here with specific procedures and schemes for pH control and graduated peroxide addition seems like a new and promising technique for thiocyanate remediation.

6.3.3 Kinetics for Advanced Photo-oxidation of Thiocyanate

According to the results of experiments and discussions in the previous section, homogenous photolysis of thiocyanate with hydrogen peroxide (advanced photo-oxidation processes) had different oxidation pathways under different experimental conditions. In this section, kinetics for the advanced photo-oxidation processes will be calculated under both conditions: without pH control and with pH control.

6.3.3.1 Without pH Control

As stated earlier, when there was no pH control, UV/H₂O₂ processes for thiocyanate led to a rapid drop in pH and produced cyanide as almost the only nitrogen-related product (97%). Table 6-1 presents the data from a typical experiment carried out in this study, based on which the kinetic calculation was carried out.

Table 6-1. Thiocyanate Conc. Variation at Typical APPs without pH Control

Time (H)	pH	[SCN] (mM)	-ln [SCN/SCN ₀]	1/[SCN]
0	10.17	3.51	0.00	0.28
1	5.61	1.78	0.68	0.56
2	5.82	1.00	1.26	1.00
3	4.93	0.38	2.23	2.64
4	4.01	0.06	4.00	15.61
5	3.61	0.02	5.17	50.00

Note: [SCN]₀=3.45 mM, 1:1 molar ratio H₂O₂ put at Time 0 in One shot, initial pH 10, no pH control all time, experiment duration time 5 h.

With no pH control, the pH dropped to a low value and under this condition no cyanate was produced. Effectively, in the general oxidation reaction 6-2, the reaction CN to CNO does not proceed.

Therefore the reaction kinetics were evaluated based on reaction 6-3:

The reaction order with respect to the thiocyanate concentration was determined using the standard methods of analysis (Levenspiel, 1972).

The kinetic model for a second-order reaction with respect to SCN concentrations is as follows:

$$\frac{d[SCN]}{dt} = k[SCN]^2 \quad (6-4)$$

Equation 6-4 is integrated as:

$$\frac{1}{[SCN]} - \frac{1}{[SCN]_0} = kt \quad (6-5)$$

If the reaction is second order, a plot of $1/[SCN]$ versus t (time) should yield a straight line.

Figure 6-13. $1/[SCN]$ Vs. Time

As can be seen, the experimental data in Figure 6-13 does not yield a straight trendline and hence the second-order model is rejected.

Next the first-order model was evaluated. The kinetic model for a first-order reaction with respect to SCN concentrations is as follows:

$$\frac{d[SCN]}{dt} = -k[SCN] \quad (6-6)$$

Equation 6-6 is integrated as:

$$\ln \frac{[SCN]}{[SCN_0]} = -kt \quad (6-7)$$

If the reaction is first order, a plot of $-\ln[SCN/SCN_0]$ Vs. Time should yield a straight line.

Figure 6-14. $-\ln[SCN/SCN_0]$ Vs. Time

As can be seen, Figure 6-14 of $-\ln[SCN/SCN_0]$ Vs. Time gives a straight trendline with the equation of $y=0.9407x$.

This indicates that the reaction of advanced photo-oxidation of SCN with UV/H₂O₂ without pH control is first-order (or close to first-order) with respect to

thiocyanate concentration. From Figure 6-14, the first-order reaction rate constant (k) is determined as 0.94 h^{-1} .

6.3.3.2 With pH Control

As stated earlier, when there was pH control, UV/H₂O₂ processes produced cyanate as the main nitrogen-related product. Table 6-2 presents a typical experiment carried out in this study, and reaction kinetics will be evaluated based on it.

Table 6-2. Thiocyanate Conc. Variation at Typical APPs with pH Control

Time (h)	pH	SCN (mM)	CN (mM)	CNO (mM)	SO4 (mM)	NH3 (mM)	NO2 (mM)	NO3 (mM)	Total N (mM)
0	10.30	3.53	0.00	0.05	0.26				3.58
1	10.30	2.46	0.61	0.50					3.58
2	10.20	1.55	0.50	1.26					3.31
3	10.20	0.81	0.12	2.05	2.86	0.00	0.00	0.00	2.97
4	7.28	0.19	0.00	2.62		0.32	0.03	0.08	3.24
5	6.91	0.03	0.00	2.28		0.36	0.12	0.30	3.10
6	6.86	0.03	0.00	1.62	3.59	0.59	0.07	0.67	2.99
7	7.00	0.09	0.00	1.07		0.68	0.11	1.04	2.99
8	7.00	0.03	0.00	0.59		0.71	0.08	1.36	2.78
9	7.00	0.03	0.00	0.31	3.56	0.82	0.10	1.55	2.82

Note: [SCN]₀=3.45 mM, Every 3 hours, 2:1 molar ratio H₂O₂ put at Time 0, 1, 2, 3, 4, 5, 6, 7, 8 stepwise, every time, 6.90/3 mM H₂O₂ added, initial pH 10, pH control for first 3 h, then no pH control, experiment duration time 9 h

Based on the product distribution obtained from the table, the reaction was roughly divided into two periods roughly. Period I, from 0 to 3 h, in which thiocyanate was oxidized to cyanate through intermediate cyanide. Period II, from 4 to 9 h, in which cyanate was oxidized to ammonia, nitrite, nitrate, and nitrogen gas through different pathways. Ammonia oxidation may also occur.

In this section, Period I is analyzed to determine the kinetics of the variations of thiocyanate, cyanate and cyanide concentrations in the solution. As Period II involves complex reactions that occur simultaneously (cyanate oxidation by hydroxyl radicals, cyanate hydrolysis, and ammonia oxidation may all occur), only the variation of cyanate concentration with respect to time is analyzed.

Kinetics Model for Reactions in Period I (0 to 3 h):

Reactions:

The rate Equations for the three components are:

$$\frac{dC_{SCN}}{dt} = -k_1 C_{SCN} \quad (6-9)$$

$$\frac{dC_{CN}}{dt} = k_1 C_{SCN} - k_2 C_{CN} \quad (6-10)$$

$$\frac{dC_{CNO}}{dt} = k_2 C_{CN} \quad (6-11)$$

Nitrogen Balance:

$$C_{SCN_0} + C_{CN_0} + C_{CNO_0} = C_{SCN} + C_{CN} + C_{CNO} \quad (6-12)$$

Initial Conditions: at $t = 0$:

$$C_{SCN} = C_{SCN_0} = 3.53mM, C_{CN} = C_{CN_0} = 0mM, C_{CNO} = C_{CNO_0} = 0.05mM \quad (6-13)$$

Concentration Expressions:

$$C_{SCN} = C_{SCN_0} e^{-k_1 t} \quad (6-14)$$

$$C_{CN} = \frac{k_1}{k_2 - k_1} C_{SCN_0} (e^{-k_1 t} - e^{-k_2 t}) \quad (6-15)$$

$$C_{CNO} = C_{SCN_0} - C_{SCN_0} e^{-k_1 t} - \frac{k_1}{k_2 - k_1} C_{SCN_0} (e^{-k_1 t} - e^{-k_2 t}) + C_{CNO_0} \quad (6-16)$$

Equations 6-14 – 6-16 describe the concentration variations during thiocyanate oxidation process under the typical experimental conditions presented in Table 6-2. The advanced photo-oxidation of thiocyanate to cyanate was a first-order reaction.

The concentrations of different compounds obtained from the experiment and those calculated from the kinetic model versus the radiation time are presented in Figure 6-15.

Figure 6-15. Distribution of Products of Advanced Photo-oxidation of Thiocyanate with UV/H₂O₂

As shown, the experimental data points fit the kinetic model (solid lines) reasonably well.

The kinetic rate constants k_1 and k_2 used in rate equations 6-14 to 6-16 are $k_1=0.26 \text{ h}^{-1}$, $k_2=1.80 \text{ h}^{-1}$.

Kinetics Model for Reactions in Period II (4 to 9h):

In Period II, thiocyanate and cyanide in the solution were all gone. Cyanate was oxidized by UV/H₂O₂. Table 6-3 presents the variation of cyanate concentration with respect to time from 4 to 9 h.

Table 6-3. Variation of Cyanate Conc. in Period II

Time (h)	Time for Period II (h)	pH	CNO (mM)
Period I			
4	0	7.28	2.62
5	1	6.91	2.28
6	2	6.86	1.62
7	3	7.00	1.07
8	4	7.00	0.59
9	5	7.00	0.31

Note: Conditions same to Table 6-2.

Plot Variation of cyanate conc. vs. time in Figure 6-16:

Figure 6-16. Variation of Cyanate Conc. in Period II
(Conditions same to Table 6-2)

As can be seen, Figure 6-16 (Cyanate conc. vs. time) gives a straight trendline with the equation of $y = -0.4903x + 2.642$.

It indicates that removal of cyanate in Period II is a zero-order reaction with respect to the cyanate concentration. The reaction rate constant is 0.49 h^{-1} .

Chapter 7 Conclusions and Recommendations

7.1 *Conclusions*

Both biological and photochemical processes for thiocyanate remediation were studied in detail as regards their feasibility and operating characteristics.

In the biological study, two continuous Aerated Biological Filters were operated to cause thiocyanate oxidation and subsequent nitrification of the ammonia produced. One was operated at room temperature (18-30 °C depending on seasons, average 24°C), and the other was in a cold room maintained at 8.5 °C. The results indicated that both the ABFs operated in a stable manner and the thiocyanate feed was oxidized to ammonia and further on to nitrate as the final product both at room temperature and 8.5 °C. The treatment capacity of the ABF with respect to thiocyanate loading was reduced by approximately 50% when the operating temperature was changed from room temperature to 8.5 °C.

