University of Alberta

Pilot Testing of Electrochemical Oxidation Technology for Centrate Ammonia Reduction

by

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Abstract

A pilot scale ammonia oxidation system has been commissioned and its ability to remove ammonia from a centrate waste stream has been tested. The system, termed AmmEl by its manufacturer (Enpar Technologies), uses a stripping column and scrubbing tower to transfer ammonia from the waste stream to a brine solution that is pumped through an electrochemical reactor in which the ammonia is oxidized to nitrogen gas which is released to the atmosphere. Within the range of controlled settings tested, the system proved to be capable of removing up to 90 percent of the ammonia in the waste stream. The average cost is $7.17/m^3 centrate for 76 percent ammonia removal from centrate having a mean initial ammonia concentration of 853 mg/L. Caustic soda accounted for the major portion of the treatment cost; this was followed by the energy costs. This operating cost may be reduced by 30% if centrate is treated in summer (20 to 25 °C).

Acknowledgements

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CHAPTER I INTRODUCTION

Centrate and supernatant are two wastewater streams which usually contain high ammonia concentrations. In municipal wastewater treatment plants, centrifugation is often used to dewater wastewater sludge (Tchobanoglous et al, 2003). Centrate is a liquid side stream generated from centrifugation processes. Centrate is usually recycled back to the main wastewater treatment process and becomes a significant contributor to the total nitrogen load. Supernatant from sludge lagoons is another main contributor to nitrogen loading. Storage lagoons are widely used in municipal wastewater treatment to store and digest waste activated sludge. Activated sludge can remain in lagoons for years allowing the biosolids to thicken and stabilize further. As the biosolids thicken, the upper liquid fraction, termed supernatant, becomes a rich ammonia stream and is pumped back to the plant for further treatment. At the Gold Bar Wastewater Treatment Plant (GBWWTP), primary and thickened waste activated sludge is decomposed in the plant's six anaerobic digesters. Anaerobic digestion of sludge is a relatively slow process, taking 15 to 20 days. At the end of that period, the digested sludge is pumped to lagoons at Clover Bar composting site, which is about 11 kilometres from GBWWTP. At this stage, the transported sludge, referred to as biosolids, is made up of about 97% water and 3% solids. The sludge remains in the lagoons for several years. As the biosolids thicken, the supernatant is pumped back to the Plant for treatment. To ensure adequate storage space in the lagoons for incoming sludge, timely pumping of the supernatant is necessary. Part of the thickened biosolids in the lagoons is pumped out and passed through centrifuges.

The centrifuged solids are used in co-composting activities at Clove Bar. Liquid generated from the centrifuging process, termed centrate, is pumped back to the lagoons or delivered to the wastewater treatment plant for further treatment. Centrate from composting operations and supernatant from digested biosolids lagoons at the Clover Bar site contain concentrations of ammonia in the range of 800 to 1,300 mg/L. These waste streams can overwhelm the nitrification process at GBWWTP, especially in the cold weather, and lead to a relatively high ammonia discharge in the plant's final effluent. Un-ionized ammonia concentrations over 5 mg/L and ammonium concentrations over 1000 mg/L start to have an inhibition on nitrification (Environment Canada, 2003). Ammonia concentrations in plant final effluent in 2003 are shown in Figure 1-1. Detailed data records of ammonia concentrations in centrate, lagoon supernatant, and GBWWTP influent and effluent are shown in Appendix A.

Ammonia in industrial and municipal discharges poses threats to the environment that include increased oxygen demand, increased nutrient loading, and toxicity to aquatic organisms. With increasingly stringent requirements for ammonia contaminant control, effective treatment systems need to be developed. In order to protect receiving waters, Alberta Environment has limited the allowable ammonia concentration in discharges from Edmonton's Gold Bar Wastewater Treatment Plant (GBWWTP) to 10 mg/L during winter months, and 5 mg/L in the summer, as of June 1 2005. In addition, GBWWTP is on an expansion project to provide enhanced primary treatment to flows from Edmonton's combined sewer overflow, which will lead to a significant increase of sludge volume. Correspondingly, centrate and supernatant volume will increase notably.

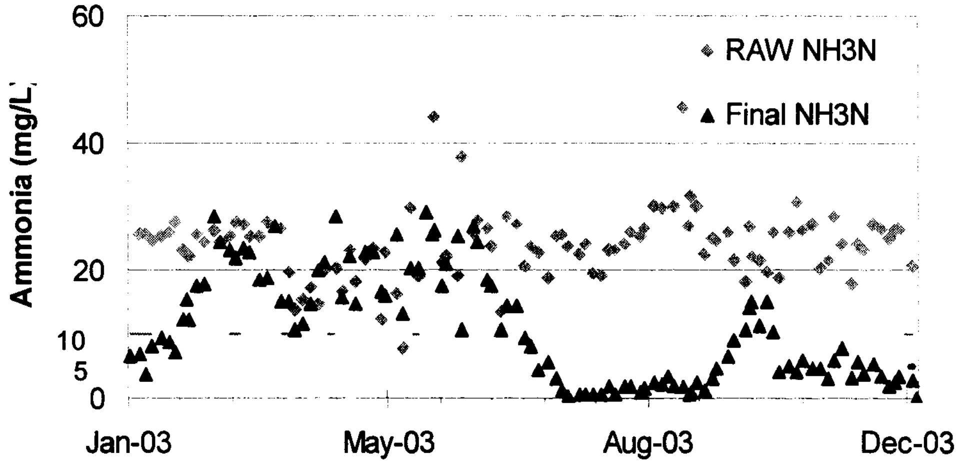


Figure 1-1 Ammonia concentrations in raw wastewater and final effluent at the GBWWTP in 2003

In order to eliminate the potentially deleterious effect of high ammonia concentrations in the waste streams returned from the Cover Bar activities, the ammonia concentration in these waste streams should be reduced before they are returned to the GBWWTP. The City of Edmonton wastewater engineers are considering an electrochemical technology called the AmmEl process for this purpose.

AmmEl (ammonia elimination) technology is an emerging proprietary technology that was developed at the university of Guelph in1995, and has been under development for the last ten years and is claimed to be a cost-effective solution for ammonia removal from wastewater from variety of sources. The proprietary core of the process applies electrochemical methods to convert ammonia directly to nitrogen gas. The manufacturer has conducted pilot-scale testing of the AmmEl system at the City of Guelph WWTP to removal ammonia from the sludge dewatering wastewater and from secondary effluent (Seed, L.P et al, 2001). The system tested in Guelph used ion exchange to capture ammonia from wastewater and provide a concentrated feed to the electrochemical oxidation unit. In comparison, the AmmEl system proposed for Edmonton uses a stripper and a scrubber column to transfer ammonia from wastewater to a concentrated ammonia stream that is treated electrochemically. This configuration has not been used previously, Therefore, the current project was undertaken to assess the effectiveness of the technology at pilot-scale.

The objectives of this research were to:

1) Operate a pilot-scale AmmEl plant at Gold Bar Wastewater Treatment Plant, to assess the applicability of AmmEl technology to centrate ammonia removal;

2) Demonstrate the effectiveness and economic viability of AmmEl technology in northern climates;

3) Seek the optimum operating conditions for the AmmEl system with respect to cost and ammonia reduction efficiency;

4) Investigate possible lower operating cost in summer time.

CHAPTER II LITERATURE REVIEW

2.1 Introduction

Ammonia in wastewater presents two potential threats to the environment. It exerts an oxygen demand that must be satisfied before its discharge, and it represents a nutrient load to the receiving waters that can promote eutrophication. Municipal wastewater treatment has traditionally sought to satisfy the nitrogenous biochemical oxygen demand by providing biological nitrification. Over the past twenty years, improved understanding of the mechanisms of biological nutrient removal (BNR) has led to its widespread application in new and upgraded biological wastewater treatment facilities (Tchobanoglous et al, 2003).

This report comprises a summary of biological, physical, and chemical methods that have been applied to control nitrogen discharge from municipal wastewater treatment facilities.

2.2 Forms of nitrogen in wastewater

Nitrogen exists in wastewater as organic nitrogen, ammonia, nitrite, and nitrate. The forms of nitrogen found in raw municipal wastewater are almost exclusively organic and ammonia nitrogen, which are measured by the Total Kjeldahl Nitrogen (TKN) procedure. Between 60 and 70 percent of the TKN concentration in raw municipal wastewater is in the form of NH_4^+-N, that is readily available for bacterial synthesis and nitrification (Tchobanoglous et al, 2003). Thus, ammonia-nitrogen removal or conversion is an essential step in total nitrogen removal.

Organic nitrogen consists of a complex mixture of compounds including amino acids, amino sugars, and proteins (polymers of amino acids). The nitrogen in these compounds is readily converted to ammonium through the action of microorganisms in the aquatic or soil environment. Urea, readily converted to ammonium, is seldom found in untreated municipal wastewaters.

Ammonia nitrogen exists in aqueous solutions as either the ammonium ion (NH_4^+) or as ammonia gas (NH_3), depending on the pH of the solution. Un-ionized ammonia is recognized to be responsible for toxicity to aquatic life, while ammonium is considered to be of relatively low toxicity to aquatic life (Environment Canada, 2003).

Nitrite nitrogen (NO_2^-) is relatively unstable and easily oxidized to the nitrate form (NO_3^-). It is an indicator of past pollution in the process of stabilization and seldom exceeds 1 mg/L in wastewater or 0.1 mg/L in surface waters or ground waters. Although present in low concentration, nitrite can be very important in wastewater or water pollution studies because it is extremely toxic to most fish and other aquatic species.

Nitrate nitrogen is the most oxidized form of nitrogen found in wastewaters. Where secondary effluent is to be reclaimed for groundwater recharge, the nitrate concentration is important. The U.S. EPA primary drinking water standards (USEPA, 1977) limit nitrogen to 45 mg/L as NO_3^-, because of its serious and occasionally fatal effects on infants. Assuming complete nitrification has taken place, the typical range found in treated effluents is from 15 to 20 mg/L as N. The nitrate concentration is typically determined by colorimetric methods or with ion-specific electrodes (Tchobanoglous et al, 2003).

2.3 Fundamentals of biological nitrogen transformations in wastewater treatment

During biological treatment processes for ammonia nitrogen removal from wastewater, nitrogen will go through ammonification, assimilation, nitrification and denitrification.

2.3.1 Ammonification

Ammonification is the process of organic nitrogen being degraded into ammonia or ammonium. Energy is produced during the ammonification, the process of converting organic matter into basic compounds, including organic nitrogen to ammonia/ammonium, which is used for cellular maintenance and biomass synthesis.

2.3.2 Assimilation

Ammonia nitrogen is assimilated directly into microbial mass to support cell growth. Upon the death and lysis of the bacterium, a portion of the ammonia is returned to the wastewater. Algae and green plants, present in lagoons and wetlands, can use nitrate as a nitrogen source for cell synthesis.

Ammonia-oxidizing microorganisms are considered to be the major contributors to ammonia removal in wastewater treatment systems. However, Nakai *et al.* (1999 and 2001) have shown that ammonia assimilation by microorganisms can also be important in agricultural waste stabilization. Investigation of the ability of many species of microbes to assimilate ammonia through glutamine synthesis indicated that ammonia assimilation by microbes contributed to ammonia removal in aerated and aerobic lagoons (Merrick and Edwards 1995, Patriarca *et al.* 2002, Sasaki *et al.* 2002). Hiraku *et al.* (2004) investigated the dominance of ammonia-assimilating microorganisms in natural lagoons and reported that only a small number of high ammonia-assimilating isolates are present in a lagoon microbial community. Results indicated that only 16 out a total of total 82 isolates exhibited ammonia-assimilating capacities. The predominant ammonia assimilating isolates were different with temperature changes, as *Janthinobacterium lividum* and *Bacillus* sp. were predominant at 10°C and 37°C, respectively. Hiraku *et al.* (2004) also pointed out that ammonia assimilating microbes were not the dominant genus in wastewater treatment systems by referring to many former studies including Wagner *et al.* 1993, 1994; Manz et al, 1994; Snaidr *et al.* 1997; Sekiguchi *et al.* 1998.

2.3.3 Nitrification

Nitrification is a two stage biological process in which ammonium is oxidized to nitrite and nitrate by bacteria. Oxidation of ammonium to nitrite by *Nitrosomonas*, proceeds as shown in reaction 2-[1]:

$$55\ NH_4^+ + 76\ O_2 + 109\ HCO_3^- \rightarrow C_5H_7O_2N + 54\ NO_2^- + 104\ H_2CO_3 + 57\ H_2O \qquad 2\text{-}[1]$$

Nitrite is then oxidized to nitrate by *Nitrobacter* as shown in reaction 2-[2]:

$$400NO_2^- + NH_4^+ + 4\ H_2CO_3 + HCO_3^- + 195\ O_2 \rightarrow C_5H_7O_2N + 3\ H_2O + 400\ NO_3^- \qquad 2\text{-}[2]$$

Generally, the reactions are coupled and advance quickly toward the nitrate form. Therefore, nitrite levels at any given time are usually low.

Combining reactions [1] and [2] yields the reaction for the overall conversion of ammonium to nitrate (Tchobanoglous et al, 2003):

$$408.4\ NH_4^+ + 758\ O_2 + 808.4\ HCO_3^- \rightarrow 8.4\ C_5H_7O_2N + 769.4\ H_2CO_3 + 425.2\ H_2O + 400\ NO_3^- \qquad 2\text{-}[3]$$

Reaction 2-[3] indicates that 3.3 mg O_2 and 11.0 mg/L alkalinity (as $CaCO_3$) are consumed for each mg of ammonium (as NH_4^+) converted to nitrate.

The maximum specific growth rate of nitrifiers is lower than that of heterotrophic bateria that are responsible for degrading organic carbon compounds. At 20°C, the maximum specific growth rates (μ_{Nmax}) typical of nitrifying bacteria and heterotrophic bacteria are 0.8 d^{-1} and 3.0 d^{-1}, respectively. Therefore, a sufficiently long sludge retention time (SRT) is needed to obtain stable nitrification. Design SRT values for carbonaceous and nitrogenous BOD removal in single stage activated sludge systems range from 4 to 7 days (Tchobanoglous et al, 2003).

Because nitrifiers are strict aerobes, an adequate dissolved oxygen (DO) concentration must be maintained. Nitrification is adversely affected below a dissolved oxygen concentration of 1 mg/L. In practice, dissolved oxygen in aeration tanks is maintained at no less than 2 mg/L. *Nitrosomonas* and *Nitrobacter* can also be inhibited by high concentrations of free ammonia and free nitrous acid, respectively (Tchobanoglous et al, 2003).

As is evident from reaction 2-[1], oxidation of ammonium produces acid which can lower the solution pH and reduce the nitrifier growth rate if sufficient alkalinity is not present. The optimal pH for nitrification ranges from 7.5 to 8.6. Nitrification ceases at pH values below 6.0 (Environment Canada, 2003; Tchobanoglous et al, 2003)

The growth rate of nitrifiers is significantly affected by water temperature. Nitrification reaches a maximum rate in the temperatures of 30 to 35 °C. At temperatures higher than 40 °C, nitrification rates fall to near zero. Temperature effect on microbial reactions in water can be expressed by equation 2-[4]:

$$\mu_{mT} = \mu_{m15} e^{0.098(T-15)} \qquad 2\text{-}[4]$$

where μ_{m15} and μ_{mT} are the specific growth rates at 15°C and at an arbitrary temperature, T, respectively. According to equation 2-[4], the maximum specific growth rate would undergo a 2.7 fold decrease as the wastewater temperature falls from 20°C to 10°C (Environment Canada, 2003; Tchobanoglous et al, 2003).

2.3.4 Denitrification

Nitrification satisfies the nitrogenous oxygen demand of a waste stream, but does not remove nitrogen from the system. Denitrification is required to accomplish this latter goal. A wide range of bacteria are capable of denitrification. Examples are *Achromobacter, Acinetobacter, Agrobacterium,* and *Pseudomonas*. Denitrification is an anaerobic respiration process in which nitrate and nitrite serve as electron acceptors during the biological oxidation of organic substrates. This occurs when oxygen levels are low and nitrate or nitrite becomes the dominant oxygen source for bacteria. The biological reduction processes are from nitrate (NO_3^-) to nitrite (NO_2^-), to nitric oxide (NO), nitrous oxide (N_2O), and finally to nitrogen gas (N_2):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

In denitrification processes, as nitrate and nitrite are the terminal electron acceptors, the electron donors are mainly from three sources: 1) the biodegradable soluble COD (bsCOD) in the influent wastewater, 2) the bsCOD produced during endogenous decay, and 3) an exogenous source such as methanol or acetate. The energy yielding reactions are shown in 2-[5], 2-[6], and 2-[7] for each of these organic carbon sources (the term $C_{10}H_{19}O_3$ is often used to represent the biodegradable organic matter in wastewater) (USEPA. 1993):

Using organic carbon in wastewater:

$C_{10}H_{19}O_3 + 10NO_3^- \rightarrow 5N_2 + 10CO_2 + 3H_2O + NH_3 + 10OH^-$ 2-[5]

Using methanol:

$5CH_3OH + 6NO_3^- \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^-$ 2-[6]

Using acetate:

$5CH_3COOH + 8NO_3^- \rightarrow 4N_2 + 10CO_2 + 6H_2O + 8OH^-$ 2-[7]

In practice, an additional 25 to 30 percent of the organic carbon substrate required for energy production is required for cell synthesis.

Denitrifying bacteria metabolize more slowly than do aerobic heterotrophs. The maximum specific growth rate of denitrifying bacteria ranges from 0.3 d^{-1} to 0.9 d^{-1}, with 0.3 d-1 being typical for municipal wastewater treatment. Anoxic conditions are needed to ensure denitrification. Denitrifying bacteria are facultative organisms, and when oxygen and nitrate are both present, will use oxygen for metabolism and oxidation of organic matter because of the higher energy yield. As shown in reactions 2-[5] through 2-[7], denitrification produces alkalinity and increases pH. The optimum pH range for denitrification is 6.5 to 7.5 (Environment Canada 2003).

The effect of temperature on denitrifying bacteria is more pronounced than its effect on heterotrophic aerobic bacteria. The dependence of the maximum specific growth rate of denitrifying bacteria is modeled as shown in equation 2-[8]:

$$\mu_{mT} = \mu_{m20}\Theta^{T-20} \qquad 2\text{-}[8]$$

where μ_{mT} and μ_{m20} are maximum specific growth rate values at T°C and 20°C, respectively, and Θ is a temperature coefficient between 1.14 to 1.16 (Tchobanoglous et al, 2003). Although denitrification can occur between 5°C to 30°C, equation [2-8] shows that a decrease in wastewater temperature from 20°C to 10°C would result in approximately a four-fold reduction in the denitrification rate.

2.4 Biological methods applied to remove nitrogen from municipal wastewater

Nitrogen removal from municipal wastewaters largely relies on biological treatment in which various populations of bacteria carry out nitrification and denitrification of the flows. These processes can be carried out in either suspended growth or attached growth systems.

2.4.1 Nitrogen removal by suspended-growth biological processes

Suspended growth systems consist of an aeration chamber. By a means of aeration, the bacteria are kept in suspension in the wastewater stream in the chamber. The bacteria digest the solids and nutrients in the wastewater and turn it into new bacteria cell, carbon dioxide, nitrogen gas and water. Activated sludge systems and lagoon systems are the most widely applied suspended-growth systems. Lagoons are used by smaller communities, but are not appropriate for larger cities due to the large land requirements. Activated sludge systems are most commonly used for large wastewater treatment plants.

As nitrifying bacteria are slow growing organisms, activated sludge systems require a long enough sludge retention time (SRT) to ensure an adequate population of nitrifying bacteria. Oxygen is usually supplied by high-efficiency aeration systems, which also helps to keep the mixed liquor in suspension. The main types of suspended growth systems include conventional activated sludge systems, oxidation ditches, sequencing batch reactors, aerated and facultative lagoons, and membrane bioreactors (Environment Canada, 2003). Aerated lagoon systems, including aerated lagoons and aerated facultative lagoons, consist of relatively large basins equipped with surface mechanical aerators or diffused aeration systems. These processes offer potential capacity for nitrification and effective conversion of ammonia nitrogen under ideal conditions. Conversion of ammonia nitrogen in aerated lagoons is usually less effective than in facultative lagoons because of shorter detention times (for usually no sludge recycling in lagoon systems, the hydraulic retention time equals to sludge retention time). The facultative lagoons are capable of converting up to 80% of ammonia nitrogen in municipal wastewaters provided that a sufficiently long hydraulic retention time is allowed (USEPA, 2002). Because nitrification is highly dependant on temperature, the systems may not be able to sustain ammonia conversion over the winter.

