Application of Sequential Microwave/Aeration Process for the Removal of Ammonia from Landfill Leachate

By

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A thesis submitted
Under the supervision of Dr. Majid Sartaj
A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Applied Science
In
Environmental Engineering

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ABSTRACT

Application of microwave (MW) radiation followed by aeration (A) for the purpose of ammonia removal from both synthetic solutions and landfill leachate was investigated in this study. Four sets of experiments: water bath (WB), microwave (MW), sequential microwave/aeration process (MW+A), and sequential water bath/aeration process (WB+A) were conducted using synthetic solution. MW and MW+A tests were applied on the landfill leachate as well. For each test, either 100 mL of synthetic solution or landfill leachate was used. All the tests were conducted with three replicates in batch scale. For both economic and safety concerns, the samples' temperature were maintained below the boiling point.

One-way ANOVA tests and T-tests were conducted to analyze the differences of ammonia removal efficiencies among different methods. Both thermal and non-thermal effects for the sequential microwave/aeration process were investigated. Factorial design and response surface methodology (RSM) were applied to evaluate and optimize the effects of pH, MW energy level and microwave power output.

Results confirmed that the sequential microwave/aeration process was an effective approach for removal of ammonia from aqueous systems. Maximum ammonia removal of 81.7 % for synthetic solution and 70% for landfill leachate was achieved by applying 7.8 KJ MW energy output/L sample and 10 minutes aeration. When apply the sequential microwave/aeration process to synthetic solution, at optimum condition of pH 10.5, 7.8 KJ MW energy output/L sample and 10 minutes aeration time, the contribution of thermal process was 39%, while 61% for non-thermal processes (33% for aeration and 28% for EMF).

Statistical analysis of synthetic solution tests data using RSM showed that ammonia removal efficiency strongly depended on pH and MW energy output. R^2 of 0.941 indicates that observed results fitted well with the model prediction. Optimum pH and MW energy output level for ammonia removal was 11 and 7.8 KJ MW energy output/L sample respectively, and under this condition, maximum ammonia removal efficiency predicted for synthetic solution was 76.3%.

ACKNOWLEDGEMENTS

First of all, I would like to express my gratitude to my academic supervisor, Dr. Majid Sartaj, who was exceedingly professional, patient and supportive in all the time I took to complete this research. He showed his great patience guiding me through my master study.

I would like to thank my colleague and friend Yuanhao Ding for helping me both in the research and reviewing my thesis. I would also like to thank Dr. Nuno Migule Gabriel Coelho and Rania Alqaralleh for the encouragement and suggestions they gave to me on my research.

Special thanks to Gary Cui for his time, effort, great patience and professional attitude in reviewing, correcting the thesis and giving useful suggestions.

This would not have been possible without the support of my family and beloved friends. To my parents, I give my deepest thanks for their support, not only this journey, but also all the past years of my life; I dedicate this thesis to them.

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List of Abbreviations

A: aeration;

AC: activated carbon;

ANOVA: analysis of variance;

AO7: azo dye acid Orange 7;

BOD: biochemical oxygen demand;

CA: Canada;

CH: traditional heating;

CH/PS: conventional heating activated persulfate;

CI: confidence interval;

CN: China;

COD: chemical oxygen demand;

CEPA: Canadian Environmental Protection Agency;

DF: degree of freedom;

DW: distilled water;

EMF: electromagnetic field;

ISWM: integrated solid waste management;

JP: Japan;

MG: malachite green;

MSW: municipal solid waste;

MW: microwave;

MW+A: microwave followed by aeration;

MW-APO: microwave activated persulfate oxidation;

PAC: powered activated carbon;

PAC-SBR: sequencing batch reactor combined with powdered activated carbon;

RAS: return activated sludge;

RSM: response surface methodology;

SBR: sequencing batch reactor;

SG: Singapore;

SMX: sulfamethoxazole;

SS: suspended solids;

SAS: surplus activated sludge;

TAN: total ammonia nitrogen;

TKN: total Kjeldahl nitrogen;

TOC: total organic carbon;

UASB: up-flow anaerobic sludge blanket;

WB: water bath;

WB+A: water bath followed by aeration.

CHAPTER I

INTRODUCTION

1.1 Background

Ammonia is one of the major inorganic pollutants in surface water. Total ammonia nitrogen (TAN) exists in aqueous solutions as two forms: un-ionized ammonia (NH_3) and ionized ammonia (NH_4^+). Wastewater from steel, fertilizer, petroleum, and meat-processing industries and landfill leachate are the main sources of ammonia in natural water bodies (Metcalf and Eddy, 2003).

Landfilling is one of the most common municipal solid waste (MSW) management approaches due to its easy operational procedures and low cost. It had been widely used in countries with access to large land area, for example Canada, Australia and China (Raffaello, 2009). Landfill leachate and potential migration into water resources is one of the main concerns of landfill management and operation.

Landfill leachate can contain relatively high NH_3-N concentrations up to 13,000 mg/L (Renou et al., 2008). High ammonia concentration in aqueous systems could inhibit microbial activities during biological treatments including the nitrification process. The inhibition is mainly due to the presence of un-ionized ammonia (NH_3), which is the toxic form and dependent on the total nitrogen concentration, temperature and pH. US Environmental Protection Agency (USEPA) has designated 1.9 mg TAN/L (20°C, pH of 7) as the chronic toxicity criteria for aquatic organisms (USEPA, 2013). Ammonia was added to the list of toxic substances by the Canadian Environmental Protection Agency (CEPA) in 1999 (Environment Canada, 2001) and the discharge concentration from wastewater treatment plant is limited by federal regulations. In addition, ammonia serves as one of the primary inorganic nitrogen sources and at high levels can cause eutrophication in natural aqueous systems (Dachs et al, 2000). All treatment plants with a daily discharge of greater than 100 m^3 is subject to a maximum concentration of 1.25 mg/L NH_3 expressed as nitrogen at 15°C (Canada Gazette, 2012).

Conventional treatment processes for ammonia removal from aqueous solution include biological nitrification/denitrification, air stripping, adsorption and ion-exchange. Microwave radiation (MW) has been also used in environmental field for sludge and wastewater treatments such as MW enhanced oxidation processes and MW enhanced ammonia-stripping processes (Lin et al., 20009a; Lin et al., 2009b; Teroci et al., 2009; Remya and Lin, 2011). Application of different removal technologies at reasonable cost as a treatment or pre-treatment method has been an important area of research in recent years.

1.2 Objectives

The main objective of this research was to investigate the feasibility and performance of a sequential microwave/aeration process for the removal of ammonia from both synthetic solutions and real landfill leachate at laboratory scale. Four sets of experiments were carried out for the synthetic solution: water bath (WB), MW, microwave followed by aeration (MW+A), and water bath followed by aeration (WB+A). WB and WB+A tests were used as control groups to measure thermal contributions. MW and MW+A tests were also carried out for the ammonia removal from real landfill leachate. Objectives of this research are:

1. Investigate the effect of parameters such as pH, ammonia concentrations, MW energy levels, MW power levels and radiation time on the performance of MW+A application;

2. Assess the contribution of the thermal and non-thermal effects of the MW+A processes;

3. Evaluate and optimize ammonia removal from aqueous system by application of MW+A method using statistical analysis, i.e., factorial design and response surface methodology (RSM);

4. Evaluate ammonia removal efficiency and optimize the experimental conditions for ammonia removal from real landfill leachate using MW+A.

1.3 Thesis Layout

This thesis is presented in the form of technical papers with six main chapters. Chapter I is introduction, containing the background, objectives and layout of the thesis. Chapter II is the literature review of the aqueous systems with high amount ammonia and ammonia removal approaches. Chapter III is the materials and methodology of this study. Chapter IV is the first technical paper entitled "Thermal and Non-thermal Effects of Sequential Microwave/Aeration Process for the Removal of Ammonia from Aqueous Solution". Chapter V is the second paper entitled "Statistical Analysis and Optimization of Ammonia Removal from Landfill Leachate by Sequential Microwave/Aeration Process Using Factorial Design and Response Surface". Chapter VI summarizes the conclusions of the thesis and presents potential future work for this study area. It is necessary to mention that due to the paper based format, there could be some repeated information appearing in different chapters.

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CHAPTER II

LITERATURE REVIEW

2.1 Solid Waste Management

Solid waste usually refers to any garbage, refuse, sludge from water or wastewater treatment plants or any other discarded material from the urban community (Tchobanoglous et. al, 1993). It is also conventionally defined as material that is unwanted or of no immediate use at the point of generation (Chandrappa and Das, 2012). Solid wastes can be generated from residential, commercial and industrial activities. Generally, municipal solid waste (MSW) is used to refer to the solid or semi-solid residential, commercial, and institutional wastes generated in urban areas excluding industrial hazardous wastes (US EPA, 2008).

The main elements of an Integrated Solid Waste Management (ISWM) plan include collection, transportation, storage, recycle, treatment and final disposal. Minimizing the impacts on the environment during the solid waste management process is the main objective of any ISWM plan. Among all these processes, the final disposal (thermal treatment and/or landfilling) is the main component due to significant amount of MSW to be disposed of, and pollutants generated during this stage (Raffaello, 2009). Fig. 2.1 shows the three most common solid waste treatment strategies used by different countries. The three axes represent the percentages of three different treatment methods used by different countries (Cossu and Piovesan, 2007). As seen in this figure, engineered landfilling is the most common solid waste management approach for most countries due to its easy operation procedure and low cost. Countries with abundant land resources, such as Canada (CA) and China (CN), tend to use this method more than any other methods.

