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ADVANCED PHOTO-OXIDATION PROCESS FOR AMMONIA REMOVAL FROM INDUSTRIAL WASTEWATER

by

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A thesis submitted to

the Faculty of Graduate Studies and Research

in partial fulfillment of the requirements for the degree of

Master of Engineering

Department of Civil and Environmental Engineering

Carleton University

Ottawa, Ontario, Canada

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**Advanced Photo-oxidation Process for Ammonia Removal
From Industrial Wastewater**

submitted by
XINHUA YANG, B.Eng.
in partial fulfillment of the requirements for the degree of
Master of Engineering

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ABSTRACT

An advanced photo-oxidation process (APP) for the removal of ammonia from industrial wastewater has been developed. Detailed investigations on the effect of operating parameters indicate that pH is the most important process parameter for the effective conversion or nitrification of ammonia. In the acidic range, irrespective of the oxidant used, the conversion of ammonia is not significant. While in the basic range, the reaction proceeds at a considerable rate. Therefore, it is concluded that unprotonated ammonia is the form most amenable for photo-oxidation. Besides the pH, the photo-oxidation of ammonia was also affected by UV dose, initial ammonia concentration and oxidant concentration.

A very significant result obtained in this study is the dramatic dependence of the product distribution on the type of the oxidant employed. In the case of UV/H₂O₂ oxidation process, nitrate is the predominant product, whereas, in the case of UV/K₂S₂O₈, nitrogen gas is the predominant product.

Reaction schemes are postulated to indicate the most probable mechanism for the overall photo-oxidation reactions. A competitive-consecutive reaction model is found to fit the data for the UV/H₂O₂ process, while a competitive-parallel reaction model fitted the UV/K₂S₂O₈ process well.

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GLOSSARY

1. APP: The advanced photo-oxidation process. the process involving the generation of highly reactive radicals by the photolysis of the oxidants and the subsequent photochemical oxidation reactions initiated by the radical attack.
2. Dissociation Energy: The energy required to break a bond, usually expressed in kcal/mole or kJ/mole.
3. Molar Extinction Coefficient (ϵ): Also called molar absorptivity ϵ ($M^{-1}.cm^{-1}$). It is defined as $\epsilon = A/cl$, where A is the absorbance of an absorbing species at a fixed wavelength, c is the molar concentration (M) of the absorbing species, l is the thickness (cm) of the layer for the beam of light to pass through.
4. Osmosis: Diffusion of a solvent through a semipermeable membrane into a more concentrated solution, tending to equalize the concentration on both sides of the membrane.
5. Oxidant: Also called oxidizing agent. Atom, ion, or molecule that takes up electrons in a reaction.
6. Quantum yield: The quantum yield for the primary process in the photolysis of a molecule M ($M + h\nu \rightarrow A + B$) is defined as the number of molecules of M that decompose divided by the number of photons absorbed by M, as determined in a fixed period of time.

7. Radicals: Reactive species with unpaired electrons. They can react with other species through 3 possible pathways: electron transfer, H atom abstraction and addition to multiple bonds.
8. Reducing agent: Atom, ion, or molecule that gives up electrons in a reaction.
9. Toxicity: The inherent potential or capacity of a material to cause adverse effects in a living organism.
10. UV Dose: A measure of the total UV lamp electrical energy applied to a fixed volume of water to be treated, usually measured in kWh/1000 US gallons or kWh/m³.
11. Zeolite: A natural hydrated silicate of aluminum and either sodium or calcium or both; or of an artificial ion-exchange resin. Both natural and artificial zeolites are used extensively for water softening and as detergent builders.

1. INTRODUCTION

1.1 General

At ambient temperature and pressure, ammonia (NH_3) is a colorless gas. It is very soluble in water, with a distinct pungent odor when the concentration exceeds 50 ppm. Its solubility is 90g /100 ml water at 0°C .

Ammonia is produced commercially by a catalyzed reaction between nitrogen and hydrogen. It is mainly used in the production of fertilizers, and it is also used in the manufacture of explosives, chemicals, plastic and synthetic fibers. Moreover, ammonia is used in refrigeration plants, pulp & paper, mining and petroleum refining industries.^[1]

Ammonia is present in most waters as a result of the biological degradation of nitrogenous organic substances which are from the biological wastes of plants and animals. It is also present in a limited number of foodstuff, such as cheeses, aged or stored meats and vegetables due to fermentation and autolytic deamination and deamidation.

Many of the industrial effluents containing ammonia are currently discharged into surface water streams, deep wells and unlined lagoons, from where it migrates into the ground water. In view of the potential negative impacts of ammonia and its by-products nitrite and nitrate on aquatic life and human health, it is currently recognized that destruction or conversion of ammonia to an

environmentally benign product - nitrogen gas may be necessary to mitigate its negative environmental impact.

There are quite a few technologies available for ammonia removal, some of which are currently in use in certain jurisdictions. Many of these technologies merely end up in transferring ammonia from one phase to another, with the result that it may be deposited elsewhere while it is removed from the treatment location. Such is the case with air stripping technology. Other technologies also have several drawbacks as will be detailed in the following chapter.

1.2 Objectives

For the reasons cited above, there is a need for developing an ammonia removal technology that can convert the ammonia to more environmentally benign products that can be discharged directly into the environment. Such a process should also preferably be efficient as well as economic. The objectives of this research are to develop an advanced photo-oxidation process (APP) for ammonia removal, determine the kinetics of the major photochemical reactions in the APP, investigate the most probable mechanism of the APP, study the effects of the various operating parameters, and establish the process feasibility.

1.3 Scope of Research

This research forms a part of the research proposed earlier^[2] for the development of a combined photolytic-biological process called Modified Advanced Photo-oxidation Process (MAP) for ammonia removal from industrial

wastewater as an improvement over the currently favored processes. The schematic for the MAP process is shown in Figure 1-1.

Figure 1-1. Schematic for Combined Photolytic Nitrification and Biological Denitrification (MAP Process)

The MAP flowsheet was based on the concept that the photo-oxidation of ammonia will yield a mixture of nitrate and nitrite, which will be subsequently denitrified in the denitrification column as shown in Figure 1-1. MAP process research, as proposed, consisted of two phases: phase I for photolytic nitrification and phase II for biological denitrification. Under phase I, the research was split into two parts. Part 1, which is the subject of this thesis, consisted of the

development of a new advanced photo-oxidation process and the determination of the reaction kinetics and the probable reaction mechanisms. Part 2 will focus on the photochemical reactor design and modeling.

This study which focused on the process feasibility, was conducted in a custom-modified RAYOX UV reactor (Figure 5-4). The research work included: assembling, commissioning and operation of RAYOX advanced oxidation system, development and study of the photochemical process with RAYOX UV reactor for ammonia removal, including selection of ammonia precursors and oxidants, direct photolysis of ammonia precursors, advanced photo-oxidation of precursors, study of the effect of the major process parameters and delineation of reaction kinetics and the probable reaction mechanisms. Experimental procedures, sampling procedures and chemical analyses protocols were also developed and standardized.

1.4 Organization of Thesis

The rest of the thesis consists of 6 chapters, each of which examines an aspect of the process development study for ammonia removal from industrial wastewater. Chapter 2 reviews the environmental impact, regulations and guidelines, available ammonia removal technologies and their limitations. Photolytic process for ammonia removal is described in chapter 3. Chapter 4 deals with the basic chemistry and photochemistry of the major nitrogen compounds and oxidants encountered in APP. Chapter 5 consists of the experimental section, including the process scheme, experimental procedures, and analyses protocols

Chapter 6 is on data interpretation and a discussion of the results. Finally, Chapter 7 presents the conclusions and recommendations.

2. BACKGROUND REVIEW

2.1 Environmental Impact of Ammonia

Ammonia is very soluble in water. When it is dissolved, it reacts with water and results in the following equilibrium with ammonium ion:

The concentration of NH_3 in aqueous solution is dependent primarily upon pH, temperature and total ammonia concentration ($\text{NH}_3 + \text{NH}_4^+$).

The corrosive alkali nature of ammonia is a hazard to human health. It is an irritant that most commonly affects the eyes, the skin, the mucous membrane of the upper respiratory tract and lungs. Chronic exposure to ammonia results in throat irritation, headache, hoarseness, cough, hemoptysis, nausea, nervousness, and loss of appetite. Acute exposure to ammonia results in laryngeal edema with asphyxia, pulmonary edema, and bronchopneumonia. When ingested, it has corrosive effect on the mouth, esophagus, and stomach. It also causes headache, insomnia, nausea and diarrhea.

Ammonia undergoes the natural nitrification process to form nitrite and nitrate. So it is considered as a potential source of nitrite and nitrate in aqueous systems. Nitrite could be harmful in humans. It can react with amides or amines to form N-nitroso compounds, some of which are potential carcinogens. Nitrate can cause methemoglobinaemia because it or nitrite oxidizes the iron(II) (the oxygen

carrier in haemoglobin in the blood) to iron(III) and result in methemoglobin which is unable to release the oxygen to body tissues^[1,3].

Ammonia and nitrates are nutrients that can stimulate the growth of algae in water that receive either treated or untreated effluents. Undesirable excess nitrogen in the form of nitrate or ammonia will lead to eutrophication, thus deteriorate the water quality in the receiving body. Besides the unpleasant odour, the resulting low dissolved oxygen level can adversely affect the respiration of fish and benthic aquatic animals.

Ammonia (NH_3) is toxic to fish and other aquatic life as well as many animals. Ammonia is present in most natural water, primarily due to the normal biological degradation of proteins. The endogenous concentration is usually very low because of the continuous conversion of ammonia to nitrate. However, ammonia in polluted water may be high enough to be lethal to fish because the acceptance value for the aquatic life is quite low^[3].

Ammonia will increase the chlorine demand during the disinfection process. It reacts with aqueous chlorine to produce chloramines, which may in turn, result in unacceptable tastes and odours in the treated water.

2.2. Regulations and Guidelines for Effluent Quality and Water Quality

In addition to natural discharge of ammonia by biological degradation, ammonia is also discharged from human-caused sources, including industrial effluent, application of fertilizer and other agricultural practices, sewage effluent,

animal wastes, landfill leachates, septic tanks, and leaching fields. For this reason, many regulations and guidelines have been established to control the man-made discharges of ammonia in order to maintain good water quality for the protection of the environment.

2.2.1. Guidelines for Industrial Effluent Quality

2.2.1.1 Industries Required to Comply with Effluent Regulations

Industrial wastewater is the liquid waste emanating from various industrial processes. An estimate shows that the percentage of industrial wastewater discharge is much larger than municipal wastewater. Two-thirds of the total industrial wastewater are released from cooling operations.^[5] In addition to this, large quantities of water are also used in process operations, which are usually altered and contaminated in the industrial process and may contain contaminants that will degrade the water quality when they are discharged to the receiving waters.

The composition of industrial wastewater varies from industry to industry. Different contaminants will be encountered in different industrial wastewater. Significant pollutant parameters typically found in the discharge from major industries are presented in Appendix 2. Effluent quality standards have also been established for those parameters^[5].

Table 2-1 presents the industries which are required to comply with effluent regulations for ammonia and nitrate.^[5]

Table 2-1. Industries Required to Comply with Effluent Regulations^[5]

	Industry *													
Parameters	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ammonia	x			x		x	x		x	x	x	x		
Nitrate	x			x		x			x	x	x		x	

* 1-Automobile, 2-Beverage, 3-Canning, 4-Fertilizer, 5-Inorganic Chemicals, 6-Organic Chemicals, 7-Meat Products, 8-Metal Finishing, 9-Plastics & Synthetics, 10-Pulp & Paper, 11-Petroleum Refining, 12-Steel, 13-Textiles, 14- Dairy

2.2.1.2 Effluent Quality Guidelines for the Fertilizer Industry

The principal uses of ammonia are in the fertilizer industry, which accounts for 95%, while the mining, petroleum refining, pulp & paper, amines/nitriles production and other industries account for 4.3%. Miscellaneous uses account for another 0.7%.

Commercial fertilizers (such as urea, ammonium phosphate, ammonium nitrate, ammonium sulfate and anhydrous ammonia) contain highly soluble ammonia and ammonium salts. Ammonia could enter the aquatic system via the wastewater discharge and air emission from fertilizer plants, runoff from fertilized agricultural lands and irrigation water. The main contaminants present in the process wastewater from nitrogen fertilizer plants are ammonia nitrogen, nitrate nitrogen and organic nitrogen. Typical wastewater characteristics from nitrogen fertilizer plants are shown in Table 2-2 ^[8]. Some provincial effluent limits or guidelines for fertilizer industry are presented in Table 2-3 ^[8].

When the wastewater containing excessive and high concentration of

Table 2-2. Final Effluent Characteristics of Nitrogen Fertilizer Plants
in Canada 1985 ^[8]

Fertilizer Plant	pH	ammonia nitrogen (mg/L)	organic nitrogen (mg/L)	nitrate nitrogen (mg/L)	Discharged to
CIL	7.6	0.8	0.07	0.47	St.Clair River
Cyanamid of Canada	8.5	61	40	34	Welland River
Nitrochem	8.8	700	-	480	St.Lawrence River
Canadian Fertilizer Ltd.	8.4	1.4	-	-	South Saskatchewan River
Cominco Ltd. Calgary	7.2	2	0.7	0.9	Bow River
Cominco Ltd. Trail	2.8	25	-	-	Columbia River
Esso Chemical	7.7	22	-	13	90% injection well, 10% North Saskatchewan River
Sheritt Gordon	8.5	130	30	25	North Saskatchewan River
Simplot Chemical	6.9	61.5	6.9	14	Assiniboine River
Western Co-op Calgary	8.8	31	-	35	Bow River

nitrogen enters the receiving body of water, it will deplete the oxygen concentration, stimulate excess growth of algae and lead to eutrophication. Ammonia will also be toxic to fish and other aquatic life in the receiving body of water. Therefore, treatment of industrial wastewater before discharge is necessary.

Table 2-3. Provincial Guidelines and Standards for Effluent Quality in the Canadian Fertilizer Industry 1987 ^[8]

Parameter	Limitation in Given Jurisdiction (all units in mg/L)		
	Ontario	Alberta	British Columbia *
ammonia nitrogen	10	35	A-10, B-15
organic nitrogen	-	10	A-15, B-25
nitrate	-	20	A-10, B-50
phosphate	1.0	5	A-1.0, B-10
suspended solids	15	25	A, B-20
pH	5.5 - 9.5	6.5 - 9.5	6.5 - 8.5

* Level A required for all new operations, level B required for all existing plants

2.2.1.3 Effluent Quality Guidelines for the Mining Industry

The wastewater from mining industry is the waterborne liquid wastes generated from mine drainage, mill process effluents and surface runoff. The major contaminants encountered in mining effluent are heavy metals, free acid and radioactive contaminants. The regulations for mine effluent quality are presented in Table 2-4. ^[9,10]

With the widespread use of explosives in mining operations, it becomes the significant source of ammonia and nitrate in mining effluent. The most commonly used explosive is ANFO (Ammonium Nitrate and Fuel Oil), which contains 94% ammonium nitrate and 6% fuel oil. Since ANFO has no water resistance and high solubility, it easily enters the water system through spillage, leaching, mill, and mine effluents ^[11] and results in the high concentration of ammonia in mining effluent. The concentrations of ammonia in mining effluents vary from 10-50 ppm

and can be even as high as 300 ppm for some mine effluents. There are no effluent quality guidelines specific to ammonia for mining industry. With the increasing concern of ammonia contamination in receiving water from mine effluent, it is anticipated that the discharge of ammonia or ammonium ion will eventually be regulated in the future^[12].

Table 2-4. Federal Regulations for Effluent Quality in the Canadian Mining Industry 1992 ^[10]

Parameters	Unit	Authorized Concentration	
		Max. Acceptable Arithmetic Monthly	Max. Acceptable in a Grab Sample
Arsenic	mg/L	0.5	1.0
Copper	mg/L	0.3	0.6
Lead	mg/L	0.2	0.4
Nickel	mg/L	0.5	1.0
Zinc	mg/L	0.5	1.0
Radium-226	Bq/L	0.37	1.11
Total suspended solids	mg/L	25	50
pH	pH	6.0 or greater	5.0 or greater

2.2.2. Guidelines for the Protection of Freshwater Aquatic Life

The un-ionized ammonia is the most toxic form of ammonia. Its toxicity will be affected by DO concentration, CO₂ concentration, pH, salinity and temperature. U.S. EPA (1976) has established a limit of 0.02 mg/l for un-ionized ammonia (NH₃) and 1.0 mg/L for ionized ammonia (NH₄⁺) to protect aquatic life in the receiving water^[13]. The International Joint Commission (IJC) revised U.S.

EPA (1976) value for un-ionized ammonia from 0.02 mg/L to 0.03 mg/L for all waters except special use zones^[14]. The U.S. EPA (1985j) value which is the revision of U.S. EPA (1976) has been adopted as a Canadian guideline and is presented in Table 2-5.^[15]

The concentration of ammonia in receiving body of water should not exceed those shown in Table 2-5. The toxicity of un-ionized ammonia varies with pH and temperature, as the portion of total ammonia that is un-ionized varies with pH and temperature. The total ammonia guidelines recommended in Table 2-5 reflect both of these variations^[3].

Table 2-5. Recommended Guidelines for Total Ammonia ($\text{NH}_3 + \text{NH}_4^+$) 1987^[3]

pH	Ammonia concentration (mg/L) at following temperature						
	0°C	5°C	10°C	15°C	20°C	25°C	30°C
6.50	2.5	2.4	2.2	2.2	1.49	1.04	0.73
6.75	2.5	2.4	2.2	2.2	1.49	1.04	0.73
7.00	2.5	2.4	2.2	2.2	1.49	1.04	0.74
7.25	2.5	2.4	2.2	2.2	1.5	1.04	0.74
7.5	2.5	2.4	2.2	2.2	1.5	1.05	0.74
7.75	2.3	2.2	2.1	2.0	1.4	0.99	0.71
8.00	1.53	1.44	1.37	1.33	0.93	0.66	0.47
8.25	0.87	0.82	0.78	0.76	0.54	0.39	0.28
8.50	0.49	0.47	0.45	0.44	0.32	0.23	0.17
8.75	0.28	0.27	0.26	0.27	0.19	0.16	0.11
9.00	0.16	0.16	0.16	0.16	0.13	0.10	0.08

Source: U.S. EPA 1985j

2.2.3 Guidelines for Municipal Effluent Quality

Municipal wastewater is the spent water originating from all aspects of human sanitary water usage. It typically constitutes a combination of flows from the kitchen, bathroom, laundry, encompassing lavatories, toilets, baths, kitchen sinks, garbage grinders, dishwashers, washing machines, and water softeners.^[5] Some commercial, institutional and industrial wastewaters will also be discharged to municipal sewer systems.

There are numerous physical, chemical and biological constituents present in municipal wastewater. Typical concentrations of ammonia, nitrite and nitrate that are present in municipal wastewater are listed in Table 2-6. Other typical composition and their concentration of untreated municipal wastewater are presented in Appendix 3.

The Ministry of Ontario states that ammonia nitrogen should not exceed 10 mg/L. Guidelines for other parameters in municipal wastewater are listed in Appendix 4.

Table 2-6. Typical Nitrogen Concentration of Untreated Municipal Wastewater ^[6]

Contaminant	Unit	Concentration		
		Weak	Medium	Strong
Total Nitrogen (total as N)	mg/L	20	40	85
Organic Nitrogen	mg/L	8	15	35
Ammonia Nitrogen	mg/L	12	25	50
Nitrites	mg/L	0	0	0
Nitrates	mg/L	0	0	0

2.2.4 Guidelines for Drinking Water

In drinking water, the guideline for nitrate nitrogen (NO_3^- -N) is 10 mg/L and for nitrite nitrogen (NO_2^- -N) is 1.0 mg/L (Table 2-7). There is no guideline for ammonia in drinking water, because it is considered that there is little risk from ammonia at the low levels (≤ 0.2 mg/L) normally encountered in drinking water. The Guidelines for Canadian Drinking Water Quality with other numerous physical and inorganic parameters are presented in Appendix 1.

Table 2-7. Guidelines for Canadian Drinking Water Quality 1978 ^[3]

Parameter	Maximum Acceptable Concentration
Nitrate Nitrogen *	10 mg/L
Nitrite Nitrogen	1 mg/L

* when both nitrate and nitrite are present, the total nitrate nitrogen plus nitrite nitrogen should not exceed 10 mg/L.

2.3 Ammonia Removal Technologies

As mentioned earlier, an advanced oxidation process is being developed as an improvement over the currently favored processes, which have their drawbacks as discussed later in this chapter. Some of the existing ammonia removal technologies are described below.