2.4.1.1 Oxidation ditches

The oxidation ditch system can be defined as an extended aeration mode activated sludge-type system. It consists of a simple racetrack aeration tank, which is often couple with an external secondary clarifier. Hong *et al.* (2003) studied a pilot-scaled phased isolation ditch system with an intra channel clarifier, a simplified novel oxidation ditch system, which was applied to achieve ammonia nitrogen and phosphorus removal from municipal wastewater simultaneously. The system consisted of two ditches with an intra-clarifier that eliminated the need for an external final clarifier, an additional pre-anaerobic reactor, and recycle of sludge and nitrified effluent. The system was operated above 10°C, and by means of alternating flow and intermittent aeration, anoxic, anaerobic, and aerobic phase separation was accomplished. The researchers reported 70 to 84 percent ammonia nitrogen removal, 65 to 90 percent total phosphorus removal, and 88 to 97 percent BOD removal when the HRT was varied from 10 to 21 hours, the SRT from 15 to 41days, and cycle times from 2 to 8 hours. Hong *et al.* (2003) concluded that extending the SRT will gradually improve removal of nitrogen and phosphorous and decrease treatment cost. In contrast, lower cycle times decreased nitrogen and phosphorus removal. The researchers set optimal parameter ranges for the system at HRT from 10 to 14 hours, SRT from 25 to 30 days, and cycle time at 4 hours.

A study by Zhou and Qian (1998) indicates that in an oxidation ditch system, the ratio of the durations of denitrification to nitrification phases is an important parameter for nitrogen removal control in municipal wastewater treatment. A full-scale triple oxidation ditch combined with a biological denitrification system having a 100,000 m3/d treatment capacity was operated to treat municipal wastewater. The system achieved effluent BOD5 below 30 mg/L and 92 percent TSS (total suspended solids) removal, but nitrogen ammonia removal was not optimal. The researchers suggested a reconstruction of the system to improve nitrification.

2.4.1.2 Membrane bioreactors

Membrane bioreactor, known as MBR, combines of a biological reactor and a membrane filtration system for retention of the activated sludge. A laboratory scale aerated submerged hollow fiber membrane system was applied to treat household wastewater. Membrane fouling was controlled by making use of the bubbles produced from the aeration period (Yeom *et al.*, 1999). Nitrogen removal efficiency reached up to 83 percent, in conditions of 8 to 15 hours of HRT and a very long SRT. Nitrification was fast and complete, and denitrification was observed to be a limiting step. TCOD and TSS removal reached up to 96 and 100 percent, respectively. Nitrogen removal efficiency was optimized by controlling intermittent aeration frequency and adjusting anoxic and aerobic phase times in the cycle. Study results showed a linear relationship between the measured specific denitrification rate and the influent BOD/TN value. Based on this, a method to optimize the denitrification phase time was proposed. Two advantages of this system over other biological treatment methods were revealed. One is that, even under high mixed-liquor volatile suspended solids (MLVSS) conditions, the denitrification could also be enhanced. The other is the system's resistance to fluctuation or the limitation of external carbon supply. The latter suggests that endogenous denitrification may play a significant role.

When organic loading is low, small-scale municipal wastewater treatment plants often cannot meet the nitrogen effluent requirements. Ahn *et al.* (1999) proposed an innovative ultrafiltration membrane-bioreactor (MBR) system to retrofit to existing municipal wastewater treatment plants. They proved that MBR, compared to direct ultrafiltraton of sewage, was more effective for the enhancement of effluent quality and fouling prevention. Applying a cross-flow membrane-bioreactor (CFMBR), COD in effluent was reduced to less than 10mg/L, independent of the influent COD value. Total nitrogen and phosphorus concentrations in the effluent were 5 and 1 mg/L, respectively. Furthermore, the system was stable and did not require chemical washing over the 40-day operation period.

2.4.2 Attached-growth biological processes

The term, *attached growth,* refers to the film of biomass that develops on inert surfaces provided by the systems. These systems rely on convection to carry organic compounds and other nutrients to the vicinity of the fixed film where they enter the biomass by diffusion. End products of bacterial metabolism are transferred to the bulk flow in a similar fashion. Establishment of a biofilm allows large microbial populations to be retained within the reactor even during periods of high hydraulic loading and low nutrient availability. However, these systems can become diffusion-limited under low organic and nutrient loadings.

Attached growth technologies include trickling filters, rotating biological contactors (RBC), aerobic submerged fixed-bed reactors, aerobic submerged mobile-bed reactors, including fluidized-bed reactors and moving-bed biofilm reactors, recirculating sand filters, intermittent sand filters and constructed wetlands (Environment Canada, 2003).

2.4.2.1 Aerobic submerged fixed-bed reactors

Aerobic submerged fixed-bed reactors referred to biological aerated filters, which are non-moving mediums submerged in a vertical mechanically aerated cell. Canziani *et al.* (1999) conducted research on nitrogen removal using pilot scale fixed-bed biofilters. The plant consisted of two fixed bed biofilm reactors in series. The first filter was used to removal carbon and the second was used to perform nitrification. Raw municipal wastewater was applied to the system. Based on four years of operation, the nitrification rate was shown to be 0.84 g NH_4-N/m^2/d at 20°C. Reduction of the nitrification rate by up to 50 percent was observed when the organic loading exceeded 2.5 g COD/ (m^2.d), indicating that ammonia oxidation was strongly affected by influent organic loading. The temperature dependence of the nitrification rate (r_n) was calculated as $r_n=r_{n20^{\circ}C}1.05^{T-20}$.

The authors also attempted denitrification of the nitrified effluent by recycling it to the first filter bed, introducing carbon sources from the raw wastewater, and allowing the bed to go anoxic. The researchers reported that that the rate limiting step in the denitrification process was the hydrolysis of organics when municipal wastewater was used as the carbon source. The denitrification rate

(r_d) was found to vary with temperature according to $r_d = r_{d20^{o}C} 1.11^{T-20}$.

2.4.2.2 Aerobic submerged mobile-bed reactors

Aerobic submerged mobile-bed reactors refer to the attached-growth nitrification chambers, in which particles or lightweight media are loaded. The particles and media are suspended or fluidized by the water and airflow velocities. Simultaneous removal of organic carbon and nitrogen was accomplished in a fluidized bed reactor composed of aerobic and anaerobic zones by Fdez-Polanco *et al.* (1994). The pilot scale unit achieved 90 percent soluble BOD_5 removal and 70 percent total nitrogen removal.

Giuseppe *et al.* (1999) tested a pilot scale moving bed sequencing batch biofilm reactor (MBSBBR), applied to treated primary settled wastewater for organic carbon, phosphorus and nitrogen removal. The system employed polyethylene biofilm carriers. Organic carbon uptake and phosphorus release took place in the anaerobic phase of the cycle. Nitrification and phosphorus uptake occurred in the aerobic phase, and deniftrification was achieved in the inner layer of biofilm among the anoxic respiration sequestered COD.

A moving bed biofilm reactor can be considered as an add-on process to meet the new requirements for nitrogen removal in cases where a municipal wastewater treatment facility was designed for organic carbon removal only. Bonomo et al (2000) employed two bench-scale oxygen moving bed biofilm reactors to treat secondary effluent from such a municipal wastewater treatment plant. The tests demonstrated the feasibility of using the moving bed biofilm technology as a full-scale add-on for nitrification of the effluent from the existing high purity oxygen activated sludge system.

2.4.2.3 Constructed wetlands

Constructed wetlands can be used in small communities for tertiary treatment of municipal wastewater for nutrient removal. In many cases, constructed wetlands cost less to build and operate, and consume less energy compared to other methods for nutrient removal from wastewater (Merlin *et al.*, 2002). Cameron et al. (2003) studied a constructed wetland system that was used to treat effluent from a municipal sewage lagoon. The system consisted of a three-cell free-surface wetland, with phosphorus adsorption slag filters, and a vegetated filter strip. The average removals during the investigation period were 34% BOD_5, 37% TKN, 52% NH_4^+, 93% TSS, 90% TP, 82% 0-PO4, 52% fecal coliforms and 58% E. coli. Effluent total nitrogen, total phosphorus and BOD_5 values were below 3.0 mg/L, 0.3 mg/L and 3.0 mg/L, respectively.

2.4.3 Combined suspended growth and attached growth systems

Combined systems are categorized as either dual biological systems or hybrid biological systems.

Dual systems are the combination of an attached growth process with a suspended growth process. These combinations could be various, such as the activated biofilter, biofilter/activated sludge, trickling filter/solids contact and series trickling filter/activated sludge processes. When properly designed, dual systems possess the combined advantages of both attached growth systems and suspended growth systems.

Hybrid biological systems consist of suspended growth biomass and attached growth biomass in the same units. The advantage of the technology is the achievement of a high level of active biomass and long sludge retention time (SRT).

Chang and Ouyang (2000) investigated the performance of a hybrid system composed of a three-stage activated sludge process having a leading anaerobic stage followed by an anoxic stage, and finally an aerated stage containing a rotating biological contactor (see Figure 2-1).

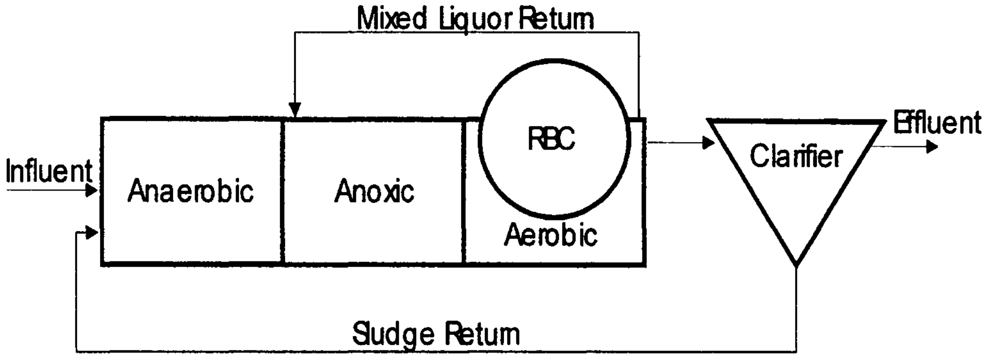


Figure 2-1 Hybrid suspended growth and fixed film process
(after Chuang and Ouyang, 2000)

The researchers reported that approximately 62% of organic matter, 48% of nitrogen and 47% of phosphorus in the influent were removed in the forms of carbon dioxide, nitrogen gas, and polyphosphate, respectively.

2.5 Physical and chemical processes used to remove nitrogen from municipal wastewater

Biological nutrient removal is a reliable and cost effective means of removing nitrogen from municipal wastewater. Physical and chemical methods are useful to remove nitrogen from intermittent flows, or to supplement biological treatment.

2.5.1 Chemical oxidation by breakpoint chlorination

Breakpoint chlorination is one alternative technology for ammonia removal from wastewater. It comprises a series of complex reactions including oxidation of ammonium-nitrogen to nitrogen gas. The overall reaction is described stoichiometrically as:

$$2NH_4^+ + 3Cl_2 \rightarrow N_2\,(g) + 6Cl^- + 8H^+ \qquad 2\text{-}[9]$$

Breakpoint chlorination can achieve over 90 percent removal of ammonium nitrogen. As may be seem in Table 2-1, the process possesses several clear advantages as well as several serious disadvantages.

Table 2-1. Advantages and disadvantages of breakpoint chlorination of wastewater (Source: Tchobanoglous et al, 2003)

Advantages	Disadvantages
Nearly all ammonia nitrogen can be oxidized	May produce high chlorine residuals that are toxic to aquatic organisms
Can be used for fine tuning of ammonia removal	Process is sensitive to pH
Limited space requirement	High operating cost
Not affected by toxic substances	Chlorine addition raises TDS
Not affected by temperature	Requires careful control to avoid formation of nitrogen trichloride gas
Low capital cost	Requires highly skilled operator

Studies on this technology were numerous in the past (Pressley *et al.*, 1972; Fertik, 1978; and Fertik and Sharpe, 1980). Operational problems were encountered primarily with respect to the long-term reliability of free chlorine and ammonia continuous analyzers. Although these problems have been resolved, the required control strategy is quite complex and although satisfactory operating performance is theoretically achievable, the process has seldom been employed in recent years. Nevertheless, breakpoint chlorination is currently used for lagoon-based water pollution control at Niagara-on-the-lake, Ontario (Environment Cananda, 2003).

2.5.2 Ion exchange

As the discharge limits of various pollutants become more stringent, ion exchange has become more attractive as possible treatment technologies (Jorgensen and Weatherley, 2002). Ion exchange is a technology that has been used in industrial wastewater and water treatment applications in the past, but which has potential in the treatment of municipal wastewater for the selective removal of ammonium nitrogen. Ion exchange technology is used for ammonium ion removal in both water treatment systems and the aquaculture industry where water is recirculated (Dryden, 1984). Organic nitrogen must be oxidized to ammonia nitrogen prior to ion exchange (Environment Canada, 2003).

Zelolite is most often applied as the ion-exchange resin for ammonia removal from wastewater. Clinoptilolite, a naturally occurring zeolite, has been proven to be one of the best natural exchange resins, with high affinity for the ammonia ion. Clinoptilolite has a classical aluminosilicate cage-like structure, so it presents a significant macroporosity, which allows its use to treat wastewater with high molecular weight contaminants such as proteins (Greig, 1996). Varieties of synthetic zeolites such as potassic zeolite (K-Zeo), magnestic zeolite (Mg-Zeo), sodic zeolite (Na-Zeo) and calcic zeolite (Ca-Zeo), have all proven to be effective resins (Milan *et al.* 1996).

Jorgensen and Weatherley (2002) conducted a study into the removal of ammonium from simulated wastewater by ion exchange and concluded that ion exchange offers a number of advantages, including the ability to handle shock loadings and the ability to operate over a wide range of temperatures. These researchers also suggested that the presence of soluble organic compounds enhanced the uptake of ammonium ion onto the exchange resins. One possible explanation offered for the observed enhancement in ammonia uptake is that the presence of organics may reduce the surface tension of the aqueous phase to the point of enhancing access of the aqueous phase to the macropores of the exchanger. The presence of citric acid reduced the surface tension of water. Clinoptilolite and Purolite MN500 both contain micropores and macropores and were the two exchangers to show enhancement in presence of an organic. Dowex 50w-x8, which does not contain macropores, did not show any NH_4^+ enhancement in the presence of any organic. However, further detailed experimentation would be required to determine any definitude link between surface tension and changes in ion exchange uptake (Jorgensen *et al.* 2003).

An ion-exchange system is designed based on mass loading. At high contaminant concentrations, the ion-exchange beds get loaded very rapidly and so very large ion exchange vessels are usually needed. In these scenarios, the construction and operation cost will be high. An ion exchange system is better suited for ammonia concentrations less than 70 mg/L. Pretreatment to control solids loading to columns is generally required to reduce clogging. Ion exchange has had limited application due to the extensive pretreatment required, concerns regarding the life of the ion-exchange resins, and the complex regeneration system required (Metcalf and Eddy, 2003).

2.5.3 Air stripping

Air stripping can be used to transfer ammonia from the aqueous phase to the gaseous phase. The process relies on pH adjustment to convert ammonium ion to aqueous ammonia, and on aeration to transfer the ammonia to the gaseous phase. The mass transfer is generally accomplished in a stripping tower, packed with inert media to increase the liquid-gas interface area. Air stripping has found wide application in municipal wastewater treatment for the capture of ammonia, malodorous gases, and volatile organic compounds (VOCs). Of the available methods to remove nitrogen from wastewater, ammonia stripping is the simplest and easiest to control. However, ammonia stripping has two main limitations: (1) In cold climates, provisions must be made to prevent ice forming in the stripping column, and (2) the column media may have to be acid washed on a regular basis to remove calcium carbonate scale that tends to form in hard waters or if lime is used for pH adjustment (Culp, *et al.*, 1977).

Ammonia is a weak base that reacts with water to form ammonium hydroxide. In ammonia stripping, caustic soda is added to the wastewater until the pH reaches 10.8 to 11.5 which converts the majority of dissociated ammonium ions to aqueous ammonia according reaction 2-[10]:

$$NH_{3\ (g)} \leftrightarrow NH_{3\ (aq)} + H^{+} \quad (pKa = 9.25) \qquad 2\text{-}[10]$$

Ammonia stripping has been shown to work well for wastewaters that have ammonia concentrations between 10 and 100 mg/L. In this concentration range, the solubility of ammonia in water obeys Henry's law, which states that the amount of ammonia present in air (transferred from water) is directly proportional to its equilibrium concentration in the water and can be expressed as following:

$$C_{NH_3} = HC_{NH_4^+} \qquad 2\text{-}[11]$$

Where C_{NH_3} is the ammonia concentration in air; $C_{NH^+_4}$ is the ammonia ion concentration in water; H is a Henry's law constant. Henry's Law constant is a strong function of temperature and increases with a temperature increase. Under the atmospheric pressure, H can be calculated from the following empirical equation:

$$\log_{10}H = 1477.8/T - 1.6937 \qquad 2\text{-}[12]$$

Equation 2-[12] shows that the higher the temperature, the lower the solubility of the ammonia in water, and the easier the contaminant is stripped (NRC, 1979).

For high ammonia content (more than 100 mg/L), it may be more economical to use alternate ammonia removal techniques, such as steam stripping or biological methods (EPA, 2000).

2.5.4 Electrochemical Treatment

Both ion exchange and air stripping processes produce waste streams that require subsequent treatment. Electrochemical treatment has been proposed as a means of dealing these streams. Electrochemical technology has found several water and wastewater treatment applications. Table 2-2 contains examples of these applications.

Table 2-2. Application of electrochemical systems to water and wastewater treatment.

Classification	Waste Treated	Substance or Reaction	Reference
Denitrification	Nuclear waste	NO_3^-, $NO_2^- \rightarrow N_2$, NH_4^+	Genders and Hartsough (1996)
Denitrification	Tannery waste	$NH_3 \rightarrow N_2$	Szpyrkowicz (1995)
Denitrification	Groundwater	$NO_3^- \rightarrow N_2$	Sakakibara *et al.* (1993, 1997)

The electrode reactions proposed to date are the electrolysis of water coupled with enzymatic denitrification (Sakakibara and Kuroda, 1993; Sakakibara *et al.*, 1997). In addition, most studies have demonstrated the simplicity of operation and maintenance of the systems.

2.6 Nitrogen removal from digested sludge supernatant and dewatering centrate

Ammonia concentrations in the supernatant from anaerobically digested biological sludges and centrate from centrifugal sludge dewatering are in the range of 100 to 1000 mg/L (as N). The removal of nitrogen from these concentrated waste streams presents challenges not encountered in the treatment of raw municipal sewage, and is an issue of increasing prevalence. Specialized physical-chemical and biological methods are employed, many of which are still in the research and development stage.

2.6.1 Nitrogen removal from digested sludge supernatant

2.6.1.1 Biological Methods

Biological treatment technology for ammonia nitrogen removal has been the most prevailing practice in municipal wastewater treatment for decades, but the high ammonia concentrations in supernatant recycled to the head of the plant often causes a shock to the entire process (Gee and Kim, 2004; Prakasam and Loehr, 1972). An alternative solution is to employ biological technology to pre-treat supernatant prior its introduction to the main process. In order to reduce aeration costs and organic carbon requirements, research on a short-cut ammonia removal method in which nitrite is accumulated in a reactor and subsequently converted directly to nitrogen gas was studied in the early the 1980s. Gee and Kim (2004) employed a sequencing batch reactor (SBR) to test this concept for ammonia removal from digester supernatant. These researchers demonstrated that nitrite accumulation in a reactor is feasible and identified the important parameters affecting the accumulation of nitrite, and the effects of these parameters on process performance (Gee, and Kim, 2004).

A new promising system for nitrogen elimination via nitrite is the SHARON process (single reactor system for high activity ammonia removal over nitrite). The process uses a continuous flow reactor without sludge retention (Fux *et al.*, 2003). Seigrist (1996) also tested this process for ammonia removal from digester supernatant and reported a nitrogen removal efficiency of over 90 percent in both the SBR and SHARON modes.

The Sjolunda wastewater treatment plant in Malmo, Sweden applied a new process concept to remove the nitrogen from digester supernatant. An existing trickling filter was used to nitrify the supernatant, which was then introduced to a moving bed biofilm reactor to which an external carbon source was added to accomplish denitrification. After implementing the upgraded system in the plant, the average effluent concentrations of phosphorus and nitrogen were 0.21 mg/L and 5.4 mg/L, respectively, which were stable despite varying loading conditions (Hanner *et al.*, 2003; Bortone *et al.*, 1994).