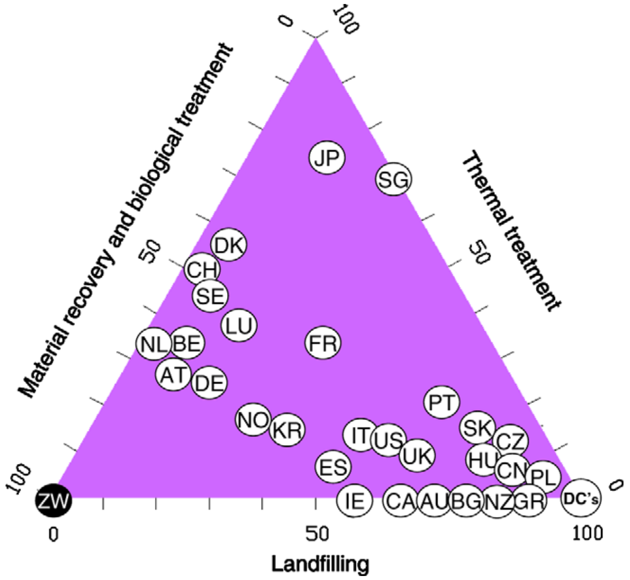


Fig. 2.1 Percentage of different solid waste treatment method of different countries (Adapted from Cossu and Piovesan, 2007)

In contrast, countries with limited land area such as Japan (JP) and Singapore (SG) prefer to use thermal processes due to the benefit of volume reduction. Moreover, a facility for thermal treatment method requires less area. Thus, it is possible to operate this process even in densely populated cities. However, the main issue of thermal processes is toxic air emissions, which contain SO_2, NO_x, CO, dioxins and pollutant particles (Beylot & Villeneuve, 2013; Zhou, et al., 2014).

As the most widely used waste disposal approach, the main components of an engineered landfill are the containment systems, and the gas and leachate collection systems (Morris & Barlaz, 2011). After gases and leachate are collected, there are several treatment processes to remove or reduce the harmful substances in leachate or gas before utilization or release into the environment. Nevertheless, there are several short-term and long-term issues involved in landfilling operation, as shown in Fig. 2.2.

The most common problems during the construction, operation and post-closure phases are: wind-blown litter and dust, noise, odorous gases, birds, vermin and insects attracted by the waste, surface runoff, and generation of leachate and landfill gas (Christensen et al., 2012). Landfill leachate might not be a significant concern at the beginning depending on the characteristics of the wastes in the landfill. However, it will become the major issue during operation and at the post-closure stage.

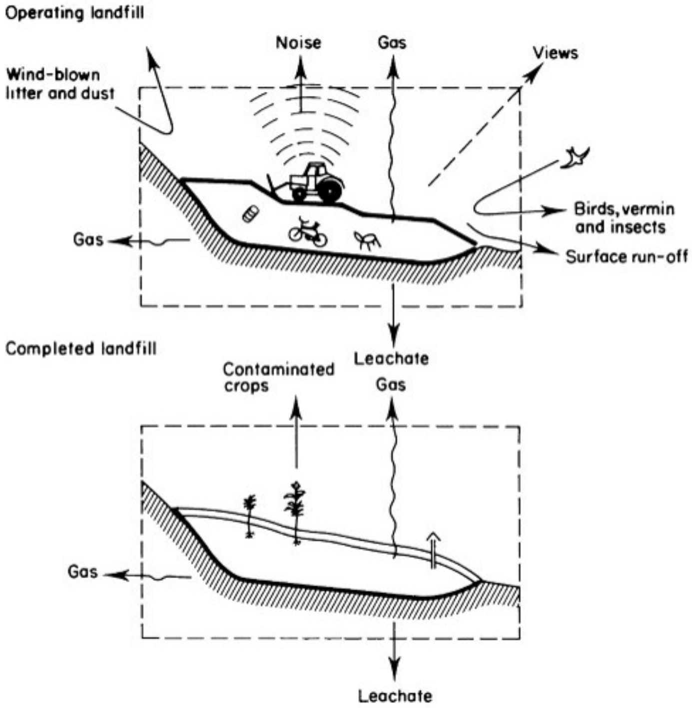


Fig. 2.2 Illustration of the major environmental aspects related to sanitary landfilling. (Adapted from Christensen, et al., 2012)

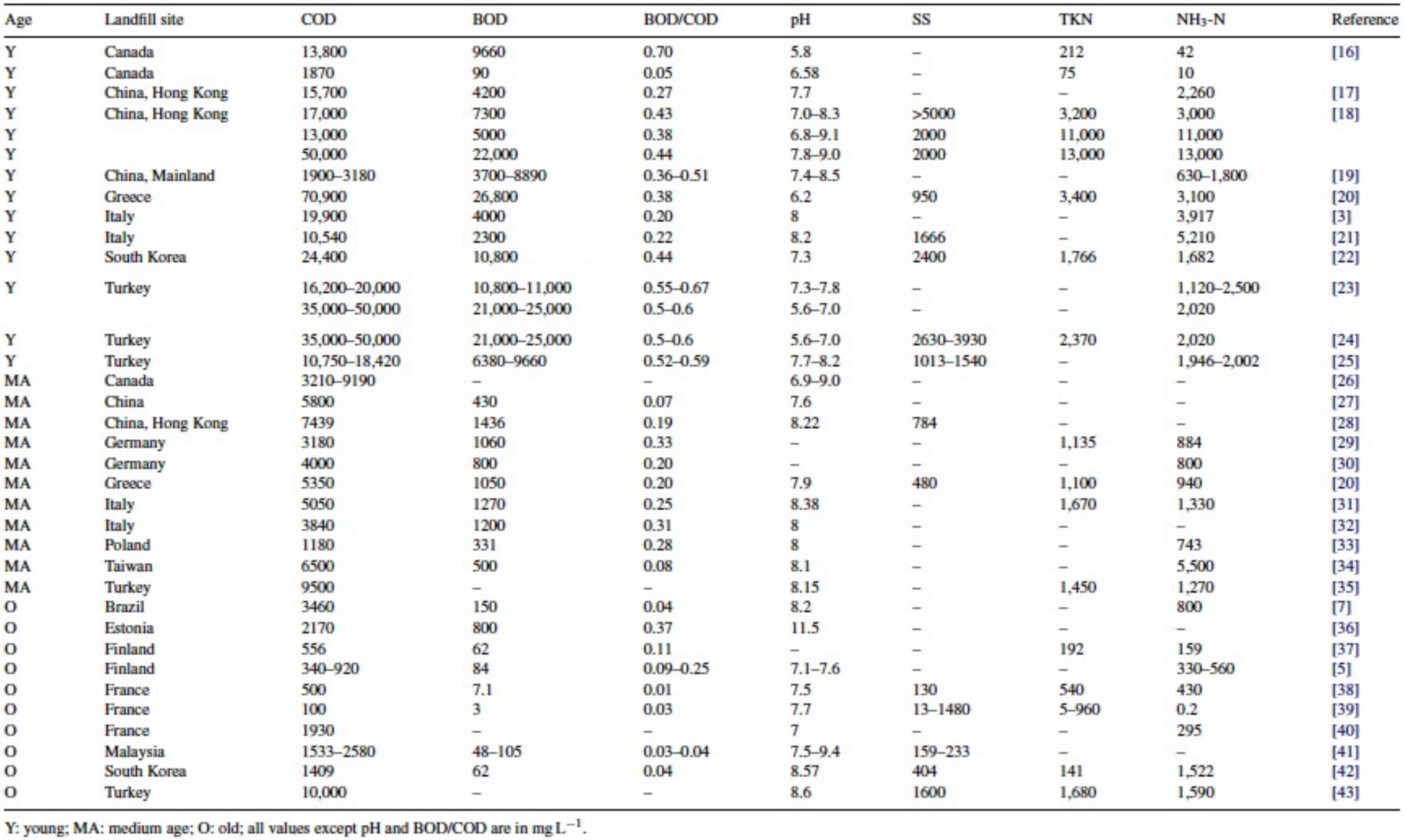
2.2 Landfill Leachate

Leachate is one kind of hazardous and severely polluted wastewater that contains large amounts of organic matters, ammonia nitrogen, heavy metals, chlorinated organic and inorganic salts (Wang et al., 2008). Many factors such as climatology (precipitation), the age of a landfill, the solid waste type and composition can affect the quantity and quality of the landfill leachate (Ludwing et al., 2003; Sartaj et al., 2010; Emenike et al., 2012; Nair et al., 2014).

Several parameters, such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), the BOD/COD ratio, suspended solids (SS), pH, ammonia nitrogen (NH_3-N), total Kjeldahl nitrogen (TKN) and heavy metals can be used to characterize the quality of landfill leachate. According to Table 2.1, the COD value is in the range of 100 mg/L to 70900 mg/L. The lowest value reported was for a 10-year old landfill near Marseille (France). The pH values can range from 5.8 to 8.5 (with the exception of a few extraordinary high values) depending on the biological activities inside the landfill. TKN value can range from as low as 0.2 up to 13000 mg/L. And BOD/COD ratio decreases rapidly with the increase in age of the landfills from 0.70 to 0.04.