2.3.1 Physical / Chemical Treatment Technologies

2.3.1.1 Ammonia Stripping

Ammonia Stripping is based on the acidic dissociation equilibrium for ammonia in aqueous solution:

At 25°C, atmospheric pressure, the equilibrium constant for equation (2-2) is: $K_a = 5.637 \times 10^{-10}$, $\text{p}K_a = 9.25$. From equation (2-2) and $\text{p}K_a$ value, it is calculated that 99.4 % of ammonia is present as ammonium ions at pH 7. As the pH is raised, the reaction is driven to the right and the dissolved ammonia gas increases with the increase of pH. About 99.5 % of ammonium ions are converted to ammonia gas at pH 11.5. At this pH or higher, the gaseous ammonia dissolved in the wastewater may be removed by ammonia stripping.^[16]

Ammonia stripping process consists of three major steps: raising the pH of the wastewater to the range of 10.5 to 11.5, formation and reformation of water droplets in a stripping tower, and providing sufficient air-water contact to strip the ammonia gas from the wastewater. Lime or hydroxide may be used for pH adjustment. The amount of air required for stripping can be predicted by Henry's Law. There are two basic types of stripping towers used in full-scale application: countercurrent towers and cross-flow towers. The countercurrent towers have been found best suited to ammonia stripping as opposed to cross-flow towers.^[17]

2.3.1.2 Selective Ion Exchange

Selective ion exchange is accomplished by passing the wastewater through an ion exchange column filled with ion exchange resin which is highly selective for ammonium ion over other cations that are normally present in wastewater. A natural zeolite, called clinoptilolite, has been found to be suitable for this application. It is selective for ammonium ion relative to calcium, magnesium and

sodium, whose order of ion selectivity is reported as : $K^+ > NH_4^+ > Na^+ > Ca^{2+} > Mg^{2+}$. When the effluent ammonium ion exceeds the acceptable level, regeneration of clinoptilolite is required. Regeneration is carried out by passing a regenerant solution through the clinoptilolite bed (column), and the spent regenerant can be recovered and reused by removing the ammonium from it. There are various ways to remove ammonium ion from the regenerant during the regenerant recovery. It can be removed by air stripping of high pH regenerant, the ammonia gas formed from which may be directly discharged to atmosphere or absorbed in a sulphuric acid solution. It may also be converted to nitrogen gas by electrolytic treatment during the regenerant recovery.

2.3.1.3 Reverse Osmosis

Reverse osmosis was originally selected as a demineralization technology for sea waters and brackish waters. It involves separating a solvent, such as water from wastewater by the use of a semipermeable membrane and hydrostatic pressure. In environmental engineering application, the wastewater feed is pressurized so that the pressure difference between the two sides of the membrane (the wastewater side and the solvent side) is greater than osmotic pressure. At this time, the solvent starts to transfer. Its transfer rate increases with the increase in the pressure difference.

The most common membrane used in this application is cellulose acetate membrane, which has low water permeability and can reject over 99% of the salts. The pilot plant studies showed that some organics in the wastewater will foul the

membrane and lead to its incapacity. So periodic cleaning of the membranes is required in order to control the fouling.

Pilot plant studies showed that typical removal from secondary effluents treated by reverse osmosis are as follows^[4] : total organic carbon, 90%; total dissolved solids, 93%; phosphate, 94%; organic nitrogen, 86%; ammonia nitrogen, 85%; and nitrate nitrogen, 65%. It is observed that nitrate is more difficult to remove than ammonia and the average removal rate for ammonium nitrogen by reverse osmosis is about 85 %.

2.3.1.4 Breakpoint Chlorination

Breakpoint chlorination is accomplished by the addition of chlorine to the wastewater to oxidize the ammonia nitrogen. The primary final product is nitrogen gas.

When chlorine gas is dissolved in water, hydrolysis occurs in water:

HOCl thus formed will dissociate to give OCl^- according to the reaction:

The active forms of the chlorine are hypochlorous acid (HOCl) and hypochlorite (OCl^-). At the process pH, which is pH 7, HOCl is dominant. Ammonium reacts with chlorine according to the following pathways:

The reactions are dependent on certain process variables, including pH, temperature, contact time, and the initial chlorine to ammonia nitrogen ratio. At the breakpoint, the sufficient chlorine added will oxidize ammonia to a simple product - nitrogen gas, the reactions are as follows:

The overall reaction at the breakpoint is :

The optimum pH for the breakpoint is near pH 7.0 and the weight ratio of chlorine to ammonia nitrogen is theoretically at 7.6: 1. In practice, the actual ratio has ranged from 8: 1 to 10: 1.

Laboratory studies showed that the breakpoint reactions proceed very rapidly. At a pH of 6 to 7, the breakpoint reaction will be completed in less than 15 seconds.

Breakpoint chlorination is applicable only to certain types of wastewater such as those containing mainly ammonia nitrogen.

Because of large amount of chlorine used in breakpoint chlorination, dechlorination is required as a companion process to breakpoint chlorination in many cases.

2.3.2 Biological Treatment Technologies

The biological treatment process is currently the most favored process by various jurisdictions, which is also the one under intensive study. The overall process consists two steps of treatment: biological nitrification and the denitrification. Biological nitrification is usually the first step in which ammonium ion is converted to nitrate and nitrite. It is followed by denitrification in which the nitrate and nitrite formed from the first step are converted to nitrogen gas. In view of the importance of the biological process as well as the possible adoption of the biological denitrification step in the MAP Process, detailed description of the process is given below:

2.3.2.1 Biological Nitrification

Biological nitrification is carried out by bacteria that sequentially oxidize ammonium to nitrate with intermediate formation of nitrite. Over one hundred species of bacteria have been cited as forming nitrite from ammonia^[18]. But the major nitrifying bacteria are *Nitrosomonas* and *Nitrobacter*. Both of these two groups are classified as autotrophic organisms because they derive energy from the oxidation of organic matter. In nitrification process, ammonia and organic nitrogen are converted to nitrite by *Nitrosomonas* (eq. 2-12), while nitrite is oxidized to nitrate by *Nitrobacter* (eq. 2-13).

The reaction for the oxidation of nitrite to nitrate by *Nitrobacter* is :

The overall oxidation of ammonium by both bacteria groups is obtained by adding the above two equations (2-12) and (2-13):

Equations (2-12) showed that hydrogen ion is formed during the oxidation of ammonium ion. Oxygen is utilized for both reactions as shown in equations (2-12) and (2-13).

Nitrosomonas and *Nitrobacter* have their specific oxidizing ability on nitrogen compounds. *Nitrosomonas* is limited to oxidizing ammonium to nitrite, its growth is thus limited by the concentration of ammonium. *Nitrobacter* is limited to oxidation of nitrite to nitrate and its growth is limited by the concentration of nitrite. The kinetic equation proposed by Monod^[18] is used to describe the kinetics of biological growth of either *Nitrosomonas* or *Nitrobacter*:

$$\mu = \mu_m S / (K_s + S) \quad (2-15)$$

where:

μ = specific growth rate of microorganisms, d^{-1}

μ_m = maximum specific growth rate of microorganisms, d^{-1}

K_s = half-saturation or half-velocity coefficient (equivalent to the growth-limiting substrate concentration at half the maximum specific growth rate) , mg/L

S = growth -limiting substrate concentration, mg/L

The rate of ammonium oxidation is controlled by the growth of *Nitrosomonas*.

There are many factors that influence the biological nitrification, which include:

(1) Temperature: Temperature has a strong effect on the growth rate of nitrifying bacteria. The process occurs over a range of approximately 4-45°C, with about 35°C optimum for *Nitrosomonas* and 35-42°C optimum for *Nitrobacter*.^[18] The nitrification rate will decrease with the reduction of the temperature. Nitrification ceases to proceed when it is below 4°C or above 45°C.

(2) Dissolved Oxygen (DO) Concentration: Equations (2-12) and (2-13) show that oxidation of ammonium requires the consumption of oxygen. So the concentration of DO has a significant effect on the rates of nitrifier growth and nitrification process. The reaction proceeds at a reasonable rate only at DO more than 3 mg/L. When DO is less than 0.5 mg/L, it will have negative influence on nitrification.

(3) pH: In the nitrification process, alkalinity is destroyed and H^+ is formed during the process, as can be seen from equations (2-12) and (2-14). Optimum pH for the process is reported at 8.0 to 8.6. It is also reported that the rate of ammonium oxidation declines when pH is less than 6.3.^[4]

(4) Alkalinity: Alkalinity is destroyed by the oxidation of ammonia to nitrate, thus sufficient alkalinity needs to be maintained in order to balance the acid production by nitrification. In practice, alkalinity required may be 10 times greater than the amount of ammonium nitrified in order to maintain a pH greater than 6.0^[4].

(5) Inhibitors: Nitrifiers are very sensitive. Even a small concentration of inhibitory substances will affect the rate of nitrification. A wide range of organic, inorganic, and metal compounds are identified as nitrification inhibitors.^[4] When

a high concentration of inhibitors are present, removal of inhibitors is required in order to improve the nitrification rate.

2.3.2.2 Biological Denitrification

Biological denitrification involves the microbial reduction of nitrate to nitrite, and ultimately nitrite to nitrogen gas, with very little amount of nitrous oxide or nitric oxide. It occurs in an anaerobic environment with various denitrifiers. A broad range of bacteria can denitrify. An organic source is needed to act as an electron donor and supply carbon for biological synthesis, and nitrate and nitrite are electron acceptors. Methanol is widely used as the electron donor [16]. The reactions are as follows:

The overall transformation is obtained by addition of equations (2-16) and (2-17):

In the denitrification process, bicarbonate alkalinity is produced and carbonic acids are reduced. The tendency of denitrification is to partially reverse of the effect from nitrification. The pH will rise during denitrification.

The Monod-type expression can be employed to describe the effect of nitrate concentration on the growth rate of denitrifying microorganisms, taking into consideration the effects of solid retention time, concentration of organic substrate and the oxygen concentration. Similar to nitrification, there are some

variables that affect the denitrification, including temperature, pH, alkalinity and inhibitors. Denitrification is much less sensitive to these parameters than nitrification. Therefore, denitrification process is much easier to control and operate as well as having a faster reaction rate.

2.3.3 Other Ammonia Removal Technologies

In addition to the technologies listed above, there are some other methods for ammonia removal, most of which are in the experimental stage of development and need to be scaled up.

Ozonation has been used in oxidation of ammonia over the past few years, in which ammonia and nitrite will be oxidized to mainly nitrate.^[19] The process is strongly affected by pH and temperature. In general, the ozonation process is quite expensive, and the environmental impact of ozone needs to be taken into account.

Electro-oxidation method is also being investigated for removal of ammonia, in which ammonia is oxidized anodically into nitrogen gas by using a platinum electrode. No nitrite, nitrate, hydrazine or hydroxylamine was detected in the product mixture.^[20] A chloride mediated electro-oxidation method for ammonia and cyanide removal from mine/mill wastewaters has been studied.^[21] The method has its technological merits, but further R & D on development of cost-effective electrodes and cost estimates for the process are required.

2.4 Need for New Technology

2.4.1 Limitations with Existing Technologies

The existing technologies for ammonia removal have been described in section 2.3. Each of them has its limitations and disadvantages, and some of these are highlighted below:

Air stripping is a simple and low cost process. But its temperature dependency, and air pollution problems lead to its limitations in application. Air stripping has been impractical at the ambient air temperature below 0°C. Its efficiency reduced with the decrease of the temperature. Also, air pollution, washout of ammonia from the atmosphere and noise generation from the ammonia stripping towers due to air blowers are other environmental concerns.

Selective ion exchange overcomes the temperature sensitivity associated with air stripping. It has high efficiency in ammonia removal. But its complex operation and high capital costs limit its application. In fact, it consists of two or more operations in one process: ion exchange and air stripping. In practice, air stripping may be substituted by another alternative for ammonia removal from the regenerant recovery, such as absorption into an acid solution or electrolytic treatment. Interference of selectivity from the other cations will also occur in the ion exchange process.

Reverse osmosis is good for the demineralization of wastewater. But membrane fouling and operation maintenance are limitations with this process.

Further treatment of the effluent residuals from this process may be required. Even though it has good removal efficiency for organics and dissolved solids, reverse osmosis is not very good for ammonia and nitrate removal.

Breakpoint chlorination is rapid and high in efficiency for ammonia removal. Its technical merit is that the final product is nitrogen gas. But the requirement of a large amount of chlorine, complex pH control for breakpoint, contribution of total dissolved solids, formation of potential carcinogenic chlorine by-products and the requirement of dechlorination of toxic residual chlorine in effluent prior to discharge are limitations with this process. Breakpoint chlorination has no effect on the removal of nitrite and nitrate.

Biological nitrification under proper operating conditions could be one of the less costly processes among all the alternatives. Its disadvantages are complex process control, including pH, alkalinity, temperature, DO and inhibitor removal. Any change of these parameters from optimum ranges will affect the nitrification rate significantly and reduce the efficiency of the process.

2.4.2. Need for New Technology for Ammonia Removal

In view of the limitations listed above for the existing ammonia removal technologies, it was decided to evaluate the feasibility of photolytic processes for the destruction of ammonia in wastewater.

3. UV Irradiation and the Photolytic Process

UV irradiation is the process in which UV rays are employed to effect photochemical reactions.

3.1 Ultraviolet Radiation

This section describes the electromagnetic radiation, UV light and energy, the Beer-Lambert absorption law, the laws of photochemistry, and sources of UV radiation.

3.1.1. Electromagnetic Radiation

Electromagnetic radiation has been classified into many parts in accordance with its wavelengths. The electromagnetic spectrum is shown in Figure 3-1 and Table 3-1. Ultraviolet is one type of electromagnetic radiation which is adjacent to and greater in energy than visible light. The Ultraviolet spectrum extends from 180 nm to 400 nm and is divided into three categories: short-wave (UVC), medium-wave(UVB), and long-wave(UVA).

UVC extends from 180 to 280 nm with a peak in energy at about 254 nm. This region UV is ideal for mutation studies, toxicology, fluorochemistry and germicidal applications. UVB extends from 280 to 320 nm with a peak in energy at about 312 nm and are generally used in electrophoresis documentation procedures and in mineral identification by their fluorescent responses. UVA extends from 320 to 400 nm with a peak in energy at about 365 nm. This long

wave UV is used as leak detector in conjunction with fluorescent dyes as well as for mineral studies.

γ rays	X rays	UV	Visible light	Infrared	Microwave	Radiowaves
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Figure 3-1. The Electromagnetic Spectrum

Table 3-1. Range of Wavelengths for Different Electromagnetic Radiation

Electromagnetic Radiation	Range of Wavelengths
γ rays	below $0.1 \text{ \AA}^0$
X rays	$0.1 \text{ \AA}^0 \sim 400 \text{ \AA}^0$
Ultraviolet	$180\text{nm} \sim 400\text{nm}$
Visible Light	$400\text{nm} \sim 780\text{nm}$
Infrared	$780\text{nm} \sim 300\mu\text{m}$
Microwaves	$0.3\text{mm} \sim 1\text{m}$
Radiowaves	$1\text{m} \sim 1000\text{m}$

3.1.2 UV light and Energy

Electromagnetic radiation has a dual nature and may be considered as a wave or a particle. It may be considered as a wave when one is discussing its physical optics. When discussing its photoelectric effect, it is convenient to regard it as a particle, a photon or a packet of energy.

The UV radiation consists of discrete light quanta (photons). The energy of each photon, E is related to its wavelength (λ) as defined by the quantum theory, as follows:

$$E = h\nu = hc / \lambda \quad (3-1)$$

where h is Plank's constant and $h = 6.626 \times 10^{-34}$ J.s, ν is the frequency of the light and $\nu = c / \lambda$, c is the velocity of light and $c = 2.998 \times 10^8$ m / s.

Therefore, for the wavelength in nanometers, The energy of one photon E (per photon) = $1.986 \times 10^{-16} / \lambda$ Joules. One mole of photons, is also known as an "Einstein", its energy may be calculated by multiplying E (per photon) by the Avogadro's number N , which is 6.022×10^{23} , so E (per einstein) = $1.196 \times 10^5 / \lambda$ kJ = $2.859 \times 10^4 / \lambda$ kcal.

UV energies of various wavelengths of UV light are presented in Table 3-2.

Table 3-2. Energies per Einstein at Various Wavelength of UV light

Wavelength	E (kcal/einstein)	E (kJ/einstein)
200	143	600
220	130	546
240	119	500
260	110	462
280	102	428
300	95	399
320	89.4	375
340	84.1	353
360	79.4	333
380	75.3	316
400	71.5	300

3.1.3 The Beer-Lambert Absorption Law

The absorption of a monochromatic beam of light by a homogenous absorbing system is described well by the Beer-Lambert law. The law states that when a beam of incident intensity I_0 passes through a layer of thickness l , its intensity is reduced to I , and $I = I_0 10^{-\epsilon c l}$, where ϵ ($M^{-1} \text{ cm}^{-1}$) is the molar extinction coefficient, also called molar absorptivity, c (M) is the molar concentration of the absorbing species.

So the absorbance of a layer A is defined as

$$A = \log_{10} (I_0 / I) = \epsilon c l. \quad (3-2)$$

The transmittance T is defined as I / I_0 ,

$$\text{so } T = 10^{-A} \quad (3-3)$$

$$A = -\log T \quad (3-4)$$

If there are more than one absorbing species present in a homogeneous mixture, the total absorbance is the sum of the absorbances of the individual components.

3.1.4 The Laws of Photochemistry

There are two basic laws of photochemistry. The first law, known as the Grotthus-Draper law, states that only the light which is absorbed by a molecule can be effective in producing photochemical change in the molecule. Thus for photochemical transformations, it is necessary to know the absorption spectrum of the compound being photolyzed, the emission spectrum of the light source, the absorption spectra of the filter as well as the amount of light absorbed by the reactants in the system.

The second law, the Stark-Einstein law, states that when an atom or molecule undergoes a photochemical change, it is the result of the absorption of a single photon by this atom or molecule. The law applies to the primary process and it reveals that the numbers of molecules reacting will be equal to the number of quanta absorbed. The one-quantum-absorbed-per-molecule aspect might not apply to the secondary processes that result in chain reactions.

Applying the above two laws of photochemistry in photochemical processes, it is easy to understand that the rate of photoreaction of a chemical is a function of the rate at which light is absorbed and it is also the function of the efficiency with which the absorbed light transforms the chemical into products.

3.1.5 Sources of UV Radiation

According to the first law of photochemistry, light must be absorbed to effect a photochemical change. So the choice of light source that is suitable for the process is important, which is dictated by the absorption spectrum of those reactants to be studied.

The most widely used source of UV light for photolytic application is the mercury vapor arc. Mercury arcs are classified into three types according to the pressure within the arc envelope: low-pressure, medium-pressure and high-pressure mercury lamps. Each type emits a characteristic spectrum and intensity, which has specific applications for the various experimental needs. The following is a brief summary of their characteristics and applications.

3.1.5.1 Low-Pressure Mercury Lamp

A low pressure mercury lamp emits primarily two bands of radiation centered at 253.7 nm and 184.9 nm, but 90 % of the light is centered around 253.7 nm. Low-pressure mercury lamp is widely used in disinfection and germicidal applications. It is also used in the UV-ozone system for wastewater treatment since ozone absorbs strongly at 253.7 nm. It is reported that it is not effective for treating refractory compounds which require UV energy at wavelength below 240 nm for photodissociation. Its narrow band and low power input and UV output restrict its application in wastewater treatment and other applications even though it has the advantages of long lifetime and dependability.

3.1.5.2 Medium-Pressure Mercury Lamp

The intensity of the medium pressure mercury lamp increases because the pressure of the lamp increases, from low to medium (1 atm). It emits light over a wide range, including the UV, visible and IR regions. The efficiency in the UV range 200-300 nm is about 5- 20%. The relative energy distribution of typical low-pressure and medium-pressure mercury lamps are listed in Table 3-3^[63].

The higher UV light intensity, higher UV energy and the broadened UV band make it widely used in wastewater treatment for destruction of contaminants in advanced photo-oxidation process. Its life time is not as long as the low-pressure mercury lamp.

A medium-pressure mercury lamp with known spectral distribution and output is employed in this research, details of which are given later in chapter 5.

3.1.5.3 High-Pressure Mercury Lamp

The most intense source of ultraviolet radiation is the high-pressure mercury lamp. It operates at internal pressures of several hundred atms and temperature of 5500 to 8000 K. Its spectrum consists broad bands instead of the discrete line spectrum of low-pressure or medium-pressure lamps. Its output per unit length of arc is about ten times of that of a medium-pressure lamp and 1000 times of that of a low-pressure mercury lamp.