To remove nitrogen from the digester supernatant in nutrient removal plants, increasing the anoxic volume or using a carbon source, such as methanol could be considered. Denitrification in tertiary filtration is an alternative mode when the activated sludge volume cannot be extended after the nitrification. To improve the nitrogen removal, a full-scale experiment was conducted by using existing filter cells to achieve further denitrification. Methanol was administered according to influent nitrate concentration in this process. Within the range of 12 to 15°C, denitrification reached up to 1.0 kg N m^{-3} of filter volume. Dependable results were achieved, expect during rainy weather when efficiency of denitrification decreased (Koah and Siegrist, 1997; Purtschert et al, 1996; Siegrist, 1996).

Separate treatment of digester supernatant with intermittent nitrification-denitrification is another interesting solution if the treatment reactor, has extra volume. The design of this process is influenced by different conditions such as solids retention time, the maximum growth rate of nitrifiers, and other factors (Fux *et al.*, 2003; Siegrist, 1996). A SBR with separate intermittent nitrification-denitrification was used successfully to treat digester supernatant containing 800 to 1000 mg NH_4-N/L and 70 to 80 mM alkalinity at a 250 to 300 m^3d^{-1} flowrate. Hydrolysed starch was used as a carbon source for denitrification. Seventy-five percent total nitrogen removal was obtained (Karsson, 1994; Siegrist, 1996).

2.6.1.2 Physical-Chemical Methods

ANAMMOX (ANaerobic AMMonium OXidation) is a new developing technology aimed at coping with ammonium-rich digester supernatant. The concept of this biological process is to convert ammonia nitrogen under anoxic conditions using nitrite as the electron acceptor, and the end product is nitrogen gas.

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \qquad \text{2-[13]}$$

It is estimated that using this method, the aeration and carbon source demand are reduced over 50 percent and 100 percent, respectively. A pilot scale experiment was carried out by treating digester supernatant from two wastewater treatment plants where the ammonia nitrogen loads were approximately 657 mg NH_4^+-N /L and 619 mg NH_4^+-N/L, respectively. Nitrification was conducted in a continuously stirred tank reactor without sludge retention, and a sequencing batch reactor was used to perform anaerobic ammonium oxidation. Results indicted that over 90 percent of the influent nitrogen load to the ANAMMOX reactor was removed, with negligible sludge production (Fux et al, 2002).

Magnesium ammonium phosphate precipitation (MAP) is a chemical process to precipitate ammonium from digester supernatant as ammonium phosphate through the addition of phosphoric acid and magnesium oxide and pH control. In a study carried out by Siegrist (1996), the MAP method was tested at pilot scale. During the process, phosphoric acid and magnesium oxide were added to the inlet of the first and the second of the three reactors, respectively. pH adjustment was carried out in the third reactor to promote precipitation of ammonium phosphate. The process was demonstrated to remove 85 to 90 percent of the 600 to 1000 g NH_4-N m^{-3} from a digester supernatant at a 0.5 m^3h^{-1} flow rate. The authors suggested the process would be most suitable for plants where phosphate is a by-product from an internal process because of the cost of phosphoric acid.

Siegrist (1996) also tested the use of ammonia stripping and scrubbing for ammonia removal from digester supernatant. NaOH or $Ca(OH)_2$ were employed to increase pH to 10, thereby converting ammonium into free ammonia. Ammonia released from the stripping unit was absorbed with sulfuric acid in a scrubbing column. For the same supernatant used in the MAP tests, approximately 97 percent of the ammonia was removed in a pilot scale unit at aqueous flow rates of 150 to 300 L/h, and liquid temperatures between 10 and 22 °C. The process produces an ammonium sulfate solution that can theoretically be used as feed stock for fertilizer production. However, an economical method to convert the solution to usable fertilizer has yet to be developed, due to current market fertilizer costs and the cost for drying the solution. The continuous consumption of NaOH or $Ca(OH)_2$ and sulfuric acid is a disadvantage of this technology in practice.

2.6.2 Nitrogen removal from centrate

The literature offers few reports of ammonia removal from centrate. Carrio *et al.* (2003) conducted a review of ammonia removal from centrate produced in New York City over the past 10 years. Fourteen wastewater treatment plants treat wastewater produced in New York City, and since 1992 all the sludge has been treated in eight plant locations where centrate is produced.

Centrate, produced from dewatering anaerobically treated sludge, is a special wastewater extreme, which varies greatly in both quality and quantity. The quantity varies with the amount of sludge produced, while sludge type, polymer type, and centrifuge operating mode are the factors that affect the centrate quality. The New York City centrate contained from 500 to 1,000 mg NH_4-N/L, compared to a typical ammonia concentration of 15 mg NH_4-N/L in raw municipal wastewater.

The treatment technologies applied to centrate are similar to those applied to sludge supernatant (Carrio *et al.* 2003). Physical-chemical processes and biological centrate treatment are all employed. Magnesium and phosphorous salts can be added to centrate to precipitate the ammonia ion as struvite (magnesium ammonium phosphate). Steam stripping and hot air stripping are other alternative methods. Ion-exchange, defined as Ammonia Recovery Process (ARP), a patented process developed by the ThermoEnergy Corporation, was studied at a demonstration plant. Biological centrate treatment includes separate centrate treatment and combined centrate treatment. In the full-scale practice, biological treatment was dominant in New York City, and studies on physical-chemical technologies were conducted at bench scale, pilot scale or as demonstrations at various New York City plants.

The SHARON process has been employed for ammonia removal from centrate as well as from supernatant, which suggests it to be one of the more promising strategies in the future for ammonia nitrogen removal due to energy-saving and chemical dose reduction.

Studies at full-scale activated sludge plants indicated that the location of centrate addition affects the ammonia removal efficiency. Centate addition to the return sludge line resulted in better nitrification results than addition to primary effluent (Carrio *et al.* 2003).

Separate centrate hybrid systems achieved high rates of nitrification at bench scale, but due to operational concerns regarding the durability of the media among others, few such technologies have been implemented at full scale. Further studies are needed to develop and demonstrate these technologies.

2.7 The AmmEl Process

The AmmEl (Ammonia elimination) process is an emerging proprietary technology that was developed at the University of Guelph in 1995, and has been patented in Canada, the U.S., and the European Union. The core of the process applies electrochemical methods to convert ammonia directly to nitrogen gas. The technology has been under development for the past ten years and is claimed to be a cost-effective solution for ammonia removal from wastewater from a variety of sources.

The manufacturer has conducted pilot-scale testing of the system in the City of Guelph to remove ammonia from several municipal and industrial waste streams. Due to limited amount of operating experience and the relatively small number of applications of the technology, the process should not be selected for full-scale implementation at a new site without first being tested at pilot-scale. Figure 2-2 depicted a schematic drawing of the AmmEl system.
One of the AmmEl (Ammonia elimination) process, as shown in Figure 2-2, consists of three main components: stripper column, scrubber column and electrochemical cells. The stripper separates ammonia from the centrate

stream. Sodium hydroxide is added to the influent centrate to elevate the stream pH value. This drives ammonium ions to the un-ionized ammonia form prior to the second stage of the system, the scrubber column. To concentrate ammonia, sodium chloride solution functions as the scrubber stream, entering the scrubber at the column top. Plastic packing material is installed inside the scrubber unit, as well as the stripper unit. Inside the scrubber column, two countercurrent streams, ammonia air and sodium chloride solution are well mixed and ammonia is concentrated into the liquid phase. The ammonia rich sodium chloride solution is directed to the final stage, the electrochemical cells, where ammonia is converted to nitrogen gas and released to the atmosphere. For a detailed depiction refer to chapter 2, literature review section. A detailed introduction of each unit follows.

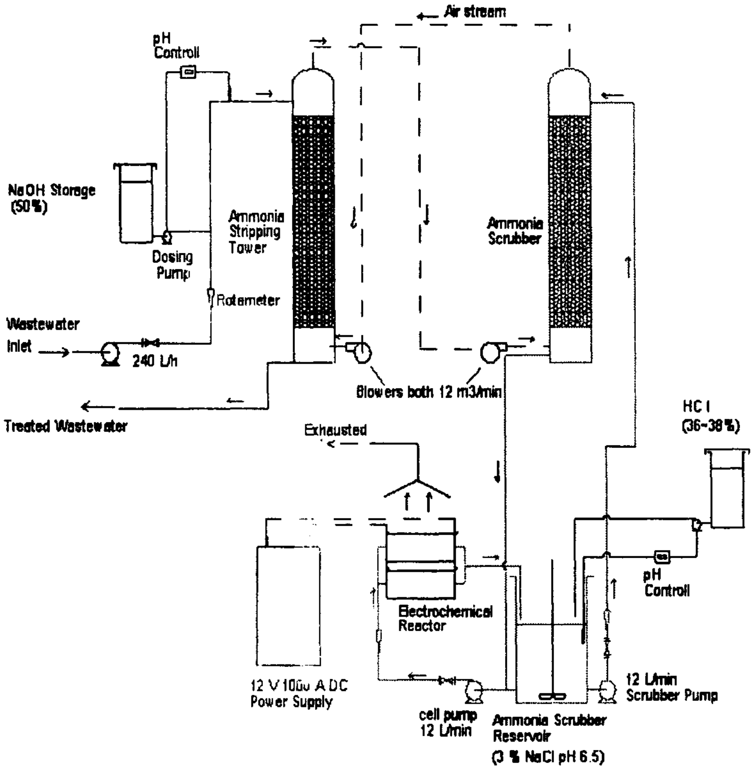


Figure 2-2 Schematic drawing of an AmmEl system (after Enpar Technology)

2.7.1 Stripping Tower

Ammonia stripping tower operations are affected by pH, the ratio of airflow to wastewater flow and, to a lesser extent, wastewater temperature. The pH of the water is considered to exert a major effect on the efficiency of the ammonia stripping process. The pH must be raised to the point where the majority of ammonium ions are converted to ammonia gas. Research has shown that removal efficiency improves with increasing feed stream pH up to a value of 10.5, and remains relatively constant as pH is increased further (Enpar Technologies Inc. 2004). Sodium hydroxide is preferred for pH adjustment because additions of lime would increase the formation of calcium carbonate scale within the stripping tower. This reduces the system efficiency and cause maintenance problems (USEPA, 1973).

Gas transfer relationships indicate that an increase in ammonia removal can be achieved by increasing the rate of airflow for a given tower height. However, there is a practical limit because of the increase in air pressure drop with increasing flow rate. This results in higher capital investment for fans and increased power costs (Liao *et al.* 1995).

Air temperature is another important factor in air stripping operations. The temperatures of the air and liquid streams reach equilibrium at a value near the initial air temperature in the top few inches of the stripping tower. As the wastewater temperature decreases, the solubility of ammonia in solution increases and it becomes more difficult to remove by stripping. This effect is most pronounced when lower than optimal pH values are maintained in the liquid feed stream (Enpar Technologies Inc. 2004).

2.7.2 Scrubber tower

Discharge of ammonia into the atmosphere is limited by environmental regulation. To deal with the ammonia stripped out of wastewater, packed column scrubbers are also commonly employed to remove ammonia from gas streams. These comprise a vessel in which counter-current two-phase flow occurs, and media that provide a relatively large gas-fluid interface per unit volume of column volume. Because of the nature of the packing media, a packed column can operate using strongly corrosive fluids. Packed columns are often more economical to build and operate than their plate or bubble-cap column counterparts, although pressure drops can be high, which require larger gas blowers with high energy consumption.

Packed-column media for gas-liquid contact in gas stripping or chemical scrubbing have been made in myriad shapes and of numerous materials, including wood, rock, ceramic, metal, plastic and woven filaments. Plastic of the various thermoplastic fabrications has become the predominant packed-column media material because of its chemical resistance and low material density (Rafson, 1998)

2.7.3 Electro-chemical units

The sodium chloride and ammonium rich scrubbing tower effluent flows into the electrochemical unit where electrochemical oxidation of ammonium to N_2

gas occurs. The system of reactions that take place is given in equations 2-[14] to 2-[18]:

Electrode (anode) reactions:

$$2NH_4^+ \rightarrow 6\ N_2 + 8H^+ + 6e^- \qquad 2\text{-}[14]$$

$$2Cl^- \rightarrow 6\ Cl_2 + 2e^- \qquad 2\text{-}[15]$$

Electrode (cathode) reaction:

$$2H^+ + 2e^- \rightarrow H_2 \qquad 2\text{-}[16]$$

Bulk reactions:

$$Cl_2 + H_2O \rightarrow HOCl + HCl^- \qquad 2\text{-}[17]$$

$$2NH_4^+ + 3HOCl \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \qquad 2\text{-}[18]$$

Enpar Technologies Inc. claims a power input of 20.4 kWh is required per kilogram of ammonia removed (Enpar Technologies, 2004).

2.8 Summary

This literature review presents the development in nitrogen removal technologies. Nitrification and denitrification are the predominant means of nitrogen removal from municipal wastewaters. However, nitrogen removal by biological methods suffers from a loss in efficiency at low wastewater temperatures. Recent advances in dual and hybrid biological treatment systems may increase reliability and flexibility of biological treatment systems in the future.

Physical-chemical treatment methods are used primarily to supplement biological nitrogen removal either as a pretreatment or a polishing step. These systems may be particularly attractive to centrate and supplement nitrogen removal in cold climates. The AmmEl system captures ammonia from wastewater streams by stripping and scrubbing, and oxidizes the ammonia to nitrogen gas in an electrochemical reactor.

CHAPTER III METHODOLOGY

3.1 Material, analytical equipment and methods

3.1.1 Centrate

The centrate used in this experiment was obtained from the centrifuges at the co-composting facilities at Edmonton's Clover Bar site, Alberta, Canada. Major chemical characteristics of the centrate are listed in Table 3-1. TKN, NH_3-N and TSS values were from composite samples of centrate for the dates indicated obtained from the Gold Bar laboratory database (see Appendix A).

Table 3-1. Characteristics of Clover Bar Centrates

Component	Concentration	Component	Concentration
TKN	950~1200 (mg/L)		
NH_3-N*	800~900 (mg/L)	TSS	300~2200 (mg/L)
Alkalinity	3300 mg $CaCO_3$/L	pH	7.8~8.3

* NH_3-N denotes total ammonia nitrogen

TSS in the raw centrate was extremely high, which posed a possible clogging problem to the AmmEl system, especially to the stripper tower. Figures 3-1 and 3-2 show the TSS loading in raw centrate. Alkalinity was determined by titration with 0.50382 N H_2SO_4 (supplied by GBWWTP laboratory). For detailed calculation of alkalinity, see Appendix B. pH was measured on site.

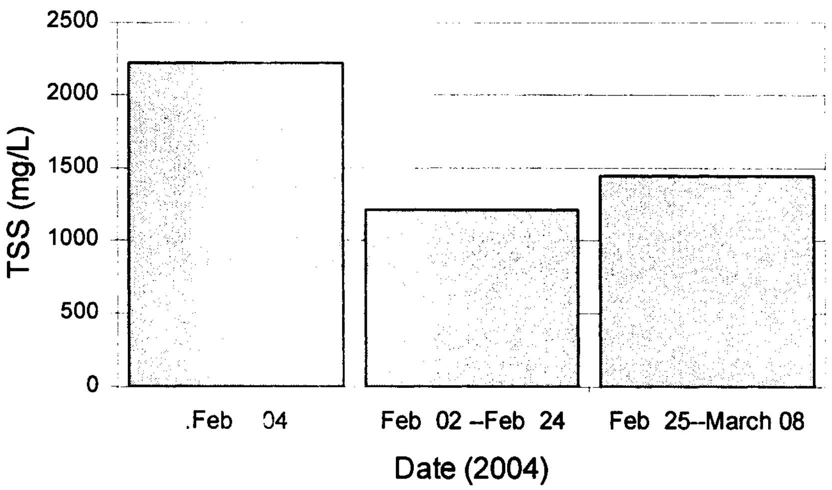


Figure 3-1 TSS values in raw centrate (early 2004)

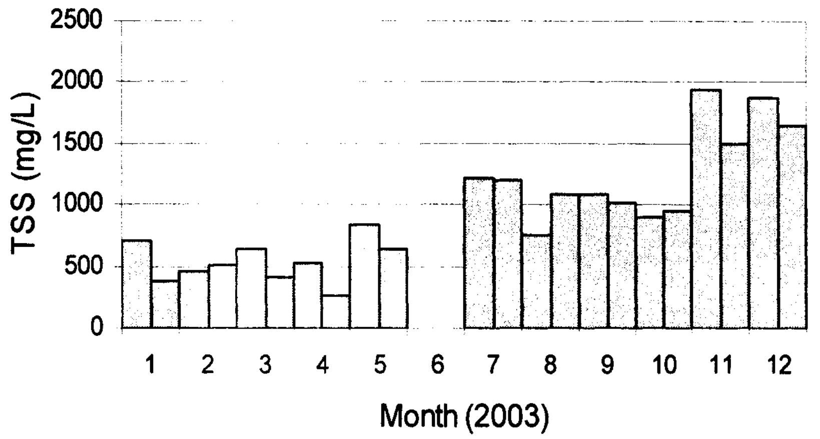


Figure 3-2 TSS values in centrate (2003)

As shown in Figures 3-1 and 3-2, TSS concentrations in the raw centrate can be as great as 2000 mg/L. In this project, an 800-micron strainer was used to pre-treat the centrate to reduce the potential clogging of stripper unit. The TSS of the centrate before and after the straining was shown in tables 3-1 and 3-2. This step aptly coped with the clogging risk with a high TSS reduction between the inlet and outlet ports of the stripper tower. Acid back-wash could be used as a back-up in case of clogging. As recommended by the manufacturer, 5% hydrochloric acid could be used for this purpose.

Table 3-2. Characteristics of Clover Bar Centrates (after strainer)

Component	Concentration (mg/L)	Component	Concentration (mg/L)
TKN	~900	COD	400~500
*N-NH_3	~850	Temp	4~11
Alkalinity	3308	pH	7~8
TSS	30~180		

*N-NH_3 denotes total ammonia nitrogen

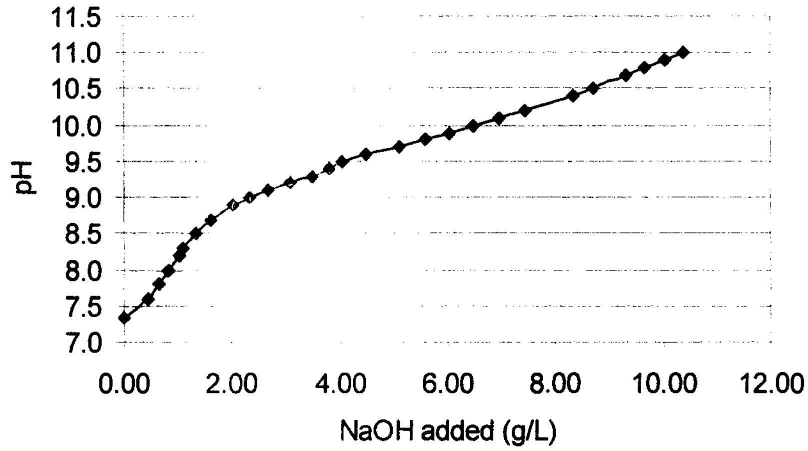


Figure 3-3. Titration of strained Centrate.

The strainer also showed benefit from saving NaOH chemical usage. Based on laboratory titration results, NaOH demands to elevate raw centrate pH were over 2 times that required for centrate pH adjustment after straining (See Figures 3-3 and 4-5). The reason is not clear. A possible explanation is that the strainer intercepts solids and organic matter that contains metal ions, like magnesium and calcium, which are potential alkalinity consuming substances. Solids separated by the straining can be delivered to lagoons for further treatment.

3.1.2 Chemicals

36~38% (w/w) Hydrochloric Acid: manufactured by EMD chemicals Inc., was used for pH control of the scrubber solution.

50% (w/w) NaOH was employed to adjust the pH of the centrate stream before it entered the stripper column.

Sodium chloride: 99% purification, used to complement the salt solution in scrubber tank.

1N sodium hydroxide: supplied by GBWWTP, to titration centrate prior to the operation for sodium usage estimation.

ISA (Ionic Stregth Adjustor): ordered by GBWWTP, manufactured by Thermo Electron Corporation, used in ammonia concentration test with Orion Ammonia Electrode.

0.5038N Sulfuric acid: supplied by GBWWTP, for titration of alkalinity measurement.

0.5N Hydrochloric Acid, pH4.0, 7.0, 11.0 buffers: supplied by GBWWTP laboratory, for probes calibration and maintenance.