Results from the experimental data showed recycle ratio and alkalinity did not influence the thiocyanate oxidation to ammonia but did influence nitrification of ammonia significantly. For the synthetic wastewater with the SCN concentration level of 200 mg/L used in these experiments, the results on the effect of alkalinity indicate that the preferred alkalinity is achieved at a concentration of 0.55 g/L of sodium bicarbonate.

In the photochemical study, direct photolysis and advanced photo-oxidation processes by UV/H₂O₂ were conducted. The results indicated that the direct photolysis of thiocyanate produced primarily cyanide. The rate of conversion of thiocyanate to cyanide fell with increasing pH. As the cyanide product is even more toxic than thiocyanate, direct photolysis would not be a suitable process for the remediation of thiocyanate.

The Advanced Photo-oxidation Process using a combination of UV/H₂O₂ can degrade thiocyanate quickly and efficiently. The results showed that the process seemed to follow different oxidation pathways under different solution pH values. When there was no pH control, thiocyanate was oxidized to cyanide fairly rapidly while the solution pH value fell (end point about 3.5). Very little cyanate was produced.

However with pH control (pH always above 10), thiocyanate was oxidized to cyanate completely while little cyanide was formed. On continued irradiation, the cyanate was further oxidized to ammonia, nitrite, nitrate, or nitrogen gas depending on different dosages of UV/H₂O₂. The existence of different pathways of thiocyanate oxidation is one of the primary findings in the photochemical study.

By following the course of the reaction, which provided the information on the products distribution and their concentration profiles with time, a detailed reaction scheme was postulated for the advanced photo-oxidation process, based on which a kinetic model was developed. The postulated model fitted the experimental data reasonably well and the kinetic parameters were evaluated.

7.2 Recommendations

In the biological area, more experimental runs should be conducted at 8.5 °C or lower to investigate the performance variations of the aerated biological filters for the oxidation of thiocyanate to nitrate. The experimental study should be expanded to a system of ABFs connected in series which would be able to handle much larger hydraulic loadings and effect complete nitrification. Such a system with a series of ABFs can be expected to have higher ability to withstand hydraulic loading variations than a single ABF.

To mimic the mill conditions and simulate the typical wastewater from gold mills, ABF experiments should be carried out with cyanide added to the synthetic feed solution.

In the photochemical area, the nature of reaction mechanism of advanced photo-oxidation processes are quite complex. Therefore more experiments should be carried out to investigate possible intermediates and their distribution at various stages of the photolytic reaction. Higher hydrogen peroxide dosages should be used to compare the effect of H_2O_2 to determine the optimum H_2O_2 dose. The APP should be extended to the use of photocatalysts such as copper salts. That may prove beneficial in the photo-oxidation of thiocyanate and improve the kinetics significantly.

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Appendix A

Biological experiments: Data from Column A

TF Overall Data	Feed Flow Rate (mL/min)	Recycle Flow Rate (mL/min)	SCN (mg/L)		Hach NH ₃ -N (mg/L)		Hach NO ₃ -N (mg/L)		Hach NO ₂ -N (mg/L)		pH		Temperature (°C)	
			Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Feed pH	Effluent	Feed	Effluent
1-Mar-02	192.0		1324.80											
4-Mar-02	94.0			1110.60										
5-Mar-02	94.0													
6-Mar-02	94.0			890.10										
7-Mar-02	94.0													
8-Mar-02	94.0			1024.20										
11-Mar-02	192.0		728.60	697.50										
12-Mar-02	192.0													
13-Mar-02	192.0		185.10	123.60										
14-Mar-02	192.0													
15-Mar-02	192.0			69.10										
18-Mar-02	192.0			19.10										
19-Mar-02	192.0													
20-Mar-02	192.0		112.60											
21-Mar-02	46.0													
22-Mar-02	46.0			60.40										
25-Mar-02	46.0		102.30											
26-Mar-02	46.0													
27-Mar-02	46.0		0.00	0.00										
28-Mar-02	46.0		156.30											
29-Mar-02	46.0													
1-Apr-02	46.0			0.00										
2-Apr-02	46.0		126.30											
3-Apr-02	46.0													
4-Apr-02	46.0			0.00										
5-Apr-02	46.0		120.00											
8-Apr-02	46.0			0.00										
9-Apr-02	46.0		111.60											
10-Apr-02	46.0			0.00										
11-Apr-02	46.0													
12-Apr-02	35.0	10.0			2.00		0.10		1.40					
15-Apr-02	35.0	10.0	115.03	0.00	3.00	31.00	0.80	1.00	0.00	0.90	7.56	7.1		
16-Apr-02	35.0	10.0												
17-Apr-02	35.0	10.0	132.70	0.00	#N/A	#N/A	0.60	0.40	#N/A	#N/A	8.09	7.67		
18-Apr-02	35.0	10.0												
19-Apr-02	35.0	10.0												
22-Apr-02	35.0	10.0	400.70	43.00	#N/A	#N/A	0.00	0.00	#N/A	#N/A	7.98	7.20		
23-Apr-02	35.0	10.0												
24-Apr-02	35.0	10.0												
25-Apr-02	15.0	10.0	190.80	0.48	5.75	27.50	0.70	0.70	0.00	13.50	8.30	6.75		
26-Apr-02	15.0	10.0												
29-Apr-02	15.0	10.0	240.70	0.00	0.06	28.00	1.90	3.30	1.80	14.60	7.55	6.92		
30-Apr-02	15.0	10.0												
1-May-02	15.0	10.0												
2-May-02	15.0	10.0	156.00	0.00	12.00	32.00	1.20	5.20	1.00	24.80	7.89	6.95		
3-May-02	15.0	10.0												
6-May-02	15.0	10.0			9.00	31.00	1.00	6.80	1.20	23.90	7.90	6.60		
7-May-02	15.0	10.0												
8-May-02	15.0	10.0	157.30	0.00	10.00	4.00	0.60	31.30	0.00	16.20	7.89	6.63		
9-May-02	15.0	10.0												
10-May-02	15.0	10.0	220.90	0.00	2.00	3.00	1.40	29.75	0.10	3.40	8.05	7.02	22.0	21.6
13-May-02	25.0	12.5	235.20	0.00	1.00	3.00	0.60	32.10	0.00	3.20	7.87	7.50	21.0	22.3
14-May-02	25.0	12.5	216.50	0.00	3.00	3.00	1.30	39.60	0.00	8.50	8.30	7.17	22.3	23.6
15-May-02	25.0	12.5												
16-May-02	25.0	12.5	202.20	0.00	5.00	4.00	0.40	38.30	0.10	2.20	7.90	7.37	21.5	22.6
17-May-02	25.0	12.5												
20-May-02	25.0	12.5	205.30	0.00	6.00	5.00	0.60	39.00	0.00	2.10	7.96	7.26	21.7	22.3
21-May-02	25.0	12.5												
22-May-02	25.0	12.5												
23-May-02	25.0	0.0	203.50	0.00	1.00	4.00	0.00	38.60	0.40	2.80	8.00	7.30	23.8	23.7
24-May-02	25.0	0.0												
27-May-02	25.0	0.0												