Table 3-3. Energy Distribution in Low-Pressure and Medium-Pressure Mercury Lamps

Wavelength (nm)	Relative Energy	
	Medium-pressure mercury lamp	Low-pressure mercury lamp
222.4	14.0	-
232	8.0	-
236	6.0	-
238	8.6	-
240	7.3	-
248.2	8.6	0.01
253.7	16.6	100.0
257.1	6.0	-
265.2-265.5	15.3	0.05
270	4.0	-
275.3	2.7	0.03
280.4	9.3	0.02
289.4	6.0	0.04
296.7	16.6	0.2
302.2-302.8	23.9	0.06
312.6-313.2	49.9	0.6
334.1	9.3	0.03
365.0-366.3	100.0	0.54
404.5-407.8	42.2	0.39

A high-pressure mercury lamp is used in the studies where intensity is of primary importance. Its high internal temperature, high pressure, and its intense short-wavelength radiation are dangers to the process and thus require more protection and caution.

3.1.5.4 Other UV radiation Sources

Many other sources of UV radiation have been used in various applications. Medium or high-pressure Xenon lamps have been used to generate useful intensity of far-UV light. Apart from those sources of irradiation mentioned above, metal halide lamps, electrodeless lamps are also commercially available.

3.2 Photolytic Process

Photolytic processes involve the photo-oxidation of the contaminants by direct photolysis or by a cascade of photochemical reactions initiated by reactive radicals generated from the photolysis of an additive. The different photolytic process schemes can be classified into three broad categories.

- (1) Direct photolysis
- (2) Advanced photo-oxidation or photochemical oxidation
- (3) Photocatalytic oxidation

The above three photolytic processes as well as the UV irradiation are described respectively in the following section:

3.2.1 Direct Photolysis:

Direct photolysis, as the name implies, is the process in which there is direct absorption of UV photons by the contaminants as a result of which

decomposition occurs. In this type of process, which is primarily dependent on the absorption of UV by the contaminant, no oxidants or catalysts are employed. This is similar to the UV technology for disinfection whereby the contaminant is directly attacked by the energetic photons, leading to its destruction. Direct photolysis has been found to be applicable to many organic contaminants and large-scale commercial units have become available in the last few years.

Ammonia by itself is largely transparent in the visible and near-ultraviolet regions of the electromagnetic spectrum. It has a progression of diffuse absorption bands between the wavelength of 170 nm and 216.8 nm. However, it is reported that ammonia dissociates to give amino radicals ($\bullet\text{NH}_2$) when exposed to ultraviolet irradiation at wavelength less than 220 nm^[22,23]. At shorter wavelengths, the $\bullet\text{NH}$ radical is observed.

There is no report in the literature that indicated the possible application of direct photolysis of ammonia in wastewater treatment, which is probably due to the limited direct absorption over the UV range.

3.2.2 Advanced Photo-oxidation

Advanced photo-oxidation is also known as photochemical oxidation. It is a homogeneous process generally carried out in the aqueous medium, which involves the generation of highly reactive radicals (mostly hydroxyl radicals) by the photolysis of oxidants and the initiation of the subsequent photo-oxidation of

contaminants by the radical attack. The advanced photo-oxidation results in a significant increase in oxidation rate as compared to direct photolysis or the dark reaction. Unlike direct photolysis, it is not dependent on direct absorption of UV by the contaminants.

In advanced photo-oxidation process (APP), the oxidants act as the source of reactive radicals such as hydroxyl radicals. H_2O_2 , O_3 and other powerful oxidizing agents may be employed as oxidants in APP. The treatment options in APP are UV/ H_2O_2 , UV/ O_3 , UV/ $\text{H}_2\text{O}_2/\text{O}_3$ and other UV/Advanced Oxidants.

3.2.2.1. UV/ H_2O_2

The effect of radiation on the decomposition of H_2O_2 was observed as early as the end of nineteenth century^[24]. All UV radiation is absorbed by H_2O_2 , i.e. radiation of wavelength shorter than 380 nm, is photochemically active. The UV absorptivity of H_2O_2 increases as the wavelength decreases. The primary process of photolysis of hydrogen peroxide yields hydroxyl radicals.^[24,25]

These radicals then quickly attack and react with the contaminants to undergo a series of complex photochemical reactions through three probable pathways: abstraction of hydrogen atom, addition to double or triple bond, and electron transfer.^[24]

Photochemical reaction of ammonia with hydrogen peroxide has been reported by Ogata et al.^[33,37] While a probable mechanism has been suggested, no detailed kinetics and parametric studies had been carried out. Photoinitiated

reactions of H_2O_2 with other inorganic nitrogen compounds other than ammonia have also been dealt with in some papers.^[24, 34-35]

A simplified reaction scheme for photo-oxidation of ammonia in the presence of H_2O_2 could be represented as follows:

Such photo-oxidation of ammonia is also resorted to in analytical protocols for the estimation of total dissolved nitrogen.^[27-32]

Hydrogen peroxide was selected as the oxidant for ammonia removal in this study. Hydrogen peroxide, available as a liquid solution, is easily handled in a homogeneous aqueous treatment system. It has the further advantage that it leaves no residuals in the process effluent, and poses no environmental hazard in its use, as is the case with ozone.

There is no reported system on the application of UV/ H_2O_2 process for ammonia removal from wastewater.

3.2.2.2 UV/ O_3

Ozone has a strong absorption band centered at 260 nm which has an ϵ_{260} of $3000 \text{ M}^{-1}\cdot\text{cm}^{-1}$. In aqueous solution, photolysis of ozone leads to a quantitative formation of hydrogen peroxide and the subsequent generation of the hydroxyl radicals. Thus ozone is simply an expensive precursor for the hydroxyl radical. Health and safety problems in the use of ozone can make it less desirable.

3.2.2.3 UV/H₂O₂/O₃

Ozone can chemically react with hydrogen peroxide to produce hydroxyl radicals. Under irradiation, more efficient and highly reactive hydroxyl radicals are produced, resulting in an improved efficiency on contaminant removal.^[26]

3.2.2.4. Other UV/Advanced Oxidants

Besides hydrogen peroxide and ozone, many other compounds such as persulphate, permanganate, perchlorate, bromate, iodate, ceric ion, and dichromate may act as powerful oxidants in APP. But most of these oxidants or their residuals could be hazardous to the environment. Among these oxidants, persulphates are comparatively environmentally benign and hence chosen for detailed study in this research. The treatment alternative UV/K₂S₂O₈ is described in chapter 6.

3.2.3 Photocatalytic Oxidation:

The photocatalytic oxidation involves the UV irradiation of the contaminants in the presence of a catalyst. Both homogeneous catalyst (ferric ion or ferrous ion) and heterogeneous catalyst (TiO₂) may be used in the photocatalytic oxidation. The treatment options of UV/H₂O₂/Ferrous Ion, UV/H₂O₂/Ferrioxalate and UV/TiO₂ are outlined below:

3.2.3.1 Homogeneous Catalysts

UV/H₂O₂/Ferrous Ion :

In UV/H₂O₂/Ferrous Ion process, ferrous ion reacts with hydrogen peroxide to produce hydroxyl radical, which is also known as Fenton's reaction. Ferrous ion is used as the homogeneous catalyst in the reaction. The reaction has to take place in acid solution to avoid the precipitation of the ferrous hydroxide.^[26]

UV/H₂O₂/Ferrioxalate :

In UV/H₂O₂/Ferrioxalate process, the photolysis of ferrioxalate produces ferrous ion (free or complexed with oxalate), which combines with hydrogen peroxide to provide a continuous source of Fenton's reagent, leading to higher yield of hydroxyl radicals. The process has to be operated at acidic pH.^[26]

The above treatment options have been currently applied in organic degradation and destruction from wastewater,^[26,36] however, no report indicates their applications for ammonia removal from wastewater.

3.2.3.3. Heterogeneous Catalysts

UV/TiO₂ :

TiO₂ has been used as the heterogeneous photocatalyst, since it efficiently absorbs long-wavelength UV light and is chemically stable at reaction conditions. UV photons promote electrons from the TiO₂ valence band to the conduction band, creating electron-hole pairs. The photogenerated holes will react with hydroxyl anions

to produce hydroxyl radical. When $\bullet\text{OH}$ radical is formed, it will initiate the photo-oxidation reactions as does with UV/ H_2O_2 treatment. The application of photocatalytic oxidation on water treatment has been reviewed by Bahnemann et al.^[64] It is reported that the presence of H_2O_2 in the heterogeneous photocatalysis system has a positive effect on the rate of contaminant removal.^[65] The application of UV/ TiO_2 on photo-oxidation of aqueous ammonia has been reported^[66], in which it is indicated that ammonia is oxidized to a mixture of nitrate and nitrite with titania-based heterogeneous catalysts.

4. Basic Chemistry and Photochemistry

In this project, many nitrogen compounds and some oxidants are studied. These include the feed nitrogen sources, intermediate nitrogen compounds, final nitrogen compounds and oxidants. A knowledge of basic chemistry and photochemistry of these compounds is helpful in understanding the photo-oxidation of ammonia as well as understanding the probable mechanisms of the process.

Physical and chemical properties of these important chemicals and the reaction intermediates are outlined below.

4.1 Nitrogen Source - Ammonia

Physical Properties

Ammonia is a colorless gas under ambient conditions, with a sharp, intensely irritating odour. It is lighter than air and easily liquified by pressure. It is very soluble in water.

NH_3 represents the -3 valence state of nitrogen, its molecular weight is 17.03. The ammonia molecule has a pyramidal structure, with the nitrogen atom at the apex and hydrogen atoms at the base. The H—N—H bond angles have been observed to be $106^{\circ} 47'$. The physical and thermodynamic properties of ammonia are summarized in Table 4-1.

Table 4-1. Physical Properties of Ammonia^[23].

PROPERTY	VALUE
Formula	NH ₃
Molecular Weight	17.03
Specific gravity at 0 °C	0.77
Viscosity	0.135 cps
Boiling point at 1 atm	-33.37
Triple-point temperature	-77.69°C
Triple-point density of liquid	0.735 g/ml
Critical Temperature	132.45°C
Critical Pressure	112.3 atm
Heat capacity at 25 °C	8.38 cal/mole/deg.
Heat of vaporization	5.581 kcal/mole
Solubility	very soluble in water, alcohol and ether
pH of 0.01 N aq. solution	10.6
Autoignition temperature	650°C

Formation Reactions

Most ammonia is manufactured by the Haber process [eq.(4-1)]. In this process, hydrogen and nitrogen react at high temperatures and pressures in the presence of a catalyst to form ammonia. In addition to this, ammonia may be commercially produced as a byproduct of coking.

In laboratory, the most convenient means for preparation of ammonia is a simple reaction of ammonium salt with a strong base, such as sodium hydroxide:

Another method for ammonia preparation is the hydrolysis of urea [eq.(4-3)], which is particularly important because of its significance in the conversion of animal wastes in the global nitrogen balance.

Acid - Base Chemistry

Ammonia is a polar substance because of its asymmetric structure. It has a strong hydrogen bonding character. When ammonia is dissolved in water, it reacts with water to form ammonium ion and hydroxyl ion. The equilibrium is as follow:

Equation 4-4 reveals the equilibrium of unionized ammonia with ammonium ion in solution. Un-ionized ammonia concentration is quite pH and temperature dependent. It increases with an increase in pH. At pH 7, the solution contains 99.4% of ammonium ion, while at pH 12, 99.8 % is in the form of unionized ammonia (dissolved ammonia gas) in solution. The relative percentages of ammonium ions and ammonia at different pH and temperature are shown in Figure 4-1.

Figure 4-1. Distribution Diagram of Ammonia and Ammonium Ion at 25°C

Oxidation - Reduction Reactions

Ammonia represents the lowest oxidation state of nitrogen. It is oxidized by many oxidants, such as hypochlorite, persalts, ozone, hydrogen peroxide, oxygen, chlorine, and metal oxide.

Oxidation of ammonia with hypochlorite will give nitrogen gas and water [eq.(4-5)]. Oxidation with ozone, hydrogen peroxide, persulphate, permanganate or metal oxide will lead to final products nitrite and nitrate [eq.(4-6), (4-7)]^[20]. The combustion of ammonia with oxygen will give nitrogen gas [eq.(4-8)], while bacterial oxidation of ammonia under aerobic condition produces nitrite and nitrate [eq.(4-9)]. When ammonium salts and nitrite are in solution at low pH, the chemical decomposition will occur to give nitrogen gas [eq.(4-10)]^[20,23].

Photochemistry

As mentioned earlier, ammonia is mostly transparent in the visible and near- ultraviolet light regions as can be seen in the absorption spectrum in Figure 4-2. It will dissociate when exposed to radiation in the far-ultraviolet by the

following two reactions. The dissociation energy for the bond $\text{NH}_2\text{-H}$ is 104 kcal/mole and it needs the ultraviolet energy at wavelength below 270 nm to break the bond [23,44].

Figure 4-2. UV Absorption Spectrum of Ammonia in Aqueous Solution

Ammonia is known to undergo secondary reactions with photochemically excited species such as hydroxyl radicals [eq.(4-13)] and ozone [eq.(4-6)]^[23].

The following chemicals are of interest because they are the potential intermediate products in the APP for ammonia removal.

4.2 Intermediate Nitrogen Compounds

In the APP process, intermediate products N_2H_4 and NH_2OH could be formed, which would be rapidly oxidized to final products as discussed below.

4.2.1 Hydrazine

4.2.1.1 Physical Properties

Anhydrous hydrazine (N_2H_4) is a colorless oily liquid that freezes at 2°C and boils at 113.5°C . Its density is 1.004 g/ml at 25°C . It is miscible with water, methyl, ethyl, and isobutyl alcohols.

4.2.1.2. Chemical Properties

N_2H_4 represents the -2 valence of nitrogen. Its molecular weight is 32.05. At room temperature, pure hydrazine and its aqueous solutions are kinetically stable with respect to decomposition. It will decompose in the presence of catalytic materials to give nitrogen or ammonia [eq.(4-14), (4-15)]. When it is dissolved in water, it will react with water to give OH^- ion, revealing its basic nature[eq.(4-16)]. But it is not quite as strong as ammonia.

Hydrazine is a powerful reducing agent. It has the -2 valence of nitrogen and it may be oxidized by a wide variety of oxidizing agents, including molecular oxygen. Some important half-cell reactions both in acid and basic solutions together with their standard potentials (E^0) are listed below.

Table 4-2. Half-Cell Reactions and Standard Potentials of Hydrazine in Basic Solution:

Half-Cell Reaction	E^0 , volts
$N_2H_4 + 4 OH^- = N_2 + 4 H_2O + 4 e^-$ (4-17)	-1.16
$N_2H_4 + OH^- = NH_3 + 0.5 N_2 + H_2O + e^-$ (4-18)	+2.42
$N_2H_4 + 2.5 OH^- = 0.5 N_3^- + 0.5 NH_3 + 2.5 H_2O + 2 e^-$ (4-19)	+0.92

Table 4-3. Half-Cell Reactions and Standard Potentials of Hydrazine in Acid Solution:

Half-Cell Reaction	E^0 , volts
$N_2H_5^+ = N_2 + 5 H^+ + 4 e^-$ (4-20)	+ 0.23
$N_2H_5^+ = NH_4^+ + 0.5 N_2 + H^+ + e^-$ (4-21)	+ 1.74
$N_2H_5^+ = 0.5 HN_3 + 0.5 NH_4^+ + 2.5 H^+ + 2e^-$ (4-22)	- 0.11

Hydrazine is quantitatively oxidized to nitrogen gas by many oxidizing agents such as by acid iodate or bromate, neutral iodine or hypochlorite, alkaline ferricyanide, ferric, ceric, permanganate, hydrogen peroxide, and persulphate. It may also be oxidized to nitrogen by nitrite in acidic solution. Some of the reactions are presented below.

4.2.1.3 Photochemistry

Hydrazine may be formed from the irradiation of ammonia. Ammonia will dissociate to give the amino radical under UV irradiation. Two of the amino radicals combine to form hydrazine.

NH_2NH_2 absorbs longer wavelengths than ammonia. The dissociation energy for the bond $\text{NH}_2\text{—NH}_2$ is 60 kcal/mole^[44], which means that irradiation energy at a wavelength of 470nm or less is required to break the bond. The primary process for the decomposition of hydrazine under irradiation is to give the amino radical $\bullet\text{NH}_2$:

4.2.2 Hydroxylamine

4.2.2.1 Physical and Chemical Properties

Pure hydroxylamine (NH_2OH) is an extremely unstable compound that melts at 33⁰C and boils at 58⁰C. It represents -1 valence of nitrogen. Its molecular weight is 33.02. It decomposes to ammonia, water, and a mixture of nitrogen and nitrous oxide.

Aqueous acid solutions of hydroxylamine are much more stable, in which hydroxylamine is protonated as NH_3OH^+ . The equilibrium is as follows:

This reveals its weak basic nature. But it is weaker than ammonia.

Hydroxylamine is easily oxidized to a variety of oxidation states as well as reduced to ammonia. The oxidation states to which hydroxylamine is converted are highly dependent on experimental conditions, such as acidity and oxidation-reduction agent. The following presents some important half-cell reactions and their oxidation potentials.

Table 4-4. Half-Cell Reactions and Standard Potentials of Hydroxylamine

Half-Cell Reaction	E ⁰ , Volts
$\text{NH}_2\text{OH} + 2 \text{H}_2\text{O} + 2 \text{e}^- = \text{NH}_4\text{OH} + 2 \text{OH}^-$ (4-29)	0.42
$2 \text{NH}_2\text{OH} + 2 \text{e}^- = \text{N}_2\text{H}_4 + 2 \text{OH}^-$ (4-30)	0.74
$\text{N}_2\text{O} + \text{H}_2\text{O} + 6\text{H}^+ + 4 \text{e}^- = 2 \text{NH}_3\text{OH}^+$ (4-31)	-0.05
$\text{NH}_3\text{OH}^+ + 2\text{H}^+ + 2 \text{e}^- = \text{NH}_4^+ + \text{H}_2\text{O}$ (4-32)	1.35
$2 \text{NH}_3\text{OH}^+ + \text{H}^+ + 2 \text{e}^- = \text{N}_2\text{H}_5 + 2 \text{H}_2\text{O}$ (4-33)	1.46

Hydroxylamine is quantitatively oxidized by many oxidants such as ferric or ceric ion to give nitrous oxide, ferricyanide or persulphate to form nitrogen gas, bromate or iodate to give nitrate and hydrogen peroxide to give a mixture of nitrogen gas, nitrite and nitrate. It can be reduced to ammonia by titanium(III). Some of the reactions are presented below.

4.2.2.2 Photochemistry

Hydroxylamine may be formed from the photolysis of ammonia and hydrogen peroxide. Ammonia will dissociate to give the amino radical and hydrogen peroxide dissociates to produce the hydroxyl radical under UV irradiation. The Amino radical and hydroxyl radical combine to form hydroxylamine.

The dissociation energy for the bond $\text{NH}_2\text{—OH}$ is 66 kcal/mole^[44]. The irradiation energy at wavelength 430nm or less is required to break the bond. The primary process for the decomposition of hydroxylamine under irradiation is to give $\bullet\text{NH}_2$ and $\bullet\text{OH}$:

It has been reported^[32] that hydroxylamine can react with a hydrated electron to produce the amino radical in aqueous solution as follows:

The following are some possible final products formed during the photo-oxidation of ammonia in this study.

4.3 Final Nitrogen Compounds

As mentioned above, the intermediate nitrogen compounds such as hydroxylamine or hydrazine are formed during the photo-oxidation of ammonia, which are oxidized to final nitrogen compounds, including nitrate, nitrite, nitrogen gas and nitrogen oxides. The physical and chemical properties as well as their basic photochemistry are outlined below:

4.3.1 Nitrogen Gas

Nitrogen is a colorless, odorless gas, which represents the 0 valence of nitrogen. Its molecular weight is 14.0. Air constitutes about 78.06% nitrogen by volume or 75.5 % by weight. Nitrogen is sparingly soluble in water, 1.6 volumes of N_2 may be dissolved in 100 volumes of water.

Typically, all nitrogen of commerce is produced by the liquefaction and fractional distillation of air. Extremely pure nitrogen can be prepared from the thermal decomposition of sodium azide:

In laboratory, many methods have been used to prepare nitrogen gas. Hot aqueous solutions of ammonium nitrite decompose to give nitrogen, ammonium dichromate decomposes on heating to give nitrogen and the high temperature reaction between ammonia and cupric oxide produces nitrogen. Many oxidation reactions with hydrazine or hydroxylamine also produce nitrogen gas, refer to eqs.(4-23), (4-24), (4-25), (4-34) and (4-35).