3.1.3 Analytical equipment and methods

Orion Ammonia Electrode: OAE, manufactured by Thermo Electron Corporation, with a measurement range from 0.01 to 1,400 ppm N, was used to measure the ammonia concentration of the wastewater samples. The pH of samples and standards were adjusted to above pH 11. The operational temperature range of this electrode is from 0 to 50 °C and measurement reproducibility is to within 2%.

RAE Gas Detection Tubes and Pumps, manufactured by systems Inc., were used to measure the concentration of Cl_2 and NH_3 in the gas form. The measurement precision for NH_3 tubes is ±12% at 25 and 50 ppm with the measurement standard range from 25 to 500 ppm (with extention range from 12.5 to 250 ppm and from 50 to 1000 ppm). And for Cl_2 tubes the precision is ±4% at 25 and 50 ppm with the measurement standard range from 5 to 100 ppm (with extended range from 2.5 to 50 ppm and from 10 to 200 ppm). For both the operational temperature range is 0 to 40 °C.

Fisher Accumet Model 950 pH Meter: manufactured by Fisher Scientific, was used for the pH value of the water samples measurement with a relative accuracy of 0.001 pH units. Its measurement range is -2 -16 pH and its application temperature range is -5 to 105 °C.

A Traceable Hot Wire Anemometer, manufactured by Control Company, was used to measure airflow rate with an accuracy of 1% over the full scale plus 1 digit.

TSS, COD, TKN parameters were measured by the GBWWTP laboratory.

3.2 Experimental design

3.2.1 Full factorial design for low temperature centrate

To investigate which factors were of significant, a full factorial design was developed and carried out in cold temperature (centrate temperature was between 7.5 and 11°C). Seven control settings can affect ammonia removal by the AmmEl treatment process. These are the air flow rates to the scrubber (Q_{asb}) and the stripper (Q_{asp}), the pH value of the wastewater in the stripping column (pH_{out}), the pH value in brine tank (pH_{bri}), the wastewater flow rate (Q_{ww}), the brine flow rate (Q_b) and the DC current density (DC). Because the stripper and scrubber are operated as a closed system, with a common air flow, $Q_{asb} = Q_{asp} = Q_{air}$.

Ammonia is a weak base that reacts with water to form ammonium hydroxide. Hydrochloric acid solution was added to the brine water to depress its pH below 7 and convert the vast majority of aqueous ammonia to dissociated ammonium ions according to reaction 3-[1]:

$$NH_4^+ \Leftrightarrow NH_{3\,(aq)} + H^+ \quad (pKa = 9.25) \qquad 3\text{-}[1]$$

On the advice of Enpar Technologies, the pH value of the brine water was maintained constant at 6.5. The brine water flow rate entering the scrubber was also fixed at the design value of 12 L/min. This reduced the number of control variables to be optimized from 7 to 4: wastewater pH (pH_{out}), wastewater flow rate (Q_{ww}), air flow rate (Q_{air}), and the current at which the electrochemical reactor is operated (DC).

Temperature in this setting was looked as an uncontrollable nuisance factor. Before the operation, all the settings' running order was randomized. In addition, the temperature fluctuation fell into a narrow range (7.5~11.1°C), so with the complement advance of full factorial design experiments, the temperature's effects could be ignored (Montgomery, 2001).

A 2^4 factorial design with center point replication was developed and performed, requiring a total of 19 experimental runs. This would allow the effects on the performance of the pilot plant of these four independent variables and their interactions to be assessed. The 19 runs were carried out in random order to prevent unknown or uncontrollable changes in experimental conditions biasing observations.

Table 3-3. Experimental range for the 2^4 factorial design with centre point replication

	Q_{air} (m^3/min)	Reactor Current (A)	Outflow pH	Q_{ww} (L/min)
Low level	9.90	500	10.5	240
Centre point	11.12	550	11.25	270
High level	12.34	600	12.0	300

Table3-3 presents the experimental ranges for each of the 4 control variables. The centre point values were recommended by the pilot plant's manufacturer

(Enpar Technologies Inc). The experimental range of each parameter was selected in consultation with Enpar Technologies.

3.2.2 Experimental design for higher temperature centrate

Theoretically, higher temperature of centrate was expected to benefit for AmmEl process performance or lowering treatment operating cost. The principle was discussed in chapter 2 (literature review). To investigate the possibility of reducing operating cost in a warmer temperature of centrate, eight days operation (after the full factorial design experiment) plan was made, which would use Centrate being preheated and treated in 19.9~25°C. The results would be used to compare the performance and cost.

3.2.3 Data analysis

The statistical analysis consisted of estimating the effects of the factors and assessing their significance. The ANOVA method was used for this purpose. Regression tools were applied to generate an equation for operating cost estimation.

Operating cost comparison of AmmEl treatment with centrate in high temperature (19.9~25°C) and low temperature (7.5~11.1°C) was based on their average values and a specific case study.

3.3 Operation of the AmmEl pilot plant

The AmmEl pilot plant is shown in Figure 3-4. Other equipment affiliated with the plant included a 16 m^3 outdoor tanker for bulk wastewater storage, a 2m^3 indoor wastewater day tank and a 800-micron screen strainer. Centrate from the tanker was transferred to the indoor storage tank through the screen strainer when needed. The screen strainer removed solid material to prevent clogging of the pilot plant equipment. The screen strainer removed 20 to 30 percent of the solid material contained in the raw centrate.

The design wastewater flow rate for the system was 240 L/h. Centrate was pumped from the day storage tank to the top of the stripper column. At the top of the stripper column, NaOH was added and mixed with centrate in the inflow line to achieve a pH greater than 10. A pH probe was installed in the inflow line and sent a reading that was displayed on the main control panel. During preliminary testing with the pilot plant, it was found that the stripper column pH could be controlled with greater accuracy and precision if NaOH dosing was based on the pH in the wastewater as it exited the column. This "outflow pH" was measured using a field pH meter. The wastewater flow rate was measured by a rotameter, which was located in the inflow line immediately downstream of the NaOH and centrate mixing point, and was controlled manually by adjusting the appropriate valve. The stripped liquid stream was discharged to the waste flume at the Wastewater Training and Research Center, Edmonton. This was not a problem, due to the relatively small volumes used for pilot testing. However, pH adjustment would likely be required prior to effluent discharge for a full scale application.

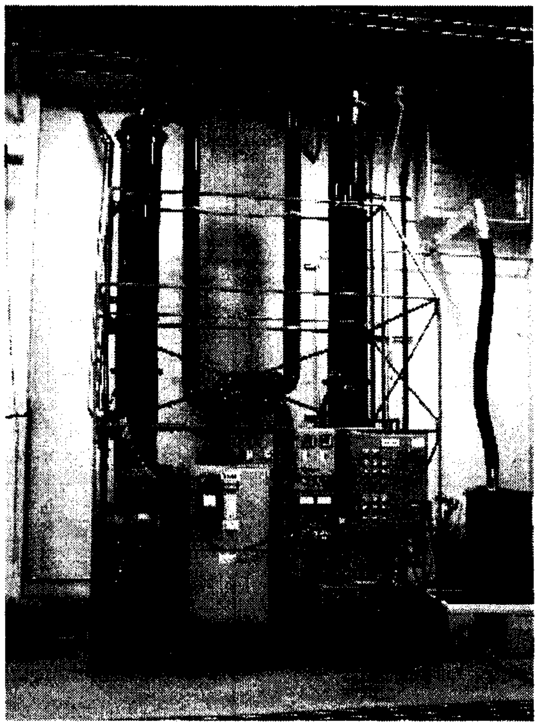


Figure 3-4 The AmmEl pilot plant.

Airflow was supplied to the bottom of the stripper by a blower. The blower's speed was controlled from the main panel. Ammonia was transferred from the high pH centrate to the air stream inside the stripper tower.

The air flow from the top of the stripper tower was transferred to the bottom of the scrubber by a second blower. Brine water with a pH of 6.5 entered the scrubber column from the top and absorbed ammonia from the air stream. The pH value in the brine tank was controlled from the main control panel by adjusting the amount of hydrochloric acid that is added.

The ammonia rich brine water exited the bottom of the scrubber column and was pumped into the two parallel electrochemical cells. The air flow exited the top of the scrubber and was recycled as inflow to the stripping tower.

Air flow rate and DC current density were controlled from the main control panel. The brine solution flow rate to the scrubber was monitored by using a rotameter, and was controlled manually by adjusting the appropriate valves.

3.4 Pilot plant commissioning and troubleshooting

The pilot plant was shipped from Ontario in mid October 2004, and its assembly at the Edmonton Waste Management Centre of Excellence was complete in early November. Commissioning took place during the first two weeks of November, after which preliminary test runs were done. A number of operational control problems were identified and remedied between November and February, after which, the pilot plant produced reliable and repeatable results. The main source of operational problems was the pH control systems for the influent wastewater and the brine solution, and obtaining a representative sample of treated wastewater. The automatic dosing systems were unable to maintain constant pH in the system, and it became apparent that manual control of pH dosing was necessary.

CHAPTER IV RESULTS

4.1 Three main sections performance

Separate investigation of each section of the whole AmmEl process was helpful for the insight into the mechanism and the integrity inside this system. Three main stages, the stripper column, the scrubber column and the electrochemical cells were studied separately for this purpose.

4.1.1 Mass balance for stripping tower

In the stripper column, it is expected that physical processes occur without chemical reaction. Ammonia enters the stripper column in liquid form, mainly as ammonium ion, and sodium hydroxide is added and mixed with the wastewater to raise the pH, so ammonia gas is stripped out and routed to the scrubber column. Therefore, the mass of ammonia entering the unit equals that flowing out of it.

A steady-state materials balance for a countercurrent continuous stripping tower used for removal of ammonia gas from wastewater is given by:

1) General word statement:

moles of solute entering in liquid stream + moles of solute entering in Gas stream = moles of solute leaving in liquid stream + moles of solute leaving in Gas stream

2) simplified word statement:

Inflow = Outflow

3) Symbolic representation:

$$LC_0 + Gy_0 = LC_e + Gy_e \qquad 4\text{-}[1]$$

$$\text{Inflow} = LC_0 + Gy_0 \qquad 4\text{-}[2]$$

$$\text{Outflow} = LC_e + Gy_e \qquad 4\text{-}[3]$$

Where L : moles of incoming liquid (i.e., wastewater) per unit time

C_0: concentration of solute in liquid entering at the top of the tower, (moles of solute per mole of liquid)

Ce: concentration of solute in liquid leaving at the bottom of the tower, (moles of solute per mole of liquid)

G: moles of incoming gas per unit time (at STP)

y_o: concentration of solute in gas entering the bottom of the tower, (moles of solute per mole of solute-free gas)

y_e: concentration of solute in gas leaving the top of the tower, (moles of solute per mole of solute-free gas)

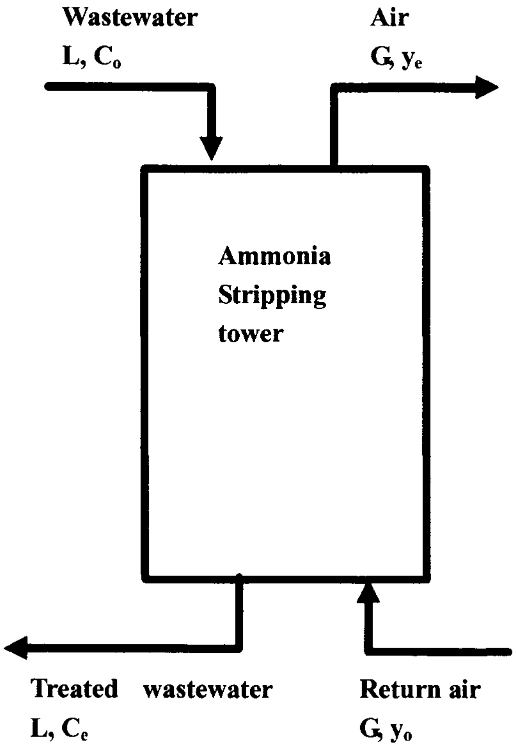


Figure 4-1 schematic of stripper unit

A mass balance on ammonia was calculated for the operation settings shown in Table 4-1. The ammonia concentrations are presented in Table 4-2.

Table 4-1. Operation settings for the mass balance process

Q_{ww} (L/h)	Q_{air} (m^3/min)	pH $_{inflow}$	DC (A)	$Q_{scrubber}$ (L/min)	T_{ww} (°C)
240	11.12	10.5	500	12	20

Table 4-2. Ammonia concentrations examined for mass balance (stripper)

L (L/h)	C_0 (mg/L)	C_e (mg/L)	G (m^3/min)	y_0 (ppm)	y_e (ppm)
240	925	176	11.12	0	400

Substituting the values in Table 4-2 into equations 4-[1], 4-[2] and 4-[3], with appropriately converted units (see Appendix C) gives

Ammonia entering stripper: $LC_0 + Gy_0 = 15.85$ mol/h

Ammonia leaving stripper: $LC_e + Gy_e = 13.28$ mol/h

These measurements and calculations indicate that the moles of ammonia entering and exiting the stripper agree to within 16.7%. As the process is a dynamic equilibrium, measured values fluctuate around their average values. Additionally, the precision of the ammonia detection tubes is ±12% precision. These factors account for the lack of complete agreement.

4.1.2 Mass balance for scrubber tower

The mass balance calculation for the scrubber unit is identical to that for stripper unit. The inputs and outputs of the scrubber column are shown in Figure 4-2. The operational settings and related measurements are shown in Tables 4-1 and 4-3, respectively.

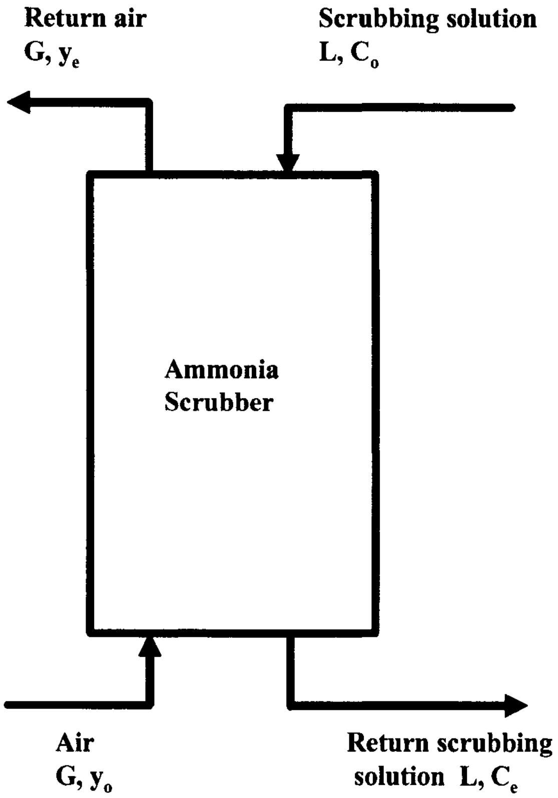


Figure 4-2. Schematic of scrubber unit

Table 4-3. Ammonia concentrations examined for mass balance(scrubber)

L (L/h)	C_0 (mg/L)	C_e (mg/L)	G (m^3/min)	y_0 (ppm)	y_e (ppm)
720	0	203	11.12	400	0

Substituting the values in Table 4-3 to equations 4-[1], 4-[2] and 4-[3], with appropriately converted units (see Appendix C) gives

Ammonia entering scrubber: $LC_0 + Gy_0 = 10.26$ mol/h

Ammonia leaving scrubber: $LC_e + Gy_e = 10.44$ mol/h

The moles of ammonia entering and exiting the scrubber agree to within 1.8%. Concentration fluctuations, due to dynamic equilibrium, and measurement error account for this discrepancy.

4.1.3 Electrical cells performance evaluation and ammonia in off gas

Electrochemical cells function as the oxidant generator and ammonium ion oxidation reactor (see Figure 4-3). Ammonia concentration loading in inflow, outflow and off gas were measured to verify the electrochemical cells' effective oxidation performance. N_2 concentration in off gas was not measured, because the nitrogen content in the atmosphere could interfere with the measurement accuracy.

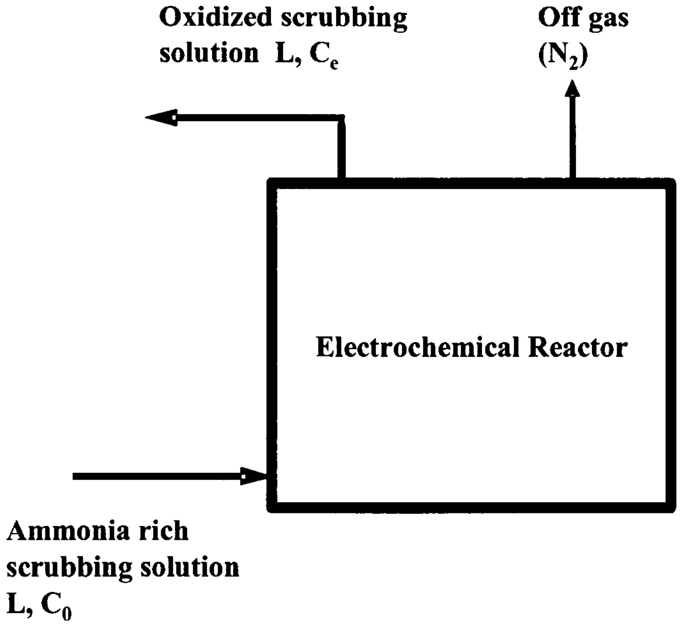


Figure 4-3. Schematic of electrochemical cell unit

Ammonia residual in the off gas was monitored and examined with RAE detection pump and tubes. With Gastec special detection tube, a very low concentration of 5 ppm ammonia can be measured. When ammonia concentration is higher than 5 ppm, the media color inside the tube will change to yellow from pink. This method has an advantage, as it does not need corrections for temperatures or humidity.

During the whole treatment process, ammonia in off gas was never detectable with this method. The electrochemical cells completely oxidized the ammonia released from centrate stream.

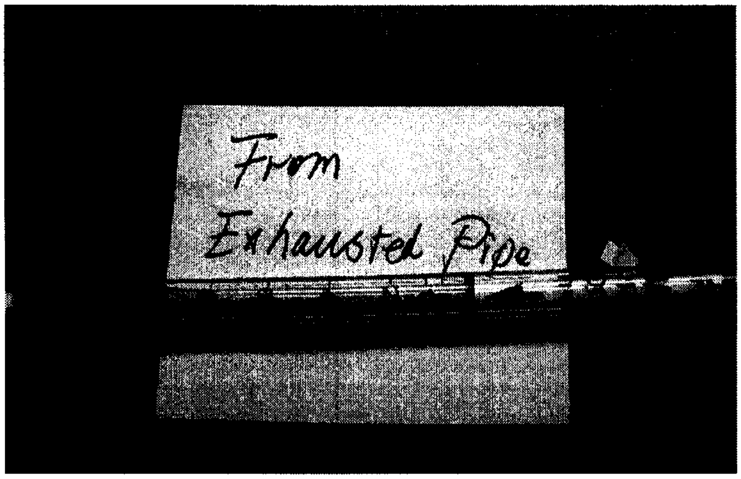


Figure 4-4. Ammonia residual in off gas stream

4.2 Ammonia abatement in low temperature centrate

As introduced previously, high concentrations of ammonia in cold weather poses a challenge in treatment processes. In this section, centrate temperature ranged between 7.5 to 11.1 °C.

4.2.1 Titration test to estimate chemical consumption to raise centrate pH

Centrate pH values are around 7.6 to 8, which need to be elevated to between

10.5 and 12 depending on the treatment conditions and the ammonia removal level requirements. Prior to the pilot plant operation, NaOH dose demand was estimated by laboratory titration of the centrate liquid with standard NaOH solution. The generated titration curves are presented in Figure 4-5. To raise pH to 10.5 and 12, approx. 4.0 and 5.3 g/L NaOH would be needed, respectively.

It can be calculated that centrate treatment at pH 10.5, rather than 12, would save 26% NaOH dosage for a centrate treatment unit.