28-May-02	25.0	0.0	202.90	0.00	0.00	7.00	0.50	39.00	0.00	3.10	7.97	7.32	25.0	26.1
29-May-02	25.0	0.0												
30-May-02	25.0	0.0	191.10	0.00	0.00	3.00	0.50	37.50	0.00	1.70	7.88	7.47	26.8	27.7
31-May-02	25.0	0.0												
3-Jun-02	25.0	0.0												
4-Jun-02	25.0	0.0	200.10	0.00	0.00	6.00	0.00	25.60	0.10	0.00	8.00	7.67	21.6	21.8
5-Jun-02	25.0	0.0												
6-Jun-02	25.0	0.0	209.10	0.00	3.00	4.00	0.50	28.70	0.00	3.10	7.67	7.48	21.5	21.5
7-Jun-02	25.0	0.0												
10-Jun-02	25.0	0.0	203.00	0.00	3.00	5.00	0.80	28.35	0.00	4.20	7.78	7.22	20.8	21.2
11-Jun-02	25.0	0.0												
12-Jun-02	25.0	0.0												
13-Jun-02	25.0	0.0	203.10	0.00	1.00	6.00	0.40	22.80	0.00	1.10	7.75	7.65	21.4	20.9
14-Jun-02	25.0	12.5												
17-Jun-02	25.0	12.5	249.40	0.00	2.00	7.80	0.50	18.90	0.20	2.60	8.01	7.88	20.3	20.0
18-Jun-02	25.0	12.5												
19-Jun-02	25.0	12.5	207.60	0.00	1.00	6.00	0.70	21.30	0.20	2.30	7.99	7.70	20.8	20.1
20-Jun-02	25.0	12.5												
21-Jun-02	25.0	12.5	194.80	0.00	3.00	7.00	0.90	20.80	0.00	1.80	7.94	7.78	22.5	22.2
24-Jun-02	25.0	12.5												
25-Jun-02	25.0	12.5	207.10	0.00	1.00	6.70	0.60	32.70	0.30	3.20	8.08	7.81	25.2	25.1
26-Jun-02	25.0	12.5												
27-Jun-02	25.0	12.5	212.30	0.00	1.20	3.00	0.80	30.10	0.50	2.20	8.04	7.83	25.3	25.1
28-Jun-02	25.0	12.5												
1-Jul-02	25.0	12.5												
2-Jul-02	25.0	12.5	201.30	0.00	1.50	6.20	0.80	29.80	0.60	1.80	8.04	7.88	26.2	26.2
3-Jul-02	25.0	12.5												
4-Jul-02	25.0	12.5	189.50	0.00	3.20	4.70	1.60	25.60	0.40	1.20	8.01	7.90	26.0	26.2
5-Jul-02	25.0	12.5												
8-Jul-02	25.0	12.5	150.70	0.00	2.00	6.00	0.30	23.60	0.00	1.90	8.12	7.85	26.2	26.2
9-Jul-02	25.0	12.5												
10-Jul-02	25.0	12.5	203.90	0.00	1.20	6.30	0.60	24.50	0.40	1.80	8.00	7.90	26.2	26.0
11-Jul-02	25.0	12.5												
12-Jul-02	25.0	12.5	196.30	0.00	2.40	5.00	0.60	28.90	0.30	2.30	8.10	7.86	26.4	26.1
15-Jul-02	25.0	12.5												
16-Jul-02	25.0	12.5	201.00	0.00	3.00	7.00	0.40	36.60	0.10	1.40	8.04	7.82	26.1	25.6
17-Jul-02	25.0	12.5												
18-Jul-02	25.0	12.5	210.60	0.00	2.00	6.60	0.50	32.30	0.20	1.00	8.05	7.79	26.5	26.0
19-Jul-02	25.0	12.5												
22-Jul-02	25.0	12.5	188.60	0.00	3.00	5.80	0.40	37.50	0.00	1.60	8.09	7.80	26.8	27.5
23-Jul-02	30.0	5.0												
24-Jul-02	30.0	5.0												
25-Jul-02	30.0	5.0	192.30	0.00	2.60	8.10	0.30	21.60	0.10	1.20	8.08	7.86	26.3	27.5
26-Jul-02	30.0	5.0												
29-Jul-02	30.0	5.0	178.00	0.00	2.00	8.30	0.40	22.50	0.10	1.80	8.04	7.96	26.7	27.2
30-Jul-02	30.0	5.0												
31-Jul-02	30.0	5.0	194.80	0.00	0.00	10.00	0.10	21.00	0.30	7.90	8.08	7.80	27.2	29.8
1-Aug-02	30.0	5.0												
2-Aug-02	30.0	5.0	201.50	0.00	1.00	5.00	0.20	20.50	0.00	4.70	8.10	7.86	27.0	27.5
5-Aug-02	30.0	5.0												
6-Aug-02	30.0	5.0	215.30	0.00	2.00	1.00	0.50	32.00	0.00	5.00	8.01	8.12	26.6	27.1
7-Aug-02	30.0	5.0												
8-Aug-02	30.0	5.0	204.70	0.00	1.00	0.00	0.10	28.40	0.10	1.40	8.00	8.15	25.7	25.9
9-Aug-02	30.0	5.0												
12-Aug-02	30.0	5.0	202.30	0.00	1.00	0.00	0.20	29.80	0.10	1.20	8.10	8.12	26.8	27.1
13-Aug-02	35.0	0.0	207.90	198.20	1.00	5.00	0.00	0.70	0.00	0.00	8.06	8.01	27.2	27.6
14-Aug-02	35.0	0.0												
15-Aug-02	35.0	0.0	203.20	0.00	2.00	22.20	0.60	24.50	0.20	0.20	8.11	8.17	28.2	27.8
16-Aug-02	35.0	0.0												
19-Aug-02	35.0	0.0												
20-Aug-02	35.0	0.0	210.30	0.00	2.00	23.00	0.30	16.00	0.00	11.00	8.02	7.86	26.4	27.0
21-Aug-02	35.0	0.0												
22-Aug-02	35.0	0.0	190.60	0.00	3.00	26.50	0.20	14.00	0.20	12.00	8.08	8.01	25.8	25.6
23-Aug-02	35.0	0.0												
26-Aug-02	35.0	0.0	219.30	0.00	4.00	17.00	0.10	5.90	0.00	28.20	7.92	8.01	24.1	24.0
27-Aug-02	35.0	0.0												
28-Aug-02	35.0	0.0	208.70	0.00	2.00	21.20	0.30	6.10	0.10	22.00	8.01	8.12	24.0	24.6
29-Aug-02	35.0	0.0												
30-Aug-02	35.0	0.0	214.50	168.70	1.00	10.00	0.10	0.40	0.20	4.20	8.09	8.17	25.1	24.3
2-Sep-02	25.0	10.0												
3-Sep-02	35.0	0.0												
4-Sep-02	35.0	17.5	228.90	0.00	3.00	21.00	0.00	4.90	0.10	27.60	7.83	8.01	25.0	25.0
5-Sep-02	35.0	17.5												
6-Sep-02	35.0	17.5												

9-Sep-02	25.0	12.5	196.50	0.00	1.00	7.00	0.10	6.90	0.00	23.00	8.07	7.89	25.1	26.2
10-Sep-02	25.0	12.5												
11-Sep-02	25.0	12.5	198.10	0.00	2.00	8.00	0.20	10.40	0.00	19.90	8.00	7.90	25.2	25.8
12-Sep-02	25.0	12.5												
13-Sep-02	25.0	12.5	208.30	0.00	2.00	5.00	0.10	11.00	0.00	18.20	7.95	7.89	23.6	24.2
16-Sep-02	25.0	12.5	201.20	0.00	1.00	1.00	0.10	12.00	0.00	17.90	7.91	7.80	23.3	24.0
17-Sep-02	25.0	12.5												
18-Sep-02	25.0	12.5	203.70	0.00	1.00	0.00	0.20	10.00	0.00	17.60	7.99	7.85	23.3	23.6
19-Sep-02	25.0	12.5												
20-Sep-02	25.0	12.5	210.60	0.00	3.00	1.00	0.10	12.60	0.10	16.90	8.02	7.90	23.5	24.0
23-Sep-02	25.0	12.5	200.60	0.00	1.00	0.00	0.30	11.20	0.00	18.00	7.96	7.80	23.1	24.1
24-Sep-02	25.0	12.5												
25-Sep-02	25.0	12.5	196.30	0.00	0.00	0.00	0.50	10.40	0.00	18.30	8.00	7.78	23.2	23.4
26-Sep-02	15.0	15.0												
27-Sep-02	15.0	15.0												
30-Sep-02	15.0	15.0	193.20	0.00	0.00	0.00	0.10	16.20	0.00	10.20	8.06	8.00	21.1	22.3
1-Oct-02	15.0	15.0												
2-Oct-02	15.0	15.0	205.30	0.00	0.00	0.00	0.10	20.10	0.10	6.10	8.02	7.80	21.2	22.2
3-Oct-02	15.0	15.0												
4-Oct-02	15.0	15.0	203.20	0.00	0.00	0.00	0.20	20.50	0.00	5.00	7.70	7.49	20.7	20.7
7-Oct-02	15.0	15.0	201.50	0.00	1.00	1.00	0.00	24.30	0.00	2.00	7.64	7.53	20.8	20.7
8-Oct-02	25.0	12.5												
9-Oct-02	25.0	12.5	207.80	0.00	1.00	2.00	0.10	20.00	0.00	1.00	7.62	7.60	21.6	22.0
10-Oct-02	25.0	12.5												
11-Oct-02	25.0	12.5	197.60	0.00	0.00	3.00	0.00	20.50	0.00	1.90	7.60	7.60	21.5	22.4
14-Oct-02	25.0	12.5												
15-Oct-02	25.0	12.5												
16-Oct-02	35.0	0.0	205.60	0.00	1.00	2.00	0.10	16.50	0.10	11.50	7.60	7.50	21.3	22.3
17-Oct-02	35.0	0.0												
18-Oct-02	35.0	0.0	202.30	0.00	1.00	3.00	0.10	17.20	0.00	12.00	7.68	7.68	22.5	23.4
21-Oct-02	35.0	0.0												
22-Oct-02	35.0	0.0												
23-Oct-02	35.0	0.0	208.60	0.00	1.00	3.00	0.00	18.80	0.00	11.00	7.37	7.40	22.0	21.5
24-Oct-02	35.0	0.0												
25-Oct-02	35.0	0.0	203.30	0.00	1.00	4.00	0.10	18.80	0.00	7.90	7.69	7.50	20.9	21.6
28-Oct-02	35.0	17.5	197.80		1.00	2.50	0.10	19.50	0.00	5.00	7.54	7.47	20.0	20.1
29-Oct-02	35.0	17.5												
30-Oct-02	35.0	17.5	204.30	0.00	0.00	1.00	0.30	18.00	0.00	4.90	7.60	7.55	20.5	22.0
31-Oct-02	35.0	17.5												
1-Nov-02	35.0	17.5	193.70	0.00	1.00	1.00	0.00	20.00	0.00	2.00	7.60	7.56	20.3	20.0
4-Nov-02	35.0	17.5	202.10	0.00	0.00	2.50	0.50	22.40	0.00	1.40	7.97	7.80	20.2	19.9
5-Nov-02	35.0	17.5												
6-Nov-02	35.0	17.5	203.50	0.00	3.00	2.00	0.20	22.30	0.00	1.00	7.89	7.70	20.0	21.0
7-Nov-02	35.0	17.5												
8-Nov-02	35.0	17.5	192.20	0.00	1.00	1.00	0.50	25.00	0.00	0.50	7.75	7.70	20.5	20.4
11-Nov-02	75.0	0.0	201.10	0.00	0.00	20.60	0.50	2.30	0.00	6.50	7.80	7.80	21.5	21.8
12-Nov-02	75.0	0.0												
13-Nov-02	75.0	0.0	200.40	0.00	0.00	19.90	0.10	3.20	0.00	5.70	7.71	7.83	22.2	22.2
14-Nov-02	75.0	0.0												
15-Nov-02	75.0	0.0	199.20	0.00	1.00	21.80	0.10	3.50	0.00	6.10	7.74	7.67	21.2	21.0
18-Nov-02	50.0	25.0	205.60	0.00	2.00	6.00	0.50	10.00	0.00	12.00	7.80	7.67	20.2	20.2
19-Nov-02	50.0	25.0												
20-Nov-02	50.0	25.0	197.80	0.00	0.00	6.00	0.00	10.70	0.10	7.30	7.80	7.70	20.0	19.5
21-Nov-02	50.0	25.0												
22-Nov-02	50.0	25.0	203.10	0.00	1.00	7.20	0.10	8.50	0.00	8.90	7.90	7.90	18.5	18.0
25-Nov-02	50.0	25.0												