During the waste stabilization processes, the quantity of biodegradable substances is reduced due to the metabolism of the microorganisms. However, most of the organic nitrogen converts into ammonium nitrogen through ammonification during this stage. Aside from the nitrogen that leaves the system in the form of free ammonia (NH_3-N), there is no removal path for the ammonia in anaerobic systems (Berge et al., 2006). Therefore, mature landfill leachate is usually characterized by its low of BOD/COD ratio and relatively high NH_3-N concentration (Renou et al., 2008).

Table 2.1 Leachate composition (COD, BOD, BOD/COD, pH, SS, TKN, NH_3-N) (Adapted from Renou, et al., 2008)



Age	Landfill site	COD	BOD	BOD/COD	pH	SS	TKN	NH_3-N	Reference
Y	Canada	13,800	9660	0.70	5.8	–	212	42	[16]
Y	Canada	1870	90	0.05	6.58	–	75	10	
Y	China, Hong Kong	15,700	4200	0.27	7.7	–	–	2,260	[17]
Y	China, Hong Kong	17,000	7300	0.43	7.0–8.3	>5000	3,200	3,000	[18]
Y		13,000	5000	0.38	6.8–9.1	2000	11,000	11,000	
Y		50,000	22,000	0.44	7.8–9.0	2000	13,000	13,000	
Y	China, Mainland	1900–3180	3700–8890	0.36–0.51	7.4–8.5	–	–	630–1,800	[19]
Y	Greece	70,900	26,800	0.38	6.2	950	3,400	3,100	[20]
Y	Italy	19,900	4000	0.20	8	–	–	3,917	[3]
Y	Italy	10,540	2300	0.22	8.2	1666	–	5,210	[21]
Y	South Korea	24,400	10,800	0.44	7.3	2400	1,766	1,682	[22]
Y	Turkey	16,200–20,000	10,800–11,000	0.55–0.67	7.3–7.8	–	–	1,120–2,500	[23]
		35,000–50,000	21,000–25,000	0.5–0.6	5.6–7.0	–	–	2,020	
Y	Turkey	35,000–50,000	21,000–25,000	0.5–0.6	5.6–7.0	2630–3930	2,370	2,020	[24]
Y	Turkey	10,750–18,420	6380–9660	0.52–0.59	7.7–8.2	1013–1540	–	1,946–2,002	[25]
MA	Canada	3210–9190	–	–	6.9–9.0	–	–	–	[26]
MA	China	5800	430	0.07	7.6	–	–	–	[27]
MA	China, Hong Kong	7439	1436	0.19	8.22	784	–	–	[28]
MA	Germany	3180	1060	0.33	–	–	1,135	884	[29]
MA	Germany	4000	800	0.20	–	–	–	800	[30]
MA	Greece	5350	1050	0.20	7.9	480	1,100	940	[20]
MA	Italy	5050	1270	0.25	8.38	–	1,670	1,330	[31]
MA	Italy	3840	1200	0.31	8	–	–	–	[32]
MA	Poland	1180	331	0.28	8	–	–	743	[33]
MA	Taiwan	6500	500	0.08	8.1	–	–	5,500	[34]
MA	Turkey	9500	–	–	8.15	–	1,450	1,270	[35]
O	Brazil	3460	150	0.04	8.2	–	–	800	[7]
O	Estonia	2170	800	0.37	11.5	–	–	–	[36]
O	Finland	556	62	0.11	–	–	192	159	[37]
O	Finland	340–920	84	0.09–0.25	7.1–7.6	–	–	330–560	[5]
O	France	500	7.1	0.01	7.5	130	540	430	[38]
O	France	100	3	0.03	7.7	13–1480	5–960	0.2	[39]
O	France	1930	–	–	7	–	–	295	[40]
O	Malaysia	1533–2580	48–105	0.03–0.04	7.5–9.4	159–233	–	–	[41]
O	South Korea	1409	62	0.04	8.57	404	141	1,522	[42]
O	Turkey	10,000	–	–	8.6	1600	1,680	1,590	[43]

Y: young; MA: medium age; O: old; all values except pH and BOD/COD are in mg L^{-1}.

2.3 Ammonia

2.3.1 Characteristics of Ammonia

Ammonia is one of the major inorganic pollutants in water resources. Ammonia exits in aqueous solution as two forms: un-ionized ammonia (NH_3) and ionized ammonia (NH_4^+). It is common in aquatic chemistry to refer to and express the sum of the two as simply ammonia or total ammonia nitrogen (TAN) (Nair et al., 2014). The equilibrium between NH_3 and NH_4^+ is heavily dependent on the pH value and temperature of the aqueous solution. The percentage of NH_3 and NH_4^+ can be derived by the following equation containing the acid ionization constant, K_a:

$$\frac{[NH_3][H^+]}{[NH_4^+]} = K_a \qquad (2.1)$$

Where $[NH_3]$ is the concentration of NH_3, and $[NH_4^+]$ stands for the concentration of NH_4^+. $[H^+]$ is the concentration of H^+ (pH). K_a is the acid ionization constant, which changes with respect to temperature. As the pH increases, the proportion of unstable and volatile NH_3 also increases.

Fig. 2.3 shows the distribution of NH_3 and NH_4^+ as a function of pH at a temperature of 20°C. The pKa value at this temperature is approximately 9.2, which means that at pH = 9.2, the ratio of NH_3 to NH_4^+ is about 1:1. For pH values lower than 7, the majority of ammonia exists as NH_4^+. At low pH conditions, the concentration of un-ionized ammonia is negligible. As pH increases over 7, the concentration of NH_3 rises and it becomes the dominant form.

According to US EPA's fresh water criteria (2013), the ammonia chronic toxicity to aquatic organisms is 1.9 mg/L as TAN at 20°C and pH of 7. Significant toxicity of leachate from a landfill in Florida was reported by Ward et al. (2000) to be due to the presence of ammonia. Other researches confirmed that the toxicity mainly comes from NH_3 (Clément and Merlin, 1995; Rutherford et al., 2000; Ward et al., 2002). High levels of ammonia nitrogen has been suggested as one of the most significant long-term challenges in landfills, and it is one of the parameters in determining the termination of the landfill post-closure monitoring (Berge et al., 2005).

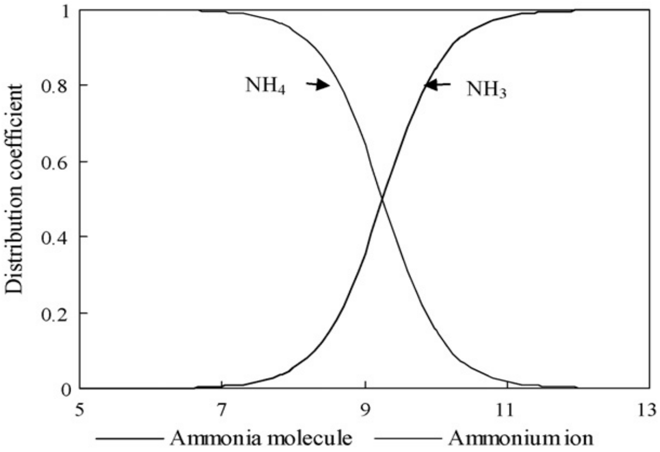


Fig. 2.3 Distribution coefficients of NH_3 and NH_4^+ at different pH levels (20°C). (Adapted from Lin et al, 2009a)

According to the United States Environmental Protection Agency (USEPA), at a pH of 7 and a water temperature of 20°C, the acute and chronic criterion magnitude is 17 mg TAN/L and 1.9 mg TAN/L, respectively (USEPA 2013). For vertebrates, the toxicity of ammonia accumulation can be characterized by over-excitation of the nervous system (Walsh et al., 2007). Moreover, the increased nitrogen level in the water bodies can also cause water eutrophication and proliferation of toxic algae blooms in the rivers, lakes and coastal waters as shown in Fig. 2.4 (Dachs et al, 2000).

Fig. 2.4 A worldwide study in 2005 noted an increase in eutrophication, which was blamed for the death of these fish in a lake near Bangalore, India. (Britannica, 2014)

Studies have shown that ammonia is the most toxic substance with inhibition effects on microbial activities, including nitrification. (Jung et al., 2004; Metcalf and Eddy, 2003). It can inhibit the NO_2-N oxidation process at the NH_4-N concentration of 20 mg/L and the NH_4-N oxidation process at a concentration of 100 mg/L (Metcalf and Eddy, 2003). Thus, the biodegradation processes will be slowed down during wastewater treatment and removal efficiency of ammonia and organic matter will be significantly reduced.

2.3.2 Sources of Ammonia

In the natural environment, ammonia is usually generated from the decomposition of dead organisms and/or excreted wastes of living organisms. The main ammonia sources from human activities are agricultural fertilization, and municipal and industrial emissions. In the United States, more than 95% of the aquatic point source emissions are from sewage treatment plants (Ip et al., 2001). Other sources include wastewater from steel, fertilizer, petroleum, meat-processing industries and landfill leachate.

2.3.3 Ammonia Removal from Aqueous System

For highly contaminated wastewaters such as landfill leachate, ammonia removal is usually achieved by a combination of physical, chemical and biological processes. This is because high ammonia concentrations are commonly accompanied by high concentrations of organic matter and heavy metals, which makes it difficult to obtain satisfactory treatment results using only one method (Ahn et al., 2002; Chiang et al., 2001; Park et al., 2001; Lin and Chang, 2000).