Nitrogen is a relatively stable gas. The dissociation energy for nitrogen is quite high, 226 kcal/mole. It requires the radiation energy at wavelength 126 nm or less to break the bond $\text{N}\equiv\text{N}$. There is insufficient energy in the ultraviolet range to break the bond.

4.3.2 Nitrogen Oxides

The three nitrogen oxides that are encountered in this process are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2).

The physical properties of the three oxides are presented in Table 4-5.

Table 4-5. Properties of Nitrogen Oxides

nitrogen oxides	oxidation state	M.W.	M.P. (°C)	B.P. (°C)	density (g/ml)	color
N ₂ O	+1	44	-90.8	-88.5	1.226*	colorless
NO	+2	30	-163.7	-151.8	1.269*	colorless
NO ₂	+4	46	-11.2	21.2	1.449**	red-brown

* at boiling point, ** at 20°C

4.3.2.1 Nitrous Oxide

Nitrous oxide is relatively inert and it is the most soluble gas of the three. It can be obtained from the thermal decomposition of ammonium nitrate, hyponitrous acid or nitramide. It is also produced by oxidation-reduction reactions with hydroxylamine or hydrazine. It reacts slowly with oxidizing and reducing agents. It decomposes to give nitrogen when heated above 600°C [eq.(4-36)]. The dissociation energy for breaking the N₂—O bond is 40 kcal/mole and for N—NO is 115 kcal/mole. So N₂—O is easier to break than N—NO bond. Under irradiation, N₂O could be dissociated to N₂ and O or N and NO if there is sufficient energy for both of the reactions.

It is reported that N₂O reacts with a hydrated electron(e_{aq}⁻) in aqueous system to produce nitrogen and the hydroxyl radical (•OH)^[25,32].

4.3.2.2 Nitric Oxide

Nitric oxide is manufactured by the atmospheric oxidation of ammonia at about 500°C in the presence of a catalyst [eq.(4-43)]. It is usually one of the

products of the oxidation and reduction reactions with hydroxylamine, nitrite or nitrate. It reacts rapidly with oxygen to form NO_2 [eq.(4-44)]. The dissociation energy for nitric oxide molecule is 151 kcal/mole. NO absorbs weakly in UV range, there is insufficient energy in UV range to dissociate the NO.

Nitrogen dioxide is industrially prepared from nitric oxide and air. In gaseous and liquid states, it always exists in equilibrium with dinitrogen tetroxide, but in gaseous state, it exists principally as nitrogen dioxide. At higher temperature, the nitrogen dioxide decomposes to nitric oxide and oxygen [eq.(4-45)].

It can be absorbed in a dilute alkaline solution to form nitrite and nitrate. It also can be oxidized by some oxidizing agents such as the ceric ion to give nitrate. The N-O bond angle is 134° and dissociation energy is 73 kcal/mole. NO_2 absorbs over most of the visible and ultraviolet spectrum. Photodissociation is energetically possible at wavelengths below 390 nm. The primary dissociation process is given by eq. (4-46).

4.3.3 Nitrite and Nitrate

4.3.3.1 Nitrite

Nitrite contains nitrogen in an intermediate and relatively unstable oxidation state (+3). It is the conjugate base of nitrous acid ($pK_a = 3.36$). The N-O bond angle is 115° for the nitrite ion. Nitrite is less stable than nitrate.

It is a weak reducing agent and may be oxidized to nitrate. It may be oxidized by oxygen, bromate, permanganate, persulphate, ferricyanide, and other oxidizing agents to nitrate. It is also a weak oxidizing agent and may be reduced to nitrous oxide, nitric oxide or nitrogen gas. It reacts with hydrazine to form nitrous oxide and nitrogen. It reacts with hydroxylamine to give nitric oxide and nitrogen.

4.3.3.2 Nitrate

Nitrate represents +5 oxidation state of nitrogen. It is the more stable form of oxidized nitrogen. Nitrate salts are very soluble and chemically unreactive in dilute aqueous solutions. Because of its relative stability, most nitrogenous materials tend to be converted to nitrates. Therefore, many sources of nitrogen, including ammonia, nitrite and organic nitrogen, could be considered as potential sources of nitrate.

Nitrate is an oxidizing agent, it may be reduced to nitrogen compounds with lower oxidation states. It is reduced by cadmium or hydrazine to give nitrite, by ferrous ion or oxalate to nitric oxide, by stannous ion (Sn^{2+}) to hydroxylamine,

or by titanous ion (Ti^{3+}) to ammonia. Some important half reactions and their standard potentials are listed in Table 4-6.

In aqueous solution, nitrates and nitrites absorb ultraviolet radiation. The absorbance increases with the decrease of wavelength. At 220 nm, the molar extinction coefficient of nitrate is about $2000 \text{ M}^{-1}\text{cm}^{-1}$, which is much higher than that of ammonia. The UV absorption spectrum of nitrate is shown in Figure 4-3.

Table 4-6. Half-Cell Reactions and Standard Potentials of Nitrate and Nitrite

Half-Cell Reaction	E^0 , Volts
$\text{NO}_2^- + \text{H}_2\text{O} + \text{e}^- = \text{NO} + 2 \text{OH}^-$ (4-49)	-0.46
$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- = \text{NO}_2^- + 2 \text{OH}^-$ (4-50)	0.01
$2\text{NO}_2^- + 3 \text{H}_2\text{O} + 4 \text{e}^- = \text{N}_2\text{O} + 6 \text{OH}^-$ (4-51)	0.15
$2 \text{NO}_3^- + 3 \text{H}^+ + 2 \text{e}^- = \text{N}_2\text{O}_4 + 2 \text{H}_2\text{O}$ (4-52)	0.81
$\text{N}_2\text{O}_4 + 2\text{e}^- = 2 \text{NO}_2^-$ (4-53)	0.88
$\text{NO}_3^- + 3 \text{H}^+ + 2\text{e}^- = \text{HNO}_2 + \text{H}_2\text{O}$ (4-54)	0.94
$\text{NO}_3^- + 4 \text{H}^+ + 3\text{e}^- = \text{NO} + 2 \text{H}_2\text{O}$ (4-55)	0.96
$\text{N}_2\text{O}_4 + 2 \text{H}^+ + 2\text{e}^- = 2 \text{HNO}_2$ (4-56)	1.07
$2\text{HNO}_2 + 4 \text{H}^+ + 4\text{e}^- = \text{N}_2\text{O} + 3 \text{H}_2\text{O}$ (4-57)	1.29

Figure 4-3. UV Absorption Spectrum of Nitrate in Aqueous Solution

Nitrogen exhibits a large number of oxidation states, from -3 to +5 in its compounds. The oxidation potentials for most important nitrogen species that exist in aqueous solutions are summarized in Figure 4-4^[44]. As can be seen, the positive number is the standard potential for the half-reaction from left to right, while the negative number is that for the reaction from right to left.

The dissociation energies for some important nitrogen species are presented in Table 4-7.

Figure 4-4. Oxidation-Potential Diagram for Nitrogen Species in Aqueous Solutions

Table 4-7. Dissociation Energies of Nitrogen Species

Species	Formula	Bond Broken	Dissociation Energy (kcal /mole)
Ammonia	NH ₃	NH ₂ — H	104
Hydrazine	N ₂ H ₄	NH ₂ — NH ₂	60
Hydroxylamine	NH ₂ OH	NH ₂ — OH	66
Nitrogen	N ₂	N≡N	226
Nitrous Oxide	N ₂ O	N ₂ — O	40
Nitric Oxide	NO	N — O	151
Nitrogen Dioxide	NO ₂	NO — O	73

4.4 Oxidants

As discussed in chapter 3, hydrogen peroxide and potassium persulphate are used as oxidants in this study. Their chemical and physical properties are outlined below.

4.4.1. Hydrogen Peroxide

Hydrogen peroxide is a clear, colorless liquid which is completely miscible with water. Its aqueous solution is acidic. Some physical constants of the main commercially available grades are recorded in Table 4-8.

Table 4-8. Physical Properties of Commercial Hydrogen Peroxide Solutions ^[46]

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 (⁰ C)	-33	-52.2	-40.3
Boiling point (⁰ C)	107.9	113.8	125.5

Hydrogen peroxide solution is rather unstable, it will decompose gradually to give water and oxygen:

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 sulphite, thiosulphate, iodide, ferrous ion (Fenton's reaction), hydrazine, hydroxylamine, etc. But its reactions with ammonia or nitrite under standard conditions are too slow to be observed. It can also behave as a reducing agent. It can be oxidized by ceric ion (Ce⁴⁺) or permanganate (MnO₄⁻) to oxygen. The two important half cell reactions and their potentials are listed in Table 4-9:

Table 4-9. Half -Cell Reactions of H₂O₂

Half-Cell Reaction	E ⁰ , Volts
$\text{H}_2\text{O}_2 = \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^-$ (4-59)	-0.682
$2 \text{H}_2\text{O} = \text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^-$ (4-60)	-1.77

Hydrogen peroxide absorbs UV light, which has been discussed in chapter 3. Figure 4-5 shows its UV absorption spectrum. Its absorption increases with a decrease of wavelength. Its dissociation energy for bond HO—OH is 52 kcal/mole and 91 kcal/mole for HOO—H. There is sufficient energy from UV light to break the bond HO—OH and generate the highly reactive hydroxyl radicals.

Figure 4-5. UV Absorption Spectrum of Aqueous Hydrogen Peroxide

Hydrogen peroxide can dissociate by absorbing UV light. The quantum yield for the photolysis of hydrogen peroxide depends on the wavelength, as shown in Table 4-10^[37]. The primary photolysis of H₂O₂ in pure water gives almost completely hydroxyl radical •OH, which may react with H₂O₂ to give HOO• radical. The photolysis mechanism is presented in eqs.(4-61) to (4-64). The active species in these cases are •OH and HOO•, of which •OH would be more important because it is involved in the initial and main pathways for the photodecomposition of H₂O₂, as shown in eq.(4-61).

Table 4-10. Summary of Primary Processes in the Photolysis of H_2O_2 ^[37]

Primary Process	Quantum Yield	
	123.6 nm	253.7 nm
$\text{H}_2\text{O}_2 \rightarrow \text{H}\bullet + \text{HOO}\bullet$ (4-65)	≥ 0.25	< 0.01
$\text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{O}_2$ (4-66)	0.25	< 0.01
$\text{H}_2\text{O}_2 \rightarrow \text{H}_2 + 2\text{O}$ (4-67)	0.25	< 0.01
$\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}(\text{singlet})$ (4-68)	< 0.01	< 0.01
$\text{H}_2\text{O}_2 \rightarrow 2 \bullet\text{OH}$ (4-69)	≤ 0.50	~ 1.0

It has been reported that hydroxyl radical is a strong oxidizing agent and it can react with a variety of substances, such as ammonia, carbonate and organics to produce other reactive radical intermediates. Table 4-11 summarizes the rate constants for some reactants with hydroxyl radical in aqueous solution. Some properties of hydroxyl radical are listed in Table 4-12.

Table 4-11. Rate Constants for the Reaction of Hydroxyl Radical with Various Compounds^[25].

Reactant	Reaction	$k \text{ (M}^{-1} \text{ s}^{-1}\text{)}$
NH ₃	$\bullet\text{OH} + \text{NH}_3 \rightarrow \bullet\text{NH}_2 + \text{H}_2\text{O}$ (4-70)	9.0×10^7
NO ₂ ⁻	$\bullet\text{OH} + \text{NO}_2^- \rightarrow \bullet\text{NO}_2 + \text{OH}^-$ (4-71)	9.1×10^9
H ₂ O ₂	$\bullet\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HOO}\bullet + \text{H}_2\text{O}$ (4-72)	2.7×10^7
HOO•	$\bullet\text{OH} + \text{HOO}\bullet \rightarrow \text{O}_2 + \text{H}_2\text{O}$ (4-73)	6.0×10^9
OH ⁻	$\bullet\text{OH} + \text{OH}^- \rightarrow \text{O}\bullet + \text{H}_2\text{O}$ (4-74)	1.2×10^{10}
CH ₃ COOH	$\bullet\text{OH} + \text{CH}_3\text{COOH} \rightarrow \bullet\text{CH}_2\text{COOH} + \text{H}_2\text{O}$ (4-75)	1.6×10^7
C ₆ H ₅ COOH	$\bullet\text{OH} + \text{C}_6\text{H}_5\text{COOH} \rightarrow [\text{HOC}_6\text{H}_5\text{COOH}]\bullet$ (4-76)	5.9×10^9
HCOOH	$\bullet\text{OH} + \text{HCOOH} \rightarrow \bullet\text{COOH} + \text{H}_2\text{O}$ (4-77)	1.3×10^8

Table 4-12. Properties of Hydroxyl Radical in Aqueous Solution^[25].

Property	Unit	Value
Max. absorption wavelength (λ_{max})	nm	230
Molar extinction coefficient at λ_{max}	M ⁻¹ .cm ⁻¹	530
pKa	-	11.9
E ⁰	V	1.77
Diffusion coefficient	cm ² /s	2.3×10^{-5}
ΔG_f^0	kJ/mol	13
ΔH_f^0	kJ/mol	-7
S ₂₉₈ ⁰	kJ.mol ⁻¹ .K ⁻¹	96

4.4.2 Potassium Persulphate

Potassium persulphate (K₂S₂O₈) is colorless or white, odorless crystals with molecular weight 270.3. 1 part of K₂S₂O₈ will dissolve in 50 parts of water and the resultant solution is acidic.

Persulphate is a powerful oxidizing agent with a high oxidation potential.

It can oxidize water to oxygen and hydrogen ion when the solution is heated.^[62]

Persulphate absorbs UV light. Its absorptivity increases with the decrease of the wavelength as shown in Figure 4-6. In aqueous solution, when $\text{S}_2\text{O}_8^{2-}$ is exposed to UV irradiation, the sulphate anion radical $\bullet\text{SO}_4^-$ is generated, which is a useful oxidant in aqueous solutions.^[67] The sulphate anion radical can effect the oxidation reactions by hydrogen abstraction or electron transfer. In aqueous solution, $\bullet\text{SO}_4^-$ can react with water to produce the hydroxyl radical, also it is capable of oxidizing the hydroxide ion to the hydroxyl radical.^[67] Therefore the photolysis of persulphate generates the hydroxyl radicals.

Under UV irradiation, oxidation-reduction reactions between persulphate and the water also occurs. The solvent water is oxidized to oxygen (O_2) and hydrogen ion (H^+), and the persulphate is reduced to sulphate, resulting in extensive bubbling and a pH change in the solution. The overall reaction is shown

in equation (4-83). As can be seen, it is identical to the reaction given by equation (4-79).

Figure 4-6. UV Absorption Spectrum of Persulphate in Aqueous Solution

5. EXPERIMENTAL

5.1 Materials

All the chemical and reagents were certified ACS grades and used as received, which included:

Precursors (Nitrogen Source):

Process precursors: ammonium sulphate, ammonium nitrate, ammonium acetate, ammonium oxalate, and ammonium hydroxide (aqueous ammonia, 29%) were provided by Fisher Scientific.

Oxidants:

Hydrogen peroxide (30%) obtained from Fisher Scientific and potassium persulphate provided by VWR Scientific were used as oxidants in the process, both of them are analytical reagent grades. Catalase from bovine liver (60,000 units/mg, 1 unit decompose 1 μmol of H_2O_2 per minute at pH 7.0 at 25°C) was used to eliminate the H_2O_2 interference during the analyses and was provided by Sigma.

Other Reagents:

Other reagents such as sodium nitrite, pH buffer reagents, reagents for various analyses were supplied by Fisher Scientific or Sigma.

Distilled water was used in all the experiments while deionized and distilled water was used for all analytical determinations.

5.2 Equipment

The advanced photo-oxidation process consists of an advanced photo-oxidation system and other equipment, which are outlined below.

5.2.1 Rayox® Advanced Oxidation System

All the experiments were carried out in the custom-modified Rayox® Advanced Oxidation System supplied by Calgon Carbon Oxidation Technologies of Markham, Ontario, Canada. The system can be operated as a true batch reactor or used as a recycle reactor. The two major components of the system: the UV reactor and the UV lamp are described below.

5.2.1.1 UV reactor

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 (Figure 5-1, 5-2, 5-4), and separated from the water 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 water.

There are some accessories equipped with the UV reactor, including a pH probe, mixer, cooling water loop, quartz sleeve wiper, UV light shutter, etc.

Figure 5-1. Front View of the UV reactor

Figure 5-2. Rear View of the UV Reactor

5.2.1.2 UV Lamp

1 kW medium pressure mercury lamp was used in this system. Its spectral distribution of emission and output are known, as shown in Figure 5-3. As can be seen, two emission peaks appeared at about 220 nm with output 1.2 kW of radiation energy and 260 nm with 1.5 kW of energy. The light intensity in the range of 200 to 500 nm was found to be $(6.45 \pm 0.16) \times 10^{-4}$ Einstein/s and the light intensity for wavelength 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 per minute or 0.556 kWh/m³ per minute for a total reaction volume of 30L. The rated lifetime of the UV lamp is about 3000 hours.

Figure 5-3. Energy Distribution of 1 kW Medium-Pressure Mercury Lamp in Rayox® Advanced Oxidation System

5.2.1.3 Other Equipment

A Masterflex peristaltic pump along with the controller (with auto dispense function) was used to pump the water from the feed tank to the UV reactor. A 800W heating tape was used to increase the initial temperature of the UV reactor, Nalgene HDPE tanks were used as the feed tanks for synthetic wastewater and narrow mouth bottles were used as sample containers. Air and water sampling equipment will be discussed in the following section, while analytical instruments will be detailed in the section of chemical analyses and protocols.

5.3. Experimental Procedure

5.3.1 Schematic for Advanced Photo-oxidation Process

In this study, the advanced photo-oxidation process for ammonia removal was carried out in the custom-modified Rayox UV reactor, which can be operated as a true batch reactor or as a recycle reactor. The process scheme is shown in Figure 5-4. Both direct photolysis and advanced photo-oxidation processes were carried out in the same UV reactor, and the experimental procedures are outlined below.

5.3.2 Direct Photolysis

In a typical batch experiment for direct photolysis of precursors, 28.5 L of the distilled water was pumped into the UV reactor through the fill port, and the pre-dissolved precursor solution was then added into the reactor through the reagent addition port with continuous complete mixing in the reactor. The pH in

Figure 5-4. Schematic for Advanced Photo-oxidation Process with UV Reactor

the reactor was adjusted by pH buffer solutions, and the total reaction volume was made up to 30 L. A sample was taken through the sample port and then the UV lamp was turned on with the lamp shutter in the closed position. At time zero, the lamp shutter was opened and the reaction time was counted. With complete mixing, the solution was irradiated by UV light and samples were taken at scheduled sampling frequencies (5 or 30 min.) and sent for analysis.

5.3.3. Advanced Photo-oxidation Process

In a typical batch experiment, 28.5 L of the distilled water was pumped into the UV reactor through the fill port, the pre-dissolved ammonium compound solution was then added into the reactor through the reagent addition port with continuous complete mixing in the reactor. The oxidant (hydrogen peroxide or dissolved persulphate solution) was added into the reactor through the reagent port. The pH in the reactor was adjusted by pH buffer solutions, and the total reaction volume was made up to 30 L. A sample was taken through the sample port and then the UV lamp was turned on. At time zero, the UV lamp shutter was opened and the run time started. With complete mixing, the solution was irradiated by UV light and samples were taken at scheduled sampling frequencies (5 or 30 min.) and sent for analysis.

5.3.4. Sampling:

Aqueous samples were collected at various time intervals. For UV/H₂O₂ process, the sample interval was 30 min., while for the UV/K₂S₂O₈ process, it was 5 min. Nalgene HDPE narrow mouth bottles were used to store the water samples. Samples were analyzed immediately when possible. If not, they were cooled at 4⁰C and analyzed within 24 hours. Sodium sulphite or catalase was used to quench the residual hydrogen peroxide in the sample.

A Gilian air sampling pump was used to pump the gas samples into the Tedlar air sampling bags.

In aqueous samples, ammonia, nitrite, nitrate, hydrazine, hydroxylamine, hydrogen peroxide, persulphate, and sulphate were analyzed. Nitrous oxide, nitric oxide, nitrogen dioxide, nitrogen and ammonia gas were analyzed in the gas samples. The chemical analysis methods are detailed in the next section.

5.4 Chemical Analyses and Protocols

Chemical analyses of the different precursors, oxidants, products and other possible intermediates for the reactions were carried out by developing specific protocols for the concentration ranges encountered in this study or following the standard protocols outlined in the literature. They are outlined below.