Appendix B

Biological experiments: Data from Column B

TF Overall Data	Feed Flow Rate (mL/min)	Recycle Flow Rate (mL/min)	SCN (mg/L)		Hach NH ₃ -N (mg/L)		Hach NO ₃ -N (mg/L)		Hach NO ₂ -N (mg/L)		pH		Temperature (°C)	
			Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Feed pH	Effluent	Feed	Effluent
25-Jul-02	15.0	15.0	192.30		2.60		0.30		0.10		8.08		26.3	
26-Jul-02	15.0	15.0												
29-Jul-02	15.0	15.0	178.00		2.00		0.40		0.10		8.04		26.7	
30-Jul-02	15.0	15.0												
31-Jul-02	15.0	15.0	194.80		0.00		0.10		0.30		8.08		27.2	
1-Aug-02	15.0	15.0												
2-Aug-02	15.0	15.0	201.50		1.00		0.20		0.00		8.10		27.0	
5-Aug-02	15.0	15.0												
6-Aug-02	15.0	15.0	215.30		2.00		0.50		0.00		8.01		26.6	
7-Aug-02	15.0	15.0												
8-Aug-02	15.0	15.0	204.70		1.00		0.10		0.10		8.00		25.7	
9-Aug-02	15.0	15.0												
12-Aug-02	15.0	15.0	202.30		1.00		0.20		0.10		8.10		26.8	
13-Aug-02	15.0	15.0	207.90		1.00		0.00		0.00		8.06		27.2	
14-Aug-02	15.0	15.0												
15-Aug-02	15.0	15.0	203.20		2.00		0.60		0.20		8.11		28.2	
16-Aug-02	15.0	15.0												
19-Aug-02	15.0	15.0												
20-Aug-02	15.0	15.0	210.30	0.00	2.00	26.00	0.30	5.90	0.00	11.60	7.95	8.10	26.4	26.6
21-Aug-02	15.0	15.0												
22-Aug-02	15.0	15.0	190.60	0.00	3.00	25.80	0.20	6.80	0.20	11.00	7.90	8.03	25.8	25.6
23-Aug-02	15.0	15.0												
26-Aug-02	15.0	15.0	219.30	0.00	2.00	23.00	0.00	8.20	0.10	10.00	7.88	7.92	24.1	23.7
27-Aug-02	15.0	15.0												
28-Aug-02	15.0	15.0	208.70	0.00	2.00	19.80	0.30	8.80	0.10	12.20	8.01	8.10	24.0	24.6
29-Aug-02	15.0	15.0												
30-Aug-02	15.0	15.0	214.50	150.00	1.00	8.00	0.10	1.00	0.20	5.00	8.09	8.02	25.1	24.3
2-Sep-02	15.0	15.0												
3-Sep-02	15.0	15.0												
4-Sep-02	15.0	15.0	228.90	0.00	3.00	10.00	0.00	25.00	0.10	4.50	7.83	7.62	25.0	25.0
5-Sep-02	15.0	15.0												
6-Sep-02	15.0	15.0												
9-Sep-02	15.0	15.0	196.50	0.00	1.00	4.00	0.10	25.60	0.00	0.90	8.07	7.80	25.1	26.4
10-Sep-02	25.0	12.5												
11-Sep-02	25.0	12.5	198.10	0.00	2.00	6.00	0.20	16.60	0.00	7.40	8.00	7.84	25.2	24.4
12-Sep-02	25.0	12.5												
13-Sep-02	25.0	12.5	208.30	0.00	2.00	7.60	0.10	16.20	0.00	10.00	7.95	7.57	23.6	23.5
16-Sep-02	25.0	12.5	201.20	0.00	1.00	8.00	0.10	18.20	0.00	9.70	7.91	7.61	23.3	22.7
17-Sep-02	25.0	12.5												
18-Sep-02	25.0	12.5	203.70	0.00	1.00	6.60	0.20	19.50	0.00	7.80	7.99	7.50	23.3	22.9
19-Sep-02	25.0	12.5												
20-Sep-02	25.0	12.5	210.60	0.00	3.00	5.90	0.10	19.00	0.10	7.80	8.02	7.62	23.5	23.0
23-Sep-02	25.0	12.5	200.60	0.00	1.00	3.00	0.30	22.60	0.00	7.00	7.96	7.52	23.1	23.1
24-Sep-02	25.0	12.5												
25-Sep-02	25.0	12.5	196.30	0.00	0.00	1.00	0.50	24.30	0.00	5.10	8.00	7.51	23.2	22.7
26-Sep-02	25.0	12.5												
27-Sep-02	25.0	12.5												
30-Sep-02	25.0	12.5	193.20	0.00	0.00	2.00	0.10	28.30	0.00	0.30	8.06	7.67	21.1	20.5
1-Oct-02	35.0	17.5												
2-Oct-02	35.0	17.5	205.30	0.00	0.00	17.60	0.10	15.60	0.10	3.10	8.02	7.60	21.2	20.6
3-Oct-02	35.0	17.5												
4-Oct-02	35.0	17.5	203.20	0.00	0.00	18.30	0.20	14.00	0.00	3.00	7.70	7.55	20.7	20.1
7-Oct-02	35.0	17.5	201.50	0.00	1.00	18.00	0.00	14.70	0.00	2.00	7.64	7.53	20.8	20.0
8-Oct-02	35.0	17.5												
9-Oct-02	35.0	17.5	207.80	0.00	1.00	16.00	0.10	15.90	0.00	1.00	7.62	7.50	21.6	21.6
10-Oct-02	35.0	17.5												
11-Oct-02	35.0	17.5	197.60	0.00	0.00	14.50	0.00	18.00	0.00	1.90	7.60	7.51	21.5	21.6
14-Oct-02	35.0	17.5												
15-Oct-02	35.0	17.5												
16-Oct-02	35.0	17.5	205.60	0.00	1.00	14.50	0.10	17.00	0.10	2.50	7.60	7.50	21.3	21.7
17-Oct-02	35.0	17.5												
18-Oct-02	35.0	17.5	202.30	0.00	1.00	14.00	0.10	17.70	0.00	3.50	7.68	7.38	22.5	22.4

21-Oct-02	35.0	0.0												
22-Oct-02	50.0	0.0												
23-Oct-02	50.0	0.0	208.60	2.10	1.00	34.00	0.00	4.40	0.00	0.50	7.37	7.50	22.0	20.9
24-Oct-02	50.0	0.0												
25-Oct-02	50.0	0.0	203.30	0.00	1.00	38.00	0.10	5.80	0.00	1.60	7.69	7.68	20.9	21.2
28-Oct-02	50.0	25.0	197.80	0.00	1.00	25.00	0.10	10.90	0.00	1.50	7.60	7.53	21.0	20.6
29-Oct-02	50.0	25.0												
30-Oct-02	50.0	25.0	204.30	0.00	0.00	20.00	0.30	12.20	0.00	0.50	7.70	7.54	20.0	21.0
31-Oct-02	15.0	15.0												
1-Nov-02	15.0	15.0												
4-Nov-02	15.0	15.0	199.80	0.00	2.00	8.00	0.60	31.40	0.00	0.50	7.75	7.50	9.1	9.5
5-Nov-02	15.0	15.0												
6-Nov-02	15.0	15.0	203.50	0.00	3.00	9.00	0.20	32.00	0.00	0.10	7.77	7.50	8.9	9.3
7-Nov-02	15.0	15.0												
8-Nov-02	15.0	15.0	192.20	0.00	1.00	10.00	0.50	31.80	0.00	0.00	7.75	7.48	9.0	9.1
11-Nov-02	15.0	15.0												
12-Nov-02	30.0	0.0												
13-Nov-02	30.0	0.0	197.80	0.00	1.00	22.00	0.50	19.40	0.00	0.20	7.65	7.46	8.9	9.2
14-Nov-02	30.0	0.0												
15-Nov-02	30.0	15.0	200.80	0.00	2.00	21.60	0.10	16.80	0.10	0.00	7.70	7.48	9.0	9.5
18-Nov-02	30.0	15.0	192.30	0.00	1.00	22.30	0.10	16.00	0.00	0.00	7.67	7.50	8.9	9.0
19-Nov-02	30.0	15.0												
20-Nov-02	30.0	15.0	201.10	0.00	1.00	24.00	0.10	18.10	0.00	0.00	7.72	7.52	9.0	9.3
21-Nov-02	30.0	15.0												
22-Nov-02	30.0	30.0	203.10	4.50	1.00	16.00	0.10	18.30	0.00	0.00	7.77	7.58	9.0	9.0
25-Nov-02	30.0	30.0	201.30	3.90	1.00	25.00	0.00	16.10	0.00	0.00	7.60	7.53	9.0	9.2
26-Nov-02	30.0	30.0												
27-Nov-02	30.0	30.0	205.10	2.30	2.00	25.00	0.20	15.60	0.00	0.00	7.52	7.48	9.1	9.1
28-Nov-02	30.0	30.0												
29-Nov-02	30.0	30.0	200.30	0.00	1.00	26.00	0.00	16.40	0.00	0.00	7.62	7.50	9.0	9.1
2-Dec-02	30.0	45.0												
3-Dec-02	30.0	45.0	196.60	0.00	2.00	30.00	0.10	13.30	0.00	0.00	7.56	7.48	9.0	9.2
4-Dec-02	30.0	45.0												
5-Dec-02	30.0	45.0	198.90	0.00	2.00	28.60	0.10	14.50	0.00	0.00	7.60	7.46	9.0	9.0
6-Dec-02	30.0	45.0												
9-Dec-02	30.0	45.0	195.60	0.00	2.00	28.10	0.10	16.10	0.00	0.00	7.70	7.52	9.1	9.2
10-Dec-02	30.0	45.0												
11-Dec-02	20.0	20.0	203.30	0.00	1.00	12.00	0.10	26.80	0.00	0.00	7.60	7.50	9.0	9.1
12-Dec-02	20.0	20.0												
13-Dec-02	20.0	20.0	201.30	0.00	1.00	10.00	0.00	29.50	0.10	0.00	7.56	7.52	9.0	9.1
16-Dec-02	20.0	20.0												
17-Dec-02	20.0	30.0	206.90	0.00	1.00	9.00	0.00	30.20	0.00	0.00	7.55	7.50	9.1	9.1
18-Dec-02	20.0	30.0												
19-Dec-02	20.0	30.0	202.10	0.00	2.00	8.00	0.00	31.00	0.00	0.00	7.60	7.48	9.0	9.1
20-Dec-02	15.0	30.0												
23-Dec-02	15.0	30.0	198.70	0.00	2.00	3.00	0.10	32.80	0.00	0.10	7.66	7.50	8.9	9.0
24-Dec-02	15.0	30.0												
27-Dec-02	15.0	30.0	201.30	0.00	1.00	2.00	0.00	33.30	0.00	0.00	7.60	7.55	9.1	9.0
30-Dec-02	15.0	30.0	204.40	0.00	1.00	2.00	0.10	33.10	0.00	0.00	7.70	7.48	8.9	9.1
31-Dec-02	15.0	30.0												

Appendix C

Direct Photolysis of Thiocyanate: Batch Reaction Data

Run: TC-BUV-1 (100ppm SCN, pH 8)

[1] 30 L tap water added with NaSCN

[2] No pH value adjusted

Time (min)	Temp.(°C)	pH	SCN (mM)	CNO (mM)	NH3-N (mM)	NO2-N (mM)	NO3-N (mM)	SCN Removal (%)
0	26/20	7.85	1.78	<0.119	0.14	0.00	0.00	0.00
60	33/30	6.74	1.50	<0.119	0.07	0.00	0.00	16.12
120	34/32	6.72	1.27	<0.119	0.14	0.00	0.00	28.86
180	34/30	6.27	1.07	<0.119	0.14	0.00	0.00	39.77

Run: TC-BUV-2 (150ppm SCN, pH 8)

[1] 30 L tap water added with NaSCN, pH value 7.71 after NaSCN added

[2] No pH value adjusted

Time (min)	Temp.(°C)	pH	SCN (mM)	CNO (mM)	NH3-N (mM)	NO2-N (mM)	NO3-N (mM)	SCN Removal (%)
0	24/20	7.70	2.83	<0.119	0.00	0.00	0.70	0.00
60	31/28	7.00	2.24	<0.119	0.00	0.00	0.00	20.75
120	34/31	6.76	1.96	<0.119	0.00	0.00	0.50	30.61
180	34/30	6.50	1.82	<0.119	0.00	0.00	0.50	35.48

Run: TC-BUV-3 (200ppm SCN, pH 8)

[1] 30 L tap water added with NaSCN

[2] No pH value adjusted

Time (min)	Temp.(°C)	pH	SCN (mM)	CNO (mM)	NH3-N (mM)	NO2-N (mM)	NO3-N (mM)	SCN Removal (%)
0	28/20	7.90	3.26	<0.119	0.07	0.00	0.00	0.00
60	34/32	5.41	2.76	<0.119	0.00	0.00	0.00	15.40
120	36/31	5.58	2.62	<0.119	0.00	0.00	0.00	19.67
180	36/30	5.40	2.35	<0.119	0.07	0.00	0.00	27.90

Run: TC-BUV-4 (400ppm SCN, pH 8)

[1] 25 L tap water added with NaSCN, pH after all chemicals added: 9.2

[2] Adjust pH value to 8 by using H2SO4, NaOH

Time (min)	Temp.(°C)	pH	SCN (mM)	CNO (mM)	NH3-N (mM)	NO2-N (mM)	NO3-N (mM)	SCN Removal (%)
0	28/20	8.20	6.82	<0.119	0.00	0.10	0.00	0.00
60	34/30	7.12	6.63	<0.119	0.64	0.50	0.00	2.78
120	34/30	6.29	5.92	<0.119	0.14	1.10	0.00	13.13
180	34/30	6.79	5.10	<0.119	0.14	1.00	0.00	25.25

Run: TC-BUV-5 (800ppm SCN, pH 8)

[1] 25 L tap water added with NaSCN

Time (min)	Temp.(°C)	pH	SCN (mM)	CNO (mM)	NH3-N (mM)	NO2-N (mM)	NO3-N (mM)	SCN Removal (%)
0	30/22	8.10	13.23	<0.119	0.21	0.00	0.00	0.00
60	36/36	7.20	12.26	<0.119	0.00	0.00	0.00	7.30
120	39/40	6.10	11.44	<0.119	0.07	0.00	0.00	13.54
180	41/40	6.80	10.50	<0.119	0.14	0.00	0.00	20.59

Run: TC-BUV-6 (100ppm SCN, pH 10)

[1] 30 L tap water added with NaSCN

[2] Adjust pH value with NaOH

Time (min)	Temp.(°C)	pH	SCN (mM)	CNO (mM)	NH3-N (mM)	NO2-N (mM)	NO3-N (mM)	SCN Removal (%)
0	20/20	9.94	1.94	<0.119	0.07	0.00	0.00	0.00
60	30/25	9.00	1.65	<0.119	0.00	0.00	0.00	14.84
120	30/25	8.31	1.38	<0.119	0.07	0.00	0.00	28.80
180	30/25	7.86	1.20	<0.119	0.00	0.00	0.00	37.96

Run: TC-BUV-7 (150ppm SCN, pH 10)

[1] 30 L tap water added with NaSCN

[2] Adjust pH value adjusted with NaOH

Time (min)	Temp.(°C)	pH	SCN (mM)	CNO (mM)	NH3-N (mM)	NO2-N (mM)	NO3-N (mM)	SCN Removal (%)
0	24/20	9.90	2.46	<0.119	0.00	0.00	0.00	0.00
60	31/28	8.66	2.14	<0.119	0.00	0.00	0.00	12.64
120	31/31	8.43	2.00	<0.119	0.00	0.00	0.00	18.72
180	31/30	8.11	1.71	<0.119	0.00	0.00	0.00	30.50

Run: TC-BUV-8 (200ppm SCN, pH 10)

[1] 30 L tap water added with NaSCN, pH value 7.93 after all chemicals added

[2] Adjust pH value with NaOH

Time (min)	Temp.(°C)	pH	SCN (mM)	CNO (mM)	NH3-N (mM)	NO2-N (mM)	NO3-N (mM)	SCN Removal (%)
0	20/20	9.70	3.40	<0.119	0.21	0.00	0.00	0.00
60	28/26	8.67	3.14	<0.119	0.14	0.00	0.00	7.65
120	30/28	8.25	2.88	<0.119	0.07	0.00	0.00	15.19
180	29/30	8.09	2.60	<0.119	0.14	0.00	0.00	23.39

Run: TC-BUV-9 (400ppm SCN, pH 10)

[1] 25 L tap water added with NaSCN

[2] Adjust pH value to 10 by using NaOH

Time (min)	Temp.(°C)	pH	SCN (mM)	CNO (mM)	NH3- N (mM)	NO2- N (mM)	NO3- N (mM)	SCN Removal (%)
0	30/22	10.03	6.86	<0.119	0.00	0.00	0.20	0.00
60	38/37	9.03	6.45	<0.119	0.00	0.00	0.00	6.05
120	39/40	9.05	6.09	<0.119	0.07	0.00	0.00	11.24
180	39/40	8.75	5.81	<0.119	0.00	0.00	0.00	15.30

Run: TC-BUV-10 (800ppm SCN, pH 10)

[1] 25 L tap water added with NaSCN

[2] Adjust pH value to 10 by using NaOH

Time (min)	Temp.(°C)	pH	SCN (mM)	CNO (mM)	NH3- N (mM)	NO2- N (mM)	NO3- N (mM)	SCN Removal (%)
0	30/22	9.89	13.23	<0.119	0.21	0.00	0.00	0.00
60	36/36	9.12	12.43	<0.119	0.00	0.00	0.00	6.00
120	39/40	9.00	11.95	<0.119	0.07	0.00	0.00	9.63
180	41/40	8.54	11.43	<0.119	0.14	0.00	0.00	13.56

Appendix D

Advanced Photo-oxidation of Thiocyanate: Batch Reaction Data

Run: TC-BUVHP-1

[1] 25 L tap water added 200ppm CNS as NaSCN

[2] 1:1 mole Ratio H₂O₂ added one shot at time 0

[3] Adjust pH value with NaOH

Time (min)	Temp. (°C)	pH	SCN (mM)	CN (mM)	CNO (mM)	SO ₄ (mM)	SCN Removal (%)
0	21/20	10.17	3.51	0.00	0.00	0.25	0.00
60	26/20	5.61	1.78				49.41
120	26/20	5.82	1.00				71.62
180	26/20	4.93	0.38	1.92	0.31	2.89	89.22
240	26/20	4.01	0.06				96.40
300	26/20	3.61	0.00	3.73	0.12	3.20	100.00

Run: TC-BUVHP-2

[1] 25 L tap water added 200ppm CNS as NaSCN

[2] 1:1 mole Ratio H₂O₂ added one shot at time 0, first 3 hours, no UV.