2.3.3.1 Chemical Precipitation

Precipitation has been confirmed as an effective pretreatment process for ammonia removal from wastewater with high ammonia concentration (Calli et al., 2005b). The researches by Li et al., (1999) and Patel & Desai (2014) reported the application of ammonia removal from landfill leachate using magnesium ammonium phosphate (MAP). In Ozturk's (2003) research, struvite precipitation with a stoichiometric ratio of Mg: NH_4^+: PO_4^+=1:1:1 was used for the pre-treatment of raw landfill leachate effluent with the initial COD concentration around 2000 mg/L and ammonia concentration of 2240 mg/L. The maximum COD removal efficiency was reported as 50% at pH 8-10. The ammonia removal efficiency reached as high as 85% at pH 9.2 (Ozturk et al., 2003). Yangin et al. (2002) investigated the MAP precipitation approach after anaerobic treatment of wastewater and landfill leachate mixture. The highest reduction (66%) in NH_4^+-N was achieved at pH of 9.3 at the stoichiometric ratio. Up to 86% of NH_4^+-N was removed at the same pH above the stoichiometric ratio. In the up-flow anaerobic sludge blanket (UASB) reactor, when applied at and above the stoichiometric ratio, NH_4^+-N concentrations were reduced to 31 mg/L and 13 mg/L, respectively. The main disadvantage of the precipitation process is the generation of contaminated sludge. Moreover, precipitation is considered to be an expensive approach in wastewater treatment due to the cost of chemical additives.

2.3.3.2 Adsorption

Adsorption involves a multi-component fluid mixture, which can be captured at the surface of a solid adsorbent and form attachments via physical or chemical bonds. The adsorption process is regarded as one of the most effective methods since different adsorbents can adsorb a variety of organic and inorganic substances. It can remove the COD, heavy metal, ammonia, and many other pollutants from the aqueous system. Activated carbon (AC) is the most widely used adsorbent in the treatment of aqueous system. AC usually has well developed pore structures, which contain an inner surface area of more than 400 m^2 per gram (Li et al., 2008). It has been widely used in water and wastewater treatment and purification of gases (Zhang et al., 2014).

Halim et al. (2010) reported high adsorption capacity of 37.88 mg COD/g AC, while only absorbing 6.08 mg ammonia/g AC. In comparison, zeolite showed higher ammonia adsorption capacity of 24.39 mg ammonia/g zeolite. The poor absorption capacity displayed by activated carbon can be attributed to the non-polar surface area of the AC (a result of high temperatures of up to 950°C during the manufacturing process), which has a relatively low adsorption capacity for the highly polar ammonia molecules. (Park and Kim, 2005; Heschel and Klose, 1995). Thus the active carbon has relatively low adsorption capacity for ammonia, which exits as polar molecular. However, the surface of zeolite is hydrophilic with regular aligned molecular level pores and the cationic exchange ability that makes it widely used as a natural ion exchanger for the removal of ammonia and other inorganic pollutants from aqueous system (Ono and Yashima, 2000).

Ding (2015) investigated the application of both zeolite and ion-exchange resin for the removal of ammonia from aqueous solutions. Up to 87% ammonia removal was achieved at neutral pH levels. For ammonia aqueous solution with initial TAN concentration of 3000 mg/L, the optimum adsorption capacity for zeolite was 22.90 mg/g at pH 7. For ion-exchange resin, maximum adsorption capacity of 28.78 mg/g was achieved at pH 6 and 3000 mg/L initial TAN concentration.

2.3.3.3 Biological Treatments

Biological processes are carried out by microorganisms, which can degrade the organic substances to carbon dioxide in the presence of oxygen; or to biogas (methane and carbon dioxide) in the absence of oxygen (Castrillón et al., 2010). Biological approaches are regarded as the primary methods for the landfill leachate treatment due to the low operation cost. Examples of biological reactors include: upflow anaerobic sludge blanket reactor (UASB), membrane biological reactor (MBR), sequencing batch reactor (SBR), and anaerobic-aerobic combined reactor (Calli et al., 2005 a; Liang and Liu, 2008; Vasel et al., 2004; Kim et al., 2006; Im et al., 2001).

Biological nitrogen removal approach mainly involves the nitrification and denitrification processes. The nitrification process is carried out by the autotrophic bacteria: *Nitrosomonas* (from ammonia to nitrite) and *Nitrobacter* (from nitrite to nitrate) (Forster, 2003).

Denitrification requires anoxic conditions since it requires nitrate as the electron acceptor instead of oxygen and a carbon source as the electron donor. The denitrification process is commonly achieved through the following processes as shown in Fig. 2.5 (Cooper et al., 1994):

1. Apply the anoxic zone right before the final settling tank. However external carbon source needs to be added since the BOD is relatively low at this stage.

2. Apply the anoxic zone prior to the beginning of the aeration stage using the BOD in the settled sewage as the carbon source.

3. Apply a two-stage process, recirculate part of the settled sewage as carbon source at the anoxic region within the aeration lane.

Where the return activated sludge (RAS) is the part of part of the sludge that returned to the head of the aeration system to re-seed the new wastewater entering the tank. Surplus activated sludge (SAS) is the part of sludge removed from the aqueous system to maintain the biomass to food supplement ratio in balance.

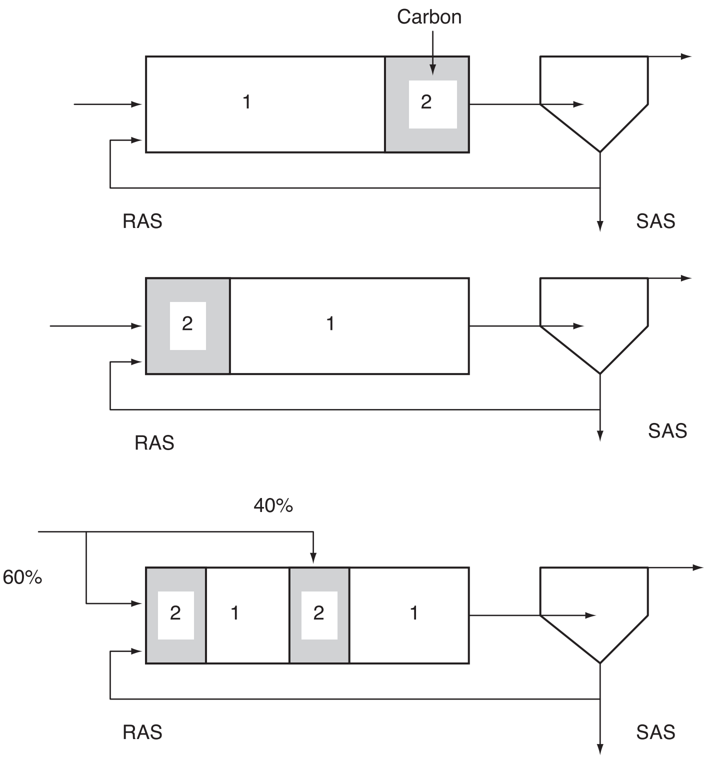


Fig. 2.5 Denitrification options: 1 aerobic zone; 2 anoxic zone (Adapted from Forster, 2003)

Uygur and Kargı (2004), carried out the SBR using the Anaerobic/Anoxic/Oxic/Anoxic/Oxic processes for the treatment of landfill leachate. The landfill leachate was pre-treated to the ideal COD:N:P ratio of 100:6:2 from 100:16.8:0.9. To reach the ideal COD:N:P ratio, the air-stripping process was applied at pH of 12 to remove part of the ammonia and PO_4^- was added in order to increase the quantity of phosphorus. The removal rates of COD, NH_4-N and PO_4-P for the five-step operations using Anaerobic/Anoxic/Oxic/Anoxic/Oxic (1/1/2/1/2 h) with total contact time of 21 h were 62%, 31% and 19%, respectively. In the second part of this research, domestic wastewater was mixed with the pre-treated leachate in equal volumes, and the mixture was treated biologically using the five-step SBR operation with and without powdered activated carbon (PAC) (1 g/L). Under the same five-step operation and the same total contact time of 21 h, the COD, ammonia and phosphate-P removal rates were 75%, 44%, and 44% for the SBR process and 64%, 23% and 26%

for the SBR combined with powdered activated carbon (PAC-SBR) process (Uygur and Kargı, 2004).

Aziz et al. (2011) conducted a study on the SBR and PAC-SBR for the treatment of landfill leachate. Six reactors were divided into two groups, three reactors for SBR and three reactors for PAC-SBR. Each group was carried out with a mixing ratio of 0.1 by using 90% return active sludge and 10% landfill leachate. Five steps for both the SBR and PAC-SBR systems were filling and mixing (20 min), settling (90 min), drawing, and idling (10 min). In the PAC-SBR group, 1.2 g PAC sized from 0.075 to 0.15 mm, was added into the reactors. The most efficient operational condition of the PAC-SBR reactor was the 1L/s aeration rate and 5.5 h contact time with the removal efficiencies of 64.1%, 71.2% and 81.4% removal of COD, color and NH3-N (Aziz et al., 2011).

2.4 Microwave Processes

2.4.1 Characteristics of Microwave

Microwaves (MW) are a type of electromagnetic wave, with a frequency range from 300 MHz to 300 GHz. When applying MW radiation to a material, it causes polarized chains of molecules to align with the direction of the electrical field and make the dipoles change their orientation in phase with the electromagnetic field at high rotating speeds. However, the intermolecular bonds restrict the movements between the dipoles, causing the delay of rotation. This resistance converts part of the radiation energy into heat (Coelho, 2012). The advantages of MW heating are:

- MW can produce homogeneous and quick thermal reactions due to the molecular-level heating;

- Selectively heat the materials that have a high dielectric factor (Remya and Lin, 2011; Metaxas and Meredith, 1983; Hong 2002).

2.4.2 Microwave Ovens

MW ovens generally have six components: MW cavity, turntable, magnetron (the device which generates the MWs), wave guide (the device directs the waves to the MW cavity), mode stirrer (the device distributes the waves inside the MW cavity) and circulator (the device directs the lost energy to a dummy load to protect the magnetron) (Coelho, 2012). A schematic of a commercial MW oven is shown in Fig. 2.6.

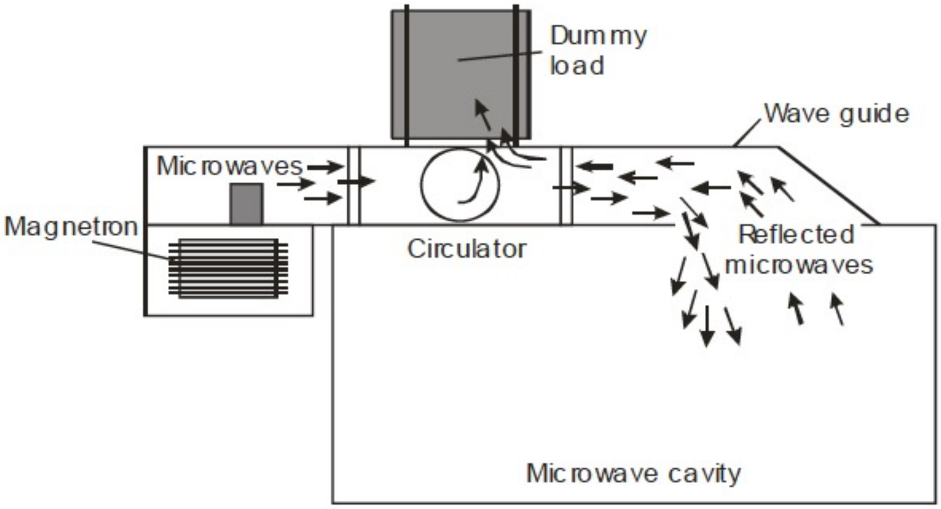


Fig. 2.6 Schematic of a MW oven with the common components (Adapted from Coelho, 2012; Kingston and Jassie, 1988)

2.4.3 Application of MW Treatment

2.4.3.1 Application of MW for Ammonia Removal

Lin et al. (2009a) investigated the application of MW for the removal of ammonia from wastewater. In this batch research, a modified MW oven was used as the basic experimental equipment, with a 300 mL glass reactor inside connected in series with a condenser and two absorption vessels. Aeration was applied during the MW radiation process. For 100 mL synthetic solution with an initial ammonia nitrogen concentration of 500 mg/L, maximum removal of 98.2% was reached at pH of 11 with 3 minutes radiation time and MW output power of 650 W. Under these conditions, the contribution from the aeration process was negligible. In this research, when applying 350W microwave output, 40% ammonia removal was achieved before sample reached its boiling point. The sample was then kept under the MW radiation for another 2 minutes after it reached the boiling point, which resulted in the removal of the rest of ammonia. Meanwhile, when the aeration process was applied at the same time with the MW radiation process, the contribution of aeration was negligible with longer radiation time. When comparing with the conventional heating (CH) process which removed less than 25% of the ammonia, the MW (350 W) process had a higher removal efficiency of 45% at the same final temperature of 100 °C at pH of 11.

Fig. 2.7 shows a pilot-scale design of the application of MW radiation for the ammonia removal from petroleum industry wastewater. Up to 84% ammonia removal was reported with no significant COD removal at pH of 12. The removal mechanism of this technology was converting the NH_4^+ to NH_3 under proper pH conditions. Then the ammonia nitrogen in wastewater was removed though the volatilization of NH_3 from the liquid phase to gas phase under MW radiation (Lin et al., 2009b). There are two contributing processes including thermal and non-thermal for the MW radiation process to remove ammonia. The general ammonia removal mechanism of the thermal process is degasification through heating. According to Henry's law, increasing temperature during the MW radiation process will lead to a decrease of gas solubility in the aqueous system, which may further contribute to the excess NH_3 volatilization. In addition, high temperature can increase the kinetic energy for both water and molecular NH_3. Comparing with low temperature, more ammonia nitrogen would leave the system during the heating process in the form of volatile ammonia nitrogen gas (NH_3). One of the possible explanations for the non-thermal contribution during the MW process is that while applying samples under the MW radiation process, the molecular bonds between water and NH_3 begin to break down, allowing the molecular ammonia to escape more easily. Thus, during the microwave radiation process, some NH_3 is eliminated due to the thermal process (increased temperature), the rest was removed due to the weakened molecular bounds and increased molecular movement caused by the electromagnetic field.

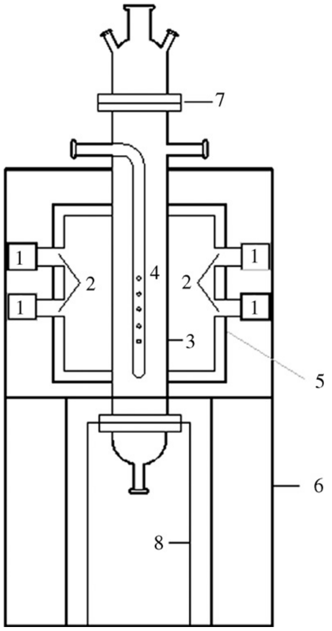


Fig. 2.7 Schematic diagram of the MW reactor. (1) magnetron, (2) wave guide, (3) glass tube, (4) bubble tube, (5) cavity chamber, (6) shell, (7) flange, (8) bracket. (Adapted from Lin et al., 2009b)

2.4.3.2 MW Enhanced Oxidation Processes

For MW enhanced oxidation processes, MW can stimulate the generation of free radicals from the oxidants and rapid polarization of the pollutant molecule (Zhang et al., 2007). Comparing with traditional thermal oxidation approaches or catalytic oxidation approaches, the combination of MW and oxidants can reach higher reaction temperatures within a shorter time, thus increasing the degradation rates of pollutants (Remya and Lin, 2011). Hydrogen peroxide (H_2O_2) and persulfate ($S_2O_8{}^{2-}$) are the two most common oxidants used along with MW.

Ju et al., (2009) studied the H_2O_2 based degradation processes of aqueous cationic triphenylmethane dye malachite green (MG) with the initial concentration of 100 mg/L under MW-enhanced and CH-enhanced conditions. The results showed that the higher discoloration rates of MG were achieved during MW-enhanced process. For 30 mL MG, when the H_2O_2 dosage was 300 mmol/L at contact time of 5 minutes, the MG degradation efficiency was 96% under MW-enhanced process and 72% for the CH-enhanced process. This suggested that the MW heating mechanism was more efficient for the generation of hydroxyl radicals than that of CH.

Chou et al. (2015) investigated the application of MW oxidation process using sodium persulfate (SPS) for the treatment of landfill leachate. The characteristics of raw leachate obtained from 2011-01 to 2014-01 are: pH (7.4 ± 0.3), BOD_5 (49 ± 32 mg/L), COD (204 ± 86 mg/L), total organic carbon (55 ± 19 mg/L) and ammonia nitrogen (187 ± 110 mg/L). The removal efficiencies at 550W microwave output and 85 °C within 30 min radiation time at pH 7.04 were: 79.4% of total organic carbon (TOC) removal, 88.4% of color removal, and 77.1% of UV254. The dosage of oxidant was that 50 mL leachate per 1 mL $Na_2S_2O_8$; and $S_2O_8{}^{2-}$ concentration was 4762 mg/L (Chou et al., 2015).

Yang et al. (2009) carried out the degradation process of azo dye acid Orange 7

(AO7) using MW activated persulfate oxidation (MW-APO). The results showed that with an initial concentration of 1000 mg/L AO7, the removal efficiency achieved 100% decolorization within 5 minutes under an 800 W microwave output when molar ratio of SPS/AO7 is 20:1. No degradation happened with MW or APO only.

Another study using microwave-activated persulfate (MW/PS) system for the degradation of sulfamethoxazole (SMX) was conducted by Qi et al. (2014). The results indicated that MW/PS degradation of SMX efficiency was higher than the conventional heating activated persulfate (CH/PS) process. For the SMX solution of 0.5 mmol/L, at a uniform temperature of 90°C, over a contact period of 16 minutes, the removal degradation can reach 100% for the MW/PS system, but only 38% of the CH/PS system.

2.5 Ammonia Stripping

Ammonia stripping involves large quantities of air passing through the liquid, which results in the increase of partial pressure of ammonia gas in the aqueous system, thus driving the ammonia from the liquid to the gas phase (Hasar et al., 2009). Several stripping approaches have been studied for the leachate treatment process:

- Free stripping without air, which is normally carried out by stirring a magnetic stirrer in the batch reactor (Ozturk et al., 2003; Hasar et al., 2009);
- Stripping with the presence of air, which is normally carried out by the air diffuser (Hasar et al., 2009);
- The combination of both.

The combined stripping process can be conducted by applying a stirring process with an air diffuser in the reactor, or by circulating the liquid through the reactor at high speeds while simultaneously diffusing air through the fluid (Degermenci et al., 2012).

Ammonia stripping is usually carried out under high pH levels for the removal of ammonia from the aqueous system where most ammonia is in the form of free ammonia. Ammonium hydroxide (NH_4OH) is formed as an intermediate product in the reaction at pH between 10 and 11 (Hasar, 2009). Lime is the most common chemical for the pH adjustment since the initial pH values of the landfill leachate are usually lower than the optimum value for the process. Previous research showed that the ammonia stripping was the most common physical–chemical method for ammonia removal from leachates and was able to remove up to 93% ammonia from leachates with high initial ammonia concentration of 5000-7000 mg N/L (Cheung et al., 1997).

Hasar et al. (2009) reported that for the free stripping process without aeration, the ammonia removal efficiency was 30% at a pH of 9 over a contact time of 6 h, with the agitation of 400rpm. By applying the same contact time, the removal efficiencies at pH values of 10, 11 and 12 were very close, but were significantly higher than that of a pH of 9. Thus, when applying this approach to the industrial scale, the optimum pH can be chosen from the range of 10-12 depending on the pH of the wastewater.

Ozturk et al. (2003) applied the air stripping process to the landfill leachate with initial pH of 7.9. The pH value had been adjusted to three pH levels (10, 11 and 12) before the air-stripping process was carried out. The maximum ammonia removal efficiency was found at 85% for a landfill leachate with approximately 1000 mg/L ammonium nitrogen, at pH of 12 with 17 h aeration and no significant changes were observed after 17h. In another similar air stripping study, 89% ammonia reduction was achieved at pH 11 within 24 h retention time with aeration rate of 10 L/h (Mattinen et al., 2010).

In terms of combination of free stripping and aeration, the ammonia removal efficiencies s increased to 76.4% at pH 10, 90.6% at pH 11, and 93.2% at pH 12 when the air flow rate was kept at 2 L/min, under the same agitation rate of 400 rpm and contact time of 6 h. When agitation rate was increased to 1100 rpm in the absence of air flow, the ammonia removal can reach up to 66.4% at pH 10, 91.7% at pH 11, and 93.3% at pH 12 with the contact time of 6 h (Hasar et al., 2009). However in a different paper, the maximum ammonia removal efficiency of the combination was 85%, which was lower than the 95% ammonia removal obtained from the free stripping process (Ozturk et al., 2003). The reason for this could be the specific structures of the different combined stripping reactors.

Degermenci et al. (2012) used a synthetic ammonia solution to study ammonia removal by jet loop reactors. Fig. 2.8 shows a schematic diagram of the semi-batch jet loop reactor. Parameters such as initial ammonia concentration (10–500 mg/L), temperature (20–50°C), air flow rate (5–50 L/min) and liquid circulation rate (35–50 L/min) were investigated.

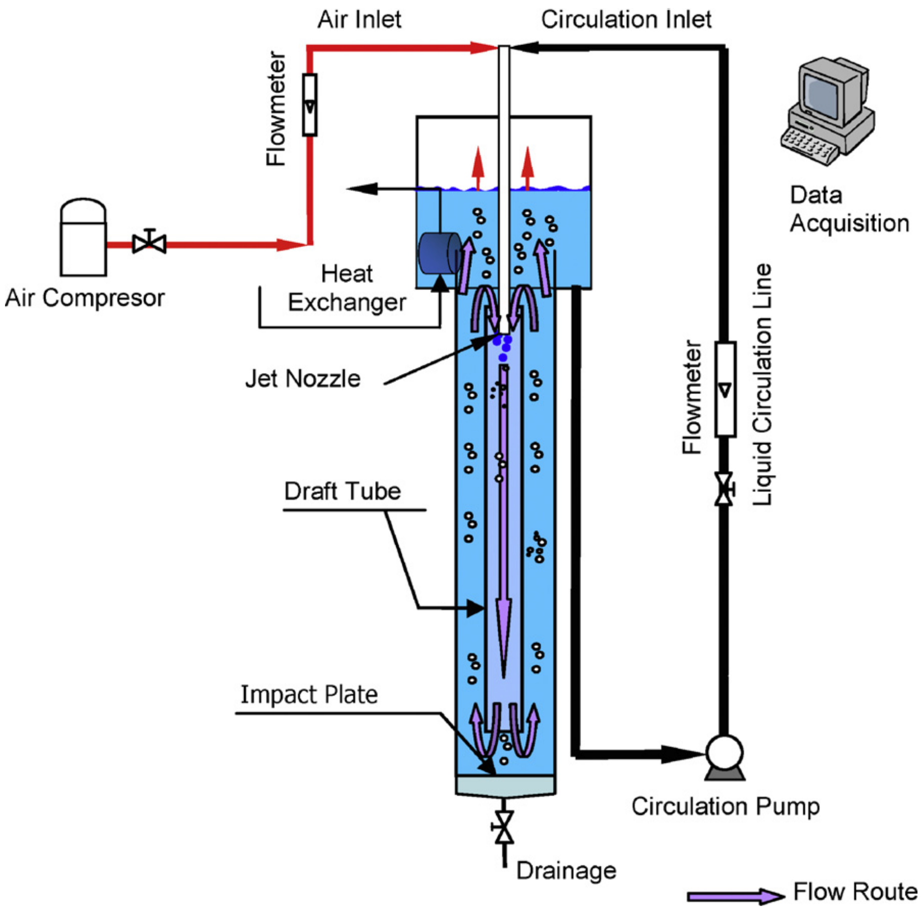


Fig. 2.8 Flow diagram of a Semi-batch jet loop reactor (Adapted from Degermenci et al., 2012)

In this semi-batch reactor, the ammonia solution was withdrawn from the bottom of the wide section at the top of the reactor and circulated back to the reactor through the liquid circulation pump. Air and circulated liquid enter the reactor through the top of the tube, which has the jet nozzle at the other end. The maximum ammonia removal efficiency can reach close to 100% with enough contact time, up to 8000 minutes. The results also showed that higher temperature and airflow rate could reduce the required reaction time (Degermenci et al., 2012). Approximately 81.4% of ammonia was removed in a similar research project and with 23% of the COD removal efficiency (Berrueta and Castrillón, 1997).

2.6 Summary and Research Gap

Landfill leachate is regarded as one highly contaminated type of wastewater with high concentrations of ammonia and organic pollutants. High ammonia concentrations can inhibit microbial activities thus decreasing the removal efficiency or even resulting in the failure of biological treatment processes (Jung et al., 2004; Metcalf and Eddy, 2003). For biological treatment, it requires an adequate C/N ratio of 20:1 for the aerobic process and 40:1 for the anaerobic process. Thus, conventional biological systems cannot significantly treat old leachates, which typically contain high levels of ammonia but low levels of biodegradable substances (Hasar et al., 2009). For the treatments of wastewaters with high ammonia concentration, the addition of an external carbon source is required for the denitrification process (Gray, 1999). However, the cost of adding carbon to an aqueous system makes biological treatment a less cost effective approach (Fudala-Ksiazek et al., 2014).

Physical and chemical methods usually have better removal efficiencies for both organic and/or inorganic components. For example the air stripping processes can achieve relatively high (more than 85%) ammonia removal efficiencies at high pH levels (higher than 10). However, the physical and chemical methods often come with high cost and other areas of concern such as the large volume of sludge for the flocculation and coagulation approach and the longer retention time during the stripping process.

Applying pretreatments followed by biological processes can be a solution for the treatment of landfill leachate with high ammonia concentration. The pretreatment approach should reduce the ammonia concentration to a certain level and retain enough organic substances for the following biological treatments so that no external carbon sources needed to be added into the system. MW radiation under high pH level can reduce the ammonia significantly and will not affect the organic compounds (Lin et al., 2009a). However, the continuous boiling process in the MW research of Lin et al. (2009a) may be a safety issue due to the high operation temperature and might generate unknown secondary pollutants when applied to the real landfill leachate. Moreover, the high effluent temperature can affect the subsequent biological treatment processes in a negative way.

In this study the sequential microwave/aeration approach was investigated for the ammonia removal. Combinations of MW and aeration process or aeration process alone had been investigated individually in previous research, but not using similar experimental conditions. No similar research has been conducted before for the sequential microwave/aeration process. In this research aeration was applied after the MW radiation process to get the maximum ammonia removal efficiency while maintaining the operational temperature below the boiling point for the MW process. The temperature of the sample was significantly increased during the MW radiation stage; then decreased in the subsequent aeration process, reaching a proper final temperature for potential biological processes. In this case ammonia removal can be achieved during both microwave and aeration process. Moreover, in this study, ammonia removal by sequential microwave/aeration process was systematically investigated using a factorial experimental design and RSM, which has not been reported in previous literatures.

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CHAPTER III

MATERIAL AND METHODOLOGY

3.1 Material and Equipment

3.1.1 Synthetic Ammonia Solution and Landfill Leachate

Synthetic solution containing approximately 2,700 mg/L TAN was prepared by dissolving 10.00 g analytical grade ammonia chloride into 990 mL distilled water. Synthetic solution was prepared and used as fresh. The initial pH of the synthetic ammonia solution was 5.5± 0.3.

Landfill leachate was obtained from a local landfill in Ottawa with an initial pH 9.0±0.2 and TAN concentration approximately 4000 mg/L. The leachate was stored in the lab fridge at an operational temperature of 4 °C. For each test, 100 mL of leachate sample was placed in the fume hood for approximately 2 hours to reach room temperature of 25 ± 3°C before the MW process was applied.

3.1.2 List of Equipment

The list of equipment for the experimental setup is shown in Table 3.1.

Table 3.1 List of equipment for experimental setup

Name	Information
Microwave Oven	Panasonic microwave oven (Model NN-S 750) with an operating frequency of 2450 MHz and power consumption of 1320 W. Full output of 1300 W and can be adjusted from 10% to 100% in 10% intervals.
Water Bath	Cole-Parmer 20 L/120 V Stable Temp Hot Water Bath. Power consumption of 1000 W (Cole-Parmer, 2015).
Aeration Pump	Model 200 MARINA pump with two outlets. Two identical air diffusers were connected to the pump with air flow rate of 110 L/h of each (Hagen, 2015) In each test, only one diffuser was placed in the batch reactor.

3.1.3 Analytical Techniques

For each test, initial pH was measured four times: 1) before adjusting to the desired pH 2) before exposure to the MW process 3) after MW radiation (before the aeration process) 4) after the aeration process. The total weight of the sample and reactor was measured every time before and after MW and aeration to monitor water loss during the sequential microwave/aeration process. The pH was measured using a glass electrode in combination with a Fisher Accumet® Model XL25 dual channel pH/ion meter (Alqaralleh, 2012).

TNT 832 ammonia vials from HACH Company were used to measure ammonia concentrations using the Salicylate Method. The HACH DR5000 Spectrophotometer was used to measure the absorbance of the samples with the measurement wavelength of

690 nm. 10 mg/L ammonia nitrogen standard solution from HACH Company was used to calibrate the spectrophotometer.

3.2 Methodology

3.2.1 Experimental Design

For this study, four series of experiments were conducted for the synthetic solution: water bath (WB), microwave (MW), sequential microwave/aeration process (MW+A), and sequential WB/A process (WB+A).

The details of the experimental design for the synthetic solution are shown in table 3.2

Table 3.2 Experimental design for the synthetic solution

(a) Experimental design of MW processes for the synthetic solution.

MW time, Sec		30		45		60		90		120	
Power Output Level (%)		50	100	50	100	50	100	50	100	50	100
	10	✓	✓	—	✓	✓	✓	✓	—	✓	—
pH	10.5	✓	✓	—	✓	✓	✓	✓	—	✓	—
	11	✓	✓	—	✓	✓	✓	✓	—	✓	—

(b) Experimental design of WB+A processes for the synthetic solution.

WB Temperature, °C		65	85	95
pH	10	✓	✓	✓
	10.5	✓	✓	✓
	11	✓	✓	✓

For landfill leachate tests, MW irradiation with and without an aeration process was applied using 50 % of the total power output with 120 seconds irradiation time under three pH levels of 10, 10.5, 11. 10 mol/L NaOH was used for the pH adjustment. For each test, either 100 mL synthetic solution or landfill leachate was used. To assess the effect of aeration rate, one set of MW+A test was conducted applying 50% of the total aeration rate for 10 minutes at pH 10.5 with 7.8 KJ MW energy output/L sample.

3.2.2 Batch Test

In this study, the application of microwave (MW) radiation followed by aeration (A) is referred as sequential microwave/aeration process. This process was carried out as a series of batch tests for the purpose of ammonia removal from both synthetic solutions and landfill leachate. For each test, the aeration process was applied after the MW radiation process. For synthetic solution tests, a 150 mL beaker was used as the batch reactor both MW and aeration tests. For landfill leachate tests, a 1 L beaker was used as the batch reactor for the microwave process and a 4 L glass container was used for the aeration process. Traditional heating using the WB was applied to the synthetic solution as well in order to compare with the MW processes. The experimental flow chart is shown in Fig. 3.1.

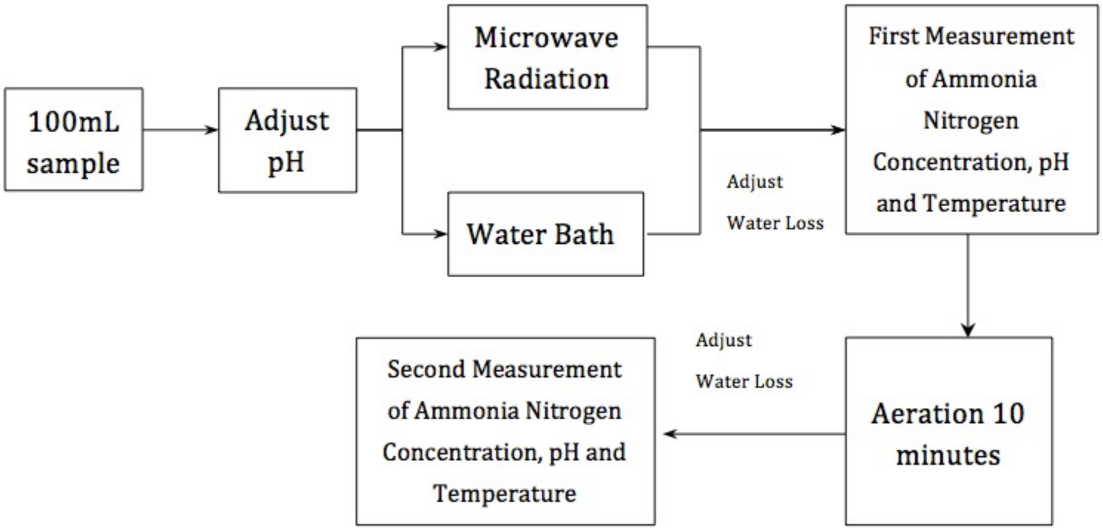

Fig. 3.1 Experimental flow chart

3.2.3 Ammonia Removal Efficiency

Ammonia removal efficiency (Y) was obtained using the following equation:

$$Y\ (\%) = \frac{C_1 - C_0}{C_0} \times 100\% \qquad (3.1)$$

Where C_1 is the ammonia nitrogen concentration after treatment,

C_0 is the initial ammonia nitrogen concentration.

3.2.4 Statistical Analysis

3.2.4.1 ANOVA and T-test

One-way ANOVA tests were performed to determine if significant differences ($p < 0.05$) existed among the ammonia removal efficiencies of different treatment methods with different radiation or thermal levels. T-Tests ($p < 0.05$) were carried out between two groups of data for further analysis.

3.2.4.2 Factorial Design Response Surface Methodology

Factorial design and response surfaces were used for experimental design optimization. These techniques are used to evaluate and optimize the pH and MW irradiation time to maximize the ammonia removal from aqueous systems. Response surface methodology (RSM) was used to acquire the optimal conditions (that obtained the highest ammonia removal efficiency) for ammonia removal by analysing the relationships between the variables and the response.

The statistical software DesignExpert® was used for the statistical analysis. Two independent variables X_1 (MW irradiation time) and X_2 (pH) were used for the response surface model and the outcome response was Y (ammonia removal efficiency). To improve the accuracy and credibility of the model, X_1 and X_2 were coded into different levels in the range of -1 to 1.

Diagnostics plots of externally studentized residuals versus predicted values, run, pH and t was used to analyze the collected data. Outliers in the diagnostics plots simply indicate the magnitude of the residuals, determining if any of the data had particularly large residuals (Salahi et al., 2013). Coefficient of determination (R^2), adjusted R^2 and predicted R^2 values were used to evaluate the fitness of the model.

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CHAPTER IV

TECHNICAL PAPER I

Statistical Analysis of Thermal and Non-Thermal effects of Sequential Microwave/Aeration Process for the Removal of Ammonia from Aqueous Solution

Sainan Dong, Majid Sartaj

Abstract

The application of microwave (MW) radiation followed by aeration (A) for the purpose of ammonia removal from synthetic solutions was investigated in this study. Results confirmed that the sequential microwave/aeration process was an effective approach for removal of ammonia from aqueous systems. Maximum ammonia removal of 81.7 % for 100 mL synthetic solution was achieved by applying 650 W microwave radiation (50% of the total MW power output) over 120 seconds MW irradiation time followed by 10 minutes aeration. One-way ANOVA tests and T-tests were conducted to analysis the differences of ammonia removal efficiencies among different methods. Among the three main contributions for the ammonia removal for the sequential microwave/aeration process (thermal effect, EMF generated by MW radiation, and aeration process), the contribution of the EMF becomes increasingly significant with the increase of MW irradiation time, except at a pH of 10. Under the optimum operation condition, the contribution of thermal process, EMF, and aeration were 39%, 28%, and 33% respectively.

Key words: Ammonia; microwave; aeration; ANOVA; T-test; thermal; non-thermal

4.1 Introduction

As one of the major inorganic pollutants in surface water, total ammonia nitrogen (TAN) can exist in liquid phase either in an unionized form (NH_3) or an ionized form (NH_4^+) depending on the pH and temperature (Ding & Sartaj, 2015; Nair et al., 2014). Ammonia nitrogen is toxic to aquatic organisms even at low levels. According to the United States Environmental Protection Agency (USEPA), at a pH of 7 and a water temperature of 20°C, the acute and chronic criterion values are 17 mg TAN/L and 1.9 mg TAN/L, respectively (USEPA 2013). Moreover, the increased nitrogen level in water bodies can cause water eutrophication and proliferation of toxic algae blooms in rivers, lakes and coastal waters as shown (Dachs et al, 2000). However, for wastewaters with high ammonia nitrogen concentrations such as those produced from the petroleum, textile, fertilizer industries, or landfill leachate, high concentrations of ammonia could inhibit microbial activities (Jung et al., 2004). Studies have shown that ammonia is the most toxic substance with inhibition effects on microbial activities, including nitrification. (Jung et al., 2004; Metcalf and Eddy, 2003). It can inhibit the NO_2-N oxidation process at an NH_4-N concentration of 20 mg/L, and can inhibit the NH_4-N oxidation process at a concentration of 100 mg/L (Metcalf and Eddy, 2003). Liu et al. (2012) reported that ammonia inhibition could occur in the range of 1500-3000 mg/L as TAN in biological anaerobic processes. Thus, it is necessary to pretreat ammonia-rich wastewater before applying biological processes to improve treatment efficiency.

Conventional methods for ammonia removal from aqueous solutions include biological treatment, air stripping, ion-exchange and adsorption (Wang et al., 2008). Biological processes incorporate nitrification and denitrification. However, these processes don't perform well at high ammonia concentrations (Karadag et al., 2006). For highly contaminated wastewaters such as landfill leachate, ammonia removal is usually achieved by a combination of physical, chemical and biological processes. This is because high ammonia concentrations are commonly accompanied by high concentrations of organic matter and heavy metals, which makes it difficult to obtain satisfactory treatment results using only one method (Ahn et al., 2002; Chiang et al., 2001; Lin and Chang, 2000).

Previous research showed that ammonia stripping was the most common physical–chemical method for ammonia removal from both ammonia-rich wastewater and landfill leachate (Hossini, H., et al., 2015). It was able to remove up to 93% ammonia from leachates with high initial ammonia concentration of 5000-7000 mg N/L (Cheung et al., 1997). Ammonia stripping is usually carried out under high pH for the removal of ammonia from aqueous systems where most ammonia is in the form of free ammonia. Ammonium hydroxide (NH_4OH) is formed as an intermediate product in the reaction at pH between 10 and 11 (Hasar, 2009). Initial heating could enhance the ammonia removal rate during the air stripping process (Değermenci et al., 2012). However the high ammonia removal is usually achieved with relatively long contact periods up to 120 h (Degermenci et al., 2012; Berrueta and Castrillón, 1997).

Microwave (MW) radiation could provide rapid heating of materials depending on the dissipation factor of the material (Kwon et al., 2015; Qi and Li, 2015; Remya et al., 2011) and has been recently used in wastewater and sludge treatment. For wastewater treatment, previous researches were mostly focused on the MW-enhanced oxidation process. Research studies conducted with different oxidants such as sodium persulfate, ozone and hydrogen peroxide reported that the application of MW can result in the increased removal efficiencies of the total organic carbon (TOC) and chemical oxygen demand (COD) while applying a MW radiation process without oxidants, the removal of TOC and COD were not significant (Remya et al., 2011; Chou et al., 2013). MW radiation reduced TAN in waters with TAN concentrations in the ranges of 25 mg/L – 5,000 mg/L

(Rabah et al., 2012; Lin et al., 2009a). Both Lin (2009a) and Rabah et al. (2012) reported pH 11 as the optimum MW radiation operation condition for ammonia removal from aqueous systems. The ammonia removal efficiency slightly increased with the increase of initial TAN concentration (Rabah et al., 2012; Lin et al., 2009a). When the pH of the wastewater was adjusted to around 11, the removal of TAN increased with irradiation time to approximately 100% in a lab batch scale (Lin et al., 2009a) and 80% in a pilot scale (Lin et al., 2009b).

Lin et al. (2009a) applied MW and aeration simultaneously to a synthetic solution with initial TAN concentration of 500 mg/L and pH of 11. When applying 350 W microwave radiation, the ammonia removal efficiency achieved approximately 40% before reaching the boiling point of 100°C. The remaining portion of the dissipated ammonia was removed in the following two minutes after the solution reached the boiling point, by a combination of MW and thermal processes. It was observed that, when the aeration process was applied concurrently with the MW radiation process, the contribution of aeration decreased with longer radiation time.

However, the continuous boiling process employed by Lin et al. (2009a) could be a safety concern due to the high operation temperatures and the possible generation of unknown secondary pollutants when applied to real landfill leachate. Moreover, when MW radiation has been used as a pretreatment approach, the high effluent temperature can have a negative effect on the subsequent biological treatment processes.

As a pre-treatment process, MW radiation processes under high pH levels could reduce ammonia significantly with negligible organic compound removal (Lin et al., 2009a). This can maintain sufficient COD supply as the carbon source for the sequential biological removal process.

The main objective of this research was to evaluate the MW irradiation followed by an aeration process for removal of ammonia from aqueous solutions under different pH and temperature. Statistical analysis was used to determine the contribution of the thermal and non-thermal effects of MW radiation approaches with and without an aeration process. For both safety and economic concerns, the samples were maintained below the boiling point.

4.2 Material and Methodology

As a sequential microwave/aeration process, aeration was applied immediately after the MW radiation process. Traditional heating using water bath (WB) with and without aeration was applied to determine the contribution of the thermal effect during the both MW and microwave/aeration process. Preliminary tests were carried out to find optimum pH and aeration levels.

Four sets of experiments were conducted: water bath (WB), microwave (MW), sequential microwave/aeration process (MW+A), and sequential water bath/aeration process (WB+A). For each test, 100 mL of synthetic solution were used. All the tests were conducted with three replicates in batch mode. For both economic and safety concerns, the synthetic solution samples were maintained below the boiling point.

4.2.1 Material and Equipment

In this study, synthetic solution which contained 2,700 mg/L total ammonia nitrogen (TAN) was prepared by dissolving ammonia chloride in distilled water. For each test, 100 mL of the fresh synthetic solution was prepared. The initial pH was around 5.5± 0.3. The pH was adjusted to the desired value using 10 mol/L NaOH. The

MW process was conducted by a Panasonic microwave oven (Model NN-S 750) with an operating frequency of 2450 MHz. The maximum power output is 1300 W and can be adjusted from 10% to 100% in 10% intervals.

The aeration process was performed using a Model 200 MARINA pump with a total aeration rate of 110 L/h with 2 air diffusers. In each test, only one diffuser was placed in the batch reactor. For the tests carried out with the synthetic solution, a 150 mL beaker was used as the batch reactor for all MW with and without aeration processes.

TNT 832 ammonia vials from Hach Company were used to test ammonia concentrations based on the Salicylate Method using a HACH DR5000 Spectrophotometer. The 10 mg/L ammonia nitrogen standard solution from HACH Company was used to calibrate the spectrophotometer. The pH was measured using a glass electrode in combination with a Fisher Accumet® Model XL25 dual channel pH/ion meter (Alqaralleh, 2012).

4.2.2 Preliminary Tests

Two sets of preliminary tests were carried out to find optimum pH and aeration levels. The first one, a MW radiation power output of 60% and MW radiation time of 100 sec were used with subsequent aeration time ranging from 5 to 15 minutes in 5 minutes intervals. The purpose was to find the optimum aeration time. According to previous research (Rabah et al., 2012; Lin et al., 2009a; and Lin et al., 2009b), pH was adjusted to 11 in this test. In the second set of preliminary test, a MW radiation power output of 50% of the total MW radiation power output, MW radiation time of 120 sec, and 10 minutes aeration were used under pH ranging from 8 to 12 with 1 pH unit interval. The purpose was to find the optimum pH.

4.2.3 Experimental Design

To determine the thermal and non-thermal contributions during the ammonia removal process using microwave radiation followed by aeration, four different sets of experiments were conducted: water bath (WB), microwave (MW), sequential microwave/aeration process (MW+A), and sequential water bath/aeration process (WB+A). These were further divided into the following categories:

1) MW with and without aeration process using synthetic solution with two MW output levels of 50% and 100% of the total power output for different irradiation time under three pH levels of 10, 10.5, 11.

2) WB with and without the aeration process using synthetic solution with different temperature under three pH levels of 10, 10.5, 11.

The details of the experimental design for WB are shown in Table 4.1.

Table 4.1 Experimental design of WB+A processes for the synthetic solution.

WB Temperature, °C		65	85	95
pH	10	✓	✓	✓
	10.5	✓	✓	✓
	11	✓	✓	✓

For the MW and MW+A tests, when using 50% of the total MW output, the radiation periods investigated were 30/60/90/120 seconds. The temperature of the sample was maintained below the boiling point. The temperatures shown in Table 4.2 for WB and WB+A tests were selected in such a way to match the temperatures measured in MW and MW+A tests when using 50% power output for comparison purposes. Based on the results of preliminary tests, for all the MW+A and WB+A tests the aeration time was 10 minutes. To verify the effect of aeration rate, one set of MW+A test was conducted applying 50% of the total aeration rate for 10 minutes at pH 10.5 with 7.8 KJ MW energy output/L sample.

Table 4.2 MW time when using 50% of the total out put and the corresponding rater bath temperature (°C)

Microwave Irradiation Time (seconds)	Water Bath Temperature (°C)
60	65
90	85
120	95

The general experimental flow diagram is shown in Fig. 4.1 For each test, 100 ml of synthetic solution was used. For the MW tests, the pH was adjusted to the desired level using 10 mol/L NaOH solution, then the batch reactor was treated by microwave radiation for the desired time period, exposed to 50% of the total MW power output. The sample temperature was measured immediately after the MW process. Distilled water was used to compensate the water loss after MW process. One mL of the irradiated sample was taken after the adjustment for the first ammonia measurement. Then, the sample was aerated for 10, immediately after the first measurement. Water loss was compensated again by distilled water after the aeration process as well. The second measurement was taken after the second adjustment.

For the WB test, the water bath tub was heated to 5°C higher than the temperature obtained from the microwave process. