Statistical Analysis and Optimization of Ammonia Nitrogen Removal from Aqueous Solutions and Landfill Leachate by Ultrasound Irradiation

By

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ABSTRACT

The application of Ultrasound (US) irradiation to remove ammonia nitrogen from aqueous solutions, including synthetic solution and landfill leachate, at 20 kHz was investigated in this thesis. Batch experiments were carried out using two synthetic solutions with initial ammonia concentrations of 3000 and 5000 mg TAN/L in addition to two leachates from new and old landfills. The results of testing showed that US irradiation is an effective treatment technology for the removal of aqueous ammonia. More specifically, it was found that increasing sonication time and pH increased ammonia removal. The maximum observed removal of ammonia was 87.4% at a pH of 11 and sonication time of 25 minutes. Also, it was found that volatilization of ammonia to the atmosphere accounted for 0-7% of removal, the thermal effect of US accounted for 21.1-52.7%, and the non-thermal effect of US accounted for 44.5-78.8% (depending on pH and sonication time). Results of factorial design and response surface methodology showed that pH, energy output (kJ), and the interaction between the two were significant parameters. The predicted two factor interaction (2FI) model was in close agreement to the observed data ($R^2 = 0.94$) and produced an optimum ammonia removal of 87% at a pH of 10.9 and energy output of 94.8 kJ. Analysis of variance tests showed that there were no significant differences in the percent removal of ammonia due to the non-thermal effects of US across all four solutions (synthetic and leachate) indicating that US irradiation is a non-selective treatment method for ammonia removal.

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List of Abbreviations

AD: anaerobic digestion;

Anammox: anaerobic ammonia oxidation;

ANOVA: analysis of variance

AOX: adsorbable organic halogens;

AS: activated sludge;

BOD: biochemical oxygen demand;

COD: chemical oxygen demand;

DF: degree of freedom;

DW: distilled water

IER: ion-exchange resin;

MAP: magnesium ammonium phosphate;

MF: microfiltration;

MLSS: mixed liquor suspended solids;

MS: mean square

NF: nanofiltration;

NMDA: N-methyl-D-aspartate;

PAC: powdered activated carbon;

PAH: polyarmatic hydrocarbons;

PCB: polychlorinated biphenyls

RO: reverse osmosis;

RSM: response surface methodology;

SBR: sequencing batch reactor;

TAN: total ammonia nitrogen;

TKN: total Kjeldahl nitrogen;

TSS: total suspended solids;

UASB: up-flow anaerobic sludge blanket;

VOC: volatile organic compound;

VSS: volatile suspended solid;

WWTP: wastewater treatment plant.

CHAPTER I
Introduction

1.1 General

Landfills, for most of post-industrial history, have been the environmental and economic choice for the disposal of solid wastes. Landfill leachate is an inevitable by-product of solid waste disposal generated by water percolating through decomposing waste, extracting both biological and chemical dissolved or suspended materials. The end product of leachate is an extremely toxic, and variable, aqueous mix of organics, heavy metals, chlorides, and NH_3/NH_4^+ (Zhang *et al.*, 2009). Ontario government regulation 232/98, section 12 states, “a person shall not establish a new landfilling site or increase the total waste disposal volume of an existing landfilling site unless a written report containing plans, specifications and descriptions for the management and disposal of any leachate collected at the site has been prepared”. Leachate may be discharged into a sewage collection system which is then treated at a wastewater treatment facility or treated on-site and discharged into a surface water body; however, leachate may need to be pre-treated before discharge (Government of Ontario, 2012).

Landfill leachate can contain anywhere from a few hundred to upwards of 13000 mg $N\text{-}NH_3/L$, depending on the source and age of the waste (Dong & Sartaj, 2016). In addition to its deleterious effects on water bodies – dissolved ammonia is on the Canadian EPA (1999) toxic substance list - ammonia has also been reported to inhibit anaerobic bacterial activity in doses as low as 1500 N-NH_3/L (Ding & Sartaj, 2015). This loss in bacterial activity leads to lower biogas yields from the wastewater treatment plant's anaerobic digesters or bioreactor landfills, which equates to a loss of energy and/or revenue or increased maintenance and monitoring costs. Methods of NH_3/NH_4^+ removal from contaminated water and leachate include biological denitrification, air-stripping, chemical precipitation, electrochemical conversion, and microwave radiation (Lin *et al.*, 2009). In the last 15 years, ultrasound technology has been explored as an alternative NH_3/NH_4^+ removal technique due to the need for environmentally-clean technology that yields minimal waste (Matouq & Al-Anber, 2006).

Ultrasound (US) technology involves the use of higher frequency (above 16 kHz) sound waves to disrupt matter. Sonication, in an aqueous solution, generates cavitation bubbles, inside of which are extremely high temperatures and pressures, which rapidly form and collapse. Sonochemical transformation is due to pyrolytic decomposition inside the cavitation bubbles or reduction and oxidation by H^+ and OH^- radicals (Adewuyi, 2001). Wang *et al.* (2008) performed laboratory tests on leachate with high NH_3 concentrations in order to find the mechanism of NH_3 removal by ultrasound irradiation. It was found that the removal of NH_3 by ultrasound is almost entirely by pyrolysis within the cavitation bubbles and produces predominantly N_2 and H_2 gas with trace amounts of NO_2 and NO_3 gas being produced (perhaps by oxidation).

1.2 Research Objective and Scope

The main objective of this thesis was to investigate the feasibility and efficiency of NH_3/NH_4^+ removal using US irradiation at anaerobically inhibitory concentrations of N-NH_3, measured in landfill leachates. Furthermore, both synthetic and actual leachates were used in testing under similar conditions to provide comparisons in NH_3/NH_4^+ ultrasonic removal between ideal and working conditions. In addition, a statistical analysis using a full factorial design was done in order to mathematically classify the relevance of the independent variables (pH, power input, and sonication time) with respect to ammonia removal. Furthermore, the contribution of thermal and non-thermal effects of US irradiation and volatilization of ammonia to the atmosphere, were explored. Finally, an assessment of the selectivity and implementation of ultrasound technology used for the removal of NH_3/NH_4^+ from landfill leachate will be made.

1.3 Thesis Structure

This thesis will consist of five main sections:

- Chapter 1: Introduces the thesis and the research objective and scope.

- Chapter 2: Presents a literature review on the thesis subject matter, including a review of landfill leachate, ammonia chemistry, known ammonia removal techniques, ultrasonic chemistry and physics, and ammonia removal by ultrasound.

- Chapter 3: Presents the materials and methodology used to perform the tests and analysis of data.

- Chapters 4 & 5: Presents the findings comprising two papers, authored by the candidate (both submitted for publication). The research was designed to study the feasibility, efficiency, and mechanisms of NH_3/NH_4^+ removal using ultrasound irradiation.

- Chapter 6: Presents the findings of all additional testing that was not discussed in the previous chapters.

- Chapter 7: Summary of concluding remarks and recommendations for future work.

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CHAPTER II
Literature Review

2.1 Ammonia

Ammonia (NH_3) is classified as a Brønsted and Lewis base due to its capacity to accept a hydrogen ion (H^+) and donate a pair of electrons. More specifically, NH_3 is a weak electrolyte/base owed to the fact that only a small percentage of dissolved NH_3 reacts with water (H_2O) to form ammonium (NH_4^+) and hydroxide ion (OH^-); this reaction is shown by Equation 2.1 (Chang & Cruickshank, 2005).

$$NH_3(aq) + H_2O(l) \Leftrightarrow NH_4^+(aq) + OH^-(aq) \tag{2.1}$$

NH_3 is a volatile compound with a boiling point of -33.4°C and, like other volatile compounds, is sensitive to pressure and temperature changes (Chang & Cruickshank, 2005). Equation 2.1 also shows the sensitivity of the NH_3/NH_4^+ equilibrium to pH; the higher the pH of a solution, or more basic, the higher the concentration ratio of NH_3 versus NH_4^+. The pKa of NH_4^+ is 9.25 at standard conditions, this translates into a pH of 9.25 being the condition where NH_3 and NH_4^+ exist in equal molar concentrations in an aqueous solution (Benjamin, 2002); Figure 2.1 illustrates this relationship.

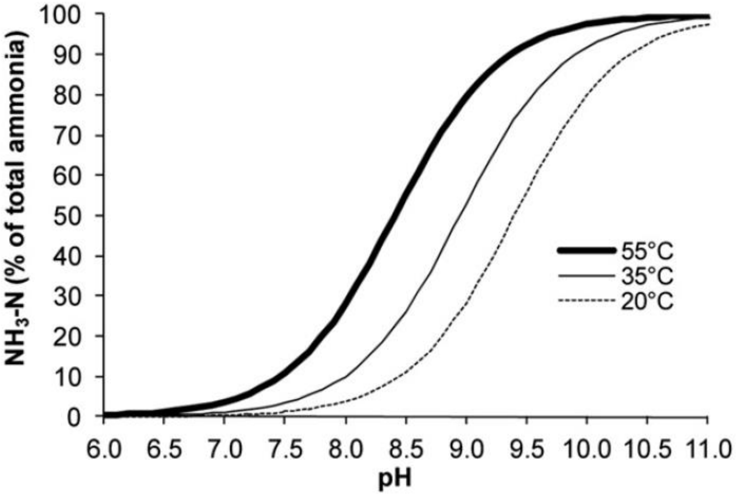

Figure 2.1 Free ammonia and ammonium percentages present in solution at 20, 35 and 55 °C and varying pH (Fernandes *et al.*, 2012)

NH_3/NH_4^+ naturally occurs in the environment from the decomposition of organics and through being excreted by plants and animals (Randall & Tsui, 2002). In these naturally occurring concentrations the NH_3/NH_4^+ system is a major nitrogen (N) nutrient source. However, in excessive concentrations NH_4^+ and, more acutely, NH_3 exhibit toxic properties to both animals and plants (Britto & Kronzucker, 2002). Furthermore, Ammonia (NH_3) is the most common liquid phase nitrogen compounds found in nature and, therefore, the most abundant nitrogen nutrient source. In addition, NH_3 is one of the most deleterious aquatic pollutants because of its toxicity in high concentrations and pervasiveness in surface water systems (Rand, 1995; USEPA, 2009).

2.2 Issues of the excess ammonia

Unfortunately, human industrial activities, including the synthesis of NH_3 for cleaning products and fertilizer as well as biological waste treatment that produces NH_3, have introduced high concentrations of ammonia into the environment. The main concern is NH_3 in aquatic systems, as terrestrial ammonia is quickly volatilized and almost all atmospheric ammonia rapidly rises and is destroyed by photolytic reactions (Randall & Tsui, 2002). An excess of ammonia in a body of water can present the following negative impacts: toxicity towards aquatic systems (fauna and flora), an increase in the abundancy of phytoplankton, and increase the oxygen demand in a receiving body of water (Beutel, 2006). Reducing the introduction of excess ammonia into all aquatic ecosystems is vital to both reduce eutrophication (the proliferation of algal blooms resulting in dead zones) and protect our drinking water sources (Conley *et al.*, 2009).

2.3 Ammonia toxicity

Free ammonia (NH_3) can traverse most biological membranes while ionized ammonia (NH_4^+) cannot; this is the reason NH_3 is much more toxic than NH_4^+. Furthermore, as temperature and pH increase so does the percentage of $N\text{-}NH_3$ versus $N\text{-}NH_4^+$ in liquid phase; this in turn increases the toxic effects of ammonia on organisms (Randall & Tsui, 2002). In aquatic chemistry, it is common to express the sum of the $N\text{-}NH_3$ and $N\text{-}NH_4^+$ as ammonia or total ammonia nitrogen (TAN) (Ding & Sartaj, 2016). Both freshwater and seawater aquatic species are intolerant to ammonia to a similar degree. Freshwater species have a tolerance limit of 2.79 mg TAN/L while seawater species possess a tolerance limit of 1.86 mg-TAN/L (USEPA, 2009).

While the amounts of ammonia tolerance differ, the nature of ammonia toxicity is similar in fish and mammals (Shingles *et al.*, 2001). High levels of ammonia in the body can produce many harmful effects mainly on the central nervous system of vertebrates, acute ammonia intoxication, and convulsion (Ip & Chew, 2010; Rao *et al.*, 1992). Some studies have indicated that the presence of high ammonia levels in the brain may cause higher levels of extracellular glutamate through stimulating glutamate release while lowering glutamate synaptic reuptake (Randall & Tsui, 2002). Also, it is known that ammonium ion displaces potassium and depolarizes neurons which, in excess, cause abnormally high activation of N-methyl-D-aspartate (NMDA) type glutamate receptors; this leads to cell death in the central nervous system due to the influx of excess calcium (Ip & Chew, 2001).

Due to an increase in knowledge and concern, the Canadian Environmental protection agency (CEPA) added ammonia to the toxic substance list in 1999 (Environment Canada, 2001). Furthermore, in 2012, the federal government regulated the maximum allowable effluent concentration of ammonia, from a WWTP with an average daily discharge greater than 100 m^3, to 1.25 mg $N\text{-}NH_3$/L at 15°C (Canada Gazette, 2012).

2.4 Ammonia inhibition

Compounding the aforementioned toxic effects is the fact that ammonia has the potential to inhibit anaerobic digestion (AD), activated sludge (AS), and other biological treatment processes (Yenigün & Demirel, 2013). Ammonia has been reported to inhibit AD and AS processes at concentrations from 1500 to 3000 mg TAN/L which renders traditional biological treatment methods far less efficient and useful (Liu *et al.*, 2012). Specifically, ammonia inhibition affects microbial activity in bioreactors which are often evaluated by looking at dehydrogenase activity, methane production rate, and volatile suspended solid (VSS) concentration (Krylova *et al.*, 1997).

Li and Zhao (1999) found that progressively increasing ammonia concentrations from 50 to 800 mg NH_4^+-N/L caused chemical oxygen demand (COD) removal in landfill leachate to decline from 95.1 to 79.1% along with a decrease in the dehydrogenase activity of the sludge from 11.04 to 4.22 μg TF/mg MLSS. Also, Lee *et al.* (2000) found that when ammonia concentrations rose above 5000 mg TAN/L dehydrogenase microbial activity decreased more than 70% for both heterotrophs and nitrifiers. Furthermore, Lee *et al.* (2000) reported that nitrifying bacteria are more sensitive to high ammonia concentrations than heterotrophic bacteria.

Akindele and Sartaj (2017) examined the effect of high concentrations of TAN on the process of anaerobic digestion of the organic fraction of municipal solid wastes. A first study was done using two shock loads of TAN and a second study examined the possibility of acclimatizing mesophilic bacteria to high ammonia concentrations by gradually increasing TAN loading over time. Both studies were done at varying pH and showed a reduction in cumulative biogas production from 32%-87% in reactors containing 7500 and 10000 mg TAN/L at pH of 7.5, 8, and 8.5. However, cumulative biogas production for a gradual increase in TAN loading vs shock loading were consistently higher.

Bioreactor landfill AD is similarly influenced by increased ammonia levels as leachate recirculation causes ammonia accumulation from the ammonification process of biodegradation (Yenigün *et al.*, 2013). Because landfill leachate is so diverse and complex in composition, high concentrations of ammonia in recirculated leachate can inhibit anaerobic bacterial activity in doses as low as 1100 mg NH_3-N/L at a pH of 8 (Hansen *et al.*, 1998).

2.5 Ammonia concentrations

Landfill leachate can contain a wide range of ammonia concentrations because of the variability in landfilled waste, landfill age, and climate (precipitation and evaporation). Landfill leachate has been reported to contain from 0.2 to 13000 mg NH_3-N/L (Renou *et al.*, 2008). Table 2.1 summarizes the range of TAN concentration from different landfill sites. As previously stated in section 2.4, ammonia is mainly produced from the ammonification process during the biodegradation of solid waste. The only removal path for ammonia in a landfill is leaching, which produces leachate, as there is no mechanism for its degradation under methanogenic conditions (Burton & Watson-Craik, 1998). A German study was conducted using 50 landfills; the results show no significant decrease of ammonia concentrations up to 30 years after a landfill's closure (Ehrig, 1989). With this in mind, coupled with potentially high concentrations, it should be no surprise that ammonia is considered to be the most significant long-term pollutant found in landfill leachate (Belevi & Baccini, 1989; Robinson *et al.*, 1995).

Table 2.1 Ammonia concentrations in landfill sites (Adapted from Renou *et al.*, 2008)

Age	Landfill Site	TAN (mg/L)	Reference
Y	Canada	42	(Henry *et al.*, 1987)
Y	China, Hong Kong	2260	(Lau *et al.*, 2001)
Y		3000	(Lo, 1996)
Y	China, Mainland	630-1800	(Wang & Shen, 2000)
Y	Greece	3100	(Tatsi *et al.*, 2003)
Y	Italy	3917	(Di Palma *et al.*, 2002)
Y		5210	(Lopez *et al.*, 2004)
Y	South Korea	1682	(Im *et al.*, 2001)
Y	Turkey	1120-2500	(Timur & Özturk, 1999)
Y		2020	(Ozturk *et al.*, 2003)
Y		1946-2002	(Çeçen & Aktaş, 2004)
MA	Germany	884	(Baumgarten & Seyfried, 1996)
MA		800	(van Dijk & Roncken, 1997)
MA	Greece	940	(Tatsi *et al.*, 2003)
MA	Italy	1330	(Frascari *et al.*, 2004)
MA	Poland	743	(Bohdziewicz *et al.*, 2001)
MA	Taiwan	5500	(Wu *et al.*, 2004)
MA	Turkey	1270	(Kargi & Pamukoglu, 2003a)
O	Brazil	800	(Silva *et al.*, 2004)
O	Finland	159	(Hoilijoki *et al.*, 2000)
O		330-560	(Marttinen *et al.*, 2002)
O	France	430	(Trebouet *et al.*, 1999)
O		0.2	(Tabet *et al.*, 2002)
O		295	(Gourdon *et al.*, 1989)
O	South Korea	1522	(Cho *et al.*, 2002)
O	Turkey	1590	(Uygur & Kargi, 2004)

Y: young MA: mature O: old

2.6 Treatments for high concentration ammonia removal

Landfill leachate's high concentration mixture of toxins and contaminants necessitates treatment before it can be discharged into sewer or surface water systems. Regrettably, a universal treatment solution covering all of the toxins and contaminants found in leachate has not yet been found. At present, a combination of different techniques must be used to mediate all of the potentially ill effects associated with landfill leachate (Wiszniowski *et al.*, 2006).

High concentration ammonia removal from an aqueous solution can be classified into four main groups (Renou *et al.*, 2008):

1) liquid transfer: mix contaminated sewage with municipal sewage to treat at a WWTP

2) biological treatments: aerobic and anaerobic processes

3) chemical methods: chemical precipitation, sorption (adsorption and ion-exchange), and ultrasound*

4) Physical methods: air stripping, microwave, and ultrasound*

*ultrasound has both chemical (oxidation) and physical (pyrolysis) removal pathways but for the purpose of this thesis will be presented under physical methods.

Historically, the preferred method has been to mix landfill leachate with municipal sewage and treat them together at a WWTP. This preference can be attributed to either a low ammonia concentration in the landfill leachate or a bias towards lowering operating and maintenance costs (Ahn *et al.*, 2002). Diamadopoulos *et al.* (1997) found the optimal ratio of leachate to total wastewater to be 1 to 9. This ratio was found using a sequencing batch reactor (SBR) which has filling, anoxic, aerobic, and settling phases. The results indicated a maximum of 95% BOD and 50% ammonia removal. A different study performed by Çeçen and Aktaş (2001) found that COD and ammonia removal decreased with an increase of the leachate to sewage ratio. Liquid transfer suffers from a lack of pre-treatment and thus does not mitigate the ill-effects of heavy metals and high ammonia concentrations. This leads to the inhibition of microorganisms critical to a properly functioning WWTP (Çeçen & Aktaş, 2004).