[3] Adjust pH value with NaOH

Time (min)	Temp. (°C)	pH	SCN (mM)	CN (mM)	CNO (mM)	SO ₄ (mM)	SCN Removal (%)
0	20/20	10.09	3.37	0.00	0.00		0.00
60	22/20	9.80	3.31				1.89
120	24/20	9.68	3.31				2.04
180	24/20	9.60	3.20	0.46	0.12		5.10
240	23/20	5.30	2.08				37.08
300	23/20	5.50	1.29	2.27	0.24		60.94

Run: TC-BUVHP-3

[1] 25 L tap water added 200ppm CNS as NaSCN

[2] 1:1 mole Ratio H₂O₂ added stepwise, every 1 hour adding 1/5, before that, adjust pH back to 10

[3] Adjust pH value with NaOH

Time (min)	Temp. (°C)	pH	SCN (mM)	CN (mM)	CNO (mM)	SO ₄ (mM)	SCN Removal (%)
0	18/20	9.99	3.22	0.00	0.00	0.30	0.00
60	22/20	6.59	2.58				19.79
120	21/20	7.06	2.17				32.46
180	21/20	8.60	1.82	0.77	0.67	1.56	43.32
240	21/20	8.85	1.48				54.01
300	21/20	9.10	1.21	0.65	1.21	2.14	62.57

Run: TC-BUVHP-4

- [1] 25 L tap water added 150ppm CNS as NaSCN
- [2] 2:1 mole Ratio H₂O₂ added 1 shot at time 0
- [3] After NaSCN added, pH 9.10, Adjust pH to 10 with NaOH

Time (min)	Temp. (°C)	pH	SCN (mM)	CN (mM)	CNO (mM)	SO ₄ (mM)	SCN Removal (%)
0	22	9.98	2.50	0.00	0.00	0.40	0.00
60	22	3.50					
120	22	3.43					
180	20	3.32	0.14	1.92	0.12	3.34	94.48
240	20	3.33					
300	20	3.38	0.00	1.69	0.12	2.89	100.00

Run: TC-BUVHP-5

[1] 25 L tap water added 200ppm CNS as NaSCN

[2] 1:1 mole Ratio H₂O₂ added 1 shot at time 0

[3] During the whole experiment, always keep pH above 10 with NaOH

Time (min)	Temp. (°C)	pH	SCN (mM)	CN (mM)	CNO (mM)	SO ₄ (mM)	SCN Removal (%)
0	21	10.13	3.48	0.00	0.00	0.32	0.00
60	21	9.97	1.93	0.61	0.90		
120	21	10.45	1.81	0.69	0.98		
180	21	10.23	1.70	0.77	1.02	1.81	50.99

Run: TC-BUVHP-6

[1] 25 L tap water added 200ppm CNS as NaSCN

[2] 2:1 mole Ratio H₂O₂ added 1 shot at time 0

[3] During the whole experiment, always keep pH above 10 with NaOH

Time (min)	Temp. (°C)	pH	SCN (mM)	CN (mM)	CNO (mM)	SO ₄ (mM)	SCN Removal (%)
0	21	11.03	3.44	0.00	0.00	0.25	0.00
60	22	10.98	1.17	0.69	1.02	2.43	
120	22	11.10	1.14	0.69	1.09	2.51	
180	22	10.96	1.05	0.69	1.19	2.69	69.50

Run: TC-BUVHP-7

- [1] 25 L tap water added 200ppm CNS as NaSCN
- [2] 2:1 mole Ratio H₂O₂ added stepwise (at time 0, 60, 120 added 1/3 every time)
- [3] During the whole experiment, always keep pH above 10 with NaOH

Time (min)	Temp. (°C)	pH	SCN (mM)	CN (mM)	CNO (mM)	SO ₄ (mM)	SCN Removal (%)
0	17	10.62	3.46	0.08	0.00	0.27	0.00
60	22	10.49	2.39	0.73	0.50	1.44	
120	21	10.50	1.50	0.77	1.21	2.07	
180	21	10.48	0.50	0.35	2.17	3.05	85.57

Run: TC-BUVHP-8

[1] 25 L tap water added 150ppm CNS as NaSCN

[2] 2:1 mole Ratio H₂O₂ added 2 shots, 1st at time 0, then first 3h, there is no pH control, 2nd shot at time 180, before that, bring pH back to 10.5 and keep it always there

Time (min)	Temp. (°C)	pH	SCN (mM)	CN (mM)	CNO (mM)	SO ₄ (mM)	SCN Removal (%)
0	17	8.36	3.43	0.31	0.00	0.26	0.00
60	18						
120	18						
180	18	5.83	0.79	2.04	0.14	1.82	76.88
240	18	10.23	0.77	0.58	1.78	2.69	
300	18	10.55	0.62	0.42	1.98	2.90	81.91

Run: TC-BUVHP-9

[1] 25 L tap water added 150ppm CNS as NaSCN

[2] 3:1 mole Ratio H₂O₂ added 2 shots, 1st shot (1:1) at time 0, then first 3h, there is no pH control, 2nd shot (2:1) at time 180, before that, bring pH back to 10.5 and keep it always there

Time (min)	Temp. (°C)	pH	SCN (mM)	CN (mM)	CNO (mM)	SO ₄ (mM)	SCN Removal (%)
0	14	8.30	3.37	0.31	0.00	0.23	0.00
60	18	4.65	2.31	1.15			
120	19	5.30	1.46	1.88			
180	19	5.20	0.84	2.27	0.14	1.69	75.00
240	17	10.20	0.24	0.27	2.52	3.02	
300	18	10.30	0.00	0.00	2.55	3.25	100.00

Run: TC-BUVHP-10

[1] 25 L tap water added 200ppm CNS as NaSCN

[2] 1:1 mole Ratio H₂O₂ diluted to 500ml and put in reactor though first 2h continuously at a small flowrate.

[3] During the whole experiment, always keep pH above 10 with NaOH

Time (min)	Temp. (°C)	pH	SCN (mM)	CN (mM)	CNO (mM)	SO ₄ (mM)	SCN Removal (%)
0	13	10.57	3.51	0.35	0.00	0.27	0.00
60	17	10.33	2.62	0.58	0.36		
120	18	10.00	1.88	0.73	0.83		
180	18	10.30	1.58	0.81	1.00	1.99	54.90

TC-BUVHP-11

[1] 25 L tap water added 200ppm CNS as NaSCN

[2] 6:1 mole Ratio H₂O₂ added stepwise (Time 0 to 480, every time adding 1/9 amount of total H₂O₂).

[3] Adjust pH value with NaOH (maintained between 10-10.5); after time 180, no pH control.

Time (min)	Temp. (°C)	pH	SCN (mM)	CN (mM)	CNO (mM)	SO ₄ (mM)	NH ₃ (mM)	NO ₂ (mM)	NO ₃ (mM)	Total N (mM)
0	23	10.30	3.53	0.00	0.05	0.26				3.58
60	19	10.30	2.46	0.61	0.50					3.58
120	18	10.20	1.55	0.50	1.26					3.31
180	18	10.20	0.81	0.12	2.05	2.86	0.00	0.00	0.00	2.97
240	17	7.28	0.19	0.00	2.62		0.32	0.03	0.08	3.24
300	18	6.91	0.03	0.00	2.28		0.36	0.12	0.30	3.10
360	18	6.86	0.03	0.00	1.62	3.59	0.59	0.07	0.67	2.99
420	19	7.00	0.09	0.00	1.07		0.68	0.11	1.04	2.99
480	17	7.00	0.03	0.00	0.59		0.71	0.08	1.36	2.78
540	18	7.00	0.03	0.00	0.31	3.56	0.82	0.10	1.55	2.82

Appendix E

Details of Chemical Analyses

Spectrophotometer DR/2010 and Colorimeter DR890 from HACH were used from chemical analyses in this study. The analytical methods following standard protocols described in the literature are outlined as follows.

Thiocyanate

A colorimetric method was used to measure thiocyanate concentration in the samples. Thiocyanate reacts with ferric ion under acidic conditions to form ferric thiocyanate, which has an intense red color. The intensity of color of the ferric thiocyanate formed is proportional to the concentration of thiocyanate ion in the sample. A spectrophotometer DR/2010 from HACH was used to measure the absorbance of the sample at 460 nm. The concentration of thiocyanate is determined from a standard calibration curve. Usually the detection range of this method is 0.1 to 2.0 mg SCN⁻/L. For higher concentrations, the sample should be diluted (Patnaik, 1997).