5.4.1 For Ammonia Nitrogen Precursors:

Ammonia (Nesslerization Method): ^[51]

Nesslerization method is applicable to natural waters or highly purified wastewaters which are low in color and in the range of 0.02 to 5 mg/L. In this method, ammonia is complexed by Nessler reagent which is potassium mercuric iodide (K_2HgI_4) in the strong alkaline solution to form a yellow-brown colloid mercury amino iodide (Hg_2OINH_2). The color intensity of the complex is directly proportional to the ammonia concentration and the yellow color can be measured at 410 nm for maximum absorbance ($\epsilon = 3.7 \times 10^3$).

Special Reagents:

(1). Nessler reagent: it was prepared by dissolving 10g HgI_2 in a 20 ml water containing 6g KI with stirring, in which 40 ml of 10M NaOH cool solution was added, the solution was made up to 100 ml and stored in a topaz bottle.

(2). Stock ammonium solution, 1000 mg/L N: it was prepared by dissolving 3.819g anhydrous NH_4Cl (dried at 100°C for 2 hours) in water and diluted to 1000 ml. This was used to prepare working standard solutions by appropriate dilution.

Procedure:

Samples were diluted to 25 ml to be in the range of 0.5 to 4 mg/L. The working standard solutions of 1, 2, 3 and 4 mg/L were prepared by appropriate dilution from the stock solution. In each 25 ml of diluted samples, blank or standard solutions, 0.5 ml of Nessler reagent was added and mixed. The color of the complex was developed for 40 min. and measured at 410 nm for absorbance by use of a UV/Vis Spectrophotometer.

A calibration curve was prepared by plotting the absorbance of ammonia standards versus their concentrations. Sample absorbance readings were compared with the calibration curve to obtain the ammonia concentration.

Nitrite (Diazotization Method)^[54] :

Diazotization method is applicable to samples free from turbidity or filtered through 0.45-micron membrane filter, in the range of 10 to 200 $\mu\text{g/L}$. In this method, nitrite reacts with sulfanilamide in acid solution to form the diazo compound. The resulting diazo compound then reacts with N-(1-naphthyl)-ethylenediamine dihydrochloride and forms a reddish purple azo dye. The intensity of azo dye is proportional to the nitrite concentration and has its maximum absorbance at 543 nm ($\epsilon = 6.6 \times 10^4$).

Special Reagents:

(1). Sulfanilamide solution, 1%: It contained 1 g sulfanilamide in 100 ml water, which was prepared by dissolving 5g sulfanilamide in a mixture of 50 ml conc. HCl and 300 ml water and diluted to 500 ml.

(2). N-(1-naphthyl)-ethylenediamine dihydrochloride, 0.1%: it contained 0.1 g of reagent in 100 ml, which was prepared by dissolving 0.5g N-(1-naphthyl)-ethylenediamine dihydrochloride in 500 ml water and stored in a dark bottle.

(3). Stock nitrite solution, 1000 mg NO_2^- -N/L: 4.929g NaNO_2 (dried at 110°C for 1 hour) were dissolved in water, and 1 ml chloroform was added as preservative, the solution was then diluted to 1000 ml and stored in a dark bottle.

Procedure:

The samples were diluted to 25 ml to be in the range of 1-200 $\mu\text{g/L}$ NO_2^- -N. The standard working solutions of 50, 100, 150 and 200 $\mu\text{g/L}$ NO_2^- -N were prepared by appropriate dilution from the stock solution. In 25 ml of standards, blank or sample solutions, 0.5 ml of 1% sulfanilamide solution was added and mixed, after a reaction time of 2-8 minutes, 0.5 ml of 0.1% N-(1-naphthyl)-ethylenediamine dihydrochloride solution was then added. The color was developed for 30 min and measured at 543 nm for absorbance.

A calibration curve was prepared by plotting the absorbance of nitrite nitrogen standards versus their concentrations. Sample absorbance readings were compared with the calibration curve to obtain the nitrite nitrogen concentration.

Nitrate, Nitrite and Sulphate (Ion Chromatography Method) ^[51,55]:

The method is applicable to surface, ground water, drinking water, and wastewater after filtration to remove particles larger than 0.2 μ m. It can be used for the analysis of solutions containing nitrate, nitrite, sulphate, chloride, thiocyanate, bromide, and phosphate. The minimum detectable concentration for nitrite is 0.1 mg/L, for nitrate is 0.1 mg/L and for sulphate is 0.25 mg/L. In this method, a solution containing anions is injected into a separator column with a stream of carbonate-bicarbonate eluent in it and the solution passes through a series of ion exchangers in the separator column. The anions in the solution are exchanged for the bicarbonate ions. A suppressor is used to lower the background conductivity of the carbonate eluent. In the suppressor, the separated anions are converted to their highly conductive acid forms and the carbonate-bicarbonate eluent is converted to weakly conductive carbonic acid. The separated anions in their acid forms are detected or measured by conductivity detector or UV detector. They are identified on the basis of retention time as compared to standards. Quantitation is by measurement of peak area or peak height.

Apparatus:

Dionex Ion Chromatograph was used, including Dionex high pressure injection valve, advanced chromatograph module, advanced gradient pump, 4 mm 4-SC separator column and guard column, anion micro membrane suppressor

(AMMS) with a pressurized suppressor solution reservoir, conductivity detector and linear UV/Vis detector.

Special Reagents:

(1). Eluent Concentrate, 0.36M Na_2CO_3 and 0.34M NaHCO_3 : this was prepared by dissolving 38.1564 g of sodium carbonate and 28.5668g sodium bicarbonate in water and the solution was diluted to 1000 ml.

(2). Standard Eluent, 1.8 mM Na_2CO_3 , 1.7 mM NaHCO_3 : this was prepared by pipetting 20 ml of eluent concentrate (1) into a 4 L container and it was diluted to 4 L.

(3). Suppressor solution, 0.025N H_2SO_4 : 2.8 ml of conc. H_2SO_4 was pipetted in a 4 L container and it was diluted to 4 L.

(4). Stock nitrate solution, 1000 mg/L NO_3^- : this was prepared by dissolving 1.3708 g NaNO_3 (dried at 105°C for 2 hr), in water and it was diluted to 1000 ml.

(5). Stock nitrite solution, 1000 mg/L NO_2^- : it was prepared by dissolving 1.4997 g NaNO_2 (dried at 105°C for 2 hr) in water and was diluted to 1000 ml.

(6). Stock sulphate solution, 1000 mg/L SO_4^{2-} : it was prepared by dissolving 1.8140 g K_2SO_4 (dried at 105°C for 2 hr) in water and diluted to 1000 ml.

Procedure:

Instrumental Parameters: eluent pressure = 7 to 10 psi, eluent flowrate = 2.0 ml/min, AMMS suppressor solution flowrate = 4 ml /min, AMMS suppressor

solution pressure = 10 psi, sample loop volume = 50 uL, conductivity detector operating range = 3, UV detector ($\lambda = 215$ nm).

The samples were diluted to 25 ml to be in the range of 0.5 to 20 mg/L for all three anions. The standards of 0.5, 1, 5 and 10 mg/L were prepared by dilution from the stock solution. Calibration standards were run first. A calibration curve was prepared by plotting peak area of standards versus anion concentration. When the correlation coefficient of the calibration curve was larger than 0.999, the samples were injected into the machine. The peak areas of the samples were compared with the calibration curve and calculated directly from the curve.

5.4.2 For Process Intermediates:

Hydrazine (p-dimethylaminobenzaldehyde Method) ^[45]:

It is applicable to samples free from turbidity or low in color, and with the concentration up to 0.77 mg/L. In this method, hydrazine reacts with p-dimethylaminobenzaldehyde to form a yellow-colored azine that rearranges in the presence of strong acid to form an intensely red-orange product. The intensity of colored product is proportional to hydrazine concentration and has its maximum absorbance at 458 nm, ($\epsilon = 3.4 \times 10^4$).

Special Reagents:

(1). p-Dimethylaminobenzaldehyde, 2%: 2g of p-Dimethylaminobenzaldehyde were dissolved in a mixture of 10 ml conc. HCl and 80 ml water, the solution was then diluted to 100 ml.

(2). Stock hydrazine solution, 1000 mg/L NH_2NH_2 : 4.0663g hydrazine sulphate ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{SO}_4$) were dissolved in water and the solution was diluted to 1000 ml.

Procedure:

The samples were diluted to 25 ml to be in the range of 0-0.77 mg/L NH_2NH_2 . The standard solutions of 0.1, 0.3, 0.5, 0.7 mg/L NH_2NH_2 were prepared by appropriate dilution from the stock solution. In 25 ml of each standards, blank or samples, 0.5 ml of 2% p-dimethylaminobenzaldehyde solution was added and mixed. The color of the solution was developed for 40 min. and measured at 458 nm for absorbance. A calibration curve was prepared by plotting the absorbance of standards versus hydrazine concentration and the sample concentrations were calculated directly from the curve.

Hydroxylamine (Modified Nesslerization Method)^[52]:

The modified Nesslerization method is applicable to samples free from turbidity or low in color and in the concentration range of 0.1 to 1.65 mg/L NH_2OH . In this method, hydroxylamine reacts with Nessler reagent to form the same yellow-colored complex as does for ammonia, its molar absorptivity is five times of that of ammonia. Addition of hydrochloric acid after the formation of the colored complex will lead to decomposition of ammonium mercuriiodide complex and keep the complex of hydroxylamine and Nessler reagent unchanged. The intensity of colored product with hydroxylamine is proportional to hydroxylamine concentration and has its maximum absorbance at 420 nm, ($\epsilon = 7.5 \times 10^3$).

Special Reagents:

(1). Perchloric acid, 4%: 6.67 ml of 60% perchloric acid (HClO_4) was pipetted and diluted to 100 ml.

(2). Stock hydroxylamine solution, 1000 mg/L NH_2OH : 2.1058g hydroxylamine hydrochloride ($\text{NH}_2\text{NH}_2\cdot\text{HCl}$) were dissolved in water and diluted to 1000 ml.

Procedure:

The samples were diluted to 25 ml to be in the range of 0.1-1.65 mg/L NH_2OH . The standard working solutions of 0.25, 0.5, 0.75, 1.0 mg/L NH_2OH were prepared by appropriate dilution from the stock solution. In 25 ml of each standard, blank or sample, 4 ml of 4% perchloric solution was added and mixed, after 2 min., 0.5 ml Nessler reagent was added into each solution and mixed, after 5 min., when precipitation occurred, 1 ml of 6N HCl was added and mixed. The color of the solution was developed for 60 min. Over the subsequent 60 min, it was observed that the precipitate was dissolved and the color formation reached its maximum. The solution was then measured at 420 nm for absorbance for all the samples, blank and standards. A calibration curve was prepared by plotting absorbance of standards versus hydroxylamine concentration and the sample concentrations were calculated directly from the curve.

5.4.3. For Photochemical Oxidants:

Hydrogen Peroxide (Iodometric Titration Method)^[53,56] :

This method is applicable to samples containing hydrogen peroxide and free from turbidity or low in color. In this method, hydrogen peroxide reacts with iodide in acid solution to form iodine and the iodine formed is titrated by the sodium thiosulphate solution with starch as the end point indicator. In this titration, thiosulphate ($\text{S}_2\text{O}_3^{2-}$) is oxidized to tetrathionate ($\text{S}_4\text{O}_6^{2-}$) by iodine.

Special Reagents:

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

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

(3). Starch solution, 2%: 2g starch were dissolved in 5 ml water and it was added into the 80 ml boiling water. The solution was kept boiling until it was clear, when it was cooled and made up to 100 ml.

(4). Potassium iodate solution, 20 mM: 4.2802 g KIO_3 (dried at 105°C for 2 hours) were dissolved in water and diluted to 1000 ml.

Procedure:

5 ml of 20% KI and 5 ml of 1M H_2SO_4 were added in a 125 ml Erlenmeyer flask, after adding 50 ml water, an appropriate sample aliquot was added in the same flask. After 15 min., the solution was titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$, when the

solution turned a straw yellow color, 2 ml of 2% starch solution was added, and the titration was continued until the solution turned to a clear (colorless) endpoint.

Standardization of 0.1N Na₂S₂O₃:

1 ml of 20 mM KIO₃, 5 ml 1M H₂SO₄ and 50 ml water were added in a 125 ml Erlenmyer flask. 5 ml 20% of KI was added in this flask and mixed. After 10 min, the solution was titrated with 0.1N Na₂S₂O₃ according to the same procedure as that for determination of H₂O₂.

Calculation:

The hydrogen peroxide concentration is calculated as follows:

$$\text{H}_2\text{O}_2 \text{ (g/L)} = N_1 \times V_1 \times \text{NW}_2 / V_2 = N_1 \times V_1 \times 17 / V_2$$

where:

V_1 = volume of standard Na₂S₂O₃ solution consumed , ml.

N_1 = normality of standard Na₂S₂O₃ solution, (approx. 0.1N).

NW_2 = equivalent weight of H₂O₂, (equals 17 in this case).

V_2 = volume of the sample taken for titration, ml.

The Normality of Na₂S₂O₃ is calculated by the following equation:

$$\text{Na}_2\text{S}_2\text{O}_3 \text{ (N)} = (N_3 \times V_3) / V_1 = 6 M_3 \times V_3 / V_1 = 0.12 / V_1$$

where:

N_3 = normality of KIO₃ solution, (equals to 6 times of M_3 in this case).

V_3 = volume of standard KIO₃ solution used, ml.

M_3 = molarity of standard KIO₃ solution, mol/L.

V_1 = standard Na₂S₂O₃ solution consumed, ml .

Persulphate (Ceric Titration Method)^[53] :

It is applicable to samples containing persulphate and free from turbidity or low in color. In this method, persulphate ($S_2O_8^{2-}$) reacts with ferrous ion (Fe^{2+}) in acid solution in the presence of bromide (Br^-) to form ferric ion and sulphate, and the excess ferrous ion is titrated by the ceric sulphate solution with ferroin as the end point indicator.

Special Reagents:

(1). Ferrous ammonium sulphate, 0.05N: obtained from Fisher Scientific and used as received.

(2). Sodium bromide solution, 5M: 51.45g NaBr were dissolved in water and diluted to 100 ml.

(3). Ferroin indicator, 0.001M: dilute 4 ml of 0.025 M ferroin indicator supplied by Fisher Scientific to 100 ml.

(4). Ceric Sulphate, 0.02N: obtained from Fisher Scientific and used as received.

Procedure:

10 ml sample was added in a solution consisting of 7 ml of 5M NaBr, 2 ml of 3M H_2SO_4 and 50 ml water and mixed, then 10 ml of 0.05N $Fe(NH_4)_2(SO_4)_2$ was added into the solution and mixed. After 20 min, 1 ml of 0.001M ferroin indicator was added in the solution and the solution was then titrated with 0.02 N ceric sulphate solution to the first colour change from orange to yellow.

Calculation:

The persulphate concentration is calculated as follows:

$$S_2O_8^{2-} \text{ (g/L) } = (N_2 \times V_2 - N_3 \times V_3) \times NW_1 / V_1 = (0.05 \times V_2 - 0.02 \times V_3) \times 96 / V_1$$

where:

V_1 = volume of sample used , ml

N_2 = normality of standard ferrous ammonium sulphate solution, 0.05N.

V_2 = volume of standard ferrous ammonium sulphate solution used, ml.

N_3 = normality of standard ceric sulphate solution, 0.02N.

V_3 = volume of standard ceric sulphate solution used, ml.

NW_1 = equivalent weight of persulphate, 96g/mole

5.4.4. For Final Products:**Nitrogen Oxides (Gas Detector Tube Method)^[58] :**

The Gastec nitrogen oxides detector tube is used to detect the NO and NO₂, in the range of 0.2 to 16.5 ppm. Halogens, chlorine dioxide, sulfur dioxide, and hydrogen sulfide when present will give plus or minus errors. In this method, the nitric oxide is oxidized to nitrogen dioxide by chromic acid in the tube. The nitrogen dioxide formed plus the original nitrogen dioxide already present in the sample reduces o-tolidine to form nitroso-o-tolidine. The reactions are as follows:

Apparatus:

Gastec Multi-stroke gas sampling pump (100 ml for 1 stroke), Gastec nitrogen oxides detector tube (measuring range 0.2 - 16.5 ppm NO₂), Masterflex tube.

Procedure:

One end of the tube was inserted into the rubber inlet of the pump with arrow on the tube pointing toward the pump, the other end was connected to the gas outlet of the UV reactor. The gas sample was pumped into the detector tube, the concentration of the NO₂ was read from the concentration mark on the tube.

Nitrogen and Nitrous Oxide (Gas Chromatography Method)^[45,59,60] :

The gas chromatography method achieves a good separation for nitrogen, nitrous oxide and nitrogen dioxide in air samples. In this method, a small volume of gas is injected into the gas chromatograph which is equipped with a thermal conductivity detector. The constantly flowing stream of carrier gas (helium) carries the gaseous constituents through a teflon chromatographic column. The gases pass through the column at different rates, as they have different retention times. Each species is detected as it emerges from the column and a gas chromatogram is obtained for each sample. Each peak in the chromatogram represents a compound and its retention time, and the area under the peak is proportional to its concentration.

Apparatus:

Gas Chromatograph (Varian Vista 6000) including a thermal conductivity detector, teflon column packed with porapak Q ($8' \times 1/8''$, 80/100 mesh), gas cylinders (helium, nitrous oxide, nitrogen), mass flow controller (Matheson), integrator, chart paper, syringe, gas sampling pump, gas sampling bottle and tedlar gas sampling bag.

Procedure:

Instrumental parameters: helium flowrate = 20ml/min, column temperature=25⁰C, thermal conductivity detector temperature=200⁰C, injection temperature=150⁰C. The helium gas was injected first to check the baseline, once the baseline was stable, the mixture of standard nitrogen compounds was injected. After the gas chromatograph had been calibrated, the samples were injected. A calibration curve was prepared by plotting the peak area of standards versus standard percentage. The sample percentage was calculated directly from the calibration curve.

6. RESULTS AND DISCUSSION

This chapter presents the results obtained in the various experiments, which are classified into the following sections: UV absorption spectra of ammonia precursors and oxidants, direct photolysis of ammonia precursors, advanced photo-oxidation of ammonia with UV/H₂O₂ and advanced photo-oxidation of ammonia with UV/K₂S₂O₈.

6.1. UV Absorption Spectra of Precursors and Oxidants

The UV absorptivity of a compound is evaluated by its UV absorption spectrum. In this study, the UV absorption spectra of the ammonia precursors (NH₄OH, (NH₄)₂SO₄, (NH₄)₂C₂O₄, NH₄Ac, and NH₄NO₃) and oxidants (H₂O₂ and K₂S₂O₈) were established with a Varian DMS 200 UV/Vis Spectrophotometer and are presented in Figure 6-1.

Figure 6-1. UV Absorption Spectra of Precursors and Oxidants

As can be seen, nitrate has the highest UV absorption among all these 7 compounds, followed by oxalate, persulphate, hydrogen peroxide, acetate, sulphate and aqueous ammonia. For all the 7 compounds, their absorption increases as the wavelength decreases. Most precursors are weak absorbers, so are oxidants persulphate and hydrogen peroxide.

As indicated earlier, the UV lamp employed in this study has broad spectral energy peaks at 220nm and 260nm. As shown in Figure 6-1, at 260 nm, all the compounds are weak in UV absorption. But at 220 nm, their absorption increases. Table 6-1 records their molar extinction coefficients at 220 nm. As can be seen, ammonium hydroxide absorbs weakly at 220 nm.

Table 6-1. The Molar Extinction Coefficients of Ammonia Precursors and Oxidants at 220 nm.

Type	Compound	ϵ (M ⁻¹ .cm ⁻¹)
Precursor	NH ₄ OH	2
Precursor	(NH ₄) ₂ SO ₄	6
Precursor	NH ₄ Ac	30
Precursor	(NH ₄) ₂ C ₂ O ₄	660
Precursor	NH ₄ NO ₃	1900
Oxidant	H ₂ O ₂	95
Oxidant	K ₂ S ₂ O ₈	240

6.2 Direct Photolysis of Ammonia Precursors

Direct photolysis was carried out by irradiating the aqueous solution containing initial nitrogen concentration of 3.57 mM at pH 10 and 25°C. The ammonia removal efficiency for the 5 precursors under direct photolysis treatment is presented in Figure 6-2. As shown, the overall ammonia removal percentage is quite low, less than 20%. Direct photolysis of a higher initial concentration of 14.28 mM nitrogen for each compound was also carried out and the overall ammonia removal efficiency was found to be less than 10%.