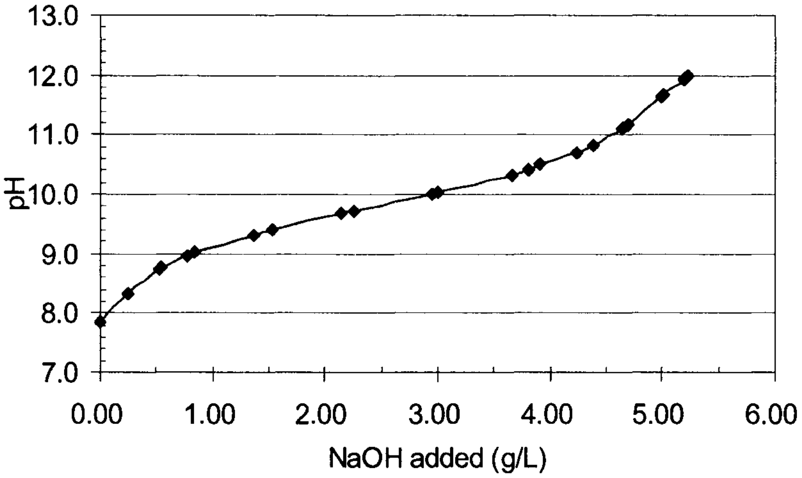


Figure 4-5. Titration of Strained Centrate.

(800 μm mess strainer used)

4.2.2 Steady state operation

The time needed for the system to reach steady state operation was determined during several preliminary tests. Figure 4-6 contains data from one of these runs that shows the ammonia nitrogen concentration and pH in the effluent wastewater from the stripping tower during the course of a run. At the start of the run, the ammonia nitrogen concentration in the outlet water is quite high and gradually decreases as the run progresses. After 100 minutes, the ammonia concentration becomes relatively constant, as does the pH, as steady-state operation is reached. Based, on these results, a 2-hour minimum operating period time was selected for each of the 19 runs.

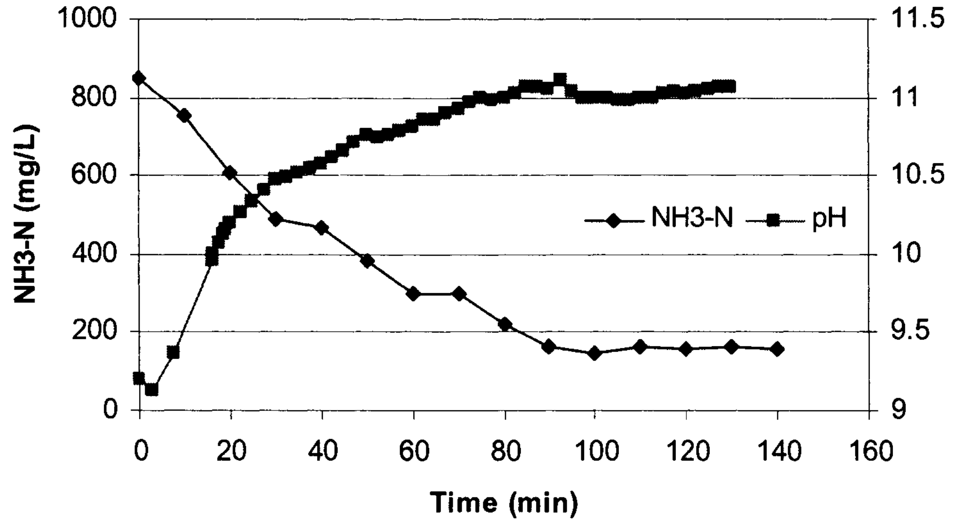


Figure 4-6. The change of Ammonia concentration and pH in outlet water with time.

4.2.3 Inlet temperature and pH

Figure 4-7 contains the pH and temperature values measured in the centrate day tank. The pH ranged from 7.4 to 8.5. In this range ammonia in the centrate was mainly in the ammonium ion form. Before its introduction to the stripping column, the wastewater's pH was increased to shift the equilibrium of reaction [10] (chapter 2) to the right and the ammonia gas form. Temperature ranged from 7.5°C to 11.1°C. Randomizing the order in which the runs were performed mitigated the effect of this uncontrolled variable on data analysis.

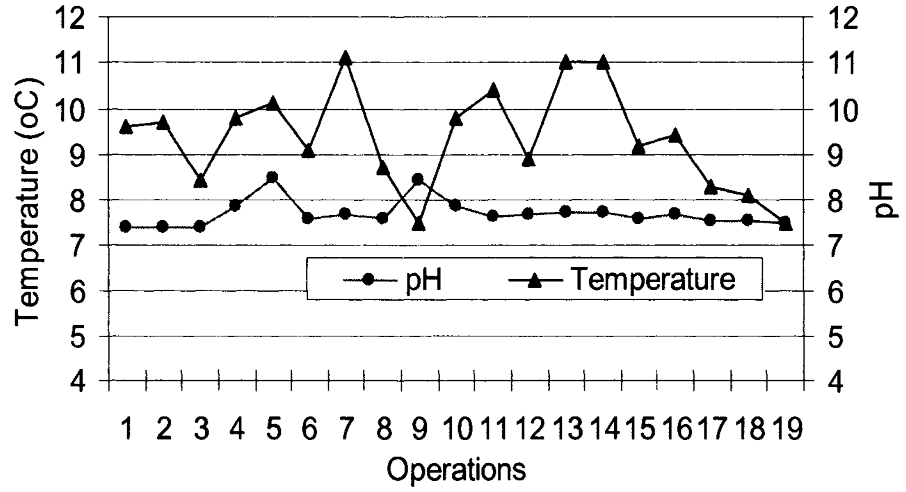


Figure 4-7. pH and temperature in centrate day tank

4.2.4 Effects of operating variables on ammonia removal

Three inlet wastewater flow rates were used in these trials, as shown in Figure Figure 4-8. Under the same flow rate, the ammonia nitrogen removal is different due to the change in the other parameters from one run to another. Nevertheless, from the average removal at a given flow rate, the figure shows presents that the ammonia nitrogen removal decreases with increasing inlet wastewater flow rate.

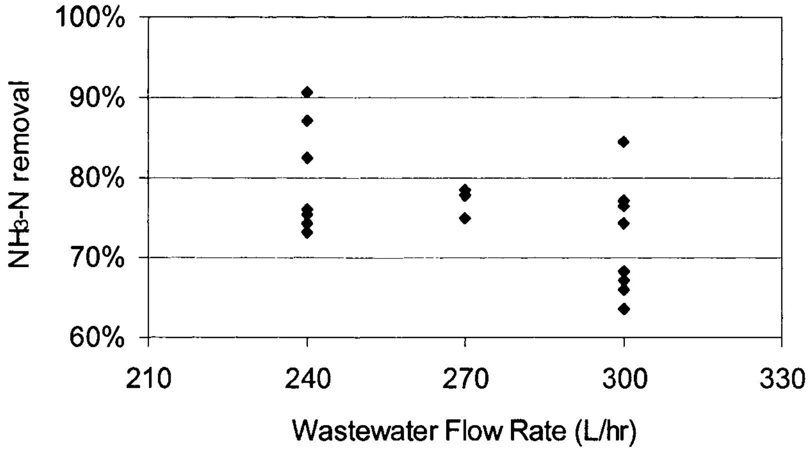


Figure 4-8. The effect of inlet WW flow rate on the NH3-N removal

Figure 4-9 shows the effect of outlet wastewater pH on NH_3-N removal. Generally higher pH values in the outlet wastewater corresponded to higher ammonia nitrogen removal in the stripping tower. As shown in equation [10] (chapter 2), with higher pH values of the wastewater, more dissociated ammonium ions are converted to aqueous ammonia.

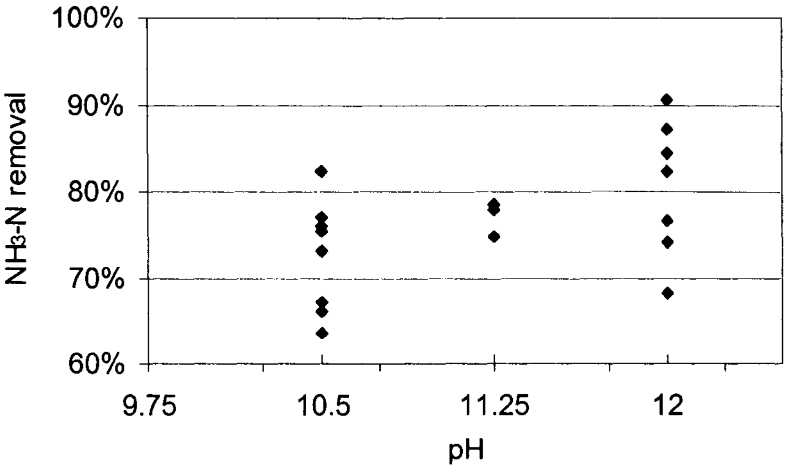


Figure 4-9. The effect of outlet WW pH on the NH_3-N removal

Figure 4-10 shows the effect of airflow rate on the ammonia removal performance. With increasing airflow rate, the average ammonia removal also increases. This trend is expected as, in the stripping tower, higher air flow rate drives more ammonia from the wastewater, which is discussed in chapter 2 (literature review).

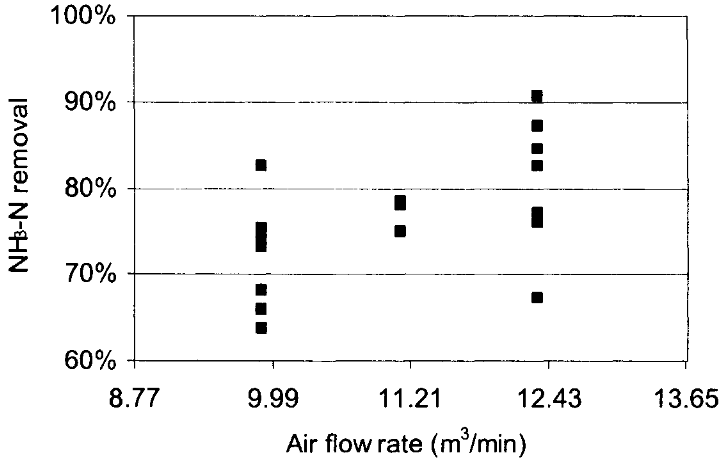


Figure 4-10. The effect of air flow rate on the NH3-N removal

As shown in Figure 4-11, the ammonia removal was essentially independent of the DC current setting of the electrochemical reactor, within the experimental range. Although the range of each control variable was selected in consultation with the manufacturer, these data indicate that the optimal range for operating the electrochemical reactor lies below that selected. Further experiments within a lower range of the DC currents will be required to optimize the operation of the pilot plant.

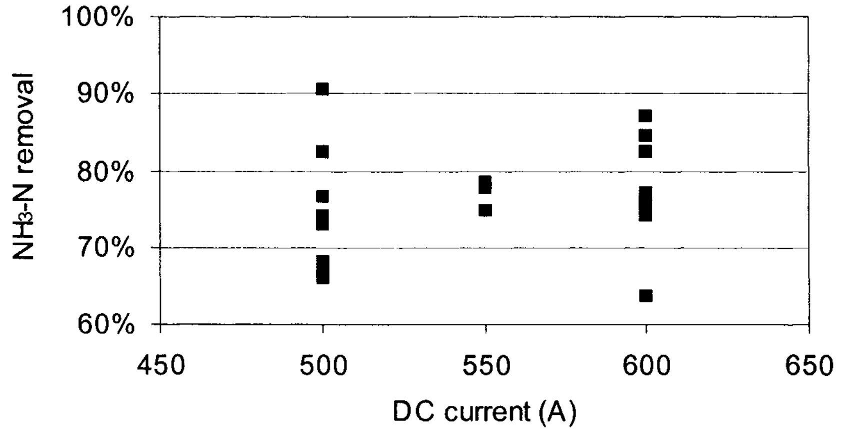


Figure 4-11. The effect of DC current density on the NH3-N removal

4.2.5 Process efficiency

Data shown in Figure 4-12 indicate that at least 60 percent removal of ammonia nitrogen was achieved in each of the experimental runs. The average removal was approximately 80 percent. The ammonia concentration in the exhaust air from the electrochemical cells was below the detection limit (5 ppm at STP) of the gas detection tubes during each of the 19 runs, indicating that virtually complete conversion of ammonia to nitrogen gas was achieved in the electrochemical reactor.

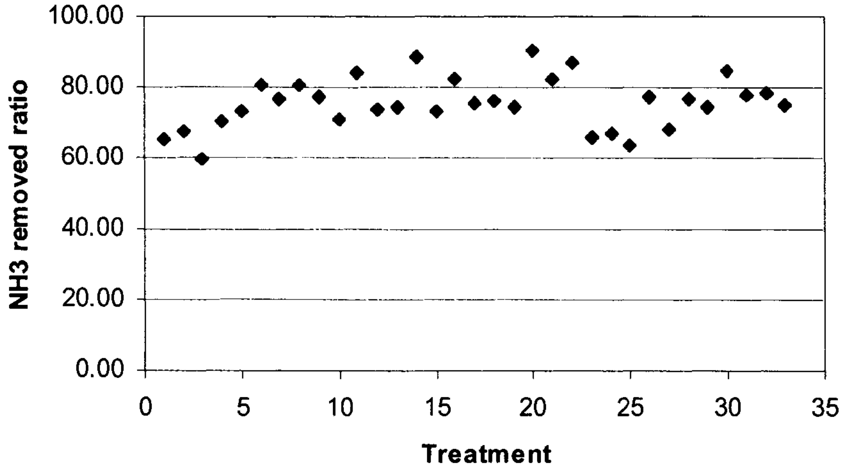


Figure 4-12. Percent removal of ammonia nitrogen during the trial period

4.2.6 Factor Analysis

The results of an analysis of variance (ANOVA) performed on the data obtained from the 19 trials are shown in Table 4-4 (for detailed recorded see Appendix E). Comparison of the F test statistic, calculated for each factor and interaction, to the critical value of the statistic (5.32) indicates that Q_{air}, outlet pH and Q_{ww} were the significant parameters affecting AmmEl system performance (at the 95 percent confidence level) (see Appendix D). The N-score normal probability plot (see Figure 4-13) and half N-score normal probability plot (see Appendix D) indicate the same outcome. The magnitude of the effects suggests that the wastewater pH, the air flow rate and the wastewater flow rate were of approximately equal importance for the removal of ammonia. The lack of significance of the DC current indicates that the optimal setting for this variable lies below the range selected for this set of trials.

Table 4-4. Results of ANOVA procedure

Parameter	Q_{air}	DC	pH	Q_{ww}	Interactions					
Designation	A	B	C	D	AB	AC	AD	BC	BD	CD
Effect	8.05	2.77	7.11	-7.99	-0.81	1.89	0.28	1.89	2.62	0.22
$^*F_{calculated}$	20.14	2.39	15.72	19.85	0.20	1.11	0.02	1.11	2.14	0.02
Significant	Y	N	Y	Y	N	N	N	N	N	N

*The critical F value was 5.32.

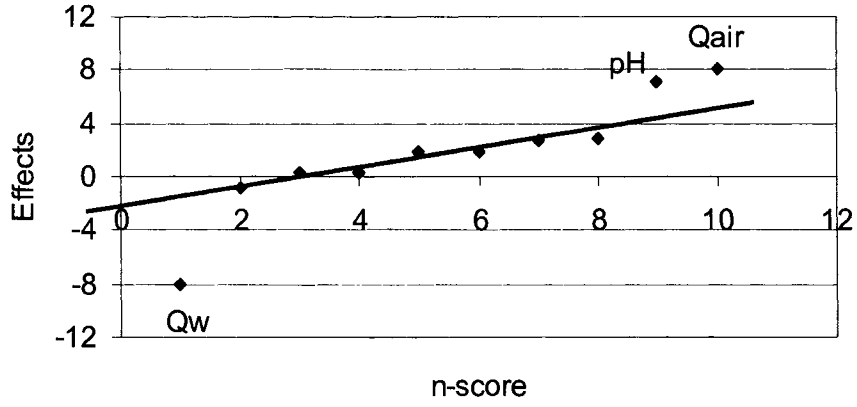


Figure 4-13. Normal plot of effects and interactions

4.2.7 Predictive performance model

To determine the linearity of the relationship between the significant independent variables and the response variable (ammonia removal), a curvature test (Montgomery, 2001) was performed, and indicated that quadratic effects were insignificant. Therefore, ammonia removal was modeled by a linear relationship between the 3 significant parameters, Q_{air}, outflow pH, and Q_{ww}. Linear regression produced the following calibration:

$$(NH_3)_{out} = (NH_3)_{in} - 51.6\,Q_{air} - 18.2\,pH + 0.48\,Q_{ww} \qquad 4\text{-}[4]$$

where $(NH_3)_{in}$ and $(NH_3)_{in}$ represent the influent and effluent total ammonia concentrations, respectively (mg/L), Q_{air} is the air flow rate (m^3/min), and Q_{ww} is the centrate flow rate (L/h).

The associated coefficient of determination (r^2) value is 0.62. The model indicates that ammonia removal will increase with increasing air flow rate and influent wastewater pH, and decrease with increasing influent wastewater flow rate. A comparison of modeled effluent total ammonia predictions to experimental results is shown in Figure 4-14.

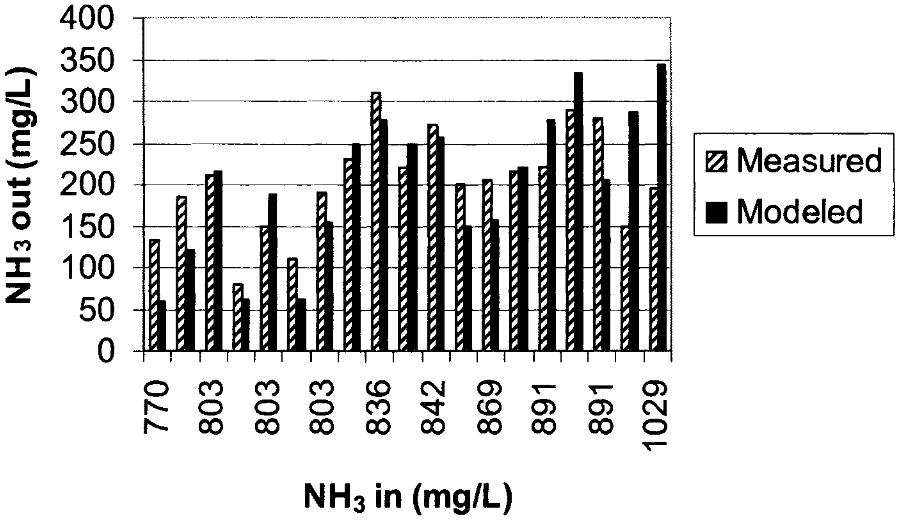


Figure 4-14. Comparison of modeled effluent ammonia concentration to measured effluent ammonia concentration

The error plot contained in Figure 4-15 shows the residuals to be randomly distributed about zero for all values within the experimental range, with a mean of 0. The maximum estimation error was 14.5 percent of the influent ammonia concentration. These larger model errors are associated with the trials in which influent ammonia concentrations exceeded 1,000 mg/L.

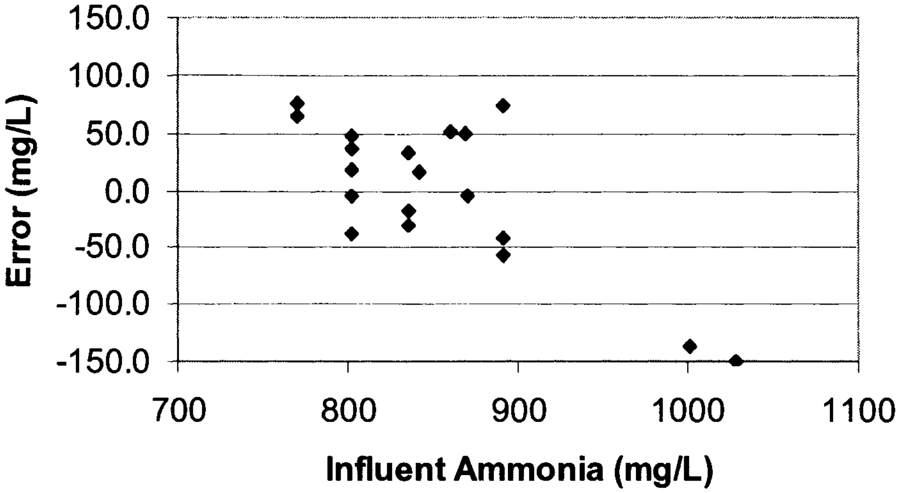


Figure 4-15. Model error plot.