Interferences:

Hexavalent chromium (Cr⁶⁺) interferes with the test and is reduced to Cr³⁺ by adding ferrous sulfate (FeSO₄) after adjusting pH below 2 with nitric acid (HNO₃). Raising the pH to 9 with 1N sodium hydroxide (NaOH) precipitates Fe³⁺ and Cr³⁺, which are then filtered out. Substances that reduce Fe³⁺ to Fe²⁺ and thus prevent formation of ferric thiocyanate complex, may be destroyed by adding a few drops of hydrogen peroxide. If a sample contains color or various interfering organic compounds, sample pretreatment is necessary. A macroreticular resin can be used to remove these interfering

materials by adsorption without affecting thiocyanate. Sulfide interferes by converting cyanide to thiocyanate, and it is necessary to precipitate the sulfide by adding lead salts. Thiocyanate is biodegradable, if immediate analysis can not be done, preserve samples at pH below 2 by adding HNO_3 and refrigerate at 4°C (Patnaik, 1997).

Apparatus:

(1). Spectrophotometer DR/2010 from HACH, for use at 460 nm, providing a light path of 5 cm.

(2). Glass adsorption column: two 10 mL cells coming with the DR/2010 above were used for absorbance determination.

Reagents:

(1). Ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) solution 1M: Dissolve 404 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 800 ml distilled water, add 80 ml conc. HNO_3 and dilute to 1 L.

(2). Stock thiocyanate solution: Dissolve 1.673 g potassium thiocyanate (KSCN) in distilled water and dilute to 1000 ml; 100 ml = 1.00 mg SCN^- .

(3). Standard thiocyanate solution: Dilute 1 ml stock solution to 100 ml with distilled water; 1.00 ml = 0.01 mg SCN^- .

(4). Nitric acid solution, 0.1N: Mix 6.4 ml conc. HNO_3 in 800 ml distilled water and dilute to 1L.

Procedure:

Prepare a calibration curve by plotting mg/L SCN^- vs. absorbance by using a series of standard thiocyanate solution from 0.1 mg/L to 10 mg/L. The absorbance plot should be linear.

Use a pretreated and diluted sample which is free of color and other interfering materials, add a few drops of conc. HNO_3 to adjust the pH to 2, pipet 10 ml portion to a beaker, add 0.5 ml ferric nitrate and mix. Fill a 10 ml absorption cell and measure absorbance against a reagent blank at 460 nm within 5 min from adding the reagent, because the color develops within 30 s and fades out in light.

Calculation:

The thiocyanate concentration is calculated by using the equation below:

$$\text{SCN}^- (\text{mg} / \text{L}) = \frac{y-b}{m} \times \text{dilution factor}$$

where:

y = absorbance of sample solution

b = intercept of standard curve, which is equal to 0.0034 in this case

m = slope of standard curve, which is equal to 0.161 in this case

Cyanate

Under acidic conditions, cyanate can be converted to an ammonium salt, the concentration of ammonia minus nitrogen before and after acid hydrolysis is measured and the cyanate concentration is equivalent to this difference (Patnaik, 1997).

Interferences:

Oxidizing agents such as chlorine may interfere and can be removed by Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$). Complex metal ions which may react with Nessler reagent to form colored complexes, they can be eliminated by EDTA.

Reagents:

(1). Sulphuric Acid (H_2SO_4), 5 N.

Sampling and Storage:

Collect samples in glass or plastic bottles and analyze as soon as possible. The presence of oxidizing agents such as chlorine, fatty acids and sulfides can cause cyanate loss during storage, pretreatment is needed to remove those materials before preservation with sodium hydroxide. Samples adjusted to pH 12 with 5.0 N NaOH and kept in the fridge at 4 °C can be stored for 14 days.

Procedure:

H₂SO₄ is added to a 100 mL portion of sample acidifying between pH 2 and 2.5. Heat the solution to boiling for 30 min. Cool to room temperature and bring up to the original volume by adding NH₃-free distilled water. The measurement for NH₃-N is carried out by colorimeter DR890, which will be detailed in the following section. Compare the ammonia nitrogen concentration between the treated sample and untreated original sample. The difference is equivalent to the cyanate concentration in the sample (Patnaik, 1997).

Ammonia Nitrogen

The Salicylate method was used to measure the ammonia nitrogen in the samples. Ammonia compounds react with chlorine to form monochloramine, which reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue-colored compound. The blue color is masked by the yellow color from the excess reagent present to give a final green-colored solution. The intensity of the color is proportional to the concentration of ammonia nitrogen in the sample. A DR890 colorimeter was used to measure the NH₃-N

concentration. Usually the detection range of this method is 0 to 0.50 mg NH₃-N/L. For higher concentrations, the sample is diluted (Hach Company, 1999).

Interferences:

Turbidity and color interfere with the test and give erroneous high values, pretreatments such as distillation and filtration are needed to eliminate the interference. Sulfide interferes positively with the analysis. Sulfide interference can be eliminated by adding the contents of one sulfide Inhibitor Reagent Powder Pillow and then filtering it through a folded filter paper. Iron may interfere at all levels and the interference should be corrected: confirm the amount of total iron in the sample, measure the iron interference by using the same amount of iron dissolved in deionized water, subtract the value from result obtained on the original sample.

Apparatus:

- (1). Colorimeter DR890 from HACH.
- (2). Sample cells 10-20-25 coming with the DR890

Reagents:

- (1). Ammonia Salicylate Reagent Powder Pillows
- (2). Ammonia Cyanurate Reagent Powder Pillows

Sampling and Storage:

Collect samples in glass or plastic bottles and analyze as soon as possible. The presence of oxidizing agents such as chlorine can cause ammonia loss during storage, the sample must be treated immediately with sodium thiosulfate. For each 0.3 mg of chlorine present in a one liter sample, one drop of Sodium Thiosulfate Standard Solution, 0.1 N is needed. Samples adjusted to pH 2 or less with conc. sulfuric acid (about 2 mL per liter)

and kept in the fridge at temperature 4 °C can be stored up to 28 days. Before testing, warm the sample to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution.

Procedure:

Fill a sample cell with 10 mL of deionized water (the blank), fill a second sample cell with 10 mL of the sample. Add the contents of one Ammonia Salicylate Reagent Powder Pillow to each sample cell, cap both cells and shake to dissolve, allow to react for 3 min. Add the contents of one Ammonia Cyanurate Reagent Powder Pillow to each sample cell, cap both cells and shake to dissolve, allow to react for 15 min (A green color will develop if ammonia nitrogen is present). After 15 min reaction, measure the ammonia nitrogen concentration of samples, first zero the DR890 with the blank, then measure the sample. Values are read as *mg/Ls* directly. The detection range is from 0 to 0.50 mg/L (Hach Company, 1999).

Nitrite Nitrogen

Diazotization method was used for the measurement of nitrite nitrogen concentration in the samples. Nitrite in the sample reacts with sulfanilic acid to form an intermediate diazonium salt. The diazonium salt reacts with chromotropic acid to produce a pink colored complex. The intensity of the color is proportional to the concentration of nitrite nitrogen in the sample. A colorimeter DR890 was used to measure the NO₂-N concentration. Usually the detection range of this method is 0 to 0.350 mg NO₂-N /L. For higher concentrations, use a diluted sample (Hach Company, 1999).

Interferences:

Turbidity and color interfere with the test and cause inaccuracy, pretreatment such as filtration is needed to eliminate interference before measuring. Strong oxidizing and reducing agents, nitrate, ferric ions, cupric ions, and lead ions interfere and should be removed before analysis.

Apparatus:

- (1). Colorimeter DR890 from HACH.
- (2). Sample cells 10-20-25 coming with the DR890

Reagents:

- (1). NitriVer 3 Nitrite Reagent Powder Pillows

Sampling and Storage:

Collect samples in glass or plastic bottles and analyze as soon as possible. Samples stored at 4 °C or lower should be measured within 48 hours. Warm the sample to room temperature before analysis. Acid preservatives are not suitable. Remove suspended solids by filtration.

Procedure:

Fill a sample cell with 10 mL of sample, add the contents of one NitriVer 3 Nitrite Reagent Powder Pillow to the cell, cap it and shake to dissolve the reagent, and allow 15 minutes to react (A pink color will develop if nitrite is present). Fill an empty sample cell with 10 mL of sample (the blank). After 15 min reaction, colorimeter DR890 was used to measure the nitrite nitrogen concentration of samples, first zero the DR890 with the blank, then measure the sample. Readings obtained from the DR890 are *mg/Ls* directly. The detection range is from 0 to 0.350 mg/L (Hach Company, 1999).

Nitrate Nitrogen

The chromotropic acid method was used for the measurement of nitrate nitrogen concentrations. Nitrate in the sample reacts with chromotropic acid under strongly acidic conditions to yield a yellow-colored product. The intensity of the color is proportional to the concentration of nitrate nitrogen in the sample. A colorimeter DR890 was used to measure the $\text{NO}_3\text{-N}$ concentration. Usually the detection range of this method is 0 to 30.0 mg $\text{NO}_3\text{-N}$ /L. For higher concentrations, use a portion of diluted sample (Hach Company, 1999).