Figure 6-2. Direct Photolysis of Ammonia Precursors
($\text{NH}_3\text{-N}]_0 = 3.57 \text{ mM}$, pH 10)

These observations suggest that direct photolysis was not a viable option for effective ammonia removal. Therefore, an advanced oxidation process for effective removal of ammonia was investigated next.

6.3 Advanced Photo-oxidation of Ammonia with UV/H₂O₂

This section presents the results obtained in the process of advanced photo-oxidation of ammonia with UV/H₂O₂ treatment, which are summarized in the following order: photolysis of hydrogen peroxide, advanced photo-oxidation of precursors, degradation of ammonia by UV/H₂O₂ treatment, parametric studies, reaction mechanism for UV/H₂O₂ oxidation of ammonia, and the kinetic model for advanced photo-oxidation of ammonia.

6.3.1 Photolysis of Hydrogen Peroxide

74 mM (2.52 g/L) of an aqueous hydrogen peroxide solution was irradiated by the same procedure as that of direct photolysis of ammonia precursors. The experimental data obtained for photolysis of hydrogen peroxide is shown in Figure 6-3. As can be seen, the photo-decomposition of H₂O₂ follows zero order kinetics with a rate expression of $dC/dt = -8.97 \times 10^{-5} \text{ M.s}^{-1}$.

Figure 6-3. Photolysis of Hydrogen Peroxide. ([H₂O₂]₀=74 mM, pH 10)

The primary process of the photolysis of hydrogen peroxide results in the generation of highly reactive hydroxyl radicals with a primary quantum yield of $\Phi=0.5$. The hydroxyl radicals then attack ammonia to initiate a series of photochemical reactions. The $\bullet\text{OH}$ radical formed readily reacts with H_2O_2 to give $\text{HOO}\bullet$ radical and thus bring about the radical chain reactions which result in higher overall quantum yield for H_2O_2 photolysis ($\Phi \geq 1$). The reaction scheme postulated by Haber-Weiss,^[37] which has been discussed in chapter 4, describes the chain reactions of H_2O_2 decomposition in aqueous solution:

The net reaction from this reaction scheme is $2\text{H}_2\text{O}_2 + h\nu \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$, which indicates the generation of oxygen. This explains the bubbling phenomenon during the photolysis of H_2O_2 . In alkaline media, formation of O_3^- , O_2^- and hydroxyl ion (OH^-) have been reported for the photolysis of H_2O_2 ,^[25] which explains the slight pH increase in the process.

Hydroxyl radical can readily react with many species including ammonia and the reaction rates are usually high. Some reactions of interest and their reaction rate constants have been presented in Table 4-11 in chapter 4.

6.3.2. Advanced Photo-oxidation of Precursors

The results obtained from the direct photolysis of the ammonia precursors suggest its limitation for ammonia removal, hence advanced photo-oxidation processes were investigated for ammonia removal. The solution containing same initial concentration, $[\text{NH}_3\text{-N}]_0 = 3.57 \text{ mM}$ (50 mg/L) of each ammonia precursors and sufficient hydrogen peroxide, $[\text{H}_2\text{O}_2]_0 = 65 \text{ mM}$ (2.2 g/L) was irradiated in the same UV reactor under the same conditions. The results are presented in Figure 6-4.

Figure 6-4. Advanced Photo-oxidation of Ammonia Precursors
 $([\text{NH}_3\text{-N}] = 3.57 \text{ mM}, \text{pH } 10)$

As can be seen, the overall percent ammonia removal (40%) has been improved as compared to direct photolysis (19%). Of the five nitrogenous compounds,

ammonium hydroxide has the highest ammonia removal. But the performance of precursor ammonium hydroxide and ammonium sulphate were close to each other. Therefore, ammonium hydroxide and ammonium sulphate were chosen as the preferred precursors for further investigation.

The advanced photo-oxidation of each precursors was also carried out at higher initial concentration $[\text{NH}_3\text{-N}]_0 = 14.28 \text{ mM}$ (200 mg/L). It was found that the overall ammonia removal obtained (17.8%) was much lower than that of lower initial concentration $[\text{NH}_3\text{-N}]_0 = 3.57 \text{ mM}$ (40.2%), as shown in Table 6-2.

Table 6-2. Ammonia Removal Efficiency for Direct Photolysis and Advanced Photo-oxidation (UV/H₂O₂) of Precursors after 2 hours UV irradiation.

Process	$[\text{NH}_3]_0$ (mM)	Ammonia Removal Efficiency (%) for Each Precursor				
		NH ₄ OH	(NH ₄) ₂ SO ₄	(NH ₄) ₂ C ₂ O ₄	NH ₄ NO ₃	NH ₄ Ac
UV only	14.28	5.9	3.8	5.9	12.8	3.0
UV only	3.57	18.7	15.1	6.9	19.3	4.5
UV/H ₂ O ₂	14.28	17.8	13.6	11.3	5.8	8.6
UV/H ₂ O ₂	3.57	40.2	36.2	30.4	18.6	12.4

These observations suggests that the initial ammonia concentration affects the ammonia removal efficiency. For the same irradiation times, ammonia removal efficiency increased with the decrease of initial ammonia concentration.

6.3.3. Degradation of Ammonia by UV/H₂O₂ treatment

The results presented above only show the removal efficiencies for 2 hours irradiation. In order to get better ammonia removal and achieve an effluent quality

which meets the regulated discharge level (10 mg/L $\text{NH}_3\text{-N}$),^[61] the prolonged treatment was carried out with the ammonium hydroxide as the preferred nitrogen source.

The synthetic wastewater containing $[\text{NH}_3\text{-N}]_0 = 3.54 \text{ mM}$ (50 mg/L) was treated with UV irradiation until the desired ammonia concentration in the effluent (less than 10 mg/L) was achieved. In this study, it is observed that the effluent concentration of 0.66 mM (9.3 mg/L N) was achieved after 6 hours of UV irradiation. The degradation of ammonia and the decomposition of hydrogen peroxide in this process are shown in Figure 6-5. The products formed during the UV irradiation were identified and monitored for their concentrations, which are discussed in the following section.

Figure 6-5. Degradation of Ammonia and Decomposition of H_2O_2 by UV/ H_2O_2 Treatment (pH 10, 25°C).

Figure 6-5 shows that the overall destruction of ammonia follows first order kinetics with an observed rate constant of $k = 0.2748 \text{ h}^{-1} = 7.63 \times 10^{-5} \text{ s}^{-1}$. The

photo-decomposition of hydrogen peroxide in the presence of ammonia, in this case, obeys zero order kinetics over the first 2 hours with a rate of $dC/dt = -5.409 \times 10^{-7} \text{ M.s}^{-1}$, which agrees well with results obtained from the photolysis of hydrogen peroxide.

6.3.4. Parametric Studies

This section presents the results of parametric studies, including effects of UV dose, initial ammonia concentration, pH, initial hydrogen peroxide concentration, temperature, the presence of photocatalyst and the presence of nitrate or nitrite.

6.3.4.1. Effect of UV Dose (Irradiation Time)

The above results actually suggest the UV dose (irradiation time) effect on ammonia removal. Thus Figure 6-5 is replotted in terms of the ammonia removal percentage which depends on the irradiation time, as shown in Figure 6-6. It is noted that one minute of UV irradiation corresponds to UV Dose of 0.556 kWh/m^3 in the UV system. A calculated dose-response equation

$$R = 100 - 103.14 e^{(-0.2748.t)} \quad (t \neq 0) \quad (6-5)$$

where R is $\text{NH}_3\text{-N}$ removal (%), t is the irradiation time (h), well describes the dependency of ammonia removal on UV irradiation for this study. The equation can be used to estimate the irradiation time required for a certain removal efficiency desired under the operating conditions employed.

Figure 6-6. Effect of UV Dose on Ammonia Removal ($[\text{NH}_3\text{-N}]_0 = 3.57 \text{ mM}$, pH 10). Each minute corresponds to 0.556 kWh of electrical energy used per m^3 of water treated.

It was also observed that the ammonia removal under the same condition for the dark reaction was too slow to be observed. As shown in Figure 6-6, only 1.3% of ammonia disappeared after 6 hours of dark reaction which indicates much lower ammonia degradation in the presence of H_2O_2 for the dark reaction.

6.3.4.2 Effect of Initial Ammonia Concentration

From the previous investigation on the direct photolysis of precursors, it appeared that the ammonia efficiency depends on the ammonia feed concentration. As shown in Table 6-2, the overall removal efficiency increased as the initial concentration decreased. Therefore, the effect of initial ammonia concentration

was investigated in detail by treating the water with initial ammonia concentrations of 50, 100, and 200 mg/L $\text{NH}_3\text{-N}$ under the same operating conditions. The experimental results are shown in Figure 6-7.

Figure 6-7. Effect of Initial Ammonia Concentration on Ammonia Removal (pH 10, 25°C)

As can be seen, the ammonia removal efficiency appears to increase with the decrease of feed ammonia concentration and the total amount of ammonia removed is greater at higher initial ammonia concentration, which could be explained by the first order kinetics of ammonia photodegradation. These observations are similar to those have been reported.^[25]

6.3.4.3 Effect of pH

The effect of pH was investigated by adjusting the pH of the feed water to 3, 7 and 10 using the pH buffer solutions, sodium hydroxide and sulphuric acid. The water thus prepared was treated under the same conditions as above. The results are shown in Figure 6-8.

Figure 6-8. Effect of pH on Ammonia Removal ($[\text{NH}_3\text{-N}]_0 = 3.57\text{mM}$, pH 10)

As can be seen, the ammonia removal was too slow to be observed in acidic solution, where ammonium ion (NH_4^+) is dominant. The reaction rate increased significantly as the pH increased, especially from pH 7 to 10. These observations suggests that unprotonated ammonia (NH_3) is oxidized by H_2O_2 much more easily than is ammonium ion, which was probably due to the faster reaction of ammonia

with hydroxyl radical to produce the more easily oxidized product (such as amino radical).

The results indicate that the process must be operated in the basic pH range in order to achieve the best ammonia removal efficiency. That is why all the experiments were carried out at pH 10 in this study .

It is also found out that the pH decreased slightly, from 10.0 to 9.7 during the 2 hour irradiation, which may be explained by the formation of hydrogen ions during the photo-oxidation of nitrogen-containing intermediate products, photodissociation of ammonia or hydrogen peroxide. Therefore, prompt pH adjustment is required in order to achieve the consistent ammonia removal efficiency. As shown in Figure 5-4, the pH controller and the buffer solutions were used for the process pH control.

6.3.4.4 Effect of initial Hydrogen Peroxide Concentration

In the advanced oxidation process, H_2O_2 was consumed in different reactions, including the self-decomposition of H_2O_2 , its reactions with ammonia and intermediate products. According to equations (4-7), (4-23) and (4-32), for complete oxidation of 1 mole of ammonia, at least 2 moles of H_2O_2 are required. Therefore, to examine the effect of initial H_2O_2 concentration, the different molar ratios of $r = [\text{H}_2\text{O}_2]_0/[\text{NH}_3\text{-N}]_0 = 2, 4, 8, 16, 64$ were prepared and water was treated under the same operating conditions as above. The ammonia removal efficiencies obtained were plotted against the irradiation time for those four molar ratios, which are shown in Figure 6-9.

Figure 6-9. Effect of Molar Ratio r on Ammonia Removal
 $(r = [\text{H}_2\text{O}_2]_0 / [\text{NH}_3\text{-N}]_0, [\text{NH}_3\text{-N}]_0 = 3.57\text{mM}, \text{pH } 10)$.

The results indicates no significant variation of ammonia removal at the various molar ratios chosen. But it is noted that it is very important to monitor the H_2O_2 concentration during the process in order to maintain the best ammonia removal.

6.3.4.5 Effect of Temperature

The effect of temperature on ammonia removal efficiency was investigated by irradiating the synthetic wastewater at different temperature under the same condition. A 800W heating tape was used to increase the temperature of the reactor. The highest temperature designed for the operating system is 60°C , therefore 20, 25, 35, and 45°C were chosen for this study and the results are shown in Figure 6-10. As can be seen, there was no significant variation of ammonia removal at various temperature from 20°C to 45°C .

Figure 6-10. Effect of Temperature on Ammonia Removal
 ($[\text{NH}_3\text{-N}]_0 = 3.57 \text{ mM}$, pH 10)

6.3.4.6 Effect of Photocatalysts

In advanced oxidation processes, photocatalysts are employed to increase the quantum yield and activity of $\bullet\text{OH}$ radical, which can lead to higher removal of contaminants. The most often used homogeneous photocatalysts for UV/ H_2O_2 treatment are ferrous ion and ferric ion.

In order to investigate the effect of those photocatalysts on ammonia removal, the experiments were carried out by adding the photocatalysts of ENOX 510 or ENOX 910 into the water under the same condition. ENOX 510, which contained mainly ferrous sulphate and ENOX 910, which contained 47% of ferrioxalate were patented homogeneous photocatalysts supplied by Calgon

Carbon Oxidation Technologies. The process has to be operated at acidic pH to avoid precipitation. In this study, 40 ppm of Fe^{2+} from ENOX 510 or 40 ppm of Fe^{3+} from ENOX 910 was added into the solution, then followed by the addition of H_2O_2 . Process pH was adjusted to 3. The observation indicated that the ammonia removal was too small to be observed in the presence of photocatalyst, which also reveals that at acidic pH, when ammonium ion is dominant, photo-oxidation of ammonium ion is not significant despite the use of photocatalysts.

6.3.4.7 Effect of Nitrite and Nitrate

From the earlier investigation, it was observed that conversion of ammonia in aqueous solution containing ammonium nitrate was lower than that in aqueous solution containing ammonium hydroxide or ammonium sulphate, which suggests that nitrate might interfere with the photo-oxidation of ammonia. Therefore the effect of nitrate and nitrite on ammonia removal was thoroughly investigated as follows:

A 13 mg/L $\text{NO}_3\text{-N}$ in NaNO_3 or 25 mg/L $\text{NO}_2\text{-N}$ in NaNO_2 was added into the feed solution containing ammonium hydroxide with $[\text{NH}_3\text{-N}]_0 = 3.57 \text{ mM}$. The water was treated under UV/ H_2O_2 oxidation for 2 hours, employing the same operating condition as those for synthetic wastewater containing only NH_4OH or NH_4NO_3 (refer to experiments No. 5, 6, 9, 10 in Appendix 5). The ammonia removal efficiencies for the different feed water containing only NH_4OH , only NH_4NO_3 , $\text{NH}_4\text{OH} + \text{NaNO}_3$ and $\text{NH}_4\text{OH} + \text{NaNO}_2$ are presented in Figure 6-11.

Figure 6-11. Effect of Nitrate and Nitrite on Ammonia Removal by UV/H₂O₂ Treatment ($[\text{NH}_3\text{-N}]_0 = 3.57 \text{ mM}$, pH 10)

As can be seen, the ammonia removal efficiency decreased when nitrate or nitrite was initially present in water. The removal of ammonia decreased with the increase of nitrate concentration. For the feed containing nitrate, a large amount of nitrite was formed after 2 hour irradiation, while for the feed containing nitrite, a large amount of nitrate was formed. These observations suggest that by UV/H₂O₂ oxidation treatment, nitrite can be oxidized to nitrate and nitrate can be reduced to nitrite.

In order to confirm these observations, the experiments were repeated by irradiating 50 mg/L NO₃-N of NaNO₃ or 50 mg/L NO₂-N of NaNO₂ solutions for both direct photolysis and UV/H₂O₂ treatment (refer to experiments No. 3, 4, 7, 8 in Appendix 5). The results indicated that under direct photolysis, nitrate was rapidly reduced to nitrite, while nitrite was oxidized to nitrate. But the oxidation

of nitrite was much slower. With UV/H₂O₂ treatment, oxidation of nitrite to nitrate was much faster than reduction of nitrate to nitrite. These observations explain why nitrate concentration is usually higher than nitrite in the final products in the UV/H₂O₂ treatment.

6.3.5 Reaction Mechanism for UV/H₂O₂ Oxidation of Ammonia

This section presents the product distribution and the postulated reaction mechanism for photo-oxidation of ammonia.

6.3.5.1 Product Yields for Photo-oxidation of Ammonia with UV/H₂O₂ Treatment

A typical experiment was carried out by irradiating the NH₄OH solution in the presence of H₂O₂. The operating parameters were: [NH₃-N]₀ = 3.57 mM (50 mg/L N), [H₂O₂]₀/[NH₃-N]₀ = 8, pH = 10, temperature = 25°C. Aqueous samples were taken every 30 minutes and sent for the analyses of ammonia, nitrite, nitrate, hydrazine and hydroxylamine. The gas samples were taken for analysis of nitrous oxide, ammonia, nitric oxide and nitrogen dioxide.

Table 6-3 shows the product yields and ammonia concentration of this typical experiment. As can be seen, NO₃⁻ is predominant among all the products. Nitrite concentration is much lower than nitrate, which may be explained by the rapid oxidation of nitrite to nitrate. Hydroxylamine and hydrazine were not detected, which may be explained by the rapid secondary oxidation by H₂O₂. In the gas stream, nitrogen is predominant and only a trace amount of nitrous oxide was detected.

Table 6-3. Product Yields for Photo-oxidation of Ammonia with UV/H₂O₂ Treatment

Time (hour)	Nitrogen Concentration of Different Species								
	Aqueous Sample						Gas Sample		
	Unit	NH ₃	NO ₂ ⁻	NO ₃ ⁻	N ₂ H ₄	NH ₂ OH	N ₂	N ₂ O	NO + NO ₂
0	(mM)	3.54	0	0	0	0	0	0	0
6	(mM)	0.66	0.079	1.99	0	0	0.80	0.016	0
P *	%	18.7	2.2	56.1	0	0	22.5	0.5	0

* the product distribution of nitrogen in percentage after 6 hours of irradiation.

The distribution of products with irradiation time are plotted together with the kinetic model in the section 6.3.6.

6.3.5.2 Reaction of Hydroxylamine with Hydrogen Peroxide

As indicated above, the hydroxylamine was not detected in the process, which could be explained by the rapid oxidation by H₂O₂ or by other radicals. To confirm these observations, the effects of H₂O₂ on oxidation of NH₂OH was investigated in detail as follows:

Four experiments were carried out for hydroxylamine with and without H₂O₂ both under UV irradiation and dark reaction. Aqueous hydroxylamine solution with [NH₂OH]₀ = 3.6 mM (calculated by assuming the complete conversion of ammonia to hydroxylamine) was used. Operating parameters were: [H₂O₂]₀=28.8mM, pH =10, temperature at 25⁰C.

For aqueous solution containing only hydroxylamine, no change of concentration was observed after it was kept standing in dark for 24 hours. For the solution containing $\text{NH}_2\text{OH} + \text{H}_2\text{O}_2$, 53% of NH_2OH was oxidized after 24 hours of dark reaction to give mainly nitrogen gas, a small amounts of nitrous oxide in the gas samples, a small amounts of nitrite and nitrate in the aqueous samples. For the solutions containing NH_2OH under direct photolysis, 19% of NH_2OH was oxidized after 2 hour irradiation to give mainly nitrogen gas and a very small amount of nitrite and nitrate. Under the same conditions, for the treatment by $\text{UV}/\text{H}_2\text{O}_2$, 67 % NH_2OH was oxidized in 1 hour to give 25% of N_2 , 27% of NO_2 , and 15% of NO_3^- . Trace amounts of N_2O , but no NO and NO_2 were detected under this treatment.

The above observation indicates that under $\text{UV}/\text{H}_2\text{O}_2$ treatment, NH_2OH is rapidly oxidized to mainly nitrite, nitrate and some nitrogen gas, which are the same products obtained from the photo-oxidation of ammonia. These observations also suggest that NH_2OH is probably one of the intermediates in the photo-oxidation of ammonia.

6.3.5.3 Reaction of Hydrazine (NH_2NH_2) with Hydrogen Peroxide

The effect of H_2O_2 on the oxidation of NH_2NH_2 was thoroughly investigated in order to confirm the rapid oxidation of NH_2NH_2 by H_2O_2 .

Four experiments were carried out for hydrazine with and without the H_2O_2 both under UV irradiation and dark reaction. The same experimental and analytical procedures as that for reaction with hydroxylamine were employed. Aqueous

hydrazine solution with $[\text{NH}_2\text{NH}_2]_0 = 1.8 \text{ mM}$ which was calculated by assuming the complete conversion of ammonia to hydrazine was used. Other operating parameters were: $[\text{H}_2\text{O}_2]_0 = 28.8 \text{ mM}$, $\text{pH} = 10$, temperature at 25°C .

For aqueous solution containing only hydrazine, no change of hydrazine concentration was observed after it was kept standing in dark for 24 hours. 62% of hydrazine was oxidized in the presence of H_2O_2 to give only nitrogen gas after 24 hours in dark. For direct photolysis, 23% of NH_2NH_2 was oxidized after 2 hours of irradiation to give only nitrogen. Under the same conditions, for the treatment by $\text{UV}/\text{H}_2\text{O}_2$, NH_2NH_2 was totally oxidized to products within 50 min., yielding solely N_2 .

The above observations indicate that under $\text{UV}/\text{H}_2\text{O}_2$ treatment, NH_2NH_2 reacts very rapidly with H_2O_2 and is easily oxidized to the sole product nitrogen, which explains why NH_2NH_2 was not detected in this treatment as an end-product. These results also suggest that NH_2NH_2 is probably one of the intermediates in photo-oxidation of ammonia. Reaction of NH_2NH_2 with H_2O_2 primarily produces nitrogen gas which was observed in the process.

6.3.5.4 Reaction Scheme

The above observations confirm the formation of the probable intermediate products and their reactions with H_2O_2 . Based on this information and the results obtained from the identification and quantitation of the final products, the following probable mechanism is postulated to describe the advanced photo-oxidation of ammonia under $\text{UV}/\text{H}_2\text{O}_2$ treatment.

(1) Initial photochemical step involves the primary photolysis of H_2O_2 to completely generate the $\bullet\text{OH}$ radicals [eq.(6-6)], which then attack the unprotonated ammonia (NH_3) to give the amino radical ($\bullet\text{NH}_2$) by reaction (6-7). Reaction (6-7) proceeds both in dark or under irradiation with rate constant reported $k = (9 \pm 1) \times 10^7 \text{ M}^{-1}.\text{s}^{-1}$ [32].

(2) The $\bullet\text{NH}_2$ formed from the equation (6-7) then reacts with $\bullet\text{OH}$ radicals to give NH_2OH [eq.(6-8)], or reacts with $\bullet\text{NH}_2$ to form NH_2NH_2 [eq.(6-9)].

(3) The NH_2OH formed from equation (6-8) then undergoes further oxidation reaction with H_2O_2 to form final products N_2 , NO_2^- and NO_3^- [eq.(6-10)], of which NO_2^- was rapidly oxidized to NO_3^- by H_2O_2 and leads to a higher nitrate concentration. At the same time, NH_2NH_2 formed from equation (6-9) reacts with H_2O_2 to give N_2 [eq.(6-11)]. Higher concentrations of NO_3^- and NO_2^- than N_2 formed in the final product suggest that the yield of intermediate NH_2OH was probably higher than that of NH_2NH_2 .

(4) Other Conceivable Pathways:

•OH radicals can also react with H_2O_2 to give $\text{HOO}\bullet$ radicals, and $\bullet\text{NH}_2$ could react with $\text{HOO}\bullet$ to form NH_2OOH [eq(6-12)], or react with O_2 to form NH_2O_2 [eq.(6-13)]^[32]. The intermediates formed from equations (6-12) and (6-13) are oxidized by H_2O_2 or other oxidizing species to give the final products NO_3^- , NO_2^- , and N_2 .

6.3.6 The Kinetic Model for Photo-oxidation of Ammonia

The major products for advanced photo-oxidation of ammonia were nitrate, nitrite and nitrogen gas. The distribution of the product yields from a typical experiment is presented in Table 6-4.

Based on the reaction scheme as shown in section 6.3.5.4 and the product distribution obtained from Table 6-4, a competitive-consecutive reaction model is proposed to simulate the experimental data. Its reaction rate and concentration expressions are presented in equations (6-14) to (6-25) in Figure 6-12.

Table 6-4 Distribution of Product Yields with the Irradiation Time

Irradiation Time (h)	Nitrogen Concentration (mM)			
	[NH ₃ -N]	[NO ₂ ⁻ -N]	[NO ₃ ⁻ -N]	[N ₂ -N]
0	3.54	0	0	0
1	2.78	0.22	0.41	0.13
2	2.12	0.22	0.94	0.26
3	1.62	0.19	1.27	0.46
4	1.31	0.12	1.75	0.36
5	0.92	0.094	1.88	0.65
6	0.66	0.079	1.99	0.81

Rate Equations:
$$\frac{dC_A}{dt} = -k_1 C_A - k_3 C_A = -(k_1 + k_3) C_A = -k C_A \quad (6-16)$$

$$\frac{dC_N}{dt} = k_3 C_A \quad (6-17)$$

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_R \quad (6-18)$$

$$\frac{dC_S}{dt} = k_2 C_R \quad (6-19)$$

$$\text{Nitrogen Balance : } C_{A0} + C_{R0} + C_{S0} + C_{N0} = C_A + C_R + C_S + C_N \quad (6-20)$$

Initial Conditions: at $t=0$:

$$C_A = C_{A0}, C_R = C_{R0} = 0, C_S = C_{S0} = 0, C_N = C_{N0} = 0 \quad (6-21)$$

$$\text{Concentration Expressions: } C_A = C_{A0} e^{-kt} \quad (6-22)$$

$$C_N = \frac{C_{A0}k_3}{k}(1 - e^{-kt}) \quad (6-23)$$

$$C_R = \frac{k_1C_{A0}}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t}) \quad (6-24)$$

$$C_S = C_{A0} - C_{A0} e^{-kt} - \frac{C_{A0}k_3}{k}(1 - e^{-kt}) - \frac{k_1C_{A0}}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t}) \quad (6-25)$$

Figure 6-12. Competitive-Consecutive Reaction Model

Several experiments have been conducted under similar conditions for advanced photo-oxidation of ammonia with UV/H₂O₂. These results are presented in Appendix 6 for 6 hour irradiation. The results indicate similar trends for the different sets of experiments. Within the concentration ranges encountered in this study, the uncertainty in the analyses of NH₃, NO₂⁻, NO₃⁻ was ± 0.054 mM, ± 0.018 mM, ± 0.11 mM respectively. Quality control procedures were followed for each analysis in which at least one mid-range standard and one duplicate were prepared for every 5 samples or per analytical run (whichever is smaller) to make sure the results meet the accuracy and repeatability tolerances of each method.

The concentration of different products obtained from a typical experiment for a 6 hour irradiation and those calculated from the kinetic model are plotted against the irradiation time and are presented in Figure 6-13.

Figure 6-13. Distribution of Products on Advanced Photo-oxidation of Ammonia with UV/H₂O₂ Treatment (pH 10, 25°C)

As could be seen, the experimental data points fit the kinetic model (solid lines) well. The kinetic rate constants k_1 , k_2 , k_3 , and k used in the rate equations in Figure 6-13 are $k_1 = 0.198 \text{ h}^{-1}$, $k_2 = 2.510 \text{ h}^{-1}$, $k_3 = 0.062 \text{ h}^{-1}$, $k = (k_1 + k_3) = 0.260 \text{ h}^{-1}$.

Beyond the visual fit that can be seen, the goodness of fit of the model and the experimental data is further confirmed by the values of the sum of residual squares from the statistical analysis on the experimental and calculated values of the concentrations of the different species over the course of the reaction. The values of $\sum R_A^2$, $\sum R_N^2$, $\sum R_R^2$, and $\sum R_S^2$ representing the sum of residual squares for [NH₃], [N₂], [NO₂⁻], and [NO₃⁻] respectively are:

$$\sum R_A^2 = 0.0137, \sum R_N^2 = 0.0632, \sum R_R^2 = 0.00184, \sum R_S^2 = 0.0280$$

6.4 Advanced Photo-oxidation of Ammonia with UV/K₂S₂O₈

As stated earlier, the presence of nitrate in feed wastewater could interfere with the photo-oxidation of ammonia by UV/H₂O₂ treatment. Hence it is necessary to choose a more powerful oxidant in order to increase the ammonia removal efficiency.

Many oxidizing agents such as hypochlorite, dichromate, bromate, iodate, persalts (e.g., permanganate, persulphate), ceric ion or other peroxides frequently encountered in analytical chemistry may be selected as an alternative to H₂O₂. But from environmental considerations, persulphate is comparatively environmentally benign among these oxidizing agents. With a high oxidation potential, persulphate easily oxidizes many reducing agents and is reduced to a very simple product - sulphate which is acceptable in the effluents of many industries (such as the mining industry) with background sulphate concentration in their wastewater. Hence, UV/K₂S₂O₈ process was selected in this study for the removal of ammonia from wastewater that may also contain a high nitrate concentration. The results for the UV/K₂S₂O₈ process for advanced photo-oxidation of ammonia are presented below.

6.4.1. Absorption Spectrum of Potassium Persulphate

The absorption spectrum of potassium persulphate has been shown in Figure 6-1, and it has also been discussed in sections 4.4.2, and 6.1.

6.4.2 Photolysis of Potassium Persulphate

The photolysis of persulphate was carried out in the same UV reactor by the same procedure as that for H_2O_2 . The initial concentration used was 7.59 mM (2.05 g/L). The results are shown in Figure 6-14. As can be seen, photolysis of persulphate follows the first order kinetics with a rate constant of $k = 5.6 \times 10^{-4} \text{ s}^{-1}$.

Figure 6-14 Photolysis of Persulphate in Aqueous Solution (pH10, 25°C)

The photolysis of persulphate leads to the generation of highly reactive sulfate anion radicals ($\bullet\text{SO}_4^-$), which is a useful oxidant particularly in aqueous

solutions. Sulfate anion radicals can react with water or hydroxyl ion in solution to produce hydroxyl radicals.^[67]

Photolysis of persulphate also leads to oxidation of water to produce oxygen and hydrogen ion, which explains the pH change and the bubbling in the solution during the photolysis, as discussed in section 4.4.2.

6.4.3. Degradation of Ammonia and Product Formation in the Presence of Nitrate by UV/K₂S₂O₈ treatment

The ammonia removal by UV/K₂S₂O₈ treatment in the presence of nitrate was investigated by irradiating the ammonium nitrate solution of [NH₃-N]₀ = 3.93 mM (55 mg/L) and [NO₃-N]₀ = 3.96 mM (55.4 mg/L) under the same conditions as that for UV/H₂O₂ treatment. Other parameters were: [K₂S₂O₈]₀/[NH₃-N]₀ = 2.0, pH = 10, temperature at 25°C. The water was treated until the desired ammonia concentration in the final sample (≤ 10 mg/L) was achieved. The samples were collected every 5 min. and sent for the analyses of NH₂NH₂, NH₂OH, NO₂⁻, NO₃⁻ and NH₃ in aqueous samples, N₂, N₂O, NO + NO₂ and NH₃ in gas samples.

The degradation of ammonia, decomposition of persulphate and product yields during the 1 hour treatment are shown in Figure 6-15.

Figure 6-15. Degradation of Ammonium Nitrate and Product Yields by UV/K₂S₂O₈ Treatment (pH 10, 25°C).

The results indicated that other than ammonia and nitrate, only nitrogen, nitrite and sulphate were detected, of which nitrogen gas was the predominant product. Nitrite concentration was very low and sulphate was the reduction product of persulphate. NH₂NH₂, NH₂OH and nitrogen oxides were not detected.

As can be seen from Figure 6-15, the overall destruction of ammonia follows first order kinetics with an observed rate constant of $k=7.7 \times 10^{-4} \text{ s}^{-1}$, which was 24 times as high as that with UV/H₂O₂ treatment ($k = 3.2 \times 10^{-5} \text{ s}^{-1}$). It only took 50 min. to destroy 90% of ammonia with UV/K₂S₂O₈ treatment, while the UV/H₂O₂ treatment could take longer than 8 hours.

UV/K₂S₂O₈ process was efficient in the conversion of ammonia in wastewater even in the presence of nitrate in the feed solution. Therefore it was studied in more detail.

For the choice of the ammonia precursor, three compounds were examined. NH₄OH which gave the best results in the UV/H₂O₂ process was one of these. The other two were (NH₄)₂SO₄ and NH₄NO₃. The above experiments were repeated for a feed solution containing ammonium hydroxide or ammonium sulphate under similar conditions. The results indicated that for 30 min of irradiation, 100% conversion of ammonia was achieved for ammonium hydroxide, 97% for ammonium sulphate and 70% for ammonium nitrate (shown in Figure 6-15).

Thus ammonium hydroxide was chosen as the precursor for further investigation, which included the study of the degradation rate, parametric studies, mechanistic and kinetic studies. The results from these studies are presented below.

6.4.4 Degradation of Ammonia by UV/K₂S₂O₈ treatment

The photo-degradation rate of ammonia was investigated by irradiating the ammonium hydroxide solution in the presence of persulphate. The parameters chosen were: [NH₃-N]₀ = 4.03 mM (56.5 mg/L), [K₂S₂O₈]₀/[NH₃-N]₀ = 1.4; pH 10 and temperature at 25°C. The solution was irradiated for 30 minutes until the final ammonia concentration was less than 10 mg/L. The experimental, sampling and analytical procedures were the same as that for the treatment of ammonium nitrate.

The photo-degradation of ammonia and the decomposition of persulphate in this process are shown in Figure 6-16.

Figure 6-16. Degradation of Ammonia by UV/K₂S₂O₈ process (pH 10, 25°C).

As shown, the overall destruction of ammonia follows first order kinetics with an observed rate constant of $k = 1.1 \times 10^{-3} \text{ s}^{-1}$, which was ~40% higher than that for treatment of ammonium nitrate solution ($k = 7.7 \times 10^{-4} \text{ s}^{-1}$) and ~14 times of that with UV/H₂O₂ treatment ($k = 7.63 \times 10^{-5} \text{ s}^{-1}$). The decomposition of persulphate obeys first order kinetics with a rate constant of $k = 1.05 \times 10^{-3} \text{ s}^{-1}$, which agrees well with the results obtained from the photolysis of persulphate.

The results also indicated that nitrogen is the predominant product in this process. The distribution of the final products is shown in Figure 6-22.

6.4.5. Parametric Studies

6.4.5.1. Effect of UV Dose (Irradiation Time)

Figure 6-16 actually showed the effect of UV Dose (irradiation time) on ammonia removal. Thus it is replotted in terms of the ammonia removal percentage versus the irradiation time and is shown in Figure 6-17.

Figure 6-17. Effect of UV Dose on Ammonia Removal
 ($[\text{NH}_3\text{-N}]_0 = 4.03 \text{ mM}$, pH 10). Each minute corresponds to
 0.556 kWh of electrical energy used per m^3 of water treated.

A calculated dose-response equation:

$$R = 100 - 102 e^{(-0.066 \cdot t)} \quad (t \neq 0) \quad (6-30)$$

where R is the $\text{NH}_3\text{-N}$ removal (%), t is the irradiation time (min), well describes the dependency of ammonia removal on UV irradiation time. The equation can be

used to estimate the irradiation time required for certain removal efficiency desired under the same operating conditions employed.

6.4.5.2 Effect of Initial Ammonia Concentration

The effect of initial ammonia concentration was investigated in detail by treating the water containing different initial ammonia concentrations under the same operating conditions. The feed concentrations chosen for this study were 50, 100, and 200 mg/L $\text{NH}_3\text{-N}$, the molar ratio of $[\text{K}_2\text{S}_2\text{O}_8]_0/[\text{NH}_3\text{-N}]_0 = 1.5$ for all the three cases. The experimental results are shown in Figure 6-18.

Figure 6-18. Effect of Initial Ammonia Concentration on Ammonia Removal (pH 10, 25°C)

As can be seen, the ammonia removal efficiency appears to increase with the decrease of feed ammonia concentration. Since the degradation of ammonia

follows first order kinetics, the total amount of ammonia converted was larger at higher concentration.

6.4.5.3 Effect of pH

The effect of pH was investigated by adjusting the pH of the feed water to 3, 7 and 10. The feed solution thus prepared was irradiated for 60 min. under the same conditions as above. The molar ratio of initial oxidant concentration over initial ammonia concentration was 1.5 for all the three cases. The results are shown in Figure 6-19.

Figure 6-19. Effect of pH on Ammonia Removal ($[\text{NH}_3\text{-N}]_0 = 3.57\text{mM}$)

At pH 3, no change of ammonia concentration was observed. The ammonia removal efficiency increases significantly with the increase of pH, which was in good agreement with the results obtained with UV/ H_2O_2 treatment. It may also be

explained by the stability of ammonium ion and its difficulty to be oxidized as compared to unprotonated ammonia which has been discussed earlier in the section on UV/H₂O₂ treatment.

The above observations indicate that the effect of pH was significant. Thus the process must be operated at basic pH in order to achieve the best ammonia removal efficiency, which is the reason why all the experiments were carried out at pH 10 in this study. It was also observed that the pH dropped during the process, which may be caused by the generation of hydrogen ion (H⁺) during the process. Therefore, prompt pH adjustment is important in order to achieve consistently high ammonia removal efficiency.

6.4.5.4 Effect of Initial Persulphate Concentration

The effect of initial persulphate concentration was investigated by irradiating the feed solution with different persulphate concentration under the same conditions. According to equation (4-23), for complete oxidation of 1 mole of hydrazine which is a probable intermediate product, the stoichiometric requirement is 2 moles of S₂O₈²⁻. For economic consideration, different molar ratios $r = [K_2S_2O_8]_0/[NH_3-N]_0 = 0.52, 1.04, 1.56$ and 2.07 were evaluated. The ammonia removal efficiency obtained was plotted against the irradiation time for the above four different molar ratios, which are shown in Figure 6-20.

Figure 6-20. Effect of Molar Ratio r on Ammonia Removal
 $(r = [\text{K}_2\text{S}_2\text{O}_8]_0/[\text{NH}_3\text{-N}]_0, [\text{NH}_3\text{-N}]_0 = 3.57\text{mM}, \text{pH } 10)$

For the first 20 minutes, the difference of ammonia removal for $r = 1.04$, 1.56, and 2.07 was small, which suggests sufficient persulphate in the solution. For ratio $r = 0.52$, ammonia removal rate increased very slowly after 15 min., which suggests insufficient or even the exhaustion of persulphate. Figure 6-21 also shows that ammonia removal efficiencies obtained for $r = 1.56$ and 2.07 were close to each other, which means no significant difference in performance exists between those two ratios. Therefore, $r = 1.56$ was chosen for most of the experiments in this study.

The above observations suggest that it is very important to monitor the persulphate concentration during the process to ensure the best ammonia removal.

6.4.5.5 Effect of Temperature

The effect of temperature on photo-oxidation of ammonia was thoroughly investigated by irradiating the ammonium sulphate solution at different temperatures 20, 25, 30, and 40°C, under the same condition employed as above. Other parameters were: $[\text{NH}_3\text{-N}]_0 = 3.57 \text{ mM}$, $[\text{K}_2\text{S}_2\text{O}_8]_0/[\text{NH}_3\text{-N}]_0=1.5$, pH 10, at 25 °C. The feed solution in the reactor was irradiated for 30 min. and the samples were collected for analysis.

The results indicate that there was no significant difference in ammonia removal at various temperatures from 20°C to 40°C. More than 97% of ammonia removal efficiency was achieved under this treatment for all the four temperatures studied, of which the relative difference in results was less than 2%.

6.4.5.6 Effect of UV/H₂O₂/K₂S₂O₈

Both UV/H₂O₂ and UV/K₂S₂O₈ have been studied separately, of which UV/K₂S₂O₈ appears to be more efficient than UV/H₂O₂, but the consumption of oxidant and pH change might also be higher than that for the UV/H₂O₂ treatment. Therefore, it was decided to evaluate this combined UV/H₂O₂/K₂S₂O₈ process that could lead to the most efficient conversion of ammonia.

The effect of UV/K₂S₂O₈/H₂O₂ was investigated by irradiating the feed solution in the presence of both H₂O₂ and K₂S₂O₈. The parameters were: $[\text{NH}_3\text{-N}]_0 = 3.57 \text{ mM}$, $[\text{K}_2\text{S}_2\text{O}_8]_0 = 1.85 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 58.82 \text{ mM}$, pH 10, 25°C. The results indicated that after 30 min. of irradiation, the ammonia removal percentage obtained (17%) was larger than that in the UV/H₂O₂ process (6%), but much lower

than that in the UV/K₂S₂O₈ process (49%). H₂O₂ consumed in this process was twice that of UV/H₂O₂ treatment.

It was concluded that UV/H₂O₂/K₂S₂O₈ treatment was less efficient than the UV/K₂S₂O₈ treatment.

6.4.6 Reaction Mechanism for UV/K₂S₂O₈ Oxidation of Ammonia

This section presents the results which were obtained from the identification and quantitation of the products formed under the UV/K₂S₂O₈ treatment. Based on the products identified and the amounts measured, a reaction scheme is postulated to account for those observations.

6.4.6.1 Product Yields for Photo-oxidation of Ammonia with UV/K₂S₂O₈ Treatment

A typical experiment was carried out by irradiating the ammonium hydroxide solution in the presence of K₂S₂O₈. The operating parameters were: [NH₃-N]₀ = 3.57 mM (50mg/L N), [K₂S₂O₈]₀/[NH₃-N]₀ = 1.5, pH= 10, temperature = 25⁰C. Aqueous samples were taken every 5 min. and sent for analysis of ammonia (NH₃), nitrite (NO₂⁻), nitrate (NO₃⁻), hydrazine (NH₂NH₂) and hydroxylamine (NH₂OH). The gas samples were taken from the top sample port at the same time interval (5 min.) and sent for analysis of nitrous oxide (N₂O), ammonia (NH₃), nitric oxide (NO) and nitrogen dioxide (NO₂).

Table 6-5 shows the product yields and ammonia concentration employed in a typical experiment.

Table 6-5. Product Yields for Photo-oxidation of Ammonia with UV/ $K_2S_2O_8$ Treatment

Time (min)	Nitrogen Concentration of Different Species								
	Aqueous Sample						Gas Sample		
	Unit	NH_3	NO_2^-	NO_3^-	N_2H_4	NH_2OH	N_2	N_2O	$NO + NO_2$
0	(mM)	4.08	0	0	0	0	0	0	0
30	(mM)	0.39	0	0.11	0	0	3.59	0	0.004
P *	%	9.5	0	2.69	0	0	88.0	0	0.1

* the percentage of nitrogen concentration in final product over the total nitrogen concentration after 30 min. of irradiation.

As can be seen, N_2 is the predominant product. Low nitrate and a trace amount of nitrogen oxides were also detected. The distribution of product yields and the kinetic model is presented later in next section.

6.4.6.2 Reaction of Hydrazine (NH_2NH_2) with Persulphate

As discussed earlier, NH_2NH_2 was not detected during the process, which suggests that it might be very easily oxidized by persulphate. Therefore the effect of persulphate on oxidation of NH_2NH_2 was thoroughly investigated as follows:

Four experiments were carried out for hydrazine with or without the persulphate both under UV irradiation and under dark reaction. Aqueous hydrazine solution with $[NH_2NH_2]_0 = 1.8$ mM which was calculated by assuming the complete convention of ammonia to hydrazine was used, other operating parameters were: $[K_2S_2O_8]_0 = 5.55$ mM, pH = 10, temperature at 25°C.

No change of concentration was observed after aqueous hydrazine solution was kept standing for 24 hours. For the solution containing $\text{NH}_2\text{NH}_2 + \text{K}_2\text{S}_2\text{O}_8$, 100% of NH_2NH_2 was oxidized after 24 hours of dark reaction, yielding solely nitrogen. For the solutions containing NH_2NH_2 under direct photolysis, 23% of NH_2NH_2 was oxidized after 2 hour irradiation and gave solely nitrogen. Under the same conditions, for the treatment by UV/ $\text{K}_2\text{S}_2\text{O}_8$, 100% of NH_2NH_2 was rapidly oxidized to products in only 5 min., yielding mainly N_2 and a very small amount of nitrate.

The above observation indicates that hydrazine could be one of the intermediates, which was rapidly oxidized to products. Under dark reaction, hydrazine reacts with persulphate to give solely nitrogen, while under UV/ $\text{K}_2\text{S}_2\text{O}_8$ treatment, NH_2NH_2 was oxidized rapidly by $\text{K}_2\text{S}_2\text{O}_8$, leading to mainly nitrogen and a small amount of nitrate. Nitrite was not detected in the process.

6.4.6.3 Reaction of Hydroxylamine with Persulphate

The effect of persulphate on oxidation of NH_2OH was investigated in detail below.

Four experiments were also carried out for hydroxylamine with and without persulphate both under the UV irradiation and under the dark reaction. Aqueous hydroxylamine solution with $[\text{NH}_2\text{OH}]_0 = 3.6 \text{ mM}$ was used. Other operating parameters were: $[\text{K}_2\text{S}_2\text{O}_8]_0 = 5.55 \text{ mM}$, $\text{pH} = 10$, temperature at 25°C .

For aqueous solution containing only hydroxylamine, no change of concentration was observed after it was kept standing for 24 hours. For the

solution containing $\text{NH}_2\text{OH} + \text{K}_2\text{S}_2\text{O}_8$, 100% of NH_2OH was oxidized to mainly nitrogen gas with a small amount of nitrate and nitrite after 24 hours of dark reaction. For the solutions containing NH_2OH under direct photolysis, 19% of NH_2OH was oxidized after 2 hours irradiation and gave mainly nitrogen and a small amount of nitrite and nitrate. Under the same conditions, for the treatment by $\text{UV/K}_2\text{S}_2\text{O}_8$, 100 % NH_2OH was oxidized in 40 min. to give mainly nitrogen and a small amount of nitrite and nitrate.

These observations indicate that under $\text{UV/K}_2\text{S}_2\text{O}_8$ treatment, NH_2OH was rapidly oxidized to mainly nitrogen and a small amount of nitrite and nitrate. NH_2OH could be one of the intermediates in the process.

6.4.6.4 Reaction Scheme

The above observations point to the formation of the probable intermediates and their reactions with persulphate. Based on this information and the results obtained from the identification and quantitation of the final products, the following probable mechanism is postulated to describe the advanced photo-oxidation of ammonia under $\text{UV/ K}_2\text{S}_2\text{O}_8$ treatment.

(1) Initial photochemical step in the process involves the photolysis of $\text{S}_2\text{O}_8^{2-}$ to generate the $\bullet\text{SO}_4^-$ radicals, which then react with water or OH^- to give $\bullet\text{OH}$ radicals.

(2) The $\bullet\text{SO}_4^-$ and $\bullet\text{OH}$ radicals generated from the equations (6-30) to (6-32) then react with unprotonated ammonia to give $\bullet\text{NH}_2$ radicals.

(3) The $\bullet\text{NH}_2$ formed from equations (6-33) and (6-34) react with $\bullet\text{OH}$ to give NH_2OH , or reacts with $\bullet\text{NH}_2$ to form NH_2NH_2 .

(4) The NH_2NH_2 formed from equation (6-35) undergoes further oxidation reaction with $\text{S}_2\text{O}_8^{2-}$ to form solely N_2 [eq.(6-37)]. At the same time, NH_2OH formed from equation (6-36) also reacts with $\text{S}_2\text{O}_8^{2-}$ to give N_2 , NO_2^- and NO_3^- [eq.(6-38)]. Formation of a very small amount of nitrate (with no nitrite) in the final products indicates that the yield of the intermediate product NH_2OH was probably not significant.

(4). Other Conceivable Pathways:

As discussed in section 6.3.5.4, $\bullet\text{NH}_2$ could react with oxygen to form NH_2O_2 , which is probably oxidized to give N_2 , NO_2^- and NO_3^- by $\text{S}_2\text{O}_8^{2-}$.

6.4.7 The Kinetic Model for Photo-oxidation of Ammonia by UV/K₂S₂O₈

As discussed above, the major products formed from the advanced photo-oxidation of ammonia were nitrogen gas with a small amount of nitrate. The distribution of the product yields with the irradiation time are presented in Table 6-6. Based on the reaction scheme as shown above and the product distribution obtained from Table 6-6, a competitive-parallel reaction model is proposed to simulate the experimental data. The reaction rate and concentration expressions are presented in equations (6-40) to (6-49) in Figure 6-21.

Table 6-6 Distribution of Product Yields with the Irradiation Time

Irradiation Time (min)	Nitrogen Concentration (mM)		
	[NH ₃ -N]	[N ₂ ⁻ -N]	[NO ₃ ⁻ -N]
0	4.08	0	0
5	3.05	0.99	0.039
10	2.21	1.81	0.062
15	1.58	2.43	0.07
20	0.89	3.12	0.08
25	0.60	3.39	0.09
30	0.39	3.59	0.11

Several experiments have been conducted under similar conditions for advanced photo-oxidation of ammonia with UV/K₂S₂O₈. These results are presented in Appendix 7 for 30 min. irradiation. The results indicate similar trends for the different sets of experiments. Within the concentration ranges encountered in this study, the uncertainty in the analyses of NH₃, NO₂⁻, NO₃⁻ was ± 0.054 mM, ± 0.018 mM, ± 0.11 mM respectively. Quality control procedures were followed for each analysis in which at least one mid-range standard and one duplicate were prepared for every 5 samples or per analytical run (whichever is smaller) to make sure the results meet the accuracy and repeatability tolerances of each method.

Rate Equations:
$$\frac{dC_A}{dt} = -k_1 C_A - k_2 C_A = -(k_1 + k_2) C_A = -k C_A \quad (6-42)$$

$$\frac{dC_N}{dt} = k_1 C_A \quad (6-43)$$

$$\frac{dC_S}{dt} = k_2 C_A \quad (6-44)$$

Nitrogen Balance :
$$C_{A0} + C_{S0} + C_{N0} = C_A + C_S + C_N \quad (6-45)$$

Initial Conditions: at $t=0$: $C_A = C_{A0}, C_S = C_{S0} = 0, C_N = C_{N0} = 0 \quad (6-46)$

Concentration Expressions:

$$C_A = C_{A0} e^{-kt} \quad (6-47)$$

$$C_N = \frac{C_{A0} k_1}{k} (1 - e^{-kt}) \quad (6-48)$$

$$C_S = \frac{C_{A0} k_2}{k} (1 - e^{-kt}) \quad (6-49)$$

Figure 6-21. Competitive-Parallel Reaction Model

irradiation time, as shown in Figure 6-22. The experimental data are shown as points and solid lines are based on the kinetic model.

Figure 6-22. Distribution of Products on Advanced Photo-oxidation of Ammonia with UV/K₂S₂O₈ Treatment (pH 10, 25⁰C)

As can be seen, the experimental data fit the model very well. The kinetic rate constants k_1 , k_2 and k used in the rate equations are $k_1 = 0.068\text{min}^{-1}$, $k_2 = 0.01\text{min}^{-1}$ and $k = 0.069\text{min}^{-1}$.

Beyond the visual fit that can be seen, the goodness of fit of the model and the experimental data is further confirmed by the values of the sum of residual squares from the statistical analysis on the experimental and calculated values of the concentrations of the different species over the course of the reaction. The values of $\sum R_A^2$, $\sum R_N^2$, and $\sum R_S^2$ representing the sum of residual squares for [NH₃], [N₂], and [NO₃⁻] respectively are:

$$\sum R_A^2 = 0.123, \quad \sum R_N^2 = 0.120, \quad \sum R_S^2 = 0.00878$$

7. Conclusions and Recommendations

7.1 Conclusions

An Advanced Photo-oxidation Process (APP) has been developed for ammonia removal from industrial wastewater using hydrogen peroxide or potassium persulphate as the oxidant. The feasibility of the process has been established in this research. In both cases (UV/H₂O₂ and UV/K₂S₂O₈), the photo-oxidation of ammonia proceeds well under alkaline conditions. In the acidic range, the oxidation of ammonium ion is not significant, hence it is imperative that for the types of oxidants and the operating conditions employed, the ammonia should be in the unprotonated form. Comparatively, the destruction of ammonia is much more rapid for the persulphate as the oxidant in APP.

One of the major findings of the study is the effect of the nature of the oxidant on the course of the photo-oxidation process, as exemplified by the significant difference in the product distribution. In the case of UV/H₂O₂ treatment, the main products are nitrate, nitrite and nitrogen with nitrate being the predominant product. The predominance of the nitrate in the products is attributed to the type of intermediates formed in the photo-oxidation process, and a reaction scheme is postulated indicating the probable course of the reaction. The experimental results of the overall photo-oxidation process were found to satisfy a kinetic model based on a competitive-consecutive reaction scheme.

In the UV/K₂S₂O₈ treatment, the main product of the photo-oxidation of ammonia was gaseous nitrogen with a small amount of nitrate. It is postulated that the primary intermediate in this process is probably hydrazine which undergoes rapid oxidation to nitrogen. A competitive-parallel reaction kinetic model simulated the experimental results satisfactorily.

In terms of practical application, if the objective is to convert the ammonia to an environmentally benign species, from the process point of view, the APP process with K₂S₂O₈ is superior to the H₂O₂ process. The predominant final product, nitrogen gas, formed in the UV/K₂S₂O₈ process, can be simply discharged to the atmosphere. In the case of the UV/H₂O₂ process, subsequent denitrification is a requirement to convert the nitrate and nitrite formed in the process. However, such process comparisons can be confirmed only after a detailed optimization and cost analysis of the processes, which is beyond the scope of this research.

7.2 Recommendations

The present work has established the feasibility of the advanced photo-oxidation process for the destruction of ammonia. The results can act as a springboard for looking into many other similar systems with the following variations.

The nature of the reaction mechanisms in the photo-oxidation processes are quite complex and the possibility of the other better-performing oxidants can not be discounted. Further search for a powerful new oxidant or a combination of oxidants may be warranted.

Only a limited number of photocatalysts were examined in this study. It is possible that these photocatalysts or others, may in combination with a specific oxidant or oxidants yield better results.

With the availability of tailored UV lamp systems, UV lamps with a different spectral distribution can also be evaluated. A large number of permutations and combinations of operating systems are conceivable to treat a particular industrial wastewater stream containing ammonia.

For the photo-oxidation processes developed in this study, optimization of the overall process, which may also include a denitrification step, would be required prior to an economic analysis.

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Appendix 1. Guidelines for Canadian Drinking Water Quality 1978 ^[2]

Parameter	Maximum Acceptable Concentration (mg/L)
Inorganic parameters:	
Arsenic	0.05
Barium	1.0
Boron	5.0
Cadium	0.005
Chloride	250
Chromium	0.05
Copper	1.0
Cyanide	0.2
Fluoride	1.5
Iron	0.3
Lead	0.05
Manganese	0.05
Mercury	0.001
Nitrate Nitrogen	10.0
Nitrite Nitrogen	1.0
pH	6.5-8.5
Selenium	0.01
Silver	0.05
Sulphate	500
Sulphide	0.05
TDS	500
Uranium	0.02
Zinc	5.0
Fluoride	1.5 mg/L
Other Parameters:	
Colour	15 TCU
Temperature	15°C
Turbidity	5 NTU
Total Coliform	10 /100 ml

Appendix 2. Industries Required to Comply with Effluent Regulations^[5]

Parameters	Industry *													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
BOD ₅	x	x	x		x	x	x		x	x	x		x	x
COD	x		x	x	x	x		x	x	x	x		x	x
pH		x	x	x	x	x	x		x	x	x	x	x	x
Suspended Solids	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Heavy metals						x		x		x			x	
Cyanide					x	x		x	x		x	x		
Chloride	x			x	x	x					x	x		x
Sulfate	x			x	x				x		x	x		
Ammonia	x			x		x	x		x	x	x	x		
Organic nitrogen				x										
Nitrate	x			x		x			x	x	x		x	
Phosphorus			x	x	x	x	x		x	x	x			x
Toxic materials		x					x		x	x	x		x	x
Temperature		x	x	x	x						x	x	x	x

* 1-Automobile, 2-Beverage, 3-Canning, 4-Fertilizer, 5-Inorganic Chemicals, 6-Organic Chemicals, 7-Meat Products, 8-Metal Finishing, 9-Plastics&Synthetics, 10-Pulp & Paper, 11-Petroleum Refining, 12-Steel, 13-Textile, 14-Dairy

Appendix 3. Typical Composition of Untreated Municipal Wastewater ^[6]

Contaminants	Unit	Concentration		
		Weak	Medium	Strong
Total Nitrogen (total as N)	mg/L	20	40	85
Organic Nitrogen	mg/L	8	15	35
Ammonia Nitrogen	mg/L	12	25	50
Nitrites	mg/L	0	0	0
Nitrates	mg/L	0	0	0
Total Phosphorus (total as P)	mg/L	4	8	15
Organic Phosphorus	mg/L	1	3	15
Inorganic Phosphorus	mg/L	3	5	10
Total Solids (TS)	mg/L	350	720	1200
Total Suspended Solids (TSS)	mg/L	100	220	350
Total Fixed Suspended Solids	mg/L	20	55	75
Total Volatile Suspended Solids	mg/L	80	165	275
Biochemical Oxygen Demand, 5-day, 20 ⁰ C (BOD ₅ , 20 ⁰ C)	mg/L	110	220	400
Total Organic Carbon (TOC)	mg/L	80	160	290
Chemical Oxygen Demand (COD)	mg/L	250	500	1000
Chlorides	mg/L	30	50	100
Sulfate	mg/L	20	30	50
Alkalinity (as CaCO ₃)	mg/L	50	100	200
Oil and Grease	mg/L	50	100	150
Total Coliform	no/100 ml	10 ⁶ -10 ⁷	10 ⁷ -10 ⁸	10 ⁸ -10 ⁹
Volatile Organic Compounds (VOCs)	mg/L	<100	100-400	>400

Appendix 4. Guidelines for Municipal Effluent Quality 1976^[7]

Parameter	Limit
BOD ₅	20 mg/L
TSS	25 mg/L
Fecal Coliform	400 / 100 ml (after disinfection)
Chlorine Residual	0.50 mg/L minimum (after 30 min contact time) 1.0 mg/L maximum
pH	6-9
Phenols	20 ug/L
Total Phosphorus (Total P)	1.0 mg/L
Oils & Grease	15 mg/L
Temperature	may not alter temperature of receiving water by more than 1 ⁰ C
Dilution is not an acceptable treatment	

Appendix 5. Oxidation of Ammonia and Formation of Nitrite and Nitrate for Different Wastewater Feed

No	Process	Feed	Time (h)	[NH ₃ -N] (mg/L)	[NO ₂ ⁻ -N] (mg/L)	[NO ₃ ⁻ -N] (mg/L)
1	UV only	NH ₄ OH	0	47.18	0	0
			0.5	45.64	0	0
			1.0	43.72	0	0
			1.5	37.95	0	0
			2.0	35.06	0	0
2	UV only	NH ₄ NO ₃	0	48.98	0	51.88
			0.5	46.21	9.59	36.49
			1.0	43.25	13.21	29.99
			1.5	41.59	15.04	27.25
			2.0	38.08	17.02	18.59
3	UV only	NaNO ₃	0	0	0	53.16
			0.5	0	12.71	39.00
			1.0	0	20.42	32.43
			1.5	0	26.17	27.37
			2.0	0	29.87	23.25
4	UV only	NaNO ₂	0	0	52.18	0
			0.5	0	51.30	0.92
			1.0	0	50.21	2.03
			1.5	0	49.77	2.39
			2.0	0	49.39	2.72
5	UV/H ₂ O ₂	NH ₄ OH	0	49.6	0	0
			0.5	44.66	3.55	1.56
			1.0	38.93	3.57	5.76
			1.5	31.23	2.57	11.58
			2.0	29.64	3.31	13.22
6	UV/H ₂ O ₂	NH ₄ NO ₃	0	47.56	0	52.38
			0.5	44.81	5.7	44.73
			1.0	43.09	7.99	44.65

			1.5	40.16	6.21	53.23
			2.0	37.75	4.60	59.04
7	UV/H ₂ O ₂	NaNO ₃	0	0	0	49.45
			0.5	0	6.85	43.00
			1.0	0	9.33	38.79
			1.5	0	13.92	38.22
			2.0	0	16.40	37.03
8	UV/H ₂ O ₂	NaNO ₂	0	0	51.96	0
			0.5	0	49.77	2.22
			1.0	0	39.61	12.42
			1.5	0	37.86	13.01
			2.0	0	32.95	18.59
9	UV/H ₂ O ₂	NH ₄ OH + NaNO ₃	0	48.94	0	13.12
			.5	47.18	5.58	9.74
			1.0	42.08	5.21	9.94
			1.5	38.56	6.08	12.61
			2.0	37.50	8.04	11.90
10	UV/H ₂ O ₂	NH ₄ OH + NaNO ₂	0	49.8	25.12	0
			0.5	47.56	21.08	3.95
			1.0	41.47	18.67	8.84
			1.5	38.12	15.95	15.32
			2.0	35.36	11.74	21.17
11	UV/H ₂ O ₂	NH ₄ OH + NaNO ₃ + NaNO ₂	0	36.97	17.22	18.65
			0.5	35.12	13.16	22.92
			1.0	34.57	11.73	25.58
			1.5	32.07	9.00	28.32
			2.0	31.79	6.18	31.33

Appendix 6. Advanced Photo-oxidation of Ammonia with UV/H₂O₂
(pH10, 25°C)

Appendix 7. Advanced Photo-oxidation of Ammonia with UV/K₂S₂O₈
(pH 10, 25⁰C)