4.2.8 Operating cost

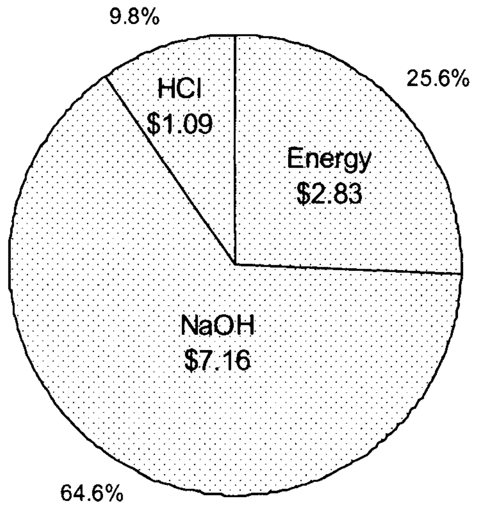
The costs of operating the pilot plant include those for the sodium hydroxide to increase the influent wastewater pH, hydrochloric acid for brine/scrubbing solution pH adjustment, and power to the air blowers (2 at 1.1 kW each), pumps (6 with a total power requirement of 0.14 kW) and the electrochemical reactor (3 kW at 500 A). An analysis of variance (ANOVA) was performed on the data to determine the relative importance of the main factors and their interactions. The ANOVA indicated all the main factors to be of significant importance, as well as the interaction between the DC current and the wastewater pH ($\alpha = 0.05$). The resulting ANOVA model is given by equation [4-5]:

$$\$/\ \text{kg}\ (NH_3)_{removed} = 11.08 - 0.71Q_{air} + 0.16DC + 0.56pH - 0.18Q_{ww} - 0.28(DC)(pH) \qquad 4\text{-}[5]$$

The intercept indicated in equation 4-[5] represents the mean operating cost. The possible values of each term in equation 4-[5] are 1- and +1, which correspond to the levels used in the experimental design: Q_{air}: for the airflow rate, -1 denotes 9.90 m^3/min and +1 denotes 12.34 m^3/min; DC: for the amperage at which the electrochemical reactor was operated, -1 denotes 500 A and +1 denotes 600 A; pH: for the wastewater pH, -1 denotes 10.5 and +1 denotes 12.0; $Q_{ww:}$: for the wastewater flow rate, -1 denotes 240 L/h and +1 denotes 300 L/h.

Factors of greatest importance (in order of decreasing effect) were the air flow rate and the wastewater pH. Although statistically significant, the wastewater flow rate and the DC current setting were of lesser importance to the treatment costs. The importance of the interaction between wastewater pH and DC current requires further investigation.

The mean cost of removing 1 kg of ammonia from the influent wastewater was \$11.08. As shown in Figure 4-16, the cost of caustic soda to adjust the pH of the influent wastewater accounted for 64.6 percent of the average treatment cost, while the energy requirements and pH control of the brine/scrubbing solution accounted for 25.6 percent and 9.8 percent, respectively.



Mean unit cost = \$1.09 + \$2.83 + \$7.16 = \$11.08

Figure 4-16. Breakdown of average operating cost per kg of ammonia removed during the 19 trials.

4.3 Ammonia abatement at 19.9 to 25.0 °C

Centrate and supernatant in the summer are warmer than in the winter at approximately 20 to 25°C. These temperatures can be expected to improve the ammonia stripper performance because a higher proportion of ammonia would exist in the unionized form at higher temperature, for a given pH value. Therefore, AmmEl system was operated using centrate heated to between 20 and 25°C. The results were used to assess the potential operating cost savings if all treatment were conducted under summer conditions.

Results presented in Figure 4-17 show that ammonia removal ranged from 69% to 92%. The pH in the stripper influent flow was maintained between 10.0 and 12.2 (see Figure 4-18). The ammonia removal was close to that achieved at 7.5 to 11.1°C. Based on the eight days operation, the average operating cost (for operation at 20 to 25.0°C) was calculated as \$5.37/m^3 centrate.

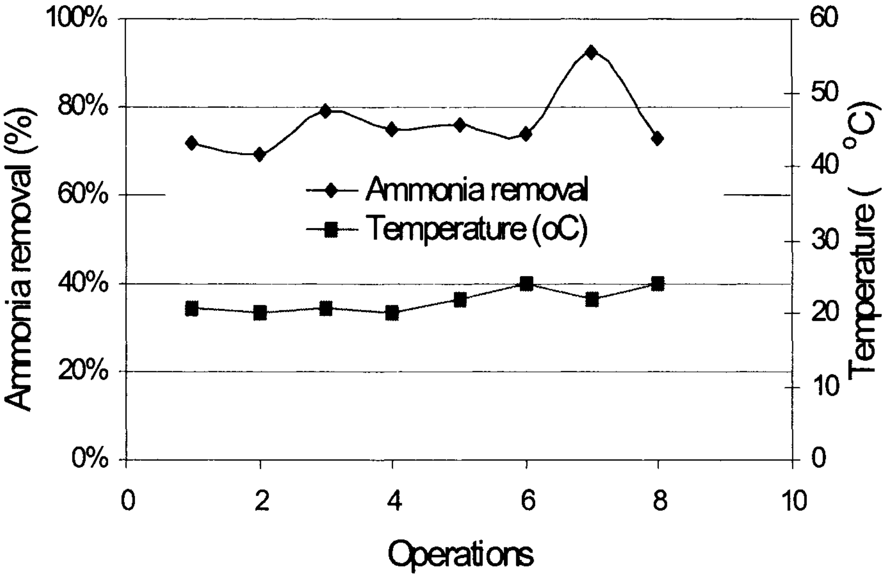


Figure 4-17. Ammonia removal at 20 to 25°C

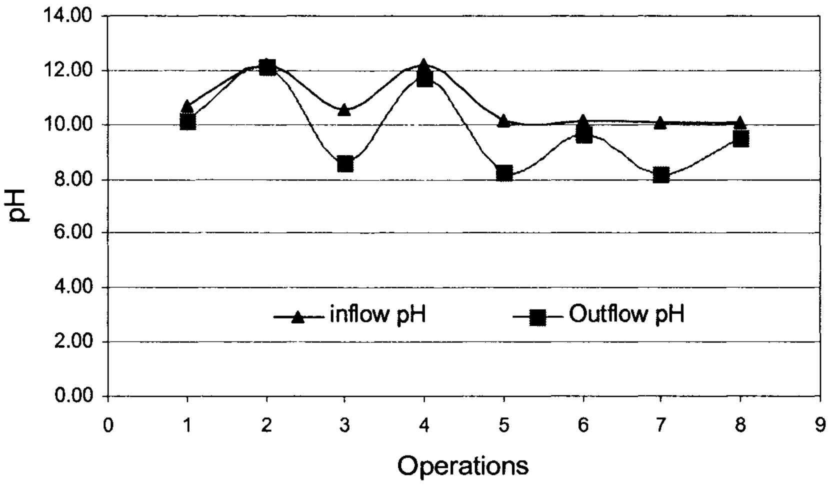


Figure 4-18. Inflow and outflow pH during operation at 20 to 25 °C

4.4 Ammonia abatement operating cost comparison at different temperatures

The average operating cost in lower temperature (7.5 to 11.1°C) and higher temperature (20 to 25°C) are listed in Table 4-5. The specific operation settings are shown in Appendices E and F. Based on these data, the saving at higher temperature is:

$$\frac{7.17-5.37}{7.17}*100\% = 25.1\%$$

Table 4-5. Ammonia abatement comparison

	Total Cost ($/m^3 centrate)	Removal Range	50% NaOH (L/m^3 centrate)	38% HCl (L/m^3 centrate)
Low Temp (7.5 to 11.1°C)	7.17	63~91%	9.23	2.37
High Temp (20 to 25°C)	5.37	69~92%	4.89	2.42
Average operating saving	25.1%		47.0%	

A comparison of runs conducted using similar operational settings, but at different temperatures is shown in Table 4-6. The slightly higher ammonia removal at 20.7°C can be attributed to the higher pH value. Nevertheless, the 13.2% lower ammonia removal at 10.4 °C would be acceptable for operational purposes, given the 19.7% cost reduction that was realized, and the overall minimum treatment objective of approximately 70% reduction in ammonia concentration.

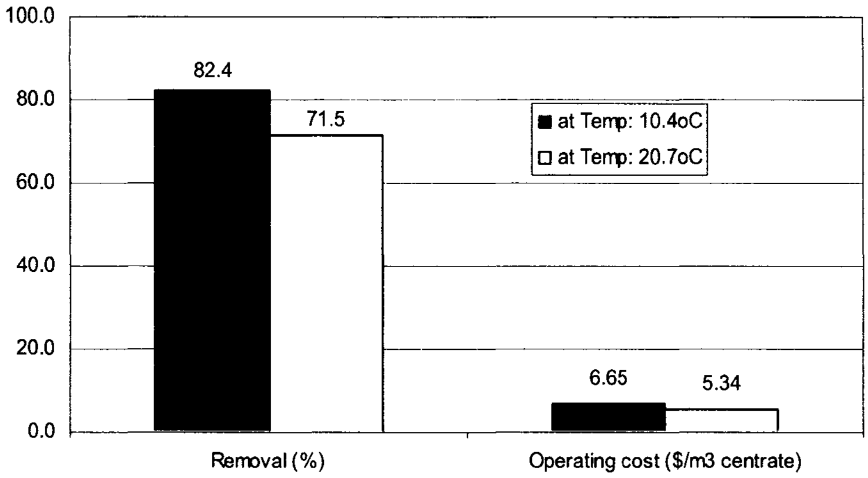


Figure 4-19. Comparison of mean ammonia removal and operating cost under "summer" and "winter" conditions.

Table 4-6 A specific pair of operation settings' comparison

Liquid Feed Flow Rate (L/h)	Temperature (°C)	DC (A)	Outflow pH	Removal (%)	NaOH added L / m^3 Centrate	Cost ($/$m^3$ centrate)
240	20.7	500	10.16	71.5	5.13	5.34
240	10.4	500	10.5	82.4	7.77	6.65

CHAPTER V CONCLUSIONS

The AmmEl pilot plant was assembled and commissioned. Preliminary trials revealed a number of operating issues that were resolved before treatment performance could be assessed. These included the automated pH control systems, and identification of sampling points and procedures.

The pilot plant was shown to remove between 60 and 90 percent of influent ammonia under winter conditions, within the range of control variables tested. The mean removal during the 19 trials was 76.3 percent. Ammonia in the exhaust air stream from the electrochemical reactor was below the 5 ppm detection limit under all conditions tested; indicating that virtually all the ammonia that was transferred to the reactor from the wastewater was converted.

The mean cost of removing 1 kg of ammonia from the influent wastewater was $11.08. Approximately 65 percent of this cost was attributed to the caustic soda used to adjust the pH of the influent wastewater. The energy required to operate the plant accounted for approximately 25 percent of the cost, and approximately 10 percent was attributed to the cost of pH adjustment of the brine/scrubbing solution. High temperature can enhance the treatment performance. Average saving of 47% in sodium hydroxide dosages was observed when centrate was pre-heated prior to the treatment. Centrate being treated in summer months largely lowered the operating cost.

A statistical analysis of the unit's ammonia removal performance indicated that the electrochemical reactor should be operated at lower amperages than were used during the current study. This would reduce the energy requirements, and may also reduce the chemical requirements for brine/scrubbing solution pH control.

CHAPTER VI RECOMMENDATIONS FOR FURTHER STUDY

6.1 Steam stripping method

Air stripping methods involve air ammonia removal and steam stripping. The former one, as was used here, is defined as removal of ammonia from the wastewater by sending ambient air countercurrent to the dripping centrate in stripping towers at ambient temperatures. The latter one uses steam to remove ammonia from the wastewater, preferably at a high pH. Although air stripping has the advantage of saving energy, steam stripping may have the benefit of saving chemical dosage. For high ammonia loading waste streams like centrate or supernatant, a recommendation of using steam stripping has been proposed (Tchobanoglous, 2003, Carrio, et al, 2003). In GBWWTP, digester off gas supplies on-site fuel energy, so steam stripping could be a promising alternative to be examined in the future research.

6.2 Ammonia Utilization

In this project, ammonia was converted directly to nitrogen gas, as a non hazardous gas released to environment atmosphere. Recently some researchers have attempted to make use of this ammonia source to produce some products, e.g., fertilizer. The principle is that, after ammonia is stripped out of the waste stream, some chemical stream, usually sulphuric acid is used to absorb the ammonia in a countercurrent absorption tower as the air is recirculated between the two columns. Some pilot scale research on that has been done in New York City Wastewater Treatment Plants (Carrio et al, 2003).

6.3 Hydrogen energy recovery

Hydrogen production in the reactor off-gas may be of interest to be quantified and evaluated for a potential energy recovery, although it was not listed in the initial scope of this research. Hydrogen is a green energy of great interest. One promising application is to use it and fuel cells to generate electricity without combustion or pollution. This electric energy can be used to power our vehicles as well as heat, cool and power our home and buildings. This will process the potential to solve several major challenges facing our country, including dependence on petroleum imports, poor air quality, and greenhouse gas emissions.

In electrical cells, chloride ion is electrolyzed at the anode to chlorine gas. Hydrogen is a byproduct at the cathode. For detailed information refer to chapter 4. Although H_2 production was not measured, theoretically calculations using Faraday's Law indicate that there would be up to 18.625 mol/h hydrogen production at a current setting at 500 A.

REFERENCES

Ahn, K. H., Cha, H. Y. and Song, K. G. (1999). Retrofitting municipal sewage treatment plants using an innovative membrane-bioreactor system. *Desalination.* **124**, 279-286

Bonomo, L., Pastorelli, G., Quinto, E. and Rinaldi, G. (2000). Tertiary nitrification in pure oxygen moving bed biofilm reactors. *Water Sci Technol.* **41**(4), 361-368.

Bortone, G, Malaspina, F. Stante, L. and Tilche, A. (1994). Biological nitrogen and phosphorus removal in an anaerobic/anoxic sequencing batch reactor with separated biofilm nitrification, *Wat. Sci. Tech.* **30** (6), 303-313.

Carrio, L., Sexton, J., Lopez, A., Gopalakrishnam, K., and Sapienza, V. (2003). Ammonia-nitrogen removal from centrate: 10 years of testing an doperating experience in New York City. *WEFTEC 2003.*

Chang, S. H. and Ouyamg. C. F. (2000). The biomass fractions of heterotrophs and phosphorus-accumulating organisms in a nitrogen and phosphorus removal system. *Wat. Res.* **34**(8), 2283-2290.

Charles, M. (1998). *Chemical scrubbing: packed columns. Odor and VOC Control Handbook.* **8**.102-8.108. McGraw-Hill.

Cameron, K., Madramootoo, C., Crolla, A. and Kinsley, C. (2003). Pollutant removal from municipal sewage lagoon effluents with a free-surface wetland. *Wat. Res. 37*, 2803-2812.

Canziani, R., Vismara, R., Basilico, D. and Zinni, L. (1999). Nitrogen removal in Fixed-Bed Submerged Biofilters without backwashing. *Water Sci. Technol.* **40**(4-5), 145-152.

Culp, R.L., George, M.W. and Culp, G., (1977). *Handbook of Advanced Wastewater Treatment*, 2^{nd}, N.Y.

Culp,G.L., and A. Slechta (1966) *Nitrogen Removal from Sewage*, Final Progress Report, U.S. Public Health Service Demonstration Grant 29-01

Dryden H. T. (1984). Ammonium ion removal from dilute solutions and fish culture water by ion exchange. PhD thesis, Heriot-Watt University, Edinburgh, UK.

Enpar Technologies Inc., http://www.enpar-tech.com/Public/280,11,Application Log accessed on Aug 10, 2004

Environmental Canada. (2003). NH_3 treatment processes for the removal of ammonia from municipal wastewater. Hydromantis (ed), Environmental Choice^M Ontario, Canada.

Fdez-Polanco, F., Real, F. J. and Garcia, P. A. (1994). Behavior of an anaerobic/aerobic pilot scale fluidized bed for the simultaneous removal of carbon and nitrogen. *Water Sci .Technol.* **29**(10-11), 339-346.

Fux, C., Lange, K., Faessler, A., Huber, P., Grueniger, B. and Siegrist, H. (2003). Nitrogen removal from digester supernatant via nitrite –SBR or SHARON? *Wat. Sci. Tech.* **48**(8), 9-18.

Fux, C., Boehler, M., Huber, P., Brunner, I. and Siegrist, H. (2002). Biological treatment of ammonium-rich wastewater by partial nitritation and subsequent anaerobic ammonium oxidation (anammox) in a pilot plant, *Journal of Biotechnology* **99**, 295-306.

Gee, C.S. and Kim, J.S. (2004). Nitrite accumulation followed by denitrification using sequencing batch reactor, *Wat. Sci. Tech.* **49**(5-6), 47–55.

Greig, J. A. (1996). Ion Exchange Depvelopments and Applications. *Novel anion exchange resins with thermal stability: synthesis and characteristics.* Kubota, H., Yano, K., Sawada, S., Aosaki, Y., Watanabe, J., Usui, T., Ono, S. Shoda, T. and Okazaki, K. 182-200.

Giuseppe, P., Roberto, C., Luca, P. and Alberto, R. (1999). Phosphorus and nitrogen removal in Moving-Bed Sequencing Batch Biofim Reactors. *Water Sci. Technol.* **40**(4-5), 169-176.

Hanner, N. Aspegren, H. Nyberg, U. and Andersson, B. (2003). Upgrading the Sjölunda WWTP according to a novel process concept. *Wat. Sci. Tech.* **47**(12), 1-7.

Jorgensen, T. C. and Weatherley, L. R. (2002). Ammonia removal from wastewater by ion exchange in the presence of organic contaminants. *Water Res.* **37**, 1723-1728.

Karsson, S. G. (1994). Experience wit the SBR process at the Linkoping WWTP. Conference on: Upgrading for nitrogen and phosphorus removal, Eslov, Sweden, 4-5 May.

Koch, G. and Siegrist, H. (1997). Denitrification with methanol in tertiary filtration at the treatment plant Zurich Werdholzli, *Wat. Sci. Tech* **36**(1), 165-172.

Llao, P. H., Chen, A. and Lo, K. V. (1995). Removal of nitrogen from swine manure wastewaters by ammonia stripping. *Bioresource Technology* **54**, 17-20.

Manz W, Wagner M, Amann RI, Schleifer KH. (1994). In situ characterization of the microbial consortia active in two wastewater treatment plants. *Water Research* **28**, 1715– 1723.

Mergaert, K. M., Vanderhaegen, B. and Verstraete, W. (1992). Applicability and trends of anaerobic pre-treatment of municipal wastewater. *Water Res.* **26**(8), 1025-1033.

Merlin, G., Pajean, J. L. and Lissolo, T. (2002). Performance of constructed wetlands for municipal wastewater treatment in rural mountainous area. *Hydrobiologia.* **469**, 87-98.

Merrick, M, Edwards, RA. (1995). Nitrogen control in bacteria. *Microbiological Review* **59**, 604-622.

Montgomery, D. C. (2001). Design and Analysis of Experiments, 5th Edition. John Wiley and Sons, Inc., New York.

Murat, S., Ates Genceli, E., Tasli, R., Artan, N.and Orhon, D. (2002). Sequencing batch reactor treatment of Tannery Wastewater for Carbon and Nitrogen Removal. *Water Sci. and Technol.* **46**(9). 219-227

Nakai Y. (2001). Animal waste management and microorganisms. *Animal Science Journal.* **72**, 1-13

Nakai Y, Abe T, Kohda C, Ando T. (1999). Water characteristics and microbial flora in a lagoon system for wastewater from a paddock of dairy cattle. *Animal Science Journal* **70**, 38–42.

OMOE (Ontario Ministry of the Environment) (1992) *Evaluation of Acute and Chronic Toxicity of Ontario Sewage Treatment Plant Effluents.* ISBN 0-7729-9401-3. August 1992

Patriarca E.J., Tate R., Iaccarino M. (2002). Key role of bacterial NH_4^+ metabolism in Rhizobium-Plant symbiosis. *Microbiology and Molecular Biology Reviews* **66**, 203-222.

Pulgarin, C., Adler, N., Peringer P. and Comninellis, C. (1994). Electrochemical detoxification of a 1.4 benzoquinone solution in wastewater treatment. *Water Res.* **28**(4), 887-893.

Purtschert, I., Siegrist, H. and Gujer, W. (1996). Enhanced denitrification with methanol at WWTP Zurich-Werdholzli, *Wat. Sci. Tech.* **33**(12), 117-126.

Sakaki, H., Kitazume, O., Sakaki, T. and Nakai, Y. (2004). Ammonia-assimilating microbes in microbial community in a lagoon for wastewater from paddock of dairy cattle. *Animal Journal. 75*, 79-84.

Sakaki H, Maruyama G, Suzuki H, Nonaka J, Sato M, Sasaki T, Ohta M, Nakai Y. (2002). Characterization of ammonia-assimilating bacteria in a lagoon for wastewater from a paddock of dairy cattle. *Animal Science Journal.* **73**, 73-76.