Interferences:

Turbidity and color interfere with the test. Pretreatment such as filtration is needed to eliminate interference before measuring. Nitrite interferes when its concentration is greater than 12 mg/L. Remove nitrite interference up to 100 mg/L by adding 400 mg of urea to 10 mL of sample and swirl to dissolve. Copper causes a positive interference at all levels and barium causes a negative interference when its concentration is greater than 1 mg/L.

Apparatus:

- (1). Colorimeter DR890 from HACH.
- (2). Nitrate Pretreatment Solution Vials

Reagents:

- (1). NitriVer X Reagent B Powder Pillows

Sampling and Storage:

Collect samples in glass or plastic bottles and analyze as soon as possible. If the analysis is conducted within 24 to 48 hours, samples should be stored at 4 °C or lower.

Warm to room temperature before running the test. For long storage periods up to 14 days, adjust sample pH to 2 or less with sulfuric acid and store at 4 °C or lower. Before running the test, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution. Remove the suspended solids by filtration.

Procedure:

Add 1 mL of sample into a Nitrate Pretreatment Vial (the blank), cap it and invert 10 times to mix. Clean the outside of the vial with a towel, then zero the DR890 with the blank. Remove the vial from the instrument and remove the cap from the vial, add the contents of one NitroVer X Reagent B Powder Pillow to the vial, cap it and invert 10 times to mix (the prepared sample), give 5 min reaction time (A yellow color will develop if nitrate nitrogen is present). Clean the outside of the vial and place it into the DR890 to measure the sample. Readings obtained from the DR890 are read as *mg/Ls* directly. The detection range is from 0 to 30.0 mg/L (Hach Company, 1999).

Sulphate

The turbididimetric method was used for the measurement of sulphate concentration in the samples. Sulfate ions in the sample react with barium in the SulfaVer 4 Sulfate Reagent to form insoluble barium sulfate. The SulfaVer 4 also contains a stabilizing agent to hold the precipitate in suspension. The amount of turbidity formed is proportional to the sulfate concentration in the sample. A colorimeter DR890 was used to measure the SO_4 concentration. Usually the detection range of this method is 0 to 70.0 mg SO_4/L . For higher concentrations, use a portion of diluted sample (Hach Company, 1999).

Interferences:

Turbidity and color interfere with the test and cause inaccuracy, pretreatment such as filtration is needed to eliminate interference before measuring. Calcium ions, magnesium ions, chloride ions and silica present in high concentrations may interfere.

Apparatus:

- (1). Colorimeter DR890 from HACH.
- (2). Sample cells 10-20-25 coming with the DR890

Reagents:

- (1). SulfaVer 4 Sulfate Reagent Powder Pillows

Sampling and Storage:

Collect samples in glass or plastic bottles and analyze as soon as possible. Samples may be stored up to 28 days if kept in fridge at 4 °C or lower. Warm to room temperature before running the test.

Procedure:

Fill a clean sample cell with 10 mL of sample, add the contents of one SulfaVer 4 Sulfate Reagent Powder Pillow into the cell (the prepared sample). Cap the cell and invert several times to mix. (A white turbidity will develop if sulfate is present), allow 5 min reaction time and let the cell sit undisturbed. Fill a second sample cell with 10 mL of sample (the blank). Zero the DR890 with the blank, then measure the sulfate concentration of the prepared sample. Readings obtained from the DR890 are *mg/Ls* directly. The detection range is from 0 to 70.0 mg/L (Hach Company, 1999).

Hydrogen Peroxide

Iodometric titration method is applicable to samples containing hydrogen peroxide that are free from turbidity or low in color (Vogel, 1961). In this method, hydrogen peroxide reacts with iodide in acidic solution to form iodine and the iodine produced is titrated by sodium thiosulphate solution with starch as the end point indicator. Thiosulphate ($\text{S}_2\text{O}_3^{2-}$) is oxidized to tetrathionate ($\text{S}_4\text{O}_6^{2-}$) by iodine during the titration process (Yang, 1998).

Reagents:

(1) Potassium iodide, 20%: 100 g KI was dissolved in distilled water and diluted to 500 mL.

(2) Sodium thiosulphate solution, 0.1 N: 24.817 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ was dissolved in distilled water and diluted to 1000 mL, 0.05 g Na_2CO_3 was added as preservative.

(3) Potassium iodate solution, 20 mM: 4.2802 g KIO_3 was dissolved in distilled water and diluted to 1000 mL.

(4) Starch solution, 2%: 2 g starch was dissolved in 5 mL distilled water and put into 80 mL boiling water. The solution was kept boiling until it was finally clear, made the cooled solution up to 100 mL.

Procedure:

5 mL of 20% KI and 5 mL of 1 M H_2SO_4 were taken in a 125 mL Erlenmyer flask, and after adding 50 ml distilled water, an appropriate sample aliquot was added to the contents. After 15 min., the solution was titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. When the solution turned to a straw yellow color, 2 mL of 2% starch solution was added, and the titration continued until the solution turned to a colorless endpoint.

Standardization of 0.1 N Sodium thiosulphate:

1 mL of 20 mM KIO₃, 5 mL 1M H₂SO₄ and 50 mL distilled water were added in a 125 mL Erlenmyer flask. 5 mL 20% of KI was added in this flask and mixed completely. After 10 min., the solution was titrated with 0.1 N Na₂S₂O₃ according to the same procedure as that for determination of hydrogen peroxide.

Calculation:

The hydrogen peroxide concentration is calculated by using the equation below:

$$H_2O_2 (g/L) = N_1 \times V_1 \times N_{w_2} / V_2 = N_1 \times V_1 \times 17 / V_2$$

where:

V₁ = volume of standard Na₂S₂O₃ consumed (mL)

N₁ = normality of standard Na₂S₂O₃ used in this case, that is 0.1 N

N_{w₂} = equivalent weight of H₂O₂, it is equal to 17

V₂ = volume of sample containing H₂O₂ taken for titration (mL)

The normality of Na₂S₂O₃ is calculated based on the following equation:

$$N_{Na_2S_2O_3} = (N_3 \times V_3) / V_1 = 6M_3 \times V_3 / V_1 = 0.12 / V_1$$

where:

N₃ = normality of KIO₃, it is equal to 6×M₃ in this case

M₃ = molarity of standard KIO₃ (mol/L). It equals 20 mM in this case

V₃ = volume of standard KIO₃ used in this case, that equals 1 ml

V₁ = standard Na₂S₂O₃ consumed for titration (mL)

Cyanide

A colorimetric method (Pyridine-Pyrazalone Method) was used to measure the cyanide concentration in the samples. Cyanide is converted to cyanogen chloride (CNCl) by using

chloramine-T at pH below 8 without hydrolyzing to cyanate (CNO^-). When adding pyridine-pyrazolone reagent, cyanogen chloride reacts with pyridine to form an intermediate nitrile which subsequently hydrolyzes to glutaconaldehyde. The glutaconaldehyde produced reacts with pyrazolone to give a blue color, its intensity is proportional to the concentration of cyanide in the sample. Usually the detection range of this method is 0 to 0.240 mg CN^-/L . For higher concentrations, a portion of diluted sample is used (Patnaik, 1997).

Interferences:

High turbidity may interfere and cause high readings. If the water sample is turbid, it should be filtered before the measurement. Sulfide interferes by converting cyanide to thiocyanate, the sulfide is precipitated by adding lead acetate. Chlorine not only decomposes cyanides during storage but also causes a milky white precipitate after the addition of the CyaniVer 5 Reagent. Sodium Arsenite Solution was used to eliminate oxidizing agents such as chlorine, and bromine water was used to eliminate the interference of reducing agents. Nickel and cobalt interfere and can be quenched by HexaVer Chelating Reagent.

Apparatus:

- (1). Colorimeter DR890 from HACH.
- (2). Sample cells 10-20-25 coming with the DR890

Reagents:

- (1). CyaniVer 3 Cyanide Reagent Powder Pillows
- (2). CyaniVer 4 Cyanide Reagent Powder Pillows
- (3). CyaniVer 5 Cyanide Reagent Powder Pillows

Sampling and Storage:

The samples are collected in glass or plastic bottles and analyzed as soon as possible. The presence of oxidizing agents such as chlorine, fatty acids and sulfides can cause cyanide loss during storage. Pretreatment is needed to remove those materials before preservation with sodium hydroxide. Samples adjusted to pH 12 with 5.0 N NaOH and kept in the fridge at temperature 4 °C can be stored for 14 days. Before testing, preserved samples should be adjusted to approximately pH 7 with 2.5 N Hydrochloric Acid Standard Solution.

Procedure:

The sample cell is filled with 10 mL pretreated sample, the temperature of sample must be kept in the range 23-25 °C. The contents of one CyaniVer 3 Cyanide Reagent Powder Pillow are added to the cell and capped. The sample cell is shaken for 30 s and then let sit undisturbed for another 30 s. The contents of one CyaniVer 4 Cyanide Reagent Powder Pillow are added and capped, and the cell shaken for 10 s. After shaking, immediately, the contents of one CyaniVer 5 Cyanide Reagent Powder Pillow are added to the cell and capped. The cell is shaken vigorously to completely dissolve the CyaniVer 5 Cyanide Reagent Powder. If cyanide is present, a pink color will develop which then turns blue after a few minutes. The blank is made by filling another 10 mL sample cell with 10 mL of sample. After 30 min reaction, colorimeter DR890 was used to measure the cyanide concentration of samples. Readings got from the DR890 are in *mg/L* directly. The detection range is from 0 to 0.240 mg/L (Hach Company, 1999).