2.6.1 Biological treatment

Biological treatments (aerobic or anaerobic) are broadly used when leachate contains ammonia concentrations in low to mid ranges. Biological treatments are favourable, with the right toxin levels, because of its comparatively simple operation and high cost-effectiveness. Because of their wide use, biological processes have been thoroughly studied and it is known that a high BOD:COD (>0.5) is needed to effectively remove ammonia from an aqueous solution (Renou *et al.*, 2008). Biological nitrogen removal includes three main processes: ammonification, nitrification/denitrification (aerobic), and anammox (anaerobic) (Metcalf & Eddy, 2014).

Ammonification occurs early in the biodegradation process and is a precursor to nitrification/denitrification and anammox. Ammonification is the enzymatic transformation of organic nitrogen into ammonia nitrogen by way of breaking down larger organic nitrogen-containing molecules into inorganic ammonia.

Nitrification begins when ammonia is oxidized in the presence of Nitrosomonas bacteria to produce nitrite, then, in the presence of Nitrobacter, nitrite is oxidized to produce nitrate. Eq. (2.2) shows the conversion of ammonia to nitrate under aerobic conditions. Denitrification is the next step of the nitrification/denitrification process. The complete process is shown in Eq. (2.3) (Metcalf & Eddy, 2014).

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \ [\Delta G'_0 = -350 \text{ kJ/mol}] \tag{2.2}$$

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2 \tag{2.3}$$

Nitrate is reduced to nitrogen gas by an assortment of denitrifying bacteria, including: Lactobacillus, Pseudomonas, Acinetobacter, Alcaligenes, Thiobacillus, Hyphomicrobium, and Spirillum (anoxic conditions) (Metcalf & Eddy, 2014).

Biological nitrification/denitrification is undoubtedly the most cost-effective process to remove ammonia nitrogen from an aqueous solution. However, this cost-effectiveness is only under optimal conditions, which is rarely the case when dealing with landfill leachate. The presence of high concentrations of TAN and its inhibitory effects, AOXs (adsorbable organic halogens), PCBs (polychlorinated biphenyls), PAHs (polyarmatic hydrocarbons), and biorefractory organics (humic substances) severely limits the performance of this process. Furthermore, microbial inhibition from high ammonia concentrations is always a factor (Lema *et al.*, 1988). In addition, heterotrophic bacteria, which consume organic matter in aqueous solution (ammonification), inhibit the activity and growth of nitrifying bacteria (Jorgensen & Weatherley, 2003). The issue of poor removal efficiency is further compounded when dealing with leachate generated from mature landfills because of its low BOD:COD (Wiszniowski *et al.*, 2006).

Anaerobic ammonium oxidation (anammox) process is a new and potentially cost-effective alternative to aerobic nitrification/denitrification. The advantage of using an anaerobic method is the elimination of the need to aerate, which accounts for the bulk of operational costs associated with aerobic nitrification/denitrification (Van de Graaf *et al.*, 1995). Eq. (2.4) shows the conversion of ammonium to nitrogen gas under anaerobic conditions (Metcalf & Eddy, 2014).

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O\ [\Delta G'_0 = -357\ kJ/mol] \qquad (2.4)$$

Strous *et al.* (1997) successfully removed ammonia from digestion effluent sludge using an anammox process in a fluidized-bed reactor. They found that 82% of ammonia was removed along with 99% of nitrite with a maximum nitrogen conversion rate of 0.7 kg/(m^3·day) during a 150-day operational cycle.

Unfortunately, the biochemistry of anammox bacteria is not fully understood and the main drawback of this process is slow and variable bacteria growth rates – anywhere from a few months to a couple of years is needed for an anammox reactor to reach its maximum design capacity (Trigo *et al*., 2006; Kuenen, 2008).

2.6.2 Chemical precipitation

For some time, chemical precipitation has been the industry standard being used to treat both ammonia and heavy metal contaminated wastewater. A wide range of industrial applications exist spanning from tannery effluent to WWTP sludge liquor (Tünay *et al.*, 1997). For highly contaminated wastewater, like landfill leachate, chemical precipitation can be used in conjunction with biological methods as a pretreatment method (Renou *et al.*, 2008). The basic chemical reaction that forms magnesium ammonium phosphate (MAP) is shown below in Eq. (5).

$$MgCl_2{\cdot}6H_2O + Na_2HPO_4{\cdot}12H_2O + NH_4^+ \rightarrow MgNH_4PO_4{\cdot}6H_2O{\downarrow} + 2NaCl \qquad (2.5)$$

A 2001 study by Li and Zhao found that the addition of $MgCl_2{\cdot}6H_2O$ and $Na_2HPO_4{\cdot}12H_2O$ with a $Mg:NH_4:PO_4$ of 1:1:1 at a pH of 8.5-9 reduced the NH_4^+-N concentration from 5600 to 110 mg/L within 15 minutes. Yangin *et al.* (2002) found a maximum NH_4^+-N reduction of 66% at a pH of 9.3 at the stoichiometric ratio compared to 86% when using the same pH above the stoichiometric ratio; this study used MAP precipitation after the wastewater and landfill leachate mixture (2% and 3% leachate) had been anaerobically treated in an up-flow sludge blanket reactor (UASB). Also, Ozturk *et al.* (2003) researched the application of struvite precipitation to remove ammonia from anaerobically treated effluents using a Mg:NH_4:PO_4 of 1:1:1. They found NH_4^+-N removal rates of 85% at a pH of 9.2, 20% at a pH of 10 to11, and 72% at a pH of 12.

While chemical precipitation is an effective means of removing ammonia from wastewater and leachate it requires a constant input of chemicals, which can be costly. Also, chemical precipitation produces large amounts of solid waste (sludge) and the precipitate formed has high concentrations of ammonia.

2.6.3 Sorption

Sorption is used here as a catch-all term referring to the removal of a compound from one phase (gas, solid, or liquid) to another (Sposito, 2008) including absorption, adsorption, and ion-exchange; the latter two will be discussed in the following sections.

2.6.3.1 Adsorption

Adsorption is a mass transfer operation that targets certain liquid constituents and transfers them to a solid phase (Metcalf & Eddy, 2014). More specifically, adsorption can capture dissolved organic and inorganic substances to a solid surface through physical or chemical bonds. Many pollutants can be adsorbed including, but not limited to: heavy metals, COD, and ammonia (Li *et al.*, 2008).

Activated carbon (AC) is the most widely used adsorbent as it has a complex pore structure with an inner surface area greater than 400 m^2/g (Li et al, 2008). AC is commonly used as an advanced stage in an integrated chemical, physical, and biological method (Foo and Hameed, 2009). Aziz *et al.* (2012) researched the equilibrium adsorption capacity (Q_e) of powdered activated carbon (PAC) for COD and ammonia removal from semi-aerobic landfill leachate and found it to be 15.41 mg/g and 6 mg/g, respectively. Similarly, Halim *et al.* (2010) found the solid phase concentrations of COD and ammonia were 37.88 mg/g and 6.08 mg/g, respectively. PAC is considered to be more efficient for organics removal due to its non-polar surface area but suffers when trying to remove ammonia, a highly polar molecule.

2.6.3.2 Ion-exchange

Ion-exchange is commonly applied in water softening and water purification processes and involves a reversible exchange of ions between liquid and solid phase. More specifically, the mobile ions of an ion-exchange resin (IER) can be replaced by similarly charged ions from the surrounding aqueous solution (Bashir et al., 2010). Cation and anion resins are the most common with cation resins attracting positively charged ions (Ca^{2+}, Mg^{2+}, NH_4^+, etc.) and anion resins attracting negatively charged ions (Cl^-, NO_3^-, etc.) (Hendershot *et al.*, 2007).

Solid ion-exchangers can be categorized as natural-inorganic particles (ex: zeolite) and synthetic-organic resins (ex: Amberlite IR120 H). Synthetic-organic resins are produced with high-molecular weight polyelectrolytes and contain a cross-linked polymer matrix attached by covalent bonds (Cheremisinoff, 2001). Synthetic ion-exchange resins (SIER) can be customized allowing several advantages over natural zeolite including faster exchange rate, longer life, and higher ion exchange capacity (Letterman, 1999).

IERs can be further classified in to the following four groups (Hendershot *et al.*, 2007):

- Strongly basic, typically featuring quaternary amino groups
- Weakly basic, typically featuring primary, secondary, and/or ternary amino groups
- Strongly acidic, typically featuring sulfonic acid groups
- Weakly acidic, typically featuring carboxylic acid groups.

Bashir *et al.* (2010a) compared the ammonia removal performance of different mobile cation forms using a SIER (INDION 225 Na). It was found that the H+ form had a higher removal efficiency than the Na+ form (92.8% and 72%, respectively). Furthermore, a 94.2% removal of ammonia was accomplished in 6 minutes by INDION 225 Na strong acid cation exchanger from a synthetic ammonia solution with an initial concentration of 1000 mg/L.

Ding and Sartaj (2015; 2016) researched the use of zeolite, a popular adsorbent with ion-exchange properties, and Amberlite IR120 H, a synthetic ion-exchange resin, in the removal of aqueous ammonia. For zeolite, an ammonia removal of up to 87% was seen at neutral pH, dose of 150 g/L, and an initial ammonia concentration of 1000 mg TAN/L. For Amberlite IR120 H, an ammonia removal of up to 84% was seen at neutral pH, dose of 100 g/L, and an initial ammonia concentration of 1000 mg TAN/L. The optimum adsorption capacities of zeolite and Amberlite IR120 H were 22.90 mg/g at pH 7 and 28.78 mg/g at pH 6, respectively, with an initial ammonia concentration of 3000 mg TAN/L.

An advantage that IERs have over chemical precipitation is that they can be regenerated by acid, base, or salt solutions at certain concentrations. The equilibrium exchange capacity decreases less than 2.5% with each regeneration, which extends the functional lifespan of SIER (Lin & Wu, 1996). However, the reuse of IERs within a WWTP still poses a logistical problem with regards to their removal from the system for regeneration.

2.6.4 Air stripping

Air stripping is one of the most common approaches for eliminating high concentration of ammonia existing in wastewater (Marttinen *et al.*, 2002). The principle of the air stripping process is relatively simple; it transfers free ammonia, which is a volatile component in liquid phase, into an air stream (Hasar *et al.*, 2009;

Metcalf & Eddy, 2003). The air stripping process is generally operated in one of the following ways (Hasar *et al.*, 2009):

1) Free stripping
    - Uses a magnetic stirrer to introduce air into an aqueous solution
2) Forced stripping
    - Uses an air diffuser to introduce air into an aqueous solution
3) Combination of both free and forced stripping

The efficacy of this process is highly dependent on the retention time of the liquid being stripped and the pH. Table 2.2 summarizes the efficiency of air stripping in removing ammonia from landfill leachate based on previous studies done by Cheung *et al.* (1997), Marttinen *et al.* (2002), Ozturk *et al.*, (2003), and Silva *et al.* (2004).

Table 2.2 Air Stripping Process Efficiency Comparison

TAN (mg/L)	Stripping time (hrs)	TAN Removal (%)	Reference
556-705	24	76-93	(Cheung *et al.*, 1997)
72-220	24	89	(Marttinen *et al.*, 2002)
1025	24	85	(Ozturk *et al.*, 2003)
750-800	96	99.5	(Silva *et al.*, 2004)

A removal of 89% TAN was achieved by Marttinen *et al.* (2002) at a pH of 11, a temperature of 20°C, stripping time of 24 hours, and an aeration rate of 10 L/hr. Cheung *et al.* (1997) reported up to 93% TAN removal with a higher initial ammonia concentration and same stripping time. Silva *et al.* (2004) reported 99.5% TAN removal with a similar high initial concentration using a 96 hour stripping time. Ozturk *et al.* (2003) accomplished 85% ammonia-nitrogen removal at a pH of 12 and 24-hour retention time, although no significant removal occurred after 17 hours.

The major drawbacks of ammonia air stripping are the energy cost associated with running the air pumps and the production of air-born ammonia, which is a known irritant.

2.6.5 Membrane filtration

Membrane filtration is classified by pore size, as follows: microfiltration (0.1-10μm), ultrafiltration (2-100 nm), nanofiltration (1-2 nm), and reverse osmosis (<1 nm) (Laitinen *et al.*, 2006). Regardless of pore size, all membrane filtration uses increased pressure to force wastewater through a membrane.

Nanofiltration (NF) membranes can remove multiple pollutants (organic, inorganic, and microbial) with a high rejection of sulfate ions and dissolved organic matter and a low rejection of chloride and sodium (Peters, 1998). Using different membrane geometries (flat, spiral wound, and tubular), pressures ranging from 6 to 30 bar, and an average velocity of 3 m/s yielded comparable ammonia removals of approximately 50% (Rautenbach & Mellis, 1994; Trebouet *et al.*, 1999; Trebouet *et al.*, 2001). Unfortunately, the variability of wastewater can lead to membrane fouling from dissolved organic and inorganic molecules along with colloidal and suspended particles (Braghetta *et al.*, 1998; Trebouet *et al.*, 2001).

Reverse Osmosis (RO) membranes show the most promise due to their extremely small pore size and capability to completely remove salt from aqueous solutions (Bilstad & Madland, 1992; Linde *et al.*, 1995). Di Palma *et al.* (2002) reported ammonia reductions greater than 97% at a pH of 6.4 using two different RO membranes. Moreover, RO membranes can be cleaned more easily and efficiently due to their surface characteristic, which lessens the impact of membrane fouling (Peters, 1998).

In order to use membrane filtration, extensive pretreatment and chemical cleaning is required. If not vigilantly monitored and maintained, the lifecycle of the membrane and process productivity decrease significantly. Furthermore, large amounts of unusable concentrate are generated and must be disposed (Rautenbach *et al.*, 2000).

2.6.6 Microwave

Microwaves (MW) are electromagnetic waves whose frequency lies somewhere between 300 MHz and 300 GHz. MW aligns polar chains of molecules to the direction of the electronic field which causes rapid dipole orientation changes in phase with the oscillating electromagnetic wave. This dipole movement is resisted by intermolecular bonds producing heat (Coelho, 2012). MW molecular-level heating leads to homogeneous and rapid thermal reactions, which is desirable in wastewater treatment (Menendez *et al.*, 2002). Also, due to the electromagnetic properties of MW, selective heating of materials with higher dielectric factors is possible (Remya & Lin, 2011).

Lin *et al.* (2009b) found that there are two general removal mechanisms when removing ammonia with MW: thermal and non-thermal. Thermal removal occurs due to volatilization, while non-thermal removal occurs due to the breakdown of molecular bonds between NH_3^+ and H_2O; both removal mechanisms are tied to the rapid dipole movement that MW produces.

Lin *et al.* (2009a) reported that pH and radiation time are important parameters affecting ammonia removal from wastewater by MW. These findings are consistent with literature regarding the increasing fraction of NH_3^+, which is the more volatile form of ammonia, with a rise in temperature and pH. A maximum ammonia removal of 98% was recorded at pH 11, duration of 3 minutes, and power output of 650 W. Also, a comparative test was done comparing the contribution of thermal and non-thermal mechanisms; using a pH of 11 conventional heating removed around 25% ammonia, while MW, operating at a power output of 350 W, removed 45%.

Dong and Sartaj (2016a; 2016b) reported an ammonia removal of 81.7% and 70% at pH

10.5, power output 650 W, duration of 120s, and 10 minutes of aeration for synthetic and actual leachate, respectively. Furthermore, it was concluded that, with the aforementioned conditions, thermal mechanisms contributed 39% of the total removal, non-thermal 28%, and aeration 33%.

Recently, MW enhanced oxidation has been investigated as a way to break down complex pollutants with great success (Qi *et al.*, 2014; Yang *et al.*,2009; Ju *et al.*, 2009). MW increases the formation of free radicals from oxidants (ex: H_2O_2, $S_2O_8^{2-}$, etc.) and yields higher reaction temperatures in less time, increasing removal efficiency (Zhang *et al.*, 2007; Remya & Lin, 2011). Unfortunately, there is yet to be targeted research as to the efficiency of ammonia removal using this method.

2.6.7 Ultrasound

The effects of ultrasound were first discovered during SONAR testing, where it was observed to be deadly to various fish populations. Research in the 1960s brought more clarity to ultrasonic mechanisms involving microbial cells, namely cavitation and the corresponding physical, sheer forces and localized heating, and chemical, free radical formation, effects (Mason & Tiehm, 2001).

Ultrasound is sound waves that oscillate at frequencies above 16 kHz or 16000 cycles per second. As these sound waves pass through a liquid with high enough energy ($> \frac{1}{3}$ W/cm^3) they create a cycle of alternating adiabatic compression and rarefaction. During rarefaction, there is adequate negative pressure to produce cavitation/microbubbles which encapsulate dissolved liquid vapor or gas. Once these microbubbles reach a critical size, which is dependent on the liquid and sound frequency applied, they collapse violently releasing the sonic energy as extremely high localized pressure and temperature, up to 1000 atm and 5000K, respectively (Adewuyi, 2001).

Cavitation in a liquid, along with pressure and temperature increase, results in the generation of free radicals (sonolysis). Furthermore, in the presence of oxygen, sonolysis produces hydroperoxyl radicals ($HO_2\cdot$) which acts as an oxidizing agent.

The formation of free radicals and hydrogen peroxide (H_2O_2) combined with the physical violence of cavitation allows ultrasound to be used as an effective industrial disinfectant method (Mason & Tiehm, 2001). Figure 2.2 shows how cavitation on a solid surface results in a liquid jet stream.

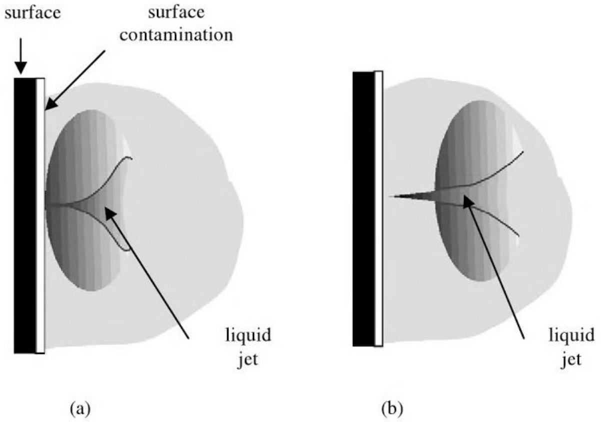

Figure 2.2 Liquid jet (a) on a surface (b) close to a surface (Mason & Tiehm, 2001)

The local liquid jet stream produced can have a velocity of up to 300 m/s which can damage nearby microorganisms, solids, and surfaces. Also, away from the bubble collapse, acoustic shockwaves, microsteaming, and sonoluminescence can occur; all of these effects contribute to ultrasonic disinfection (Gibson *et al.*, 2008).

Figure 2.3 illustrates both the chemical and physical effects produced by aqueous sonication along with their corresponding zones in the cavitation process. It can be seen that the net effect is the release of heat, free radicals, hydrogen peroxide, nitrogen gas, and hydrogen gas.

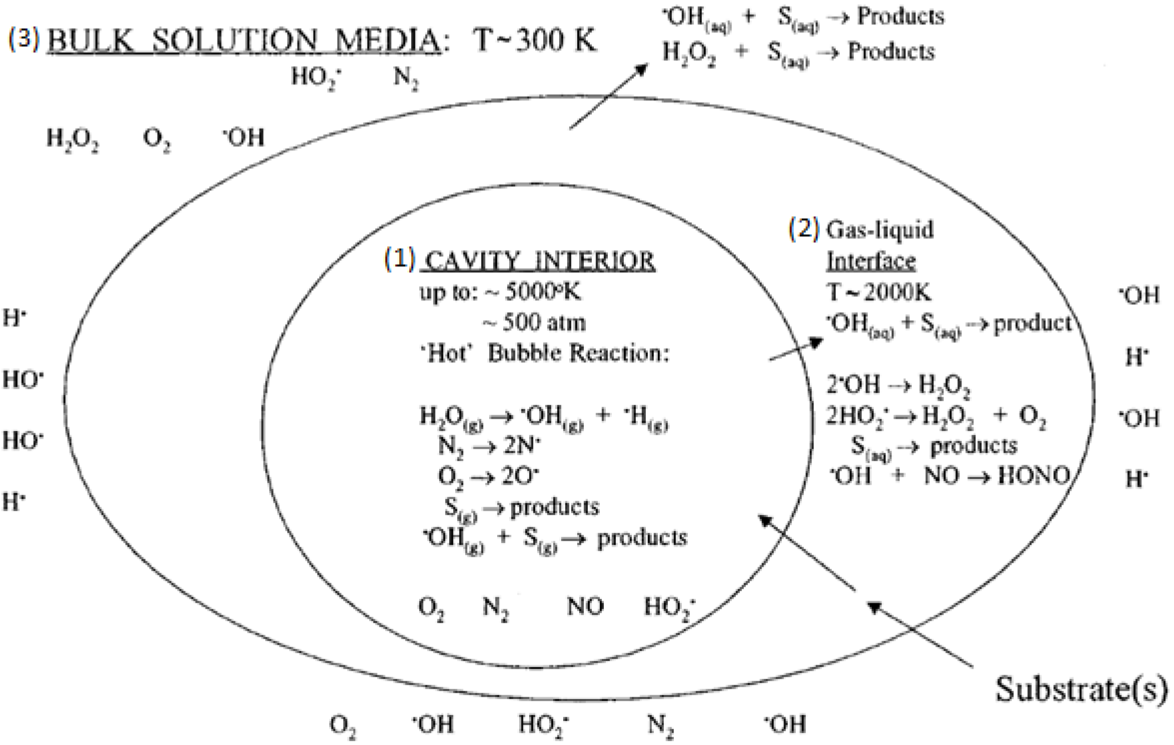

Figure 2.3 the three reaction zones of the cavitation process (Adewuyi, 2001)

Adewuyi (2001) describes the three reaction zones as follows: (1) hot, gaseous nucleus; (2) interfacial region with radial temperature gradient and local radical density; (3) bulk solution at ambient temperature.

1) In the nucleus, the extreme conditions generated by a bubble collapse cause bonds to break and dissociation as the activation energy for bond cleavage is reached. Also, the free radicals produced react with one another and form new radicals and/or diffuse into the bulk solution as oxidants.

2) In the gas-liquid interface, both free radical induced reactions and pyrolysis occur. At high solute concentrations pyrolysis dominates and at low solute concentrations free radical reactions dominate.

    - At the interface between the bubble and bulk liquid the species produced in the cavitation bubble react with the chemicals in the liquid for the first time. This zone is estimated to extend approximately 200 nm from the bubble's surface and lasts less than 2 μs.

3) In the bulk solution, the diffused free radicals react with the substrate available. Molecules close to the cavitation bubble may be volatilized, depending on the molecules present in the solution and their associated properties.

There is a plethora of research regarding the use of ultrasound as a disinfectant but far less on the use of ultrasound as a wastewater pretreatment. However, in recent years several studies have been published applying ultrasonic treatment to eliminate high concentrations of organic matter and ammonia nitrogen from wastewater and landfill leachate (Gogate, 2008).

Wang *et al*. (2008) found that up to 96% of ammonia could be removed from filtered landfill leachate after 180 minutes of US irradiation coupled with aeration at an initial pH of 11, power input of 200 W, and initial ammonia concentration of 680 mg/L; the experiments were carried out under a constant temperature of 30°C. The ultrasonic process was proven to be input power and pH dependent with ammonia removal rates increasing with the increase of power input and pH. The removal efficiency at pH 11 was approximately eight times as high as that of pH 3. This could be explained by the fact that at pH 11, almost all the ammonia is unionized ammonia rather than ionized ammonia which does not vaporize into the cavitation bubbles. In molecular state, unionized ammonia can react inside by thermal cleavage after transforming into cavitation bubbles due to ultrasound irradiation. The main mechanism of ammonia nitrogen reduction from aqueous solutions by ultrasound appears to be the entry of ammonia molecules into the cavitation bubbles and the transformation into nitrogen molecules and hydrogen molecules via pyrolysis. This was tested by adding *n*-butyl alcohol (a scavenger of hydroxyl radicals) to the leachate in order to effectively nullify the removal of ammonia by oxidation (Wang *et al.*, 2008). However, Ozturk and Bal (2015) concluded that the main mechanism of ammonia removal was advanced oxidation of ammonia–nitrogen by hydroxyl radical generation from US.

The experimental set-up used by Wang *et al.*, (2008) is relatively simple, as shown in Fig. 2.4.

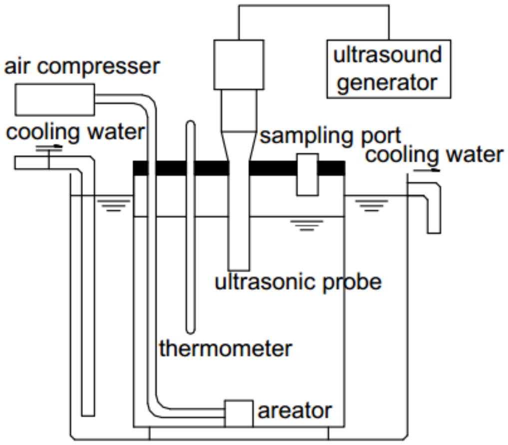

Figure 2.4 Schematic of the ultrasound set-up (Wang *et al.*, 2008)

The reactor design plays an important role in the ultrasonic irradiation process. Due to the limited penetration ability of ultrasound, as the height of liquid increases, the ammonia removal efficiency decreases. Matouq & Al-Anber (2007) reported that an optimum liquid height of 16.5 mm from the ultrasonic tip. This liquid height yielded approximately 31% ammonia removal after 90 minutes of US irradiation at an ultrasonic frequency of 2.4 MHz.

2.7 Summary and Research Gap

A wide variety of methods exist to remove high concentrations of ammonia from aqueous solutions, including landfill leachate. These methods include conventional biological nitrification/denitrification, physical adsorption, air stripping, chemical precipitation, ion-exchange, membrane filtration, microwave radiation, and ultrasound irradiation. All methods have their drawbacks: biological processes do not respond well to high ammonia levels and shock loads; air stripping, ultrasound, and microwave technologies require pH adjustment and the input of energy; Membrane fouling issue are inevitable; the costs for adsorption chemical precipitation and ion-exchange processes are relatively high and produce residuals that must be disposed of. Consequently, no single solution exists for the removal of ammonia nitrogen from highly concentrated aqueous ammonia solutions. Methods capable of reducing high levels of ammonia nitrogen from aqueous solutions, including landfill leachate, with high efficiency, relatively low cost, and minimal residuals production are highly desired.

Ultrasonic irradiation has been widely studied in industrial settings for disinfection and use as a catalyst for chemical reactions. However, few studies have been done regarding the application of US in removing ammonia nitrogen. Furthermore, there is a lack of systematic studies supported by statistical analysis. The studies that have been published show promising results. The following research is meant to build on this knowledge and provide insight into optimization through using a response surface methodology and factorial design.

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CHAPTER III
Materials & Methodology

The following chapter will explain the materials and methodology used to perform the laboratory experiments conducted for this thesis. More specifically, this chapter will explain the experimental materials, set-up, and procedure used to generate data.

3.1 Experimental Materials

The following section lists the experimental materials and equipment used to perform the experiments carried out for this thesis.

The following materials and equipment were used:

- Branson Digital Sonifier® (model 450)
- Branson 20 kHz ultrasonic converter
- Branson ½" disruptor horn
- Branson ½" disruptor horn tip
- Adjustable beaker stand
- Protective case
- 500 ml Polypropylene (PP) container with lid
- Beakers (various sizes)
- Erlenmeyer flask (various sizes)
- Distilled water (DW)
- Fisher Scientific Ammonium Chloride salt (NH_4Cl)

- Hach TNTplus 832 HR test kit
- Fisher Scientific Accumet Excel XL25 dual channel pH/ion meter
- Cole-Parmer Canada Inc. 20L/120V StableTemp hot water bath
- Encapsulated magnetic stir bar
- Mettler-Tuledo AL204 scale
- Mettler PC4400 DeltaRange scale
- Gilson Pipetman P200 & P1000 pipettes
- 0.2 ml & 1 ml pipette tips
- Kimtech Kimwipes
- Fisher Scientific Thermix 120 MR magnetic stirrer
- Fisher Scientific 10N Sodium Hydroxide (NaOH)
- Thermo Scientific Survival Legend T+ centrifuge
- 50 ml centrifuge tubes
- Top Fin AIR-500 aquarium air pump
- Top Fin aeration rocks
- Panasonic KX-P1150 Multi-Mode Printer
- Hach DR5000 spectrophotometer

3.2 Experimental Setup

The following describes the main experimental setup used for the sonication of samples. Figure 3.1 illustrates the main experimental setup as a schematic and also a photograph of the actual setup.

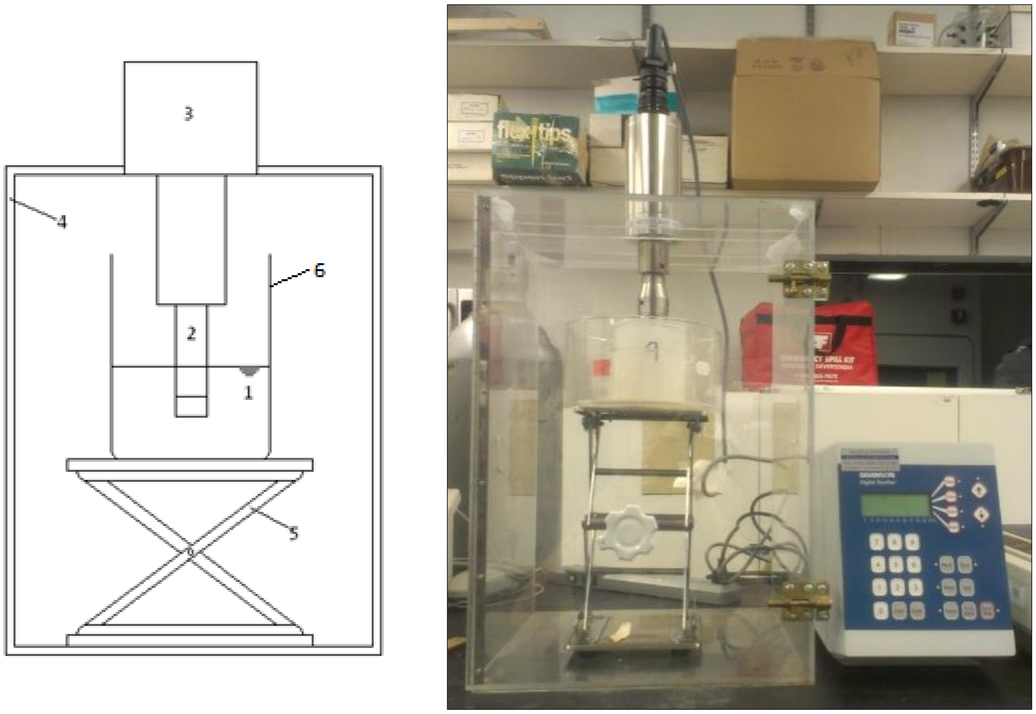


Figure 3.1 [left] Schematic of experimental setup. (1) NH_3 solution or leachate (2) disruptor horn and tip (3) ultrasonic converter (4) protective case (5) adjustable stand (6) 500 ml PP container. [right] photograph of experimental setup

3.3 Experimental Procedure

This section will outline the procedures used during experimentation, including: general procedures, synthetic NH_3 solution tests, and leachate tests.

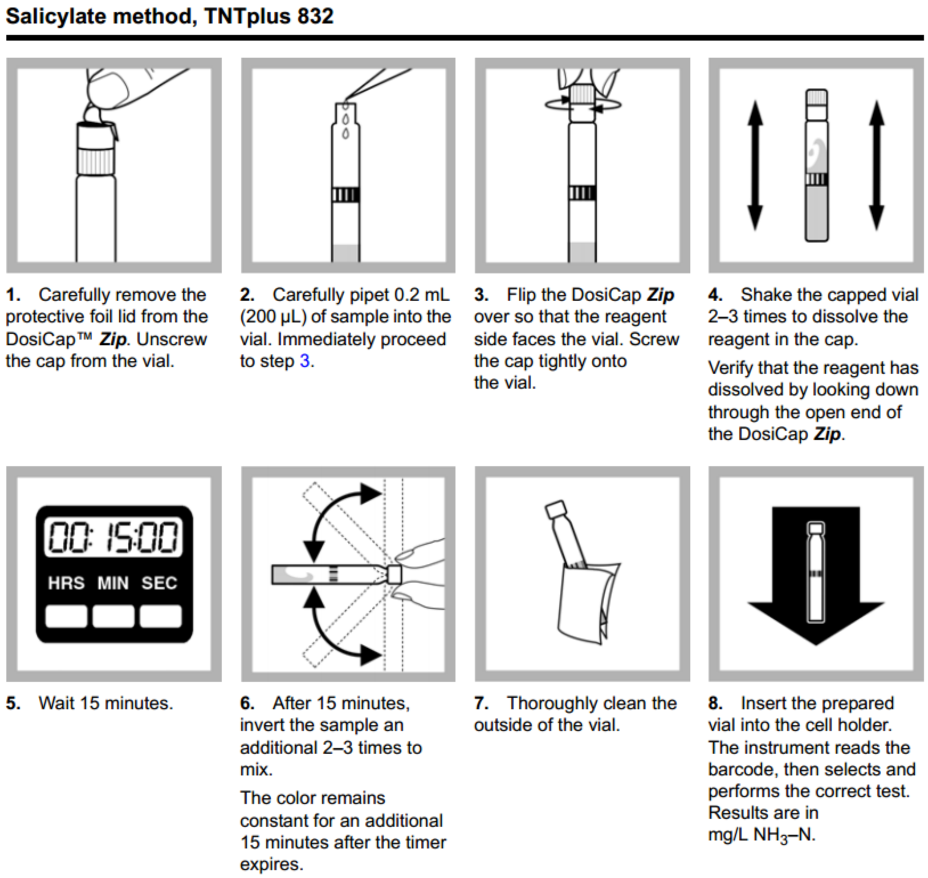
3.3.1 pH Adjustment

The pH adjustments were done using 10N NaOH in order to attain the desired pH values of 9, 10, and 11. A Fisher Scientific Accumet Excel XL25 dual channel pH/ion meter was used to monitor the adjustment process to the nearest tenth of a pH. The sample was stirred at a low speed, 3 on the speed dial, using a magnetic stirrer and magnetic stir bar to evenly distribute the NaOH within the sample while minimizing NH_3 volatilization.

3.3.2 Ammonia Concentration Testing

The following describes the procedure used in order to determine the concentration of ammonia nitrogen (mg TAN/L as NH_3-N) in a given sample.

NH_3 testing was carried out using the Hach TNTplus 832 HR testing kit coupled with a Hach DR5000 spectrophotometer. First, the sample was diluted, 1:100 for a sample with a low mg TAN/L initial concentration or 1:130 for a sample with a high mg TAN/L initial concentration, to ensure that the reading would fall within the detection range of the test kit. Second, the procedure supplied with the testing kit was followed as seen in Figure 3.2 with step 8 using the Hach DR5000 spectrophotometer.



Salicylate method, TNTplus 832

1. Carefully remove the protective foil lid from the DosiCap™ ***Zip***. Unscrew the cap from the vial.
2. Carefully pipet 0.2 mL (200 µL) of sample into the vial. Immediately proceed to step 3.
3. Flip the DosiCap ***Zip*** over so that the reagent side faces the vial. Screw the cap tightly onto the vial.
4. Shake the capped vial 2–3 times to dissolve the reagent in the cap.
   Verify that the reagent has dissolved by looking down through the open end of the DosiCap ***Zip***.
5. Wait 15 minutes.
6. After 15 minutes, invert the sample an additional 2–3 times to mix.
   The color remains constant for an additional 15 minutes after the timer expires.
7. Thoroughly clean the outside of the vial.
8. Insert the prepared vial into the cell holder. The instrument reads the barcode, then selects and performs the correct test. Results are in mg/L NH_3–N.

Figure 3.2 TNTplus 832 testing method (Hach Company, 2012)

3.3.3 Synthetic Solution Tests

This section outlines the procedures used during the synthetic solution testing which includes: test design, ammonia solution fabrication, ultrasonic testing, heat testing, and volatilization testing.

3.3.3.1 Test Design

Initial ammonia concentrations of 3000 and 5000 mg TAN/L were used as these concentrations are where the inhibitory effects of ammonia in the treatment of landfill leachate and anaerobic digestion process have been reported to occur. A 3-level factorial design was used for the 3000 mg TAN/L synthetic solution testing in order to help clarify the boundaries of the test. The 3 factors examined were the following: ultrasonic amplitude, ultrasonic duration, and initial solution pH. Ultrasonic amplitude corresponds to power output, with 100% amplitude equaling, on average, 128 W. All tests were done in triplicate, which totalled 81 tests. The levels associated with each factor can be seen below:

Table 3.1 3000 mg TAN/L synthetic solution experimental test design

Factor	Level		
	-1	0	1
Amplitude (%)	20	60	100
Duration (min)	5	15	25
pH	9	10	11

The 5000 mg TAN/L experimental design was made after the testing for the 3000 mg TAN/L was completed and the testing method refined. The new test design consisted of a pseudo 2-level factorial design using the same factors as in the 3000 mg TAN/L tests. The bottom level of both sonication duration and initial pH were dropped from the experimental design as they were deemed unnecessary – the final ammonia concentrations associated with these levels were above the determined cut-off of 1500 mg TAN/L (low-end of anaerobic inhibition). All tests were done in triplicate, which totalled 36 tests. Table 3.2 shows the test design used for the 5000 mg TAN/L tests.

Table 3.2 5000 mg TAN/L synthetic solution experimental test design

Factor	Level		
	-1	0	1
Amplitude (%)	20	60	100
Duration (min)	-	15	25
pH	-	10	11

3.3.3.2 Ammonia Solution Fabrication

The following chemical formula was used to determine the amount of Fisher Scientific analytical grade ammonium chloride (NH_4Cl) needed to attain the desired TAN concentration levels (low and high):

$$NH_4Cl \leftrightarrow NH_4^+ + Cl^- \tag{3.1}$$

After using equation 3.1 to determine the weight of NH_4Cl needed to obtain solutions with TAN concentrations of approximately 3000 and 5000 mg/L, a Mettler-Tuledo AL204 scale was used to obtain this weight to the nearest hundredth of gram. Next, the NH_4Cl was added to approximately 500 ml of distilled water in an Erlenmeyer flask and swirled gently by hand until the NH_4Cl was observed to be fully dissolved. The remaining volume of distilled water was then added to achieve the desired ammonia concentration, covered, and mixed gently by hand to ensure minimal ammonia loss due to air stripping. A fresh ammonia bulk solution was made for each laboratory session with the total volume used calculated based on the number of tests to be conducted in that session.

3.3.3.3 Ultrasonic Testing

After being made, the synthetic TAN solution was tested for its ammonia concentration (mg N-NH_3/L) and pH (see 3.3.2 and 3.3.1, respectively). Then, the pH of the solution was adjusted to one of the initial levels outlined in Table 3.1 and was again tested for its ammonia concentration (see 3.3.2). Next, approximately 165 ml of the adjusted solution was transferred to a 500 ml PP container using a Mettler PC4400 DeltaRange scale and the temperature was recorded. After, the transferred solution was sonicated using a Branson digital sonifier 450 for one of the three durations and amplitudes in Table 3.1 with the temperature recorded at completion. The sonicated solution was allowed to cool back down to its initial temperature and was then weighed to determine the water loss during sonication. The weight lost in water vapour was then added back to the sonicated solution using distilled water. Afterwards, the pH was measured then adjusted back to the initial value (9, 10, or 11) and the final concentration was measured (see 3.3.1 and 3.3.2, respectively). The pH adjusted ammonia concentration was then compared to the final ammonia concentration to determine removal efficiency.

3.3.3.4 Heat Volatilization Testing

The same procedure was used as in section 3.3.3.3, however, sonication was replaced by heating the adjusted solution in a Cole-Parmer Canada Inc. 20L/120V StableTemp hot water bath in order to replicate the final temperature of a solution after sonication for a given duration. The hot water bath temperatures used to correspond with each sonication test and solution are given below:

Table 3.3 3000 mg TAN/L synthetic ammonia solution hot water bath temperature settings

Hot Water Bath Temperature (°C)	Ultrasound Amplitude (%)	Duration (min)
78	100	5
		15
		25
70	60	5
		15
		25
50	20	5
		15
		25

Table 3.4 5000 mg TAN/L synthetic ammonia solution hot water bath temperature settings

Hot Water Bath Temperature (°C)	Ultrasound Amplitude (%)	Duration (min)
78	100	15
		25
70	60	15
		25
50	20	15
		25

3.3.3.5 Atmospheric Volatilization Testing

The same procedure was used as in section 3.3.3.3, however, sonication was replaced by leaving the adjusted solution open to the room's atmosphere. Only the initial pH, initial concentration, and duration were used as conditions as there was no amplitude to adjust.

3.3.4 Leachate Tests

The following section will outline the procedures used to analyse the removal of ammonia from landfill leachate, including: test design, ultrasonic testing, heat testing, and volatilization testing.

3.3.4.1 Test Design

A 2-level factorial design was used for the leachate testing as the relevant boundaries had been discovered after conducting the experiments outlined in section 3.3.3. Furthermore, the level of pH 11 level was dropped as it was deemed inefficient to treat leachate to a pH of this level. This is due to the non-linear relationship between NaOH added and pH increase – the higher the pH the more NaOH is needed to further increase the pH. Also, the treatment of other toxic substances, namely heavy metals, generally only requires a pH from 9-10 (Ayres *et al.*, 1994). Therefore, it was deemed useful to evaluate the leachate samples more closely to real-world conditions for treatment. The 3 factors examined were the following: ultrasonic amplitude, ultrasonic duration, and leachate sample used. All tests were done in triplicate, which totaled 24 tests. The levels associated with each factor can be seen below:

Table 3.5 Leachate Experimental Factorial Design @ pH 10

Factor	Level	
	-1	1
Amplitude (%)	60	100
Duration (min)	15	25
Leachate sample	1	2

3.3.4.2 Ultrasonic Testing

The same procedure was used as in section 3.3.3.3 with the synthetic solution being substituted by leachate.

3.3.4.3 Heat Volatilization Testing

The same procedure was used as in section 3.3.3.4 with the synthetic solution being substituted by leachate. A revised version of the temperatures needed for the hot water bath can be seen below:

Table 3.6 Leachates 1 & 2 hot water bath temperature settings

Hot Water Bath Temperature (°C)	Ultrasound Amplitude (%)	Duration (min)
78	100	15
		25
70	60	15
		25

3.3.4.4 Atmospheric Volatilization Testing

The same procedure was used as in section 3.3.3.5 with the synthetic solution being substituted for leachate.

3.4 Statistical method

The statistical methods used in this thesis are explained in the technical papers shown in chapters IV and V in order to reduce repetition.

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CHAPTER IV
Technical Paper I

Ammonia Removal from High Concentration Aqueous Solution Using Ultrasonic Irradiation Process and Statistical Analysis of Operating Parameters and Thermal/Non-Thermal effects

Majid Sartaj, Andrew Tobalt, Kevin Kennedy, Rania M. Alqaralleh

Abstract

The application of ultrasonic irradiation (20 kHz) technology for removal of ammonia from aqueous solution with high initial ammonia concentration around 3000 mg/L range where the inhibitory effects of ammonia in treatment of landfill leachate and anaerobic digestion process has been reported to occur was investigated under different pH and time duration. The application of ultrasound over a short period of time (~ 15 min) was proved to be an effective method for removal of ammonia especially at higher pH values (pH > 10). The highest ammonia removal of 87.4% was obtained at pH of 11 and 25 min duration. The ammonia removal increased with increasing pH and sonication time. Statistical analysis of data demonstrated that improvements observed in increasing sonication time from 5 to 15 min were statistically significant while improvements in increasing sonication time from 15 to 25 min were not significantly different. The contribution of volatilization (samples being exposed to the air) accounted for less than 7% of the ammonia removal. Thermal effect of US was responsible for 21.1 - 52.7% of the ammonia removal while non-thermal effect of US mechanism was responsible for 44.5 - 78.8% depending on pH and sonication time.

Keywords: Ultrasonic Irradiation; Ammonia; Statistical Analysis; pH; Sonication Time

4.1 Introduction

Increasing human population, industrialization and the subsequent anthropogenic sources of pollution such as agricultural, industrial, and municipal wastewaters contribute to the degradation of water resources (Arabgol *et al.*, 2016; Ozturk, 2015). Discharge of inadequately treated domestic, industrial and agricultural wastewaters with high ammonia–nitrogen contents can result in eutrophication and algal blooms, depletion of dissolved oxygen, and toxicity to fish even at low concentrations in receiving water bodies, and inhibitory effects on microbial activity of microorganisms responsible for biological treatment of wastewater (Ozturk & Bal, 2015; Dong & Sartaj, 2016a; Alqaralleh *et al.*, 2015; Faryadi *et al.*, 2015; Randall & Tsui, 2002; Lee & Chung, 2000). High levels of ammonia in the body can produce many harmful effects mainly on the central nervous system of vertebrates, acute ammonia intoxication, and convulsion (Ip & Chew, 2001; Rao *et al.*, 1992). Some studies have indicated that the presence of high ammonia levels in the brain may cause higher levels of extracellular glutamate through stimulating glutamate release while lowering glutamate synaptic reuptake (Randall & Tsui, 2002). Also, it is known that ammonium ion displaces potassium and depolarizes neurons which in excess causes abnormally high activation of NMDA type glutamate receptors; this leads to cell death in the central nervous system due to the influx of excess calcium (Ip *et al.*, 2001).

Total ammonia nitrogen (TAN) exists in liquid phase either in unionized form (NH_3) or ionized form (NH_4^+), with toxicity being mainly attributed to NH_3 form (Nair *et al.*, 2014; Clement & Merlin, 1995). Free ammonia (NH_3) can traverse most biological membranes while ionized ammonia (NH_4^+) cannot; this is the reason NH_3 is much more toxic than NH_4^+.

NH_3 is a volatile compound with a boiling point of -33.4°C and, like other volatile compounds, is sensitive to pressure and temperature changes (Chang & Cruickshank, 2005). The NH_3/NH_4^+ equilibrium (pKa of NH_4^+ is 9.25 at standard conditions) also depends on pH; the higher the pH of a solution or more basic, the higher the concentration of NH_3 (Ding & Sartaj, 2016; Benjamin, 2002). USEPA fresh water quality criteria for ammonia have been set at 17 mg TAN/L (acute) and 1.9 mg TAN/L (chronic) at a pH of 7 and temperature of 20 °C (USEPA, 2013). Canadian Environmental Protection Agency has set the maximum concentration of un-ionized ammonia in the effluent from any wastewater treatment plant with an average daily discharge greater than 100 m^3 to 1.25 mg/L as NH_3–N at (15±1°C) (Canada Gazette, 2012).

The leachate generated in landfills may contain a variety of different pollutants including ammonia. Landfill leachate varies in strength and composition depending on several factors, but the most significant ones are: the age of the landfill, composition of waste, and design and operation of landfill and moisture management in particular (Sartaj *et al.*, 2010; Renou *et al.*, 2008; Wang *et al.*, 2008). Ammonia is mainly produced during the anaerobic biodegradation of organic fraction of solid waste. The only removal path for ammonia in a landfill is by extraction of the produced leachate, as there is no mechanism for its degradation under methanogenic conditions (Burton & Watson-Craik, 1998). Recirculating leachate, nowadays practiced in many landfills, in fact could increase the rate of ammonification, resulting in accumulation of higher levels of NH_3, which intensifies the toxicity of the leachate (Yenigün & Demirel, 2013; Berge *et al.*, 2006). A German study was conducted on 50 landfills; the results show no significant decrease of ammonia concentrations up to 30 years after a landfill's closure (Ehrig, 1989). With this in mind, coupled with potentially high concentrations, it should be no surprise that ammonia is considered to be the most significant long-term pollutant found in landfill leachate (Dong & Sartaj, 2016b; Belevi & Baccini, 1989; Robinson, 1995). Table 4.1 presents the ammonia concentrations from a few selected landfill sites being categorized as young, mature, and old. As it can be seen, the range of ammonia concentration is very wide covering a range of a few hundreds to more than 10000 mg/L.

Table 4.1 Ammonia concentrations in landfill sites

Age	Landfill Site	Ammonia-N (mg/L)	Reference
Y	China, Hong Kong	760-11000	(Lo, 1996)
Y	Italy	5210	(Lopez *et al.*, 2004)
Y	Turkey	1120-2500	(Timur & Özturk, 1999)
MA	Poland	750	(Neczaj *et al.*, 2007)
MA	Taiwan	5500	(Wu *et al.*, 2004)
MA	Iran	864-2056	(Kheradmand *et al.*, 2010)
O	Brazil	800	(Silva *et al.*, 2004)
O	Finland	330-560	(Marttinen *et al.*, 2002)
O	Turkey	1590	(Uygur & Kargi, 2004)
	Y: young	MA: mature	O: old

Presence of ammonia in leachate is important from several different perspectives: meeting the discharge criteria; the inhibitory effect on biological treatment of leachate; and the inhibitory effect on anaerobic digestion process and biogas production within the landfill. Li and Zhao (1999) found that progressively increasing ammonia concentrations from 50 to 800 mg NH_4^+-N/L caused chemical oxygen demand (COD) removal in landfill leachate to decline from 95 to 79% along with a decrease in the dehydrogenase activity of the sludge. Lee *et al.* (2000) reported EC_{50} values (concentration of ammonia at which microbial activity reduced by 50%) of 2500 and 2700 TAN/L for ammonia inhibition of microbial activity of nitrifying and heterotrophic bacteria, respectively, in biological wastewater treatment. Hansen *et al.* (1998) reported that concentrations of ammonia in recirculated leachate in doses as low as 1100 mg NH_3-N/L and a pH of 8 could inhibit anaerobic bacterial activity while Liu *et al.* (2012) reported that TAN concentrations of 1500-3000 mg/L had inhibitory effect on anaerobic biodegradation of landfill leachates. Kayhanian (1994) and Akindele and Sartaj (2016) also reported that an inhibition of anaerobic biodegradation organic fraction of municipal solid waste occurred at 1000 and 2500 mg/L ammonia concentration, respectively. Compounding the aforementioned toxic effects is the fact that ammonia has the potential to inhibit biological treatment processes.

As discussed above, ammonia removal from wastewater has become a crucial issue, and the application of different removal strategies at reasonable costs as treatment or pre-treatment methods have been one of the main leachate management research topics in recent years. Conventional treatment processes to remove ammonia from aqueous solution include biological treatment, microwave radiation, air stripping, chemical precipitation, adsorption/ion-exchange, and ultrasonic irradiation (Ozturk & Bal, 2015; Dong & Sartaj, 2016a; Wang *et al.*, 2008; Dong & Sartaj, 2016b; Huang *et al.*, 2014; Lin *et al.*, 2009; Matouq & Al-Anber, 2007). Traditional biological processes including nitrification and denitrification are considered cost efficient, but unfortunately they do not perform efficiently in the case of high ammonia concentration or with shock ammonia loading (Huang *et al.*, 2014; Lin *et al.*, 2009; Matouq & Al-Anber, 2007; Karadag, 2006). Dong and Sartaj (2016a & 2016b) examined the effect of microwave radiation followed by aeration on ammonia removal from synthetic solutions (initial TAN concentration of 2700 mg/L) and leachate (initial TAN concentration of 4000 mg/L); they found that the proposed method was effective at removing up to 82% and 70% of the ammonia from synthetic solutions and leachate, respectively, at an optimum pH of 11. Air stripping provides satisfactory removal efficiency but only under high pH conditions where most of the ammonia is in the NH_3 (unionized) form (Marttinen *et al.*, 2002; Ferraz *et al.*, 2016). Ding and Sartaj (2015 & 2016) reported high efficiency for ammonia removal by zeolite (up to 87%) and ion-exchange resin (up to 84%) at an initial ammonia concentration of 1000 mg TAN/L and neutral pH. Huang *et al.* (2014) examined the ammonia removal from landfill leachate by struvite precipitation using waste phosphoric acid as the phosphate source, the results showed up to 83% ammonia removal. While chemical precipitation is an effective means of removing ammonia from wastewater and leachate it requires a constant input of chemicals, which can be costly. Also, chemical precipitation produces large amounts of solid waste (sludge) and the precipitate formed has high concentrations of ammonia.

Ultrasonic irradiation has been studied and shown to be a promising technology for removing high concentration of ammonia from aqueous solution. Compared with conventional methods, ultrasonication can bring several benefits such as environmentally friendly (no toxic chemicals are used or produced), low cost, selectivity and compact (allowing on-site treatment). Contrary to other processes which are negatively affected by presence of suspended solids, US efficiency may even be improved by increase of turbidity or suspended solids. In aqueous solution Ultrasound (US) application lead to formation of cavitation bubbles. Subsequent collapse of cavitation bubbles produces intense local heating (4200 - 5000 K) and pressure (up to 1000 atm) over a short period of time, which cause high energy chemical reactions (generation of free radicals) to occur and to break and decompose some compounds (Ozturk & Bal, 2015; Wang *et al.*, 2008; Matouq & Al-Anber, 2007; Deng & Zhao, 2015; Mahvi, 2009; Sivasankar & Moholkar, 2009; Ince *et al.*, 2001; Pham *et al.*, 2009). The generated free radicals are involved in the rapid oxidation of organic and inorganic matters and degradation of complex compounds in solution (Ozturk & Bal, 2015). Wang *et al.* (2008) reported that the main mechanism of ammonia nitrogen reduction from aqueous solution by US appeared to be the entry of ammonia molecules into the cavitation bubbles and the transformation into nitrogen molecules and hydrogen molecules via pyrolysis. However, Ozturk and Bal (2015) concluded that the main mechanism of ammonia removal was advanced oxidation of ammonia–nitrogen by hydroxyl radicals.

Matouq and Al-Anber (2007) studied the effect of a high US frequency (using 1.7 and 2.4 MHz) on ammonia removal from industrial wastewater with three different ammonia concentrations namely 5%, 15% and 25% (vol. %); they found that the optimum condition for ammonia removal was achieved for the solution with 5% ammonia concentration and 0.080L liquid volume. Under these conditions 31.7% and 25.7% ammonia removal was reported at 2.4 MHz and 1.7 MHz respectively. They also reported that optimum liquid height was 0.0165 m and approximately 31% of ammonia removal was achieved within 90 minutes at a radiation of 2.4 MHz. Due to the limitation of ultrasound penetration ability, as the height of liquid increases, the ammonia removal efficiency decreases.

Ozturk and Bal (2015) investigated the effect of initial concentration, initial pH, US power density and sonication period on the efficiency of ammonia removal from aqueous solutions by ultrasonic irradiation. Depending on initial conditions removal efficiencies varied between 8 - 64%. Ammonia removal efficiency increased with increasing power density, sonication period (over a range of 1 - 10 min) and pH, but decreased with increasing initial concentration (over a range of 5.6 - 415 mg/L).

Wang *et al.* (2008) investigated the removal of ammonia from an old landfill leachate by a combined US and aeration process. The leachate contained 680 mg/L TAN and had a pH of 8.1. Ammonia removal increased with increasing power and pH of the solution. After 180 min of processing at a power input of 200 W and a pH of 11, the removal efficiency for the combination of ultrasound irradiation and aeration reached 96%. The removal efficiency at pH 11 was approximately eight times as high that of pH 3.

Considering the above, the main objective of this study was to investigate the application of US technology for removal of ammonia from aqueous solution with high initial ammonia concentration around 3000 mg/L where the inhibitory effects of ammonia in treatment of landfill leachate and anaerobic digestion process has been reported to occur. Additionally, it was intended to assess the contribution of thermal and non-thermal effects as well as the effect of irradiation duration, pH, and power input through statistical analysis of the data.

4.2 Materials and Methods

To achieve the objectives a series of batch tests were carried out. All tests were carried out in triplicate. The synthetic solution of approximately 3000 mg TAN/L (approximately 2,470 mg/L as NH_3-N) was prepared by dissolving analytical grade ammonium chloride (NH_4Cl) in distilled water; after the NH_4Cl was observed to be fully dissolved the remainder of distilled water was added to achieve the desired ammonia concentration. A fresh ammonia bulk solution was made for each laboratory session with the total volume used calculated based on the number of tests to be conducted. The order of experimental activities for each test is shown in Figure 4.1. For each test, 165 mL of ammonia synthetic solution was added to a 500 mL beaker, with a removable lid used during the cooling stage to limit water loss, which was placed on top of a height adjustable stand, to achieve a desired disruptor horn tip depth of 165 mm (Matouq & Al-Anber, 2007). The pH of solution was then adjusted to the desired initial pH (9, 10, or 11) using a 10 N NaOH solution. After pH adjustment, initial TAN, pH, and temperature of the sample were measured. Afterwards, the sample was exposed to US irradiation using Branson digital sonifier 450 with a ½" disruptor horn and ½" disruptor tip for the desired duration (5, 10, or 25 minutes). The schematic and a photograph of the experimental setup are illustrated in Figure 4.2. The US vibration was generated by a 20 kHz ultrasonic converter and was transferred into the ammonia solution by putting the US probe into it. The power output could be adjusted from 10 to 100% in 5% increments and ranged from 0 to 400 W. Temperature was measured immediately after this stage. The sample was allowed to cool to room temperature before distilled water was added to account for water loss. TAN and pH were measured again and energy output recorded (kJ).

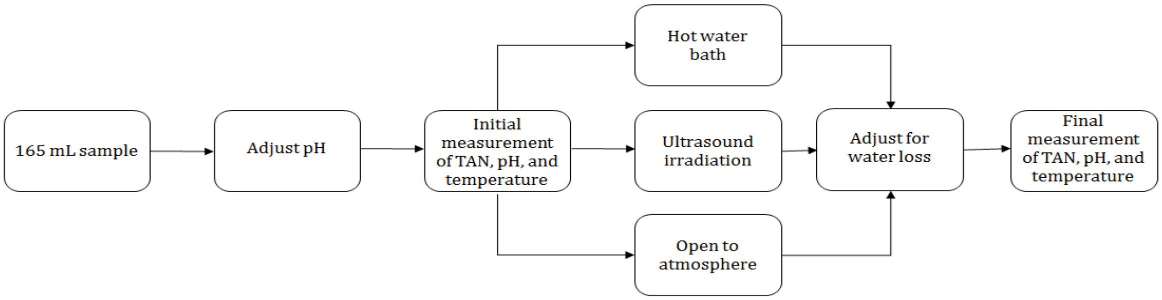

Figure 4.1 Experimental Flow-chart

In order to study the amount of ammonia removed due to temperature rise during the process, heat only experiments were conducted. This method involved the same procedure outlined above; however, instead of being sonicated, the samples were placed into a 20 L/120 V Stable Temp hot water bath (Cole-Parmer Canada Inc.) set at a temperatures that correlated to the final temperatures achieved after sonication for the desired durations. The hot water bath temperatures used for sonication test were 52, 72, and 72°C corresponding to 5, 15, and 25 min sonication duration. The contribution of evaporation on the ammonia removal was also investigated by leaving some samples open to the surrounding atmosphere instead of being heated in water bath or sonicated.

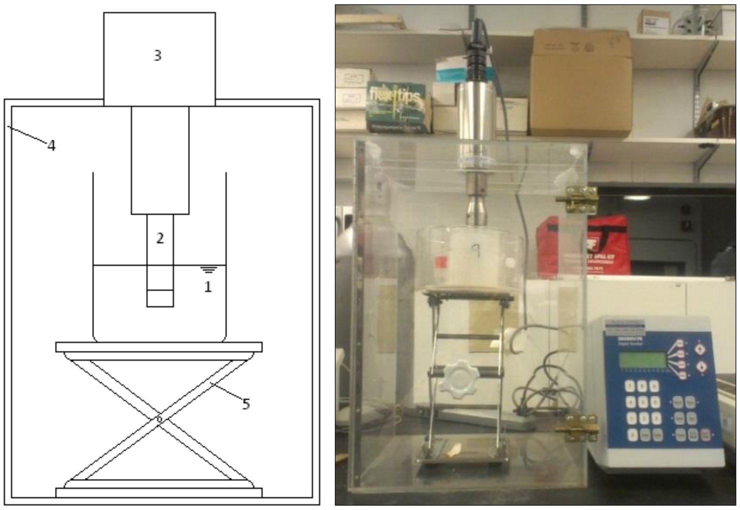

Figure 4.2 [left] Schematic of experimental setup. (1) NH_3 solution (2) disruptor horn and tip (3) ultrasonic converter (4) case (5) stand. [right] Photograph of experimental setup

4.3 Results and Discussion

The ammonia removal efficiency was calculated using the Equation below:

$$\text{TAN removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \qquad (4.1)$$

where C_o is the initial (after pH adjustment) and C_e is equilibrium TAN concentration (mg/L), respectively.

The results of the experiments are shown in Figure 4.3, where data points represent the average of triplicates. As it can be noticed the ammonia removal efficiency increased with increasing pH and duration. The lowest and highest ammonia removal observed among all the different conditions were 8% at pH of 9 and 5 min duration and 87.4% at pH of 11 and 25 min duration respectively. The above results show that application of US over a short period of time (~ 15 min) could be an effective method for removal of ammonia at higher pH values (pH > 10). Ozturk and Bal (2015) reported lower TAN removals (8 - 64%) at lower initial concentration (5.6 - 415 mg/L) and shorter sonication period (1 - 10 min) while Wang *et al.* (2008) reported high ammonia removal (96%) but with a time duration of 180 min at 680 mg/L TAN. Ozturk and Bal (2015) also reported that ammonia removal increased (18 - 64%) with sonication time (1 to 10 min) following a linear trend. The increase of removal efficiency at higher pH levels could be explained by the equilibrium shift between the two types of ammonia (NH_3 and NH_4^+), in aqueous solutions at higher pH levels the presence of NH_3 was favored compared to NH_4^+, and the presence of more NH_3 molecules that were preferred by oxidation and/or pyrolysis, should ultimately lead to a higher removal efficiency. It was suggested that ammonium ions do not vaporize into the cavitation bubble, however, free ammonia can vaporize into cavitation bubbles and react inside by thermal cleavage. Hence a higher pH would enhance the ammonia removal during US process (Ozturk & Bal, 2015; Wang *et al.*, 2008).

It can be seen that larger improvements in TAN removal were obtained by increasing US duration from 5 to 15 minutes (4.3 – 41.4%) compared to increasing it from 15 to 25 minutes (1 – 5.4%). Further statistical analysis of data proved that improvements observed in increasing sonication time from 15 to 25 min were not statistically significant. These improvements was more obvious at higher pH values, i.e. at pH 11 compared to pH 9 (41.4% vs. 5.4%). Thus it was decided to further explore this by statistical analysis of data. The first step of statistical analysis was performed using a two-way ANOVA to determine whether differences between TAN removal efficiencies at different pH and durations were statistically significant. The results are presented in Table 4.2, below.

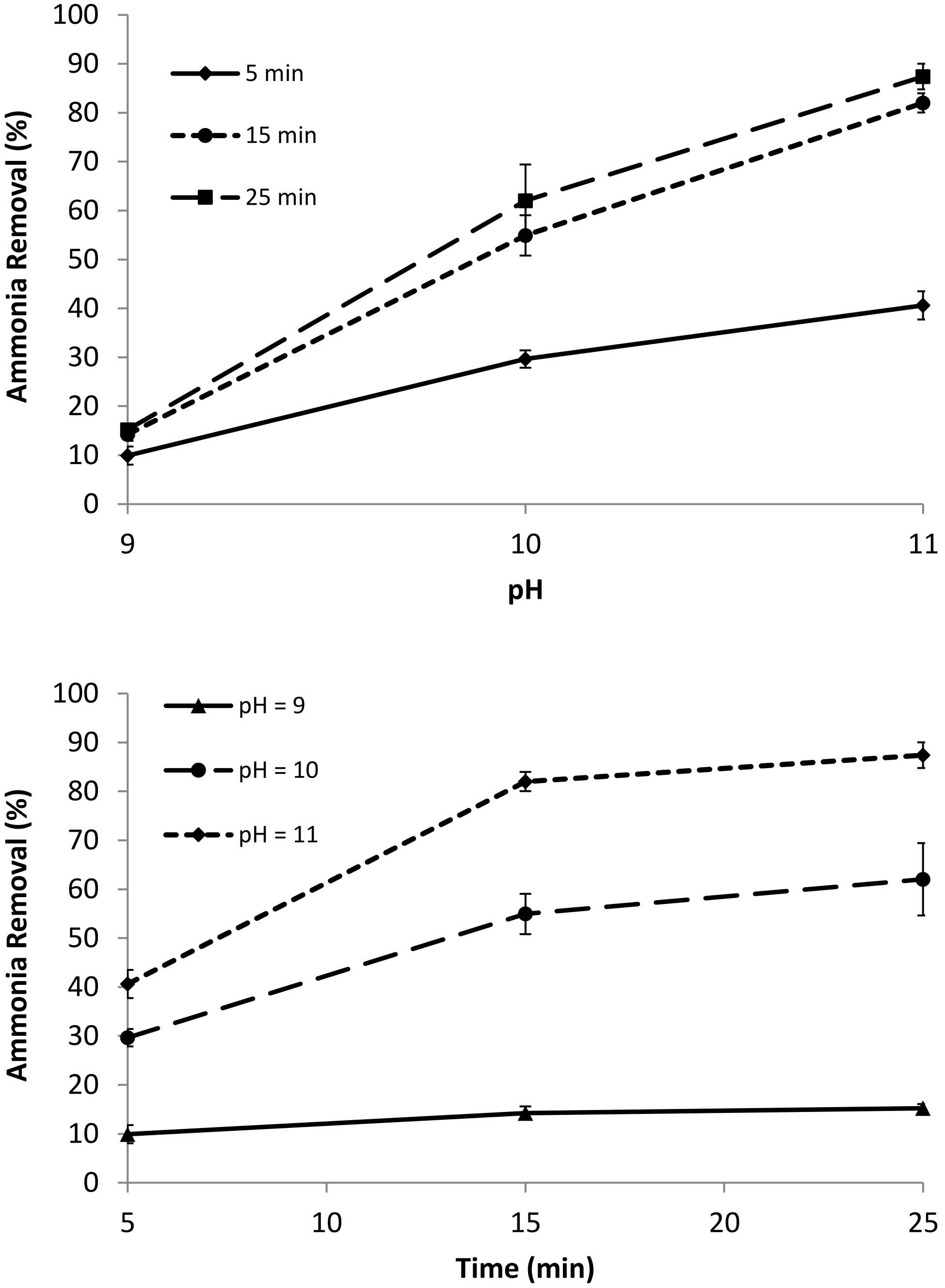

Figure 4.3 Average TAN removal by ultrasound using 100% output power at different pH and durations

Table 4.2 Two-way ANOVA for TAN removal

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
pH	14877.33	2	7438.66	670.23	1.26E-17	3.55
Duration	4118.73	2	2059.37	185.55	9.7E-13	3.55
Interaction	1597.51	4	399.38	35.98	2.33E-08	2.93
Within	199.78	18	11.10			
Total	20793.35	26				

As it can be seen, the F values were significantly larger than *F critical* values and *P-values* were significantly lower than 0.05 showing that there were significant differences between the removal efficiencies observed. Also, as it was mentioned above, the improvement in TAN between US durations of 15 and 25 min were not statistically significant. Therefore, as the next step, t-tests ($p < 0.05$) were carried out for each pair of pH and US duration for further analysis and the results are presented in Table 4.3. At all pH values, TAN removal at 5 and 15 min US duration were significantly different ($p < 0.05$), however, TAN removals at 15 and 25 min US duration were not significantly different ($p > 0.05$). This demonstrates that by applying US radiation for 25 min yields statistically insignificant TAN removals compared to US duration of 15 min was obtained.

Table 4.3 t-test for TAN removal for paired combination of pH and US duration time

	pH=9		pH=10		pH=11	
	15 min	5 min	15 min	5 min	15 min	5 min
Mean	14.26	9.92	54.93	29.65	82.01	40.62
Variance	1.80	3.45	16.98	3.16	3.86	8.29
Observations	3.00	3.00	3.00	3.00	3.00	3.00
Pooled Variance	2.62		10.07		6.08	
Hypothesized Mean Difference	0.00		0.00		0.00	
df	4.00		4.00		4.00	
t Stat	3.28		9.76		20.56	
P(T<=t) two-tail	0.03		0.00		0.00	
t Critical two-tail	2.78		2.78		2.78	
	pH=9		pH=10		pH=11	
	25 min	15 min	25 min	15 min	25 min	15 min
Mean	15.21	14.26	62.03	54.93	87.40	82.01
Variance	0.75	1.80	54.71	16.98	6.88	3.86
Observations	3.00	3.00	3.00	3.00	3.00	3.00
Pooled Variance	1.27		35.85		5.37	
Hypothesized Mean Difference	0.00		0.00		0.00	
df	4.00		4.00		4.00	
t Stat	1.04		1.45		2.85	
P(T<=t) two-tail	0.36		0.22		0.05	
t Critical two-tail	2.78		2.78		2.78	

The sonication process is accompanied by temperature rise due to the high pressure and heat produced by the collapse of cavitation bubbles. The temperature of the sonicated samples increased from 22°C to as high as 72°C, with a maximum increase in temperature was approximately 50°C. To determine the contribution of thermal and non-thermal effects of US process as well as the potential volatilization for TAN two additional sets of experiments were conducted. The effect of temperature was investigated by using a water bath to heat the samples for the same duration and temperature as under sonication (Figure 4.1). The TAN removal in water bath samples shows the combined effect of heating and volatilization and by subtracting this concentration from the TAN removal obtained in samples treated with US irradiation, it is possible to estimate the sonication or non-thermal effect. Results are presented in Figure 4.4.

With the exception of the tests with pH 11 and duration of 25 min, contribution from non-thermal effect was higher than thermal and volatilization effects, especially at higher pH values. The least TAN removal contribution came from volatilization. In fact, at pH of 9 and US duration of 5 min, TAN removal contribution by volatilization is negligible. These results were converted to percentages of total TAN removal for each case and are illustrated as pie charts in Figure 4.5. It can be noticed that the contribution of volatilization (samples being exposed to the air) only accounts for 0.0 to 6.6 % of the ammonia removal, with a general increasing trend with increasing pH and duration. It is clear that the contribution of this mechanism is minor compared to the other two mechanisms, i.e. thermal and non-thermal effects of US treatment. On the other hand, 21.2 - 33.2%, 21.1 - 39.3%, and 28.9 - 52.7% of the TAN in the aqueous solution was removed after 5, 15 and 25 minutes, respectively, because of the thermal effect of increased temperature, showing an increasing trend with increasing pH. This again could be explained by the effect of pH on distribution of ammonia species favoring NH_3. Moreover, as the cavitation bubbles were created by sonication, the NH_3 was broken down by US mechanisms which contributed 44.5 - 78.8%, 66.6 - 73.8%, and 62.9 - 70.7% of TAN removal at 5, 15 and 25 minutes duration, respectively, representing the main removal mechanism in this experiment.

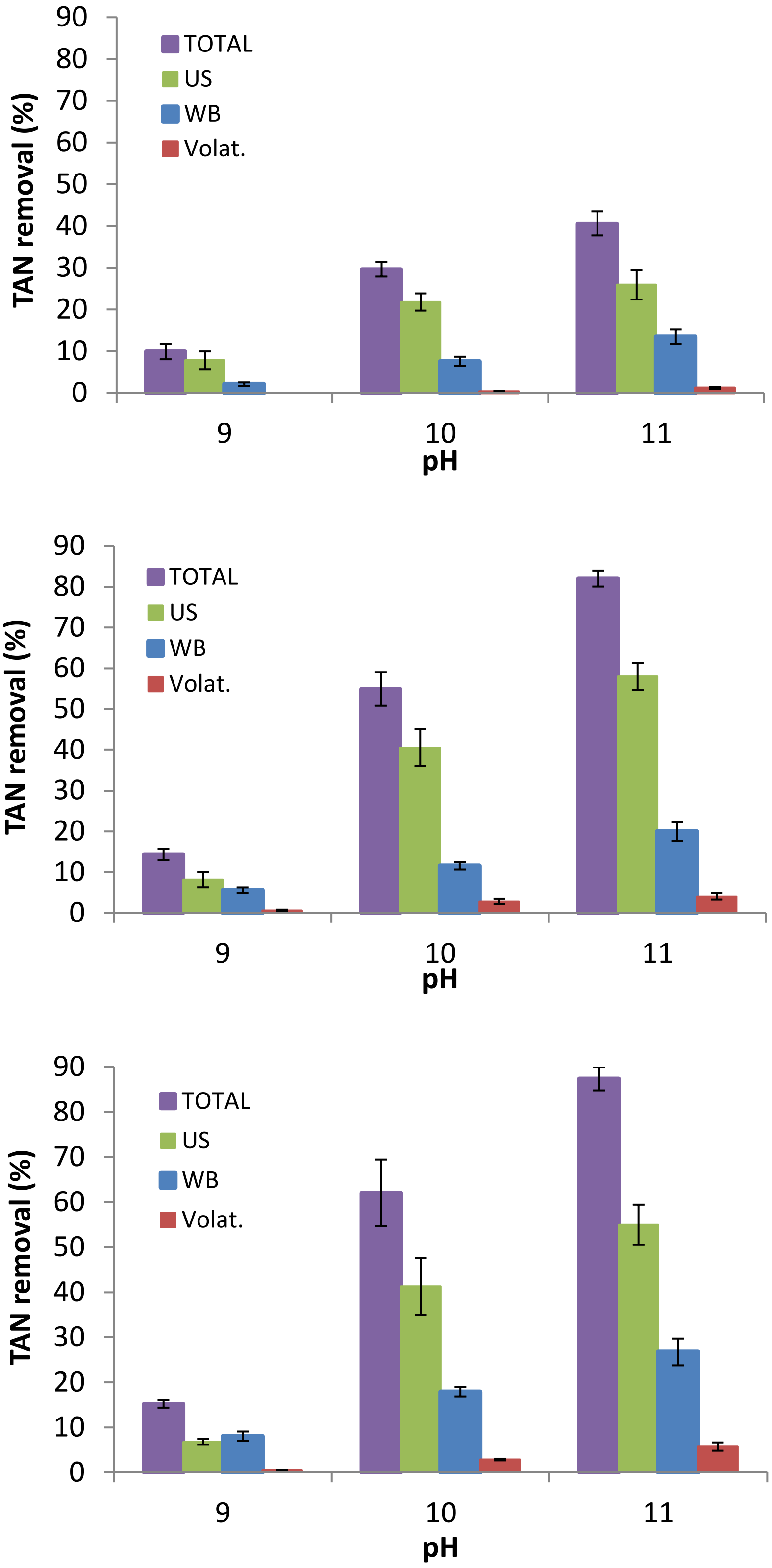

Figure 4.4 Average TAN removal by non-thermal (US), thermal (WB), volatilization (Volat.) at 5 min (top), 15 min (middle) and 25 min (bottom)

TOTAL refers to TAN removal obtained in samples treated by US; WB refers to TAN removal obtained in samples treated by water bath; US refers to the difference between TOTAL and WB or the non-thermal (sonication) effect; and Volat. refers to the effect of volatilization which was obtained for a set of samples exposed to the air with no treatment for the same duration corresponding to US tests.

Figure 4.5 Percentage of TAN removal by non-thermal (US), thermal (WB), and volatilization (Volat.) at different pH and time duration

4.4 Conclusions

The experimental results showed ammonia can be effectively removed by US irradiation from a synthetic solution with high ammonia concentration. The highest removal reached in this study was 87.4% achieved at pH 11 and sonication duration of 25 minutes. High pH conditions were preferred for the ammonia removal by US processes. Removal efficiency increased with increasing the aqueous solution pH, the optimum pH for the current study was found to be 11. Also, ammonia removal increased with increasing time duration of US application, however, after reaching a certain point no further removal was observed and extending the time would be a waste of energy as TAN removals at 15 and 25 min US duration were not statistically different. Among the 3 mechanisms considered for ammonia removal, i.e., thermal and non-thermal effects of US and volatilization to air, volatilization had the least contribution while non-thermal effects of US had the highest contribution for ammonia removal. This suggested that the main cause of ammonia molecule removal during the sonication process was due to the breaking of the ammonia molecule by the high temperature and pressure in the cavitation bubbles created by the US irradiation.

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CHAPTER V
Technical Paper II

Statistical Analysis and Optimization of Ammonia Nitrogen Removal from a High Concentration Aqueous Solution Using Ultrasonic Irradiation

Andrew Tobalt, Majid Sartaj, Kevin Kennedy

Abstract

The application of ultrasound (US) irradiation was investigated as a treatment method for the removal of ammonia nitrogen from a synthetic ammonia solution using batch experiments. 165 mL samples of synthetic ammonia solution containing approximately 3000 mg TAN/L at a pH of 9, 10, and 11 were subjected to US for 5, 15, and 25 minutes at output power amplitudes of 20%, 60%, and 100% using a 20 kHz sonifier. Results confirm that US irradiation is an effective treatment method for the removal of ammonia nitrogen from an aqueous solution. Combing the input parameters of US duration and output amplitude showed a maximum observed experimental removal rate of 83% at a pH of 11 and energy output of 101 kJ. Statistical analysis of the experimental data showed that ammonia nitrogen removal efficiency is strongly dependent on pH and energy output. Increasing percent removal was found with an increase in either parameter. A response surface methodology (RSM) was used to predict the removal efficiency of US. The RSM generated an equation for ammonia removal efficiency (%) with an R^2 of 0.94 indicating the model predicted the observed results accurately. RSM showed that an optimum pH of

10.9 and energy output of 94.8 kJ yields a maximum ammonia nitrogen removal efficiency of 87% from a synthetic ammonia solution containing approximately 3000 mg TAN/L.

Keywords: Ultrasonic Irradiation; Ammonia; Statistical Analysis; Response Surface Methodology; Optimization; Factorial Design.

5.1 Introduction

Aqueous ammonia nitrogen is one of the major inorganic pollutants of surface water and is classified as toxic by Environment Canada (2001). Ammonia and Ammonium (NH_3 & NH_4^+) naturally occur in the environment from the decomposition of organics and through being excreted by plants and animals (Randall & Tsui, 2002). The NH_3/NH_4^+ system is sensitive to pH and temperature changes, with an increase in pH and/or temperature raising the percentage of NH_3 (Fernandes *et al.*, 2012). In these naturally occurring concentrations, the NH_3/NH_4^+ system is a major nitrogen nutrient source. However, in excessive concentrations, NH_4^+ and, more acutely, NH_3 exhibit toxic properties to both animals and plants (Britto & Kronzucker, 2002). High levels of ammonia in the body can produce many harmful effects mainly on the central nervous system of vertebrates, acute ammonia intoxication, and convulsion (Ip & Chew, 2010; Rao *et al.*, 1992). Unfortunately, human industrial activities, including the synthesis of NH_3 for cleaning products and fertilizer as well as biological waste treatment that produces NH_3, have introduced high concentrations of ammonia into the environment (Randall & Tsui, 2002).

Ammonia toxicity is particularly problematic when looking at landfill leachate, which can vary greatly in composition and strength depending on the composition of the waste, design and operation (specifically for moisture content), and the age of the landfill (Sartaj *et al.*, 2010; Wang *et al.*,2008). Ammonia generated in landfills does not have a natural removal mechanism due to methanogenic conditions and will accumulate unless treated externally (Burton & Watson-Craik, 1998). Furthermore, Ehrig (1989) showed that, if left untreated, ammonia concentrations can remain constant for more than 30 years post landfill closure. All of the aforementioned factors result in leachates that contain from 0.2 to 13000 mg NH_3-N/L (Renou *et al.*, 2008). As such, ammonia is considered to be the most significant long-term pollutant found in landfill leachate (Dong & Sartaj, 2016b; Belevi & Baccini, 1989; Robinson, 1995).

Compounding the toxic effects of ammonia is the inhibitory effect it has on biological nutrient removal and anaerobic digestion. Lee *et al.* (2000) found that a concentration between 2500 and 2700 mg TAN/L reduced the microbial activity of heterotrophic and nitrifying bacteria by 50%. Also, Liu *et al.* (2012) reported that inhibitory effects on anaerobic biodegradation of landfill leachates occurred at concentrations between 1500 and 3000 mg TAN/L. Furthermore, Akindele and Sartaj (2016) found that a concentration of 2500 mg TAN/L was inhibitory to anaerobic biodegradation while Kayhanian (1994) found this limit to be 1000 mg TAN/L. It is clear from literature that ammonia nitrogen is a substance of great concern with a need for novel removal techniques.

Many treatment options exist to remove ammonia from aqueous solutions; however, a universal treatment solution covering all of the toxins and contaminants found in leachate has not been found yet. At present, a combination of different techniques must be used in tandem to mediate all of the potentially ill effects associated with landfill leachate (Wiszniowski *et al.*, 2006).

Common biological processes used to remove ammonia employ nitrification and denitrification and show degraded performance when treating higher concentrations of ammonia. The inhibition of the biological nitrification process is reported to be due to NH_3 while the presence of NH_4^+ inhibits the NO_2 oxidation process at concentrations of 20 mg-N/L, and also begins to inhibit the NH_4 oxidation process at concentrations of 100 mg-N/L (Metcalf & Eddy, 2014).

Alternatively to biological processes, ammonia may be removed by physical and chemical methods, which include air stripping, membrane filtration, microwave, and ultrasound. These methods of ammonia removal present some drawbacks: adequate results from air stripping are achieved only in high pH conditions, where ammonia is in unionized form (NH_3) (Marrtinen *et al.*, 2002); extensive pretreatment and chemical cleaning is required for membrane filtration and if not vigilantly monitored and maintained, the lifecycle of the membrane and process productivity decrease significantly (Rautenbach *et al.*, 2000). Microwave radiation has shown the ability to remove ammonia from aqueous solutions as well as leachate, though the removal rates without accompanying aeration seem low (Dong & Sartaj, 2016a).

For the purpose of this paper, ultrasound (US) irradiation was used as the method of ammonia removal. Compared to conventional treatment methods, US offers significant advantages with respect to yield and performance; the primary benefit of using this method is that there is no additional use of chemicals required. In turn, US does not release toxic compounds into the environment and reduces the associated environmental impacts (Faryadi *et al.*, 2015). Moreover, US can provide an improved yield product and selectivities, as well as enhance product recovery and quality if applications of several processes are used (Matouq & Al-Anber, 2007). Further, the use of US is a two-fold economical solution: it is easily applied and operational costs are lowered (Faryadi *et al.*, 2015).

Previous research conducted by Matouq and Al-Anber (2007) studied high frequency US waves to remove ammonia from simulated industrial wastewater. The efficiency of ammonia removal from water were examined at three different concentrations of ammonia (5%, 15%, and 25% volume), which are similar to conditions of wastewater from strippers at petroleum refineries. US frequencies of 1.7 and 2.4 MHz were used to study the effects of waves on ammonia removal. The study surmised that US removed 5% concentration ammonia, which met local wastewater standards for 0.080 L solution within less than 2 hours. Further, the study indicated that with the increase of ammonia concentration, the amount of ammonia removed with 2 hours decreased; however, the concentration of ammonia removed still met the local wastewater standards (Matouq & Al-Anber, 2007).

Neczaj *et al.* (2007) studied the effects of US on combined treatment of landfill leachate and domestic sewage in sequencing batch reactors (SBR). Their experiments used a ratio of sewage to leachate of 9:1 by volume and sonification was used to pre-treat landfill leachate. Sonification of the leachate was performed in a static condition using a disintegrator UD-20 with a field frequency of 20 kHz and amplitude of 12 μm. The mixed wastewater was seeded to a mixed suspended solids solution with a concentration of 3500 mg/L with activated sludge obtained from a biological wastewater treatment plant. The SBR operated with a 24-hour time cycle in the following operational sequence: fill, aerobic reaction, anoxic reaction, settlement, draw, and idle. Different operational factors were applied to optimize the removal of nitrogen compounds and COD. Their results indicated that bio-treatment of combined leachate and sewage was possible and that treatment efficiency was strongly dependent on operational factors. Further, it was reported that US pretreatment of raw leachate resulted in increased treatment efficiency; their results showed significant improvements to COD and nitrogen compound removal rates in SBRs operated with leachate, which had been irradiated by US as compared to biological treatment of non-pretreated leachate (Neczaj *et al.*, 2007).

Faryadi *et al.* (2015) investigated the removal of ammonia using high frequency US in two sonoreactors, a batch and a new proposed dam-weir falling reactor. The study of ammonia removal, with and without aeration, was conducted and the effects of initial concentration and US irradiation were observed. This study reported that a 4 cm liquid height on the surface of piezoelectric is an optimum height for US irritation and that aeration has a significant influence on ammonia removal. Further, as determined in previous studies, their research confirmed that aeration had an important influence on ammonia removal. It was reported that up to 80% and 49% of ammonia was removed in the dam-weir and batch systems, respectively, using US irradiation in conjunction with aeration after 120 minutes (Faryadi *et al.*, 2015).

Huang *et al.* (2014) reported on the treatment of landfill leachate using US stripping to decompose struvite and the recycling of the decomposition product. Their results specified that the ammonium in struvite could be nearly eliminated from the solution when the decomposition of struvite by US stripping is performed at 55°C for 40 minutes.

Characterization analysis indicated that magnesium phosphate and dissolved phosphate ions were the principal active derivatives and that approximately 90% of TAN in landfill leachate could be removed by reusing the decomposition product at pH 9 for 60 minutes. The TAN removal efficiency declined with an increase in the number of repeated use of the struvite decomposition product. However, the study reported that the reuse of struvite yielded approximately 90% TAN removal with the supplementation of a preformed struvite to the solution for every recycle. An economic analysis established that 79.3% of the treatment could be saved by the proposed process compared to the non-recycling process. This shows the multi-faceted advantage of using US combined with other ammonia removal techniques (Huang *et al.*, 2014).

Wang *et al.* (2008) reported that an ammonia removal efficiency of up to 96% was achieved after 180 minutes of US irradiation time. The US process was proven to be input power-dependent with the removal rate increasing with an increase in power input. It was also reported that a high pH was favorable to remove ammonia nitrogen using US irradiation. The removal efficiency at pH 11 was approximately eight times as high as that of pH 3. This was found to be the result of a higher percentage of unionized ammonia compared to ionized ammonia at high pH. Specifically, ionized ammonia does not vaporize into the ultrasonic cavitation bubbles while unionized ammonia is more volatile and does. In the molecular state, unionized ammonia can react inside the cavitation bubbles by thermal cleavage. It was found that the main mechanism of ammonia nitrogen removal was due to the entry of ammonia molecules into the cavitation bubbles and their transformation into nitrogen molecules and hydrogen molecules via pyrolysis (Wang *et al.*, 2008). However, Ozturk and Bal (2015) concluded that the main mechanism of ammonia removal was advanced oxidation of ammonia–nitrogen by hydroxyl radicals.

The main objective of this study was to evaluate and optimize ammonia removal by US using a factorial design and response surface methodology (RSM) under high TAN concentrations range.

5.2 Materials and Methods

5.2.1 Materials and Equipment

The solution used containing approximately 3000 mg TAN/L (approximately 2400 mg/L as NH_3-N) was prepared by dissolving Fisher Scientific analytical grade ammonium chloride (NH_4Cl) in approximately 500 ml of distilled water; after the NH_4Cl was observed to be fully dissolved the remainder of distilled water was added to achieve the desired ammonia concentration. A fresh ammonia bulk solution was made for each laboratory session with the total volume used calculated based on the number of tests to be conducted; approximately 4 L was used per session unless the needed laboratory equipment was not available for a full day. The initial concentration of 3000 mg TAN/L was chosen as it lies at the high end of the published range of 1500-3000 mg TAN/L that produces inhibitory effects in conventional biological treatments. The initial pH was approximately 5.5 and was adjusted to the desired levels using 10 mol/L NaOH (Fisher Scientific).

US irradiation was applied to aqueous ammonia samples using a Branson Digital Sonifier® (model 450) with included 20 kHz ultrasonic converter, ½” disruptor horn, and ½” disruptor horn tip. The maximum output power of the 450 model is 400 W and can be adjusted from 10% to 100% in 5% increments. The Branson Digital Sonifier® was connected to a printer that would produce a summary of each sample test including total energy output (J) and peak power output (W). It should be noted that the maximum output power depends on the density of the material being sonicated; the aqueous ammonia solution being used allowed for a maximum power output of approximately 130 W.

5.2.2 Analytical Method

Ammonia concentrations were tested using TNT 832 vials from HACH Company based on the Salicylate method using a spectrophotometer (model DR5000) also manufactured by HACH Company. A 10 mg TAN/L as NH_3-N standard solution (HACH Company) was used to check the calibration of the spectrophotometer. All tests were triplicated and before testing ammonia removal, a blank sample of distilled water was tested as well. The pH was measured using a glass electrode connected to a Fisher Scientific Accumet® dual channel pH/ion meter (model XL25). Also, each sample was diluted 100:1 before being sampled and tested to ensure that both the pH and ammonia concentration were within the specified range of the TNT 832 testing kit.

5.2.3 Experimental Design

The experimental design for testing ammonia removal is summarized in Table 5.1. The pH range was selected based on the results of preliminary testing that determined the low and high end effects of pH on ammonia removal. Similarly, the power output and US duration range of 100% for 25 minutes were not chosen based on preliminary tests; the removal of ammonia at these input values began to plateau and did not add statistically significant data to the experiment.

Table 5.1 Experimental design for the removal of ammonia nitrogen from a synthetic solution using US

US time (mins)		5			15			25		
Power output level (%)		20	60	100	20	60	100	20	60	100
pH	9	✓	✓	✓	✓	✓	✓	✓	✓	–
	10	✓	✓	✓	✓	✓	✓	✓	✓	–
	11	✓	✓	✓	✓	✓	✓	✓	✓	–

✓ Experiments conducted under these conditions
– No Experiments conducted under these conditions

Fig. 1 shows the order of events involved in the testing of ammonia removal from US irradiation. For each test, approximately 165 mL of synthetic solution was used to achieve the desired disruptor horn tip depth of 165 mm (Matouq & Al-Anber, 2007). The pH was adjusted to the desired initial pH (9, 10, or 11) using a 10 mol/L NaOH solution, then TAN, pH, and temperature were measured. Afterwards, the sample was exposed to US irradiation for the desired duration (5, 10, or 25 minutes) and power output (20, 60, or 100 %). The temperature was measured immediately after US irradiation. The sample was allowed to cool to its initial temperature before distilled water was added to account for water loss; water loss was calculated by weighing the sample before and after US irradiation. Finally, TAN and pH were measured and energy output recorded (kJ).

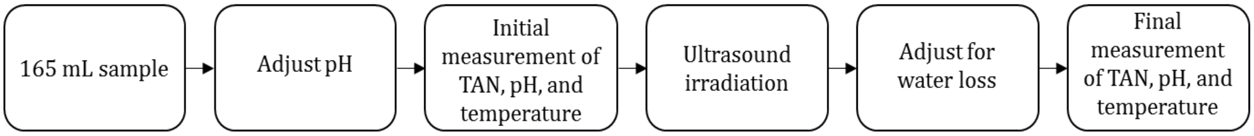

Figure 5.1 Experimental flow chart

5.2.4 Statistical method and data analysis

Both a factorial design and response surface methodology (RSM) were used to evaluate and optimize the pH and US energy input required to remove ammonia from an aqueous solution. US energy output was used as it is the product of US power output and irradiation time. The response surface model and corresponding output response, Y (ammonia removal efficiency), were based on the input of two independent variables: US energy output (X_1) and pH (X_2). Table 5.2 shows the coded levels for both X_1 and X_2, which were coded at 8 levels and 3 levels from -1 to 1, respectively. The ranges for the independent variables were determined using preliminary test results. To reduce noise and bias in the outcome response in addition to increasing standard deviation and random error accuracy, all tests were performed in triplicate.

Table 5.2 Experimental design and coded levels of independent variables used in RSM

Independent variable	Symbol	Coded Levels							
		-1	-0.75	-0.70	-0.55	-0.35	0	+0.55	+1
US energy output (kJ)	X_1	6	17.5	20.5	28	36.5	54	80.5	102
pH	X_2	9	–	–	–	–	10	–	11

Statistical analysis of the data set was done using the DesignExpert® software suite (9th version). Ammonia removal efficiency was calculated using equation (5.1), as follows:

$$Removal\ efficiency(\%) = \frac{Co - C}{Co} \times 100\% \qquad (5.1)$$

where C_o is the initial ammonia nitrogen concentration after pH adjustment and C is the US treated ammonia nitrogen concentration.

RSM is, and has been, widely used to determine the regression model and optimal operating conditions and to characterize the interactions between independent variables in both laboratory and industrial testing and processes (Sharma *et al.*, 2009). In this paper, the optimum operating conditions for ammonia nitrogen removal were found through analyzing the relationship between the independent variables (US energy output and pH) with respect to the outcome response (ammonia nitrogen removal). RSM behavior was expressed using the following second-order polynomial equation:

$$Y_1 = A_o + \sum_{i=1}^{n} A_i X_i + \sum_{i=1}^{n} A_{ii} X_i^2 + \sum_{i\neq 1,\, j=1}^{n} A_{ij} X_i X_j + \varepsilon \qquad (5.2)$$

where Y_1 is the response variable; X_i and X_j are the independent variables; Ao is the value of the fixed response at the center point of the design; A_i, A_{ii}, and A_{ij} represent the linear, quadratic, and second-order effect regression terms, respectively; n is the number of independent variables; and ε is the random error.

The coefficient of determination (R^2) was used to assess the accuracy of the model; the Fisher variation ratio (F value) and probability value (Prob > F) were used to determine the significance of the model and each of its terms (Montgomery, 2008). Lack-of-fit was evaluated to check whether there was unaccounted for variation in the model. Also, the adequate precision ratio was looked at to judge the acceptability of the model's signal-to-noise ratio (Xu *et al.*, 2015).

5.3 Results and Discussion

5.3.1 Statistical Analysis and Modelling

Ammonia nitrogen removal efficiency (Y_1) was determined by evaluating a factorial design with two independent variables and performing 71 test runs. A regression analysis was used to develop a best-fit model using the collected data. The experimental data was analyzed using DesignExpert® and the following quadratic equation was the most accurate, non-aliased, generated model to predict the response, Y_1:

$$Y_1 = 41.35 + 22.77X_1 + 21.7X_2 + 16.06X_1X_2 - 10.55X_1^2 - 3.77X_2^2 \tag{5.3}$$

Where Y_1 is the ammonia nitrogen removal efficiency, X_1 is the US energy output, and X_2 is the initial pH of the sample.

Table 5.3(a) shows the ANOVA test results of the regression model parameters for the predicted quadratic response surface describing ammonia nitrogen removal efficiency (Y_1). A model or a model term is considered statistically significant if the p-value Prob > F is less than 0.05. The model's F value of 428.86 and p-value Prob > F of <0.0001 indicate statistical significance with respect to ammonia nitrogen removal efficiency. Furthermore, this shows that there is only a 0.01% chance that an F value this large could be due to noise. The quadratic model's adequate precision ratio of 73.83 is well above the desired minimum value of 4 (Bashir *et al.*, 2010). The coefficient of determination (R^2), adjusted R^2 (R^2_{adj}), and predicted R^2 (R^2_{pred}) were used to evaluate how well-fitted the model is with regards to predicting the observed data within the experimental range. Table 5.3(a) shows the quadratic R^2, R^2_{adj}, and R^2_{pred} are 0.97, 0.97, and 0.96, respectively; these values show a very strong correlation between the model-predicted response and the observed results. Furthermore, an R^2_{adj} of 0.97 shows that only 3% of the total variation could not be accounted for by the empirical model. Contrarily, the quadratic ANOVA results show a significant lack-of-fit. This can be caused by replicate values, which are needed to estimate pure error, being very close to one another (Bashir *et al.*, 2010); this also could be due to systemic variation unaccounted for in the model (Xu *et al.*, 2015). Lastly, it can be seen from Table 5.3(a) that all the model terms (X_1, X_2, X_1X_2, X_1^2, and X_2^2) are statistically significant. Therefore, no terms need to be removed from the equation to increase its accuracy.

However, a linear two-factor interaction (2FI) model was generated to see if it could maintain the accuracy of the quadratic model using significantly less terms. The reduced linear model for ammonia nitrogen removal efficiency, Y_1, is as follows:

$$Y_1 = 34.09 + 22.99X_1 + 21.85X_2 + 16.38X_1X_2 \tag{5.4}$$

Where Y_1 is the ammonia nitrogen removal efficiency, X_1 is the US energy output, and X_2 is the initial pH of the sample.

Table 5.3(b) shows the ANOVA test results of the regression model parameters for the predicted linear response surface describing ammonia nitrogen removal efficiency (Y_1). The model's F value of 428.86 and p-value Prob > F of <0.0001 indicate statistical significance with respect to ammonia nitrogen removal efficiency. Also, this shows that there is only a 0.01% chance that an F value this large could be due to noise. The linear model's adequate precision ratio is 66.76 which, like the quadratic model's, is well above the desired minimum value of 4. Continuing to comparing the linear and quadratic response models we see very similar ANOVA results. The linear model has slightly lower R^2, R^2_{adj}, and R^2_{pred} values than the quadratic at 0.94, 0.94, and 0.93, respectively. However, these values still show a very strong correlation between the model-predicted response and the observed results; an R^2_{adj} of 0.94 shows that only 6% of the total variation could not be accounted for by the empirical model. All the linear model terms (X_1, X_2, and X_1X_2) are significant and, like the quadratic model, it has significant lack-of-fit that can be accounted for similarly. It is quite clear comparing the two models that the linear version, with less terms and only a small drop in accuracy when looking at R^2_{adj}, retains the accuracy of the quadratic model with significantly less terms.

Table 5.3 ANOVA for (a) quadratic and (b) linear (2FI) response surfaces

(a)

Source	Sum of squares	d*f*	Mean square	*F* value	*p*-value Prob > *F*	
Model	36691.68	5	7338.34	428.86	<0.0001	Significant
X_1	15076.37	1	15076.37	881.07	<0.0001	
X_2	20044.16	1	20044.16	1171.39	<0.0001	
X_1X_2	5023.58	1	5023.58	293.58	<0.0001	
X_1^2	802.41	1	802.41	46.89	<0.0001	
X_2^2	223.39	1	223.39	13.06	0.0006	
Residual	1129.35	66	17.11			
Lack-of-fit	1129.34	65	17.37	1991.02	0.0178	Significant
Pure error	8.73E^{-03}	1	8.73E^{-03}			
Total		71				
$R^2 = 0.97$	$R^2_{\text{adj}} = 0.97$		$R^2_{\text{pred}} = 0.96$		Adequate precision = 73.83	

(b)

Source	Sum of squares	d*f*	Mean square	*F* value	*p*-value Prob>*F*	
Model	35661.65	3	11887.22	374.33	<0.0001	Significant
X_1	15412.37	1	15412.37	485.34	<0.0001	
X_2	20346.57	1	20346.57	640.72	<0.0001	
X_1X_2	5231.46	1	5231.46	164.74	<0.0001	
Residual	2159.38	68	31.76			
Lack-of-fit	2159.37	67	32.23	3693.32	0.0131	Significant
Pure error	8.73E^{-03}	1	8.73E^{-03}			
Total		71				
$R^2 = 0.94$	$R^2_{\text{adj}} = 0.94$		$R^2_{\text{pred}} = 0.93$		Adequate precision = 66.76	

It should be noted from table 5.3(a) and (b) that both the quadratic and linear models do have significant lack-of-fit. A model with a low R^2 value in addition to a significant lack-of-fit would indicate a failure to properly define the correlation between the experimental factors and the variables used to generate the response (Ryan & Joiner, 2001). However, both the quadratic and linear models have very high R^2 values and, as such, are acceptable representations despite their lack-of-fit (Jabeen *et al.*, 2015; Palaniandy *et al.*, 2015). Considering that both models are adequate representations of the observed data the 2FI (linear) model was chosen due to its simplicity.

Figure 5.2 presents the predicted versus observed values with respect to the ammonia nitrogen removal efficiency for the linear model. The general linear distribution of the points along the ideal trend line show the linear model's predicted values approximate the observed values with good accuracy. Figures 5.3 and 5.4 show the externally studentized residuals versus the predicted values and runs, respectively. These diagnostic plots illustrate that the linear model is a fair representation of the data due to the randomly scattered points and lack of an observable distribution pattern. Moreover, the externally studentized plots show that the assumption of constant variance and independence holds true for all of the runs (Montgomery, 2008). Also, Figures 5.3 and 5.4 show that there are no outliers in the linear model. Figure 5.5 reinforces this by showing that the residuals follow a normal distribution; this asserts that the statistical assumptions made for this model align with the observed data.

5.3.2 Response Surface Methodology

RSM was used to evaluate the interaction between the two independent variables (pH and energy output) with respect to the response variable (removal efficiency). Figures 5.6 and 5.7 illustrate the corresponding two-dimensional contour plot and three-dimensional surface plot of ammonia removal efficiency, respectively, for the linear model. It can be seen that removal efficiency increased with an increase in both pH and energy output. The effects of pH and energy output were found to be equal within the observed experimental range. Maximizing the linear response equation yields a maximum ammonia nitrogen removal efficiency of 87% at an optimum pH of 10.9 and energy output of 94.8 kJ. It should be noted that the experimental design was chosen to limit a potential excess of output energy.

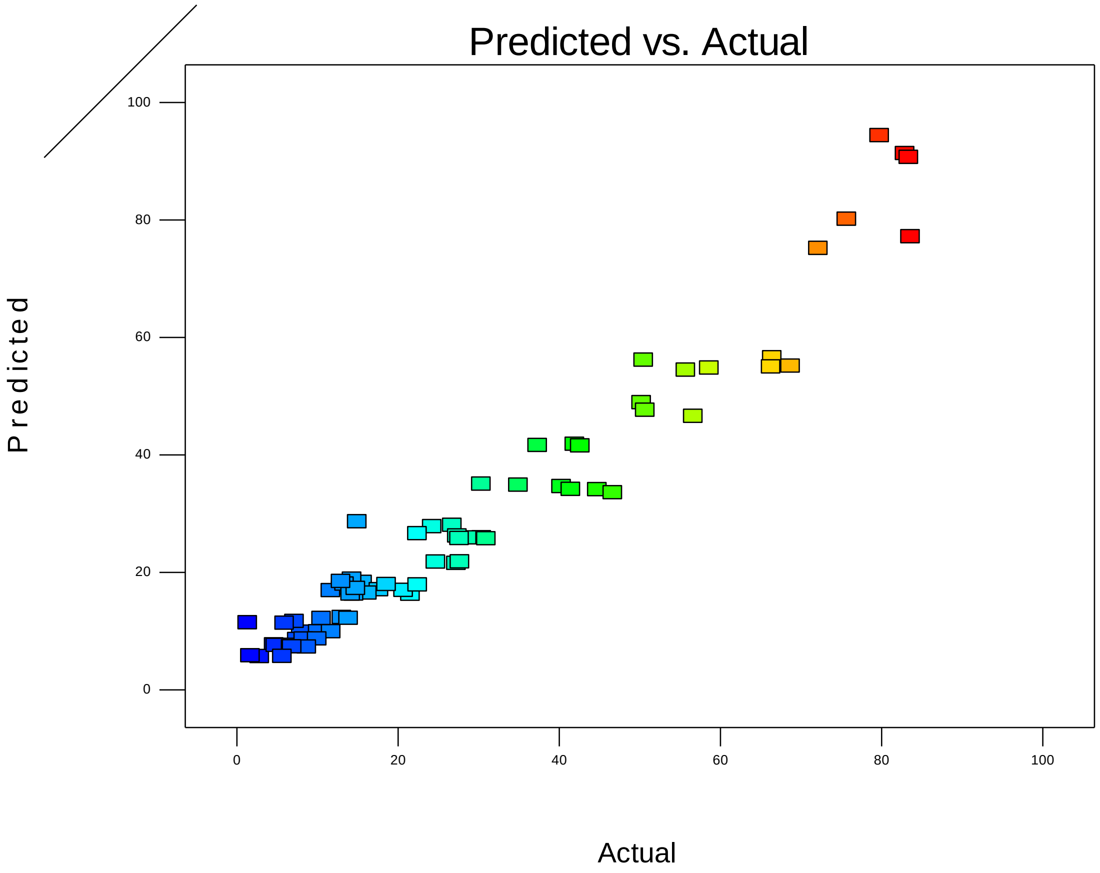

Figure 5.2 Correlation of predicted and actual values with respect to ammonia nitrogen removal for the linear model

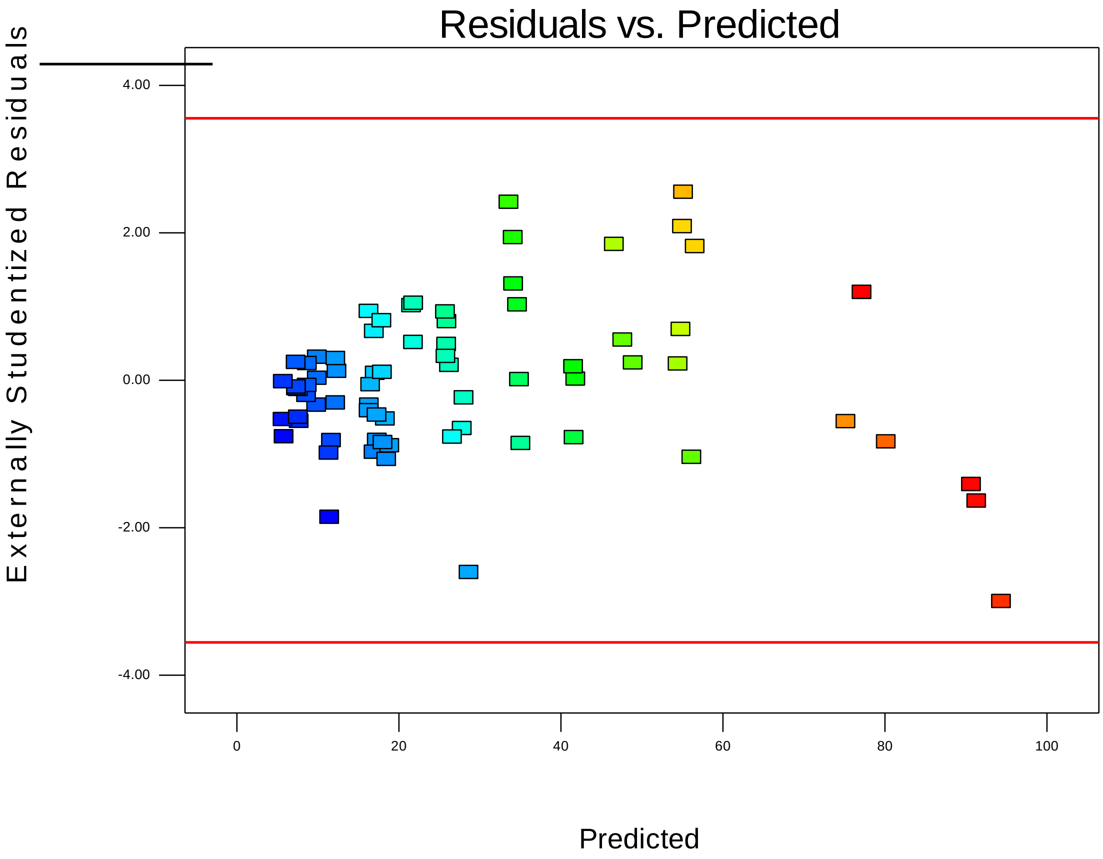

Figure 5.3 External residuals versus predicted values diagnostic plot for ammonia nitrogen removal for the linear model

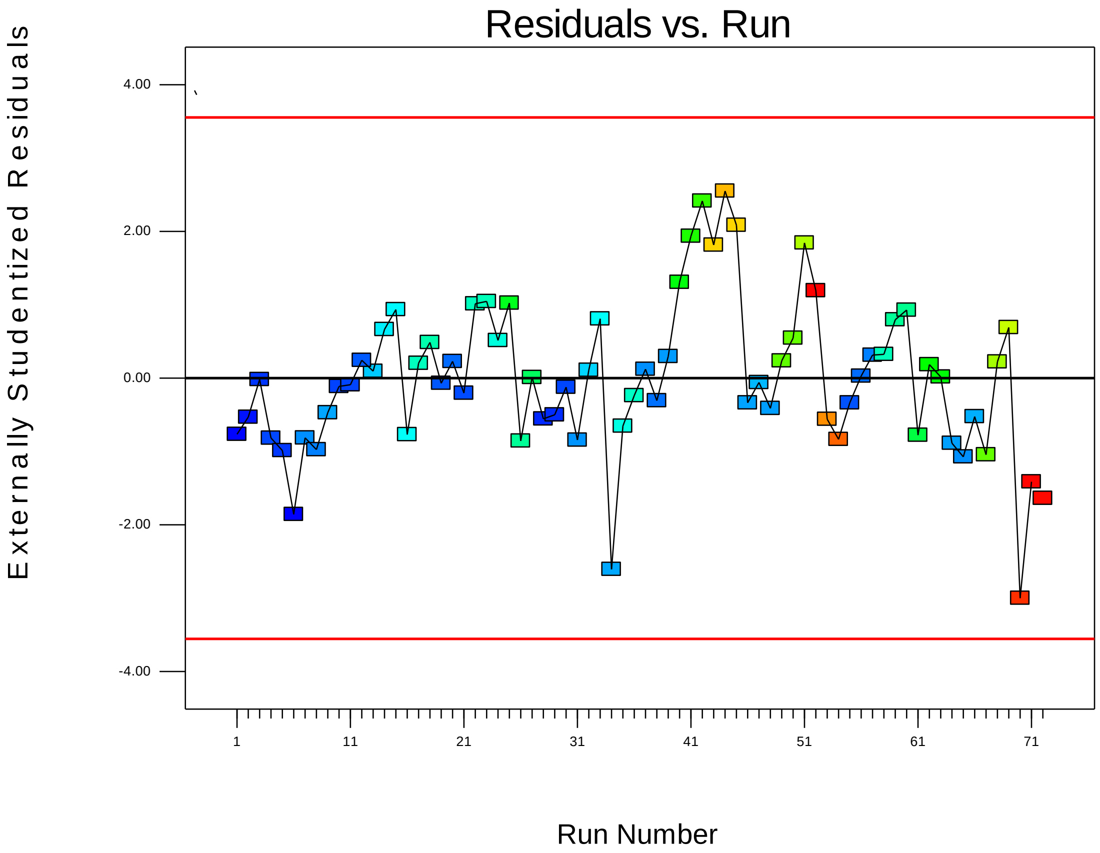

Figure 5.4 External residuals versus runs diagnostic plot for ammonia nitrogen removal for the linear model

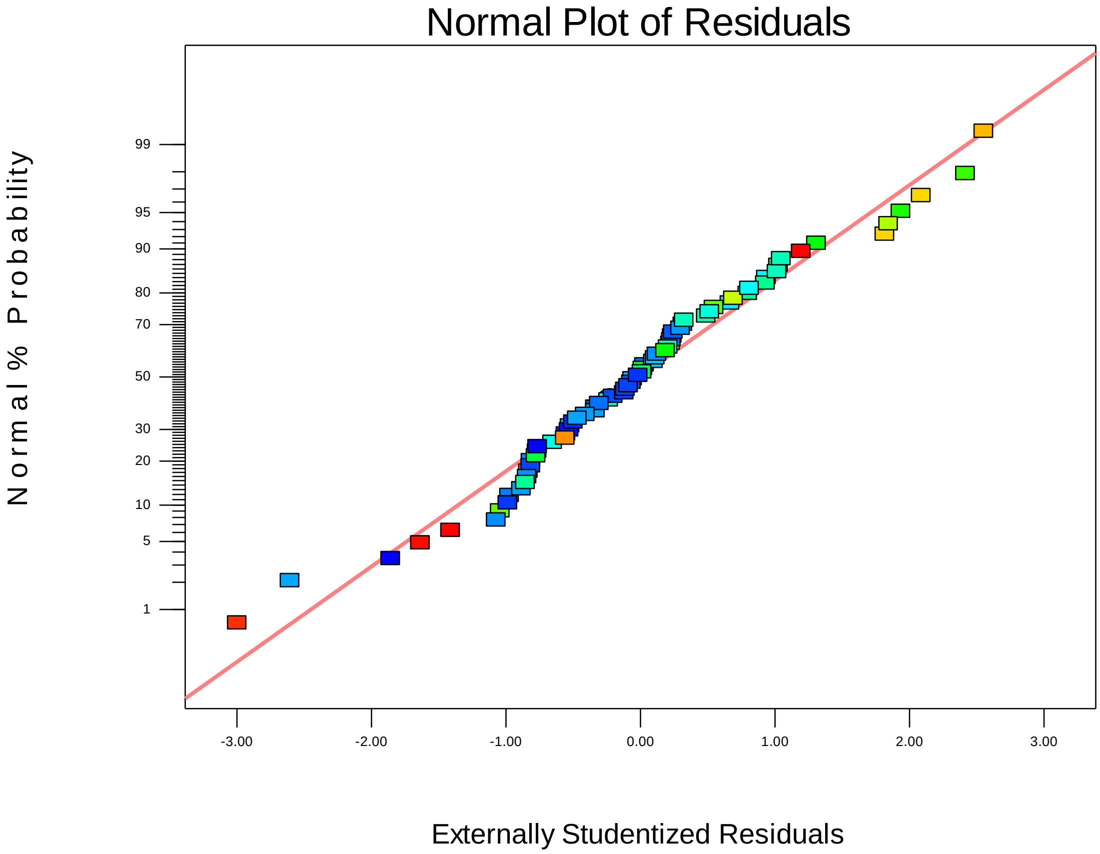

Figure 5.5 Normal probability plot of external residuals for ammonia nitrogen removal for the linear model

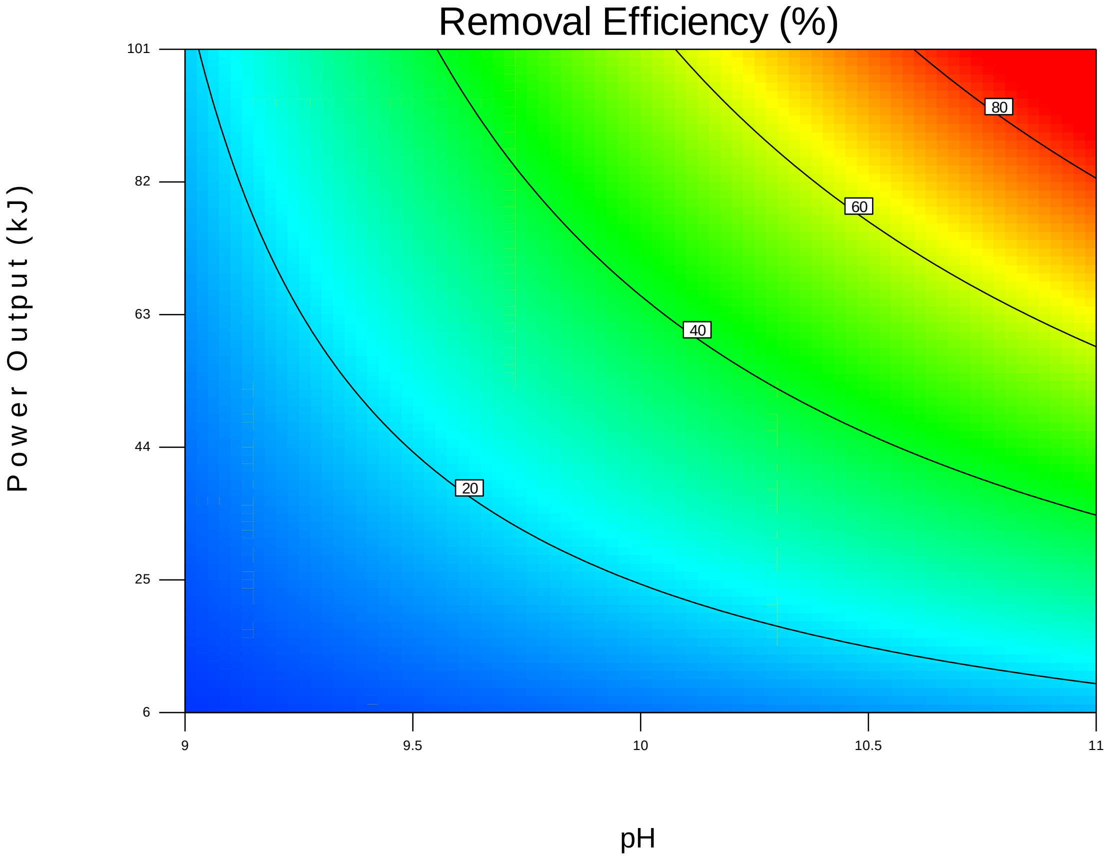

Figure 5.6 Two-dimensional surface contour plot of ammonia removal efficiency by RSM for the linear model

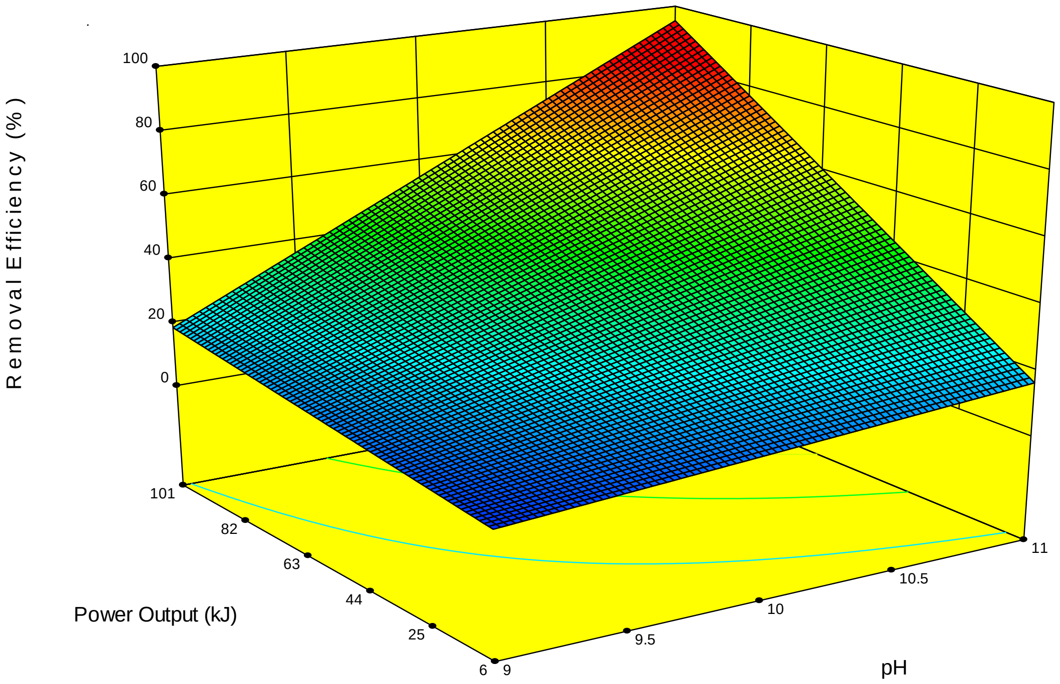

Figure 5.7 Three-dimensional surface contour plot of ammonia removal efficiency by RSM for the linear model

5.4 Conclusion

US irradiation was confirmed to be an effective treatment method for the removal of ammonia nitrogen from a synthetic ammonia solution containing 3000 mg TAN/L. A maximum observed experimental removal rate of 83% was achieved at a pH of 11 and energy output of 101 kJ.

Statistical analysis of the experimental data showed that ammonia nitrogen removal efficiency depended strongly on pH and energy output, with pH having slightly higher influence. The response surface equation's R^2 of 0.94 indicates that the linear model predicted the observed results accurately. RSM showed that an optimum pH of 10.9 and energy output of 94.8 kJ yields a maximum ammonia nitrogen removal efficiency of 87% from a synthetic ammonia solution containing 3000 mg TAN/L.

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CHAPTER VI
Additional Tests

6.1 Introduction

This chapter will cover additional tests that were performed and were not discussed in chapters 4 and 5. These additional tests involved evaluating the TAN removal efficiencies using the methods outlined in Chapter 3 using (i) a synthetic ammonia solution with an initial TAN concentration of approximately 5000 mg/L and (ii) two different leachates supplied. The following chapter will focus on comparing the results of these additional tests to the results presented in Chapter 4 which used a synthetic solution with an initial TAN concentration of approximately 3000 mg TAN/L to

6.2 Results and Discussion

Table 6.1 shows the characteristics of the two leachates used to assess the effectiveness of using ultrasound irradiation to remove ammonia nitrogen. While both leachates used had high ammonia nitrogen content they were selected to represent both old and new leachates – leachate 1 being more characteristic of a young landfill's leachate and leachate 2 more characteristic of a mature landfill's leachate. Young landfill leachate is generally characterized by the acidogenic phase of organic degradation which yields high oxygen demand (both biological and chemical) along with lower pH, alkalinity, and ammonia concentrations. Alternately, mature landfill leachate is generally characterized by the methanogenic phase of organic degradation which yields lower oxygen demand (both biological and chemical) along with higher pH, alkalinity, and ammonia concentrations (Słomczyńska & Słomczyński, 2004).

Table 6.1 Characteristics of leachates used to assess ammonia nitrogen removal by ultrasound irradiation.

	Leachate 1	Leachate 2
BOD_5 (mg/L)	18600	345
TSS (mg/L)	400	163
VSS (mg/L)	265	107
Alkalinity (mg $CaCO_3$/L)	6690	15300
COD (mg/L)	55000	6200
TKN (mg N/L)	3190	4670
$NH_3 + NH_4^+$ (mg TAN/L)	2324	5076
Nitrite (mg N/L)	18.9	0.75
Nitrate (mg N/L)	< 0.6	< 0.6
pH	5.1	8.2

Figure 6.1 shows the average total TAN removal efficiencies of US when used on the two synthetic solutions (approximately 3000 and 5000 mg TAN/L initial concentration) and the two leachates (see Table 6.1 for concentrations) adjusted to a pH 10, sonication time of 25 minutes, and US power output level of 100%. Figure 6.1 also shows the average contributions of non-thermal, thermal, and volatilization effects of total TAN removal by US; TOTAL refers to TAN removal obtained in samples treated by US; WB refers to TAN removal obtained in samples treated by water bath; US refers to the difference between TOTAL and WB or the non-thermal (sonication) effect; and Volat. refers to TAN removal due to volatilization for samples exposed to air with no treatment for an equivalent duration.

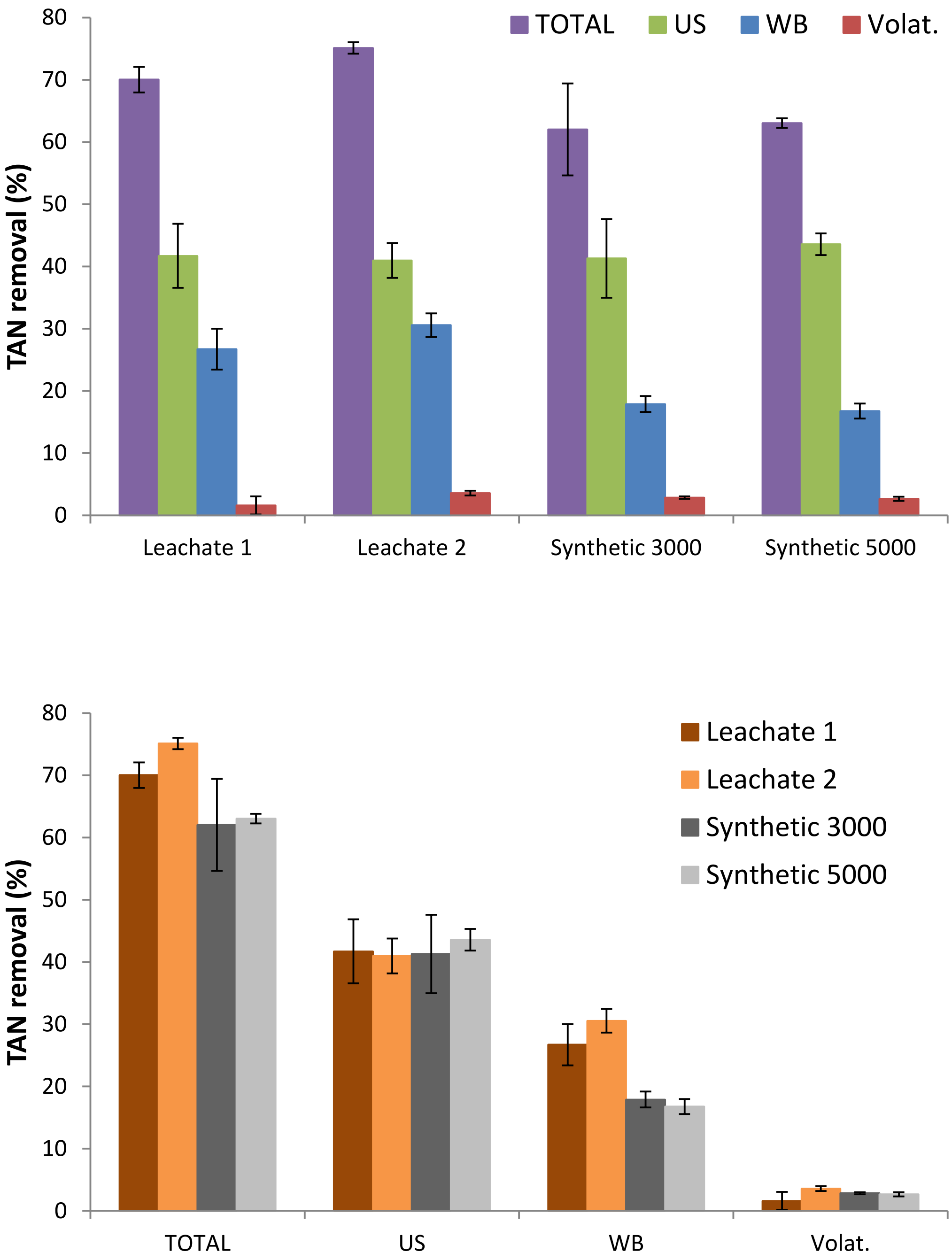

Figure 6.1 Average total, non-thermal (US), thermal (WB), and volatilization to air (Volat.) TAN removals for 4 high concentration ammonia solutions at a pH of 10, duration of 25 mins, and power output level of 100%

Looking at Figure 6.1 it can be seen that the average total TAN removal is greatest for leachate 2 at 75%. Leachate 1 has a comparable average TAN removal of 70% while the 3000 and 5000 mg TAN/L synthetic solutions have similar removal rates of 62% and 63%, respectively. The average TAN removals due to the thermal effects of US show leachate 1 and 2 have similar removals (27% and 31%, respectively) while the 3000 and 5000 mg TAN/L synthetic solutions have similar removals (18% and 17%, respectively). However, looking at the average TAN removals for the non-thermal effects of US shows very similar results across all 4 solutions (42% for leachate 1, 41% for leachate 2 and 3000 mg TAN/L synthetic solution, and 44% for 5000 mg TAN/L synthetic solution). Also, it can be seen that the TAN removals due volatilization are minimal and consistent across the 4 solutions. These results seem to indicate that the differences seen in total TAN removals are due to the thermal effects of US.

A one-way ANOVA test was used to evaluate whether significant differences in total TAN removal efficiencies exist due to changing initial concentrations; this was tested looking at the two synthetic and leachate groups separately. Also, a one-way ANOVA test was used to evaluate whether the solution being synthetic or leachate produces significant differences in the total TAN removal efficiency of US. Table 6.2 shows the results of the one-way ANOVA tests comparing (a) the total TAN removal efficiencies for the two synthetic ammonia solutions (initial concentrations of approximately 3000 and 5000 mg TAN/L), (b) the total TAN removal efficiencies for leachates 1 and 2, and (c) total TAN removal efficiencies for all four (synthetic solutions and leachates). It should be noted that total TAN removal efficiency includes the removal contributions of non-thermal US, thermal US, heat, and volatilization to the atmosphere.

Table 6.2 One-way ANOVA tests comparing total TAN removal efficiencies of (a) 3000 and 5000 mg TAN/L synthetic solutions, (b) leachates 1 and 2, and (c) all 4 solutions

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit.*
(a) Between Groups	806.67	1	806.67	1.74	0.1920	3.98
Within Groups	32531.50	70	464.74			
Total	33338.18	71				
(b) Between Groups	55.01	1	55.01	0.65	0.4288	4.30
Within Groups	1862.83	22	84.674			
Total	1917.84	23				
(c) Between Groups	2029.06	3	676.35	7.43	0.0004	2.82
Within Groups	4005.79	44	91.04			
Total	6034.85	47				

Looking at the results in table 6.2 it can be seen that the effect of initial concentration on total TAN removal efficiency between the two synthetic solutions is not significant (*P-value* > 0.05). Similarly, the results show that the effect of initial concentration on total TAN removal efficiency between the two leachates is not significant (*P-value* > 0.05). However, looking at the all four aqueous solutions (it can be seen that there are significant differences between the total TAN removal efficiencies of these groups (*P-value* < 0.05) - this will be explored more thoroughly in the paragraphs below. These findings mirror those of Wang *et al*. (2008) who found that changing the initial ammonia concentration did not produce significantly different removal rates when using US to remove ammonia from landfill leachate.

To understand whether thermal or non-thermal effects were the source of the significant total TAN removal results between synthetic solutions and leachate one-way ANOVA tests were used to compare the TAN removal efficiencies of all 4 solutions for each isolated US effect. Table 6.3 shows the results of one-way ANOVA tests where (a) compares the average TAN removal efficiencies for the four solutions (synthetic and leachate) due to non-thermal effects of US, and (b) compares the TAN removal efficiencies for the four solutions (synthetic and leachate) due to the thermal effects of US.

Table 6.3 One-way ANOVA tests with regards to TAN removal efficiencies between all 4 solutions from the effects of (a) non-thermal effects of US, and (b) thermal effects of US

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit.*
(a) Between Groups	222.37	3	74.12	1.44	0.2434	2.82
Within Groups	2261.64	44	51.40			
Total	2484.01	47				
(b) Between Groups	1637.59	3	545.86	42.06	5.56E-13	2.82
Within Groups	571.05	44	12.978			
Total	2208.64	47				

Looking at the results in table 6.3 it can be seen that when the non-thermal effects of US are isolated differences in TAN removal efficiencies between all four of the solutions are not significant (*P-value* > 0.05). Alternately, when the thermal effects of US are isolated, it can be seen that there are significant differences in the TAN removal efficiencies between the four solutions (*P-value* < 0.05).

Finally, to see whether varying initial ammonia concentration was also a source of the significant total TAN removal results when looking at the thermal effect of US, one-way

ANOVA tests were used to compare the TAN removal efficiencies within each solution group (synthetic and leachate). Table 6.4 shows the results of these one-way ANOVA tests where (a) compares the TAN removal efficiencies due to the thermal effects of US for the two synthetic ammonia solutions (initial concentrations of approximately 3000 and 5000 mg TAN/L), and (b) compares the TAN removal efficiencies due to the thermal effects of US for leachates 1 and 2 (initial concentrations of approximately 2300 and 5000 mg TAN/L).

Table 6.4 One-way ANOVA tests comparing TAN removal efficiencies due to the thermal effects of US for (a) 3000 and 5000 mg TAN/L synthetic solutions, (b) leachates 1 and 2

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit.*
(a) Between Groups	2.53	1	2.53	0.06	0.8149	3.98
Within Groups	3206.40	70	45.81			
Total	3206.93	71				
(b) Between Groups	0.84	1	0.84	0.05	0.8216	4.30
Within Groups	353.16	22	16.05			
Total	354.00	23				

Looking at the results in table 6.4 it can be seen that when looking at the thermal effects of US the differences in TAN removal efficiencies between the two synthetic solutions are not significant (*P-value* > 0.05). Also, the differences in TAN removal efficiencies between the two leachates are not significant (*P-value* > 0.05).

The findings from the ANOVA tests, along with observations from Figure 6.1, suggest that TAN removal efficiencies due to the non-thermal effects of US irradiation (no heat or atmospheric volatilization) are not influenced by any characteristic found in the tested solutions (both synthetic and leachate). This aligns with ultrasonic research done by

Kotronarou (1992) and Cost *et al.* (1993) on the effects of large and small particulate matter on the removal of hydrogen sulfide (H_2S) by US and the effects of particulate matter and alkalinity on the removal of *p*-nitrocatechol (*p*-Np) by US, respectively. Both of these studies found that particulate matter and alkalinity had no significant impact on the removal of H_2S or *p*-Np.

Alternately, the findings from the ANOVA tests, along with observations from Figure 6.1, suggest that TAN removal efficiencies due to the thermal effects of US irradiation (heat only, no atmospheric volatilization) are influenced by the characteristics found in the tested leachates (BOD, COD, TSS, TKN, Alkalinity, etc.). A hypothesis would be that the difference in saturation of the synthetic solutions versus the leachates is the cause of increased ammonia volatilization – the leachates having far more dissolved constituents than the synthetic solutions. The higher amount of dissolved molecules in leachate would cause more collisions due to molecular agitation from a heat increase. This in-turn would raise the temperature more rapidly than in the synthetic solution and increase the volatilization of the compounds with the lowest boiling points, which would include NH_3. However, it is not clear which leachate characteristic(s) contribute to these significantly different TAN removal efficiencies.

At a qualitative level, the use of US results in no foam or scum production in the leachate samples as well as no sludge or particulate production. These two observations are main benefits of US over other ammonia removal methods including electrocoagulation and chemical precipitation.

The results obtained through testing and analysis coupled with the results from literature would indicate that US irradiation, when heat production is mitigated, is a non-selective ammonia removal treatment method; non-selective meaning that the initial characteristics of the aqueous solution being sonicated have little to no impact on the removal of ammonia.

6.3 Conclusions

These additional tests show that the non-thermal effects of US irradiation presents statistically consistent removal of ammonia nitrogen across a wide range of aqueous solutions – from simple synthetic solutions to complex leachates emulating landfills of different ages. This indicates a level of non-selectivity in US irradiation which is valuable when treating a polluted aqueous source as variable as landfill leachate. However, in order to obtain these consistent removal results cooling the solution being sonicated is necessary. These findings require further investigation to more fully understand which specific characteristics of landfill leachate have the potential to influence ammonia removal by US. Also, an investigation into which characteristics of leachate contribute to the increased thermal volatilization of ammonia would be beneficial.

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CHAPTER VII
Conclusions and Recommendations

7.1 Conclusions

The application of ultrasound irradiation to remove ammonia nitrogen from aqueous solutions, including lab-made simulated landfill leachate, at 20 kHz was investigated in this thesis. Batch experiments were carried out using two synthetic solutions with initial ammonia concentrations of 3000 and 5000 mg TAN/L in addition to two leachates from new and old landfills.

The results of testing showed that US irradiation is an effective treatment technology for the removal of aqueous ammonia. More specifically, it was found that increasing sonication time and pH increased ammonia removal. The maximum observed removal efficiency of ammonia was 87.4% at a pH of 11 and sonication time of 25 minutes. Also, it was found that volatilization of ammonia to the atmosphere accounted for 0 - 7% of removal, the thermal effect of US accounted for 21.1 - 52.7%, and the non-thermal effect of US accounted for 44.5 - 78.8% (depending on pH and sonication time).

Results of factorial design and response surface methodology showed that pH, energy output (kJ), and the interaction between the two were significant parameters. The predicted two factor interaction model was in close agreement to the observed data (R^2 of 0.94) and produced an optimum ammonia removal efficiency of 87% at a pH of 10.9 and energy output of 94.8 kJ.

Additional testing showed similar average TAN removals for all solutions tested (two synthetic solutions and two leachates with initial ammonia concentrations of approximately 3000, 5000, 2400, and 5100 mg TAN/L, respectively) at a pH of 10, sonication time of 25 minutes, and US power output amplitude of 100%. Analysis of variance tests on the full data sets showed that differences in the TAN removal efficiency of ammonia due to the non-thermal effects of ultrasound between synthetic and leachate solutions were not significant. Also, that the differences in total TAN removal between different initial ammonia concentrations within a solution group (synthetic or leachate) were not significant. However, significant differences between TAN removal efficiencies were observed between synthetic and leachate solution groups when the thermal effects of US were isolated, showing higher ammonia volatilization due to heat in the leachates versus synthetic solutions.

These results indicate that ultrasound irradiation is not only an effective method for the removal of ammonia nitrogen from highly concentrated aqueous solutions, but also potentially non-selective.

7.2 Future Work

Ultrasound irradiation has been shown to be an effective method for the removal of ammonia nitrogen from highly concentrated aqueous solutions. However, all experiments were done in batches, with continuous sonication, and no heat mitigation. Also, experiments were only carried out using 4 different solutions (two synthetic and two leachates).

Future experiments could include using a continuous flow of incoming solution or leachate to simulate how ultrasonic technologies would be used in a real-world scenario; the use of various pulse settings for sonication times (ex: 30s on, 30s off, repeating) should be explored to determine the most efficient timings for the removal of ammonia nitrogen; and a cold water bath to mitigate heat production to further explore the findings regarding removal efficiency due to thermal and non-thermal effects. Also, experiments could be performed with many leachates with differing characteristics to test the findings of non-selectivity further. Furthermore, experiments could be done to find a range of ultrasonic tip depths for a given volume of solution. Lastly, due to conflicting conclusions regarding the removal pathways of ammonia by ultrasound, experiments should be carried out inhibiting ammonia removal by hydroxyl radical to determine whether removal is predominated by chemical (oxidation) or physical (pyrolysis) mechanisms.