Sakakibara, Y., Araki, K., Watanabe, T. and Kuroda, M. (1997). The denitrification and neutralization performance of an electrochemically activated biofilm reactor used to treat nitrate-contaminated groundwater. *Water Sci. Technol.* **36**(1), 61-68.

Sakakibara, Y. and Kuroda, M. (1993). Electric prompting and control of denitrification. *Biotechnol. Bioeng.* **42**, 535-537.

Seed, L. P., Yetman, D., Key, S. W. and Shelp, G. S. (2003). A novel ion-exchange/electrochemical technology for the treatment of ammonia in wastewater. Sudbury 2003 Mining and the Environment Conference

Siegrist, H. (1996). Nitrogen removal from digester supernatant – comparison of chemical and biological methods. Wat. Sci. Tech. 34(1-2), 399-406.

Sekiguchi Y, Kamagata Y, Syutsubo K, Ohashi A, Harada H, Nakamura K. (1998). Phylogenetic diversity of mesophilic and thermophilic granular sludges determined by 16S rRNA gene analysis. *Microbiology* **144**, 2655–2665.

Slechta,A., and G.L.Culp (1967) Wastewater reclamation studies at the South Lake Tahoe Public Utility District", *Journal WPCF,* **39**(5).

Snaidr J, Amann R, Huber I, Ludwig W, Schleifer KH. (1997). Phylogenetic analysis and in situ identification of bacteria in activated sludge. *Applied and Environmental Microbiology* **63**, 2884–2896.

Surampalli, R. Y., Scheible, O. K. and Banerji, S. K. (1994). Nitrification in single-stage trickling filters. *Natl Conf Environ Eng*. 694-701

Tchobanoglous, G., Burton, F. L. and Stensel, H. D. (2003). Metcalf and Eddy (2003). *Wastewater Engineering--Treatment, Disposal, and Reuse.* 4th Edition. McGraw Hill, Inc., New York.

USEPA (1993). *Nitrogen Control Manual.* EPA/625/R-93/010. Washington DC, September 1993.

USEPA (2002). *Facultative Lagoons. Wastewater Technology Fact Sheet.* EPA/832/F-02/014. September 2002.

Wagner M, Erhart R, Manz W, Amann R, Lemmer H, Wedi D, Schleifer K. (1994). Deplopment of an rRNA-targeted oligonucleotide probe specific for the genus *Acinetobacter* and its application for in situ monitoring in activated sludge. *Applied and Environmental Microbiology* **60**, 792–800.

Wagner M, Amann R, Lemmer H, Schleifer K. (1993). Probing activated sludge with oligonucleotides specific for proteobacteria: Inadequacy of culture-dependent methods for describing microbial community structure. *Applied and Environmental Microbiology* **59**, 1520–1525.

Yeom, I.T., Nah, Y. M. and Ahn, K. H. (1999). Treatment of household wastewater using an intermittently aerated membrane bioreactor *Desalination*. **124**, 193-204.

APPENDIX A. Ammonia concentration in GBWWTP effluent, centrate, supernatant and influent

1 Ammonia in Plant effluent —from Gold Bar Data base (2001~2003)

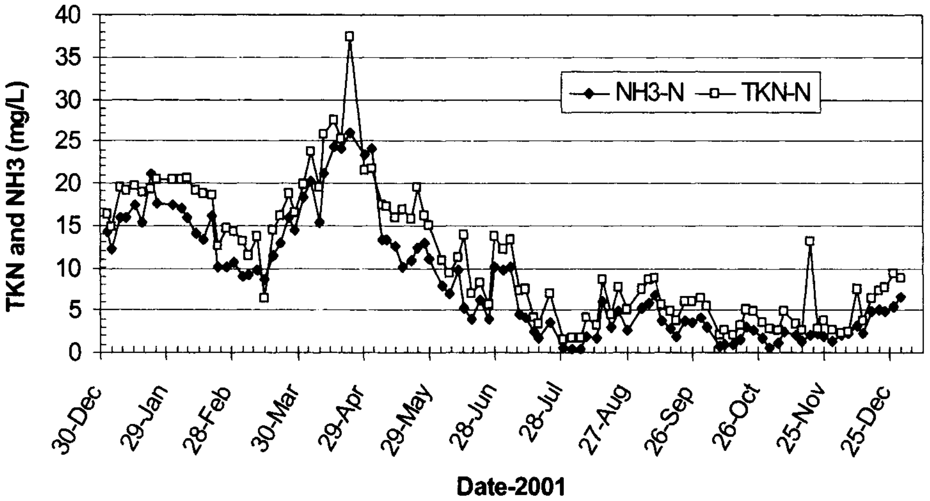


Figure A-1. GBWWTP Effluent W.W. TKN and NH3 in 2001

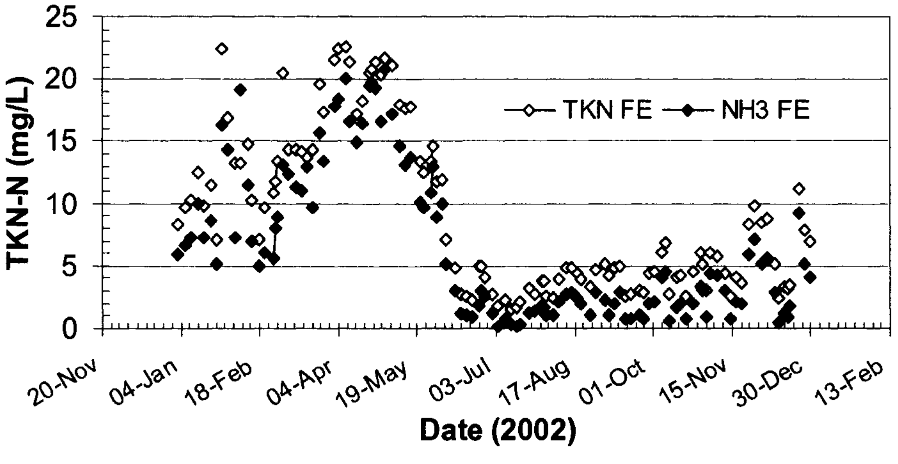


Figure A-2. WWTP Effluent W.W. TKN and NH3 in 2002

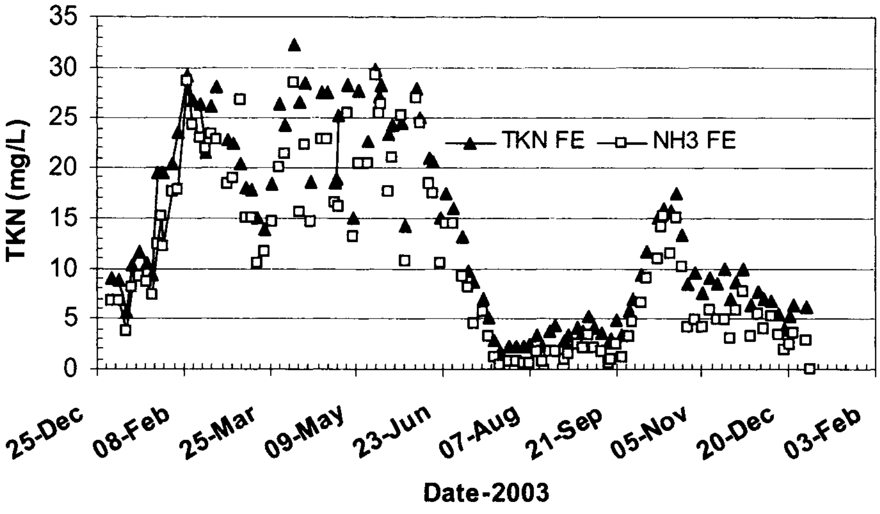


Figure A-3. Effluent W.W. TKN and NH3 in 2003

2 Ammonia in Clover Bar Supernatant (2002-2003)

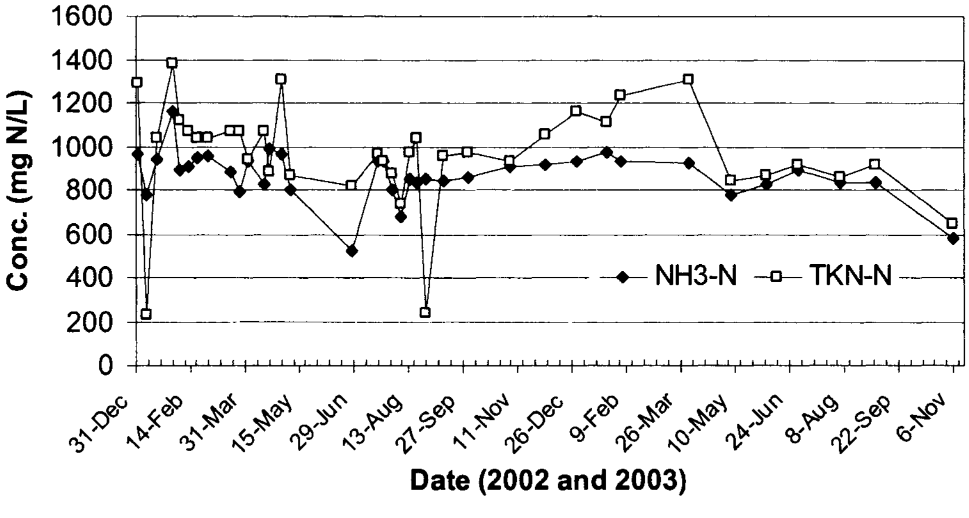


Figure A-4. Clover Bar supernatant W.W. TKN and NH3 in 2002 and 2003

3 Total Kjeldahl Nitrogen in Clover Bar Centrate (2002, 2003 and early 2004)

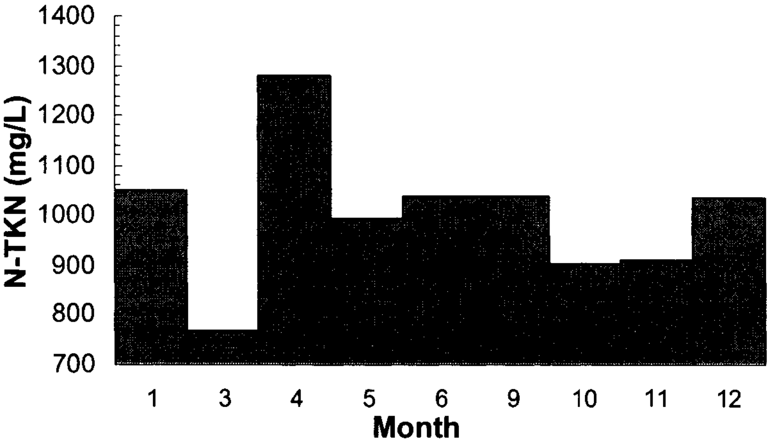


Figure A-5. N-TKN flucculation in centrate (2002)

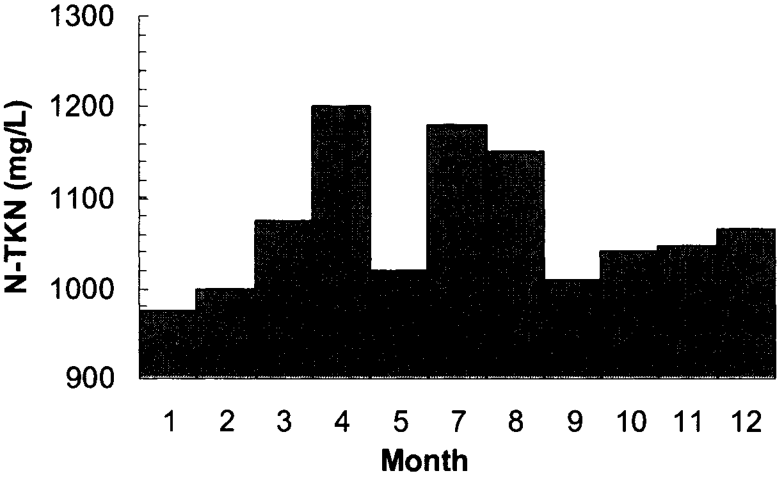


Figure A-6. N-TKN flucculation in centrate (2003)

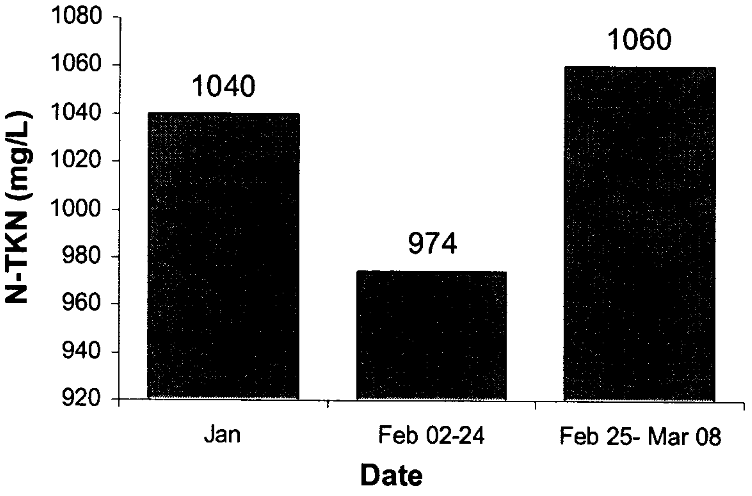


Figure A-7. N-TKN fluctuation in centrate (early 2004)

4 Ammonia in Plant influent —from Gold Bar Data base (2001~2003)

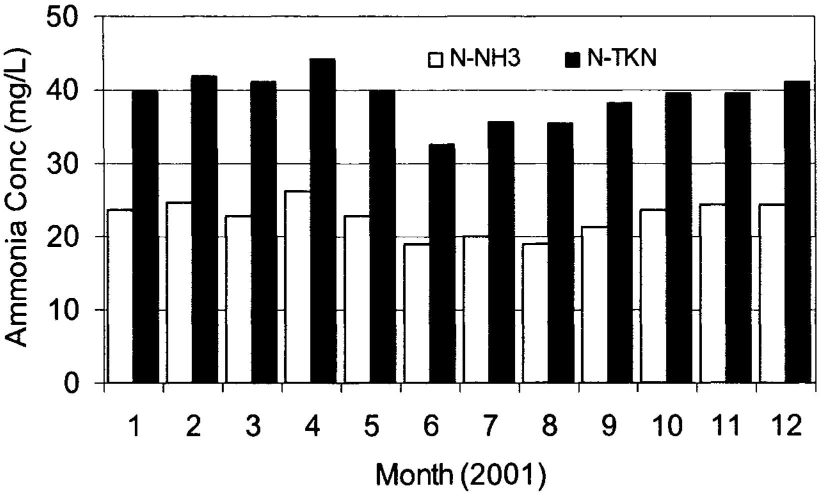


Figure A-8. Ammonia loading in GBWWTP raw wastewater (2001)

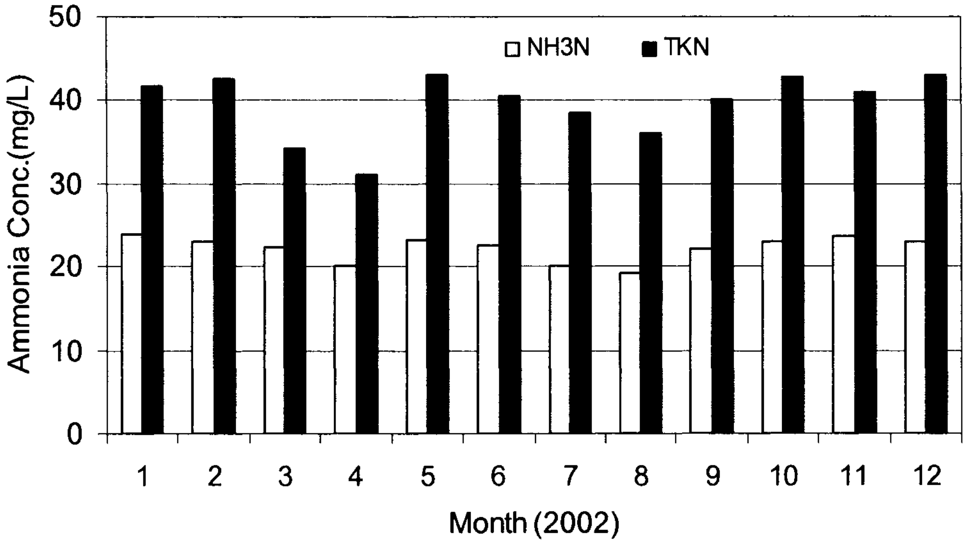


Figure A-9. Ammonia loading in GBWWTP raw wastewater (2002)

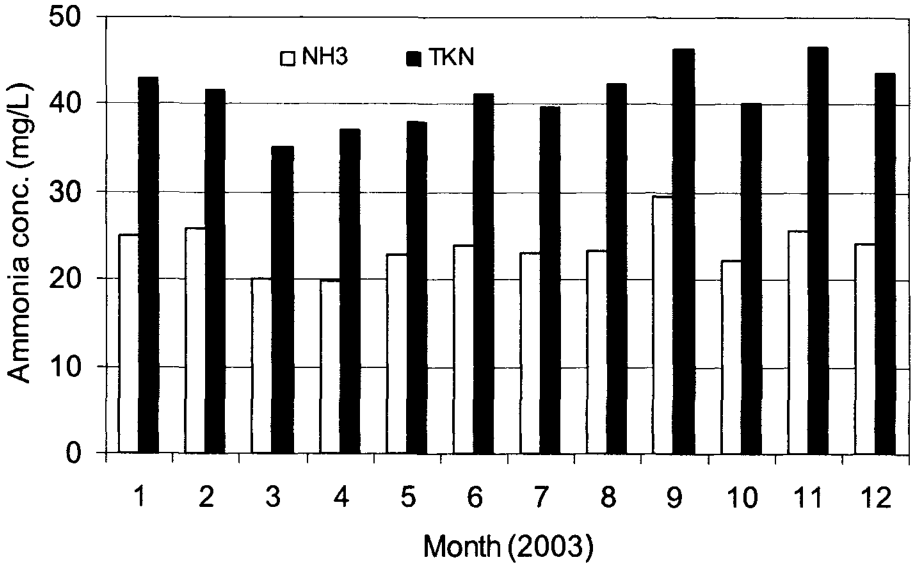


Figure A-10. Ammonia loading in GBWWTP raw wastewater (2003)

APPENDIX B. Calculations—Alkalinity

Although many materials may contributes to the alkalinity of a water, the major portion of the alkalinity in nature is caused by three major classes of materials which may be ranked in order of their association with high pH values as follows: (1) hydroxide, (2) carbonate, and (3) bicarbonate. For most practical purposes, alkalinity due to other materials in nature waters is insignificant and maybe ignored. Alkalinity is customary expressed in terms of CaCO3.

For samples have a pH of 8.3 or less, they contain mainly bicarbonate alkalinity. This is, in this case, bicarbonate alkalinity is equal to the total alkalnity. The titrition from pH (less than 8.3) to pH 4.5 measures this alkalinity.

In this experiment, the Centrate original pH is lower than 8.3. 0.50382 N H2SO4 prepared by Gold Bar lab was used to titrate Centrate sample for its alkalinity determination.

Then: $N_{H2SO4} * V_{H2SO4} = N_{Sample} * V_{Sample}$

$$X_{sample} = \frac{N_{H_2SO_4} * V_{H_2SO_4} * 50{,}000}{Vsamle}$$

Where V_{H2SO4} ... is the volume of acid titrant added, ml.

V_{sample} ... is the initial volume of the sample, ml.

N_{H2SO4} ... is the normality of the acid titrant

X_{sample} ... is the alkalinity of the sample, CaCO3 mg/L

The test result presented in talble C-1.

Table B-1. Triplication Titration record for alkalinity determination

Sample	T (°C)	pH	V_{H2SO4} (ml)	V_{sample} (ml)	N_{H2SO4}
1	20	7.84	13.1	100	0.5038
2	20	7.85	13.1	100	0.5038
3	20	7.86	13.2	100	0.5038

Substitute the values in about table to equation X, and make the average, the alkalinity is:

$$X_{sample} = (3300+3300+3325)/3=3308 \text{ mg } CaCO_3/L$$

APPENDIX C. Calculations—Mass Balance

The pressure (P_1) in the conduit is shown in the following figure. The blower used in the experiment is a HF thermoplastic centrifugal fan (HF R 160-17 D/R). From the blower's characteristic curve, we found that the pressure difference between the inlet and outlet of the blower is around 1.5KPa at the volume flow rate 11.12 m^3/min and the rotation speed of 3300 min^{-1}.

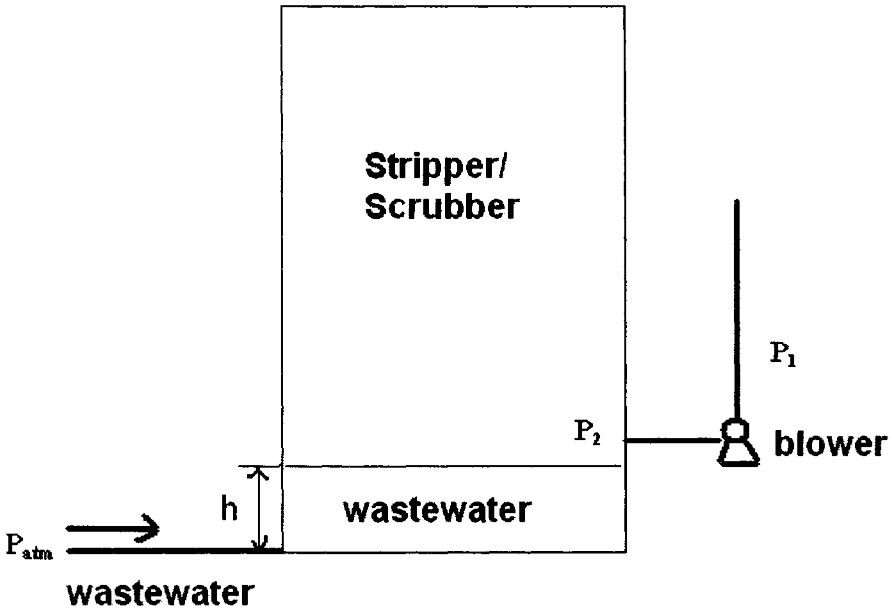


Figure C-1 Sketch figure for stripper/scrubber presure calculation

Therefore,

P_2-P_1=1.5KP_a (1)

There is a 0.6m (h) wastewater at the bottom of the tower, so

$P_{atm}-P_2=\rho gh$ (2)

From equation (1) and (2), we can get P1 as:

$P_1=P_{atm}-1.5KP_a-\rho gh$

$P_{atm}-P_1=(1.5+1*10*0.6)KP_a$

Where P_{atm} is around $101KP_a$. So the pressure in the conduit is 93.5 KP_a.

The temperature used in the experiment is around 293K. Then we can calculate the specific volume of the air in the conduit according to the ideal gas equation:

$$\frac{V}{n}=\frac{RT}{P}$$

So the volume of 1mol air is:

$$\frac{8.314*293}{93.5}=26L/mol$$

For stripper

Table C-1 Ammonia concentration distribution in stripper unit

L (L/h)	C_0 (mg/L)	C_e (mg/L)	G (m3/min)	y_0 (ppm)	y_e (ppm)
240	925	176	11.12	0	400

$G*y_0$=[(11.12*10^3*60 L/h)/26L/mol] * 0 (L/10^6L) * =0 mol/h

$G*y_e$=[(11.12*10^3*60 L/h)/26L/mol] * 400 (L/10^6L) * =10.26 mol/h

$L*C_0$=(925 mg N /L *240 L/h)/14000mgN/mol= 15.85 mol/h

$L*C_e$=(176 mg N /L *240 L/h)/14000mgN/mol= 3.02 mol/h

Inflow= $LC_0 + Gy_0$ =15.85 + 0 =15.85 mol/h

Outflow= $LC_e + Gy_e$ =3.02 + 10.26 =13.28 mol/h

$$\text{Recovery} = \frac{\text{Outflow}}{\text{Inflow}} * 100\% = 83.8\%$$

For scrubber

Table C-2 Ammonia concentration distribution in scrubber unit

L (L/h)	C_0 (mg/L)	C_e (mg/L)	G (m^3/min)	y_0 (ppm)	y_e (ppm)
720	0	203	11.12	400	0

$G*y_0$=[(11.12*10^3*60 L/h)/22.4L/mol] * 400 (L/10^6L) * =10.26 mol/h

$G*y_e$=[(11.12*10^3*60 L/h)/22.4L/mol] * 0 (L/10^6L) * =0 mol/h

$L*C_0$=(0 mg N /L *720 L/h)/14000mgN/mol= 0 mol/h

$L*C_e$=(203 mg N /L *720 L/h)/14000mgN/mol= 10.44 mol/h

Inflow= $LC_0 + Gy_0$ = 0 + 10.26 =10.26 mol/h

Outflow= $LC_e + Gy_e$ = 10.44 + 0 =10.44 mol/h

$$\text{Recovery} = \frac{\text{Outflow}}{\text{Inflow}} * 100\% = 101.8\%$$

APPENDIX D Calculations—ANOVA

1 Factorial analysis calculations

Table D-1. 24 factorial design experimental data

Removal (%)	Setting	A	B	C	D	AB	AC	AD	BC	BD	CD
73.0	-1	-1	-1	-1	-1	1	1	1	1	1	1
82.4	a	1	-1	-1	-1	-1	-1	-1	1	1	1
75.4	b	-1	1	-1	-1	-1	1	1	-1	-1	1
76.0	ab	1	1	-1	-1	1	-1	-1	-1	-1	1
74.2	c	-1	-1	1	-1	1	-1	1	-1	1	-1
90.6	ac	1	-1	1	-1	-1	1	-1	-1	1	-1
82.4	bc	-1	1	1	-1	-1	-1	1	1	-1	-1
87.1	abc	1	1	1	-1	1	1	-1	1	-1	-1
66.0	d	-1	-1	-1	1	1	1	-1	1	-1	-1
67.2	ad	1	-1	-1	1	-1	-1	1	1	-1	-1
63.7	bd	-1	1	-1	1	-1	1	-1	-1	1	-1
77.1	abd	1	1	-1	1	1	-1	1	-1	1	-1
68.1	cd	-1	-1	1	1	1	-1	-1	-1	-1	1
76.6	acd	1	-1	1	1	-1	1	1	-1	-1	1
74.2	bcd	-1	1	1	1	-1	-1	-1	1	1	1
84.4	abcd	1	1	1	1	1	1	1	1	1	1
77.8	0	0	0	0	0	0	0	0	0	0	0
78.4	0	0	0	0	0	0	0	0	0	0	0
74.8	0	0	0	0	0	0	0	0	0	0	0

Calculated with ANOVA method, using Microsoft (R) Office Excel 2003, generated following results:

Table D-2. Results of ANOVA analysis

	Qair	DC	pH	Qin	Interactions					
Fo	20.14	2.39	15.7	19.8	0.2	1.11	0.02	1.11	2.14	0.02
p-value	0.01	0.18	0.01	0.01	0.67	0.34	0.88	0.34	0.2	0.91
Significant	Y	N	Y	Y	N	N	N	N	N	N

Note: F_{crital}=5.32

Curvature Test

No.of Center Pts= 3 Center Pt. Average 77.02
No. of Factorial Pts= 16 Factorial Pt. Average 76.15

SS Pure Quadratic= 2.20
df= 1
MS Pure Quadratica = 2.20

SS Error = 7.61 df= 2
MS Error = 3.81

Fo, Pure Quadratic = 0.58
Fcritical = 18.5
p-value = 0.43

Table D-3. Curvature test

No.of Center Pts=	3	Center Pt. Average	77.02
No. of Factorial Pts=	16	Factorial Pt. Average	76.15
SS Pure Quadratic=	2.2	df=	1
MS Pure Quadratica =	2.20		
SS Error =	7.6	df=	2
MS Error =	3.81		
Fo, Pure Quadratic =	0.58		
Fcritical =	18.51		
p-value =	0.43		

Conclusion: no significant curvature.

2 half N-Score plot

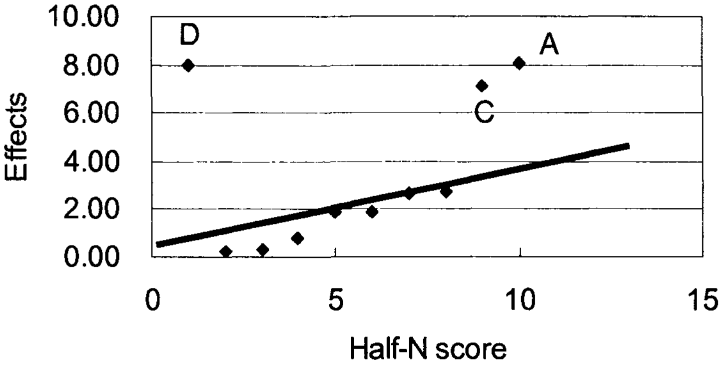


Figure D-1 half –N score test for parameters significance analysis

Table D-4.half N-Score table of ANOVA test

half-N score	1	2	3	4	5	6	7	8	9	10
main effect interactirons	D	CD	AD	AB	AC	BC	BD	B	C	A
Effects	7.99	0.22	0.28	0.81	1.89	1.89	2.62	2.77	7.11	8.05

APPENDIX E. Operation Results

Table E-1. Ammonia removal in nineteen operating settings
(Low temperature 7.5~11.1°C)

Liquid feed Temperature (oC)	Qww (L/h)	Stripper outflow pH	Mointored Outflow pH	DC (A)	Airflow rate (m3/min)	Average ammonia in WW (mg/L)	Ammonia in effluent (mg/L)	Removal %
8.3	240	10.50	10.87	500	9.90	853	230	73.0
10.4	240	10.50	10.23	500	12.34	853	150	82.4
9.7	240	10.50	10.80	600	9.90	853	210	75.4
9.2	240	10.50	10.50	600	12.34	853	205	76.0
11	240	12.00	12.02	500	9.90	853	220	74.2
8.4	240	12.00	12.07	500	12.34	853	80	90.6
9.8	240	12.00	11.75	600	9.90	853	150	82.4
9.6	240	12.00	11.80	600	12.34	853	110	87.1
8.7	300	10.50	10.28	500	9.90	853	290	66.0
11	300	10.50	10.64	500	12.34	853	280	67.2
7.5	300	10.50	10.20	600	9.90	853	310	63.7
7.5	300	10.50	10.82	600	12.34	853	195	77.1
11.1	300	12.00	11.97	500	9.90	853	272	68.1
9.1	300	12.00	11.95	500	12.34	853	200	76.6
8.1	300	12.00	12.19	600	9.90	853	220	74.2
10.1	300	12.00	11.64	600	12.34	853	133	84.4
9.8	270	11.25	10.89	550	11.12	853	189	77.8
8.9	270	11.25	11.10	550	11.12	853	184	78.4
9.4	270	11.25	11.01	550	11.12	853	215	74.8

Table E-2. Ammonia removal in high temperature operating settings
(temperature 19.9~25.0°C)

Liquid feed Temperature (oC)	Qww (L/h)	Stripper inflow pH	Mointored Outflow pH	DC (A)	Airflow rate (m3/min)	Average ammonia in WW (mg/L)	Ammonia in effluent (mg/L)	Removal %
20.7	240	10.70	10.16	500	12.34	960	301	68.6
20.7	240	10.70	10.18	500	12.34	960	278	71.0
20.7	240	10.70	10.10	500	12.34	960	267	72.2
20.7	240	10.70	10.11	500	12.34	960	246	74.4
19.9	240	12.20	12.03	500	12.34	960	314	67.3
19.9	240	12.20	12.06	500	12.34	960	301	68.6
19.9	240	12.20	12.15	500	12.34	960	289	69.9
19.9	240	12.20	12.17	500	12.34	960	278	71.0
20.5	240	10.55	9.23	600	12.34	960	218	77.3
20.5	240	10.55	8.66	600	12.34	960	218	77.3
20.5	240	10.55	8.34	600	12.34	960	201	79.0
20.5	240	10.55	8.20	600	12.34	960	178	81.4
20	240	12.20	11.37	600	12.34	960	237	75.4
18.7	240	12.20	11.94	600	12.34	960	289	69.9
20.5	240	12.17	11.74	600	12.34	960	227	76.3
20.6	240	12.16	11.72	600	12.34	960	210	78.2
22	240	10.10	8.64	600	12.34	960	227	76.3
24	240	10.10	8.04	600	12.34	960	227	76.3
24	240	10.09	7.96	600	12.34	960	246	74.4
/	240	/	/	600	12.34	960	/	/
/	240	/	/	500	12.34	823	/	/
24	240	10.14	9.58	500	12.34	823	225	72.6
24	240	10.13	9.64	500	12.34	823	208	74.8
24	240	10.07	9.65	500	12.34	823	208	74.8
25	240	10.08	9.66	500	12.34	823	216	73.7
25	240	10.10	9.65	500	12.34	823	216	73.7
22	180	10.02	8.93	500	12.34	903	90	90.0
22	180	10.08	8.47	500	12.34	903	62	93.1
23	180	10.03	8.11	500	12.34	903	47	94.8
24	180	10.07	8.00	500	12.34	903	68	92.5
24	180	10.12	7.83	500	12.34	903	71	92.2
24	180	10.06	7.59	500	12.34	903	77	91.5
24	300	10.06	9.27	600	12.34	906	230	74.6
24	300	10.00	9.20	600	12.34	906	221	75.6
24	300	10.06	9.54	600	12.34	906	261	71.2
25	300	10.08	9.66	600	12.34	906	261	71.2
25	300	10.05	9.75	600	12.34	906	261	71.2

APPENDIX F. Calculations—Operating cost

Calculation for the cost for 1 ML centrate treatment was based on the setting that ammonia conc. in raw centrate is 853 mg/L, and after treatment 76.3% ammonia has be removed.

The operating cost consists of electric energy cost and chemical cost. Former one mainly involves electric consumption on rectifier, blowers and pumps. Latter one is with respect to sodium hydroxide and hydrochloric acid consumption. Under the nineteen settings, the operation costs are listed in table F-1. This cost main components and distribution is listed in table F-2.

Table F-1. Operating cost in nineteen operating settings
(Low temperature 7.5~11.1°C)

Operating Cost ($/kg NH3-N removal)	Qair (m3/min)	DC (A)	pH	Qww (L/h)
10.67	9.9	500	10.5	240
9.35	12.34	500	10.5	240
11.54	9.9	600	10.5	240
10.95	12.34	600	10.5	240
13.52	9.9	500	12	240
10.58	12.34	500	12	240
12.56	9.9	600	12	240
11.64	12.34	600	12	240
10.71	9.9	500	10.5	300
9.97	12.34	500	10.5	300
11.85	9.9	600	10.5	300
9.89	12.34	600	10.5	300
12.49	9.9	500	12	300
10.80	12.34	500	12	300
11.71	9.9	600	12	300
10.58	12.34	600	12	300
9.78	11.12	550	11.25	270
10.83	11.12	550	11.25	270
11.14	11.12	550	11.25	270
average 11.08				

Table F-2. Operating cost main components

Average perating cost	Average NaOH cost	Average power cost	Average HCl cost
11.08	7.16 (65%)	2.83 (26%)	1.09 (10%)

unit:($/Kg NH3-N removed)

Table F-3. NaOH consumption comparison (Current at 500A)

	pH ~10.5 Temp 4~11°C	pH~10.5 Temp 20°C	pH~12 Temp 4~11°C	pH~12 Temp 20°C
NaOH consumption (L/m^3 centrate)	6.28	5.13	13.61	7.06
Ammonia removal	0.84	0.72	0.9	0.69

Table F-4. NaOH consumption comparison (Current at 600A)

	pH ~10.5 Temp 4~11°C	pH~10.5 Temp 20°C	pH~12 Temp 4~11°C	pH~12 Temp 20°C
NaOH consumption (L/m^3 centrate)	6.28	4.31	11	6.73
Ammonia removal	0.764	0.79	0.863	0.75

The cost calculation is based on:

For 50% NaOH:

- by the drum - $201, (400L)
- bulk quantities - $0.50/L

For 36-38% HCl:

- by the drum - $121.50, (405L)
- bulk quantities - $0.30/L

For power : $0.09/kWh

APPENDIX G. Calculations—Hydrogen recovery

Faraday's *law of electro*lysis can be stated as follows. The amount of a substance consumed or produced at one of the electrodes in an electrolytic cell is directly proportional to the amount of electricity that passes through the cell.

In order to use Faraday's law we need to recognize the relationship between current, time, and the amount of electric charge that flows through a circuit. By definition, one coulomb of charge is transferred when a 1-amp current flows for 1 second.

1 C = 1 amp-s

First we calculate the number of grams of sodium metal that will form at the cathode when a 500.0-amp current is passed through sodium chloride solution for a period of 1.00 hours.

We start by calculating the amount of electric charge that flows through the cell in one hour.

$$500amp * 1.00hr * \frac{60\min}{1hr} * \frac{60s}{1\min} * \frac{1C}{1amp - s} = 1800{,}000C$$

Before we can use this information, we need a bridge between this macroscopic quantity and the phenomenon that occurs on the atomic scale. This bridge is represented by Faraday's constant, which describes the number of coulombs of charge carried by a mole of electrons.

$$\frac{6.022045*10^{23}e^{-}}{1mol}*\frac{1.6021892*10^{-19}C}{1e^{-}}=96,484.56C/mol$$

Thus, the number of moles of electrons transferred when 1800,000 coulombs of electric charge flow through the cell can be calculated as follows.

$$1800,000C*\frac{1mole^{-}}{96,485C}=18.625mole^{-}$$

The H_2 gas is formed as the balancing cathodic reaction. The cathode reactions for the generation of hydrogen in acidic electrolyte are:

$$2H^{+} + 2e- = H_2$$

Therefore 2 moles of electrons are required to generate 1 mole of H_2. By using the Faraday constant (96,485 C/mol), theoretical predictions relating current to H_2 production can be calculated.

$$\text{Moles Hydrogen Gas Generated} = \frac{e^{-}mol}{2}$$

So in one hour, in two electrochemical cess, hydrogen produce is about 18.625mol/2 *2=18.625mol.

The above equation assumes a current efficiency of 100%, which is rare.

APPENDIX H. Titration records

Figure H-1. 1N NaOH titrate centrate (without pre-straining)

1N NaOH Added (mL)		**pH**	**Average 1N NaOH Added** (mL)	**NaOH Added** (g/L)
Titration 1	**Titration 2**		Average	Average
0.00	0.00	7.35	0.00	0.00
1.10	0.58	7.60	0.84	0.44
1.60	0.93	7.80	1.27	0.66
1.80	1.38	8.00	1.59	0.83
2.15	1.73	8.20	1.94	1.01
2.30	1.93	8.30	2.12	1.11
2.80	2.38	8.50	2.59	1.35
3.10	3.03	8.70	3.07	1.60
3.70	4.08	8.90	3.89	2.03
4.10	4.78	9.00	4.44	2.32
5.00	5.28	9.10	5.14	2.69
6.00	5.83	9.20	5.92	3.09
7.00	6.43	9.30	6.72	3.51
7.70	6.88	9.40	7.29	3.81
7.85	7.68	9.50	7.77	4.06
8.22	8.98	9.60	8.60	4.49
9.15	10.43	9.70	9.79	5.12
10.50	10.93	9.80	10.72	5.60
11.15	11.93	9.90	11.54	6.03
12.10	12.68	10.00	12.39	6.48
13.20	13.48	10.10	13.34	6.97
14.30	14.18	10.20	14.24	7.44
16.80	15.08	10.40	15.94	8.33
17.20	16.18	10.50	16.69	8.72
17.95	17.78	10.70	17.87	9.34
18.50	18.48	10.80	18.49	9.66
19.15	19.23	10.90	19.19	10.03
19.80	19.98	11.00	19.89	10.40

Figure H-2. 1N NaOH titrate centrate (800 μm mess strainer used)

1N NaOH Added (mL)		**pH**	**Average 1N NaOH Added** (mL)	**Average1N NaOH Added** (g/L)
Titration 1	Titration 2			
0.00	0.00	7.85	0.00	0.00
0.80	0.45	8.33	0.62	0.25
1.47	1.20	8.74	1.33	0.53
1.50	1.26	8.76	1.38	0.55
2.00	1.90	8.97	1.95	0.78
2.10	2.07	9.01	2.09	0.83
3.40	3.41	9.32	3.41	1.36
3.89	3.80	9.41	3.84	1.54
5.30	5.39	9.67	5.35	2.14
5.59	5.70	9.72	5.65	2.26
7.28	7.50	10.01	7.39	2.96
7.40	7.61	10.03	7.51	3.00
9.00	9.26	10.33	9.13	3.65
9.30	9.70	10.41	9.50	3.80
10.40	10.76	10.70	10.58	4.23
10.69	11.20	10.82	10.94	4.38
11.40	11.87	11.12	11.63	4.65
11.50	12.00	11.18	11.75	4.70
12.25	12.70	11.65	12.48	4.99
12.30	12.77	11.68	12.54	5.01
12.95	13.40	11.94	13.18	5.27
13.10	13.50	12.00	13.30	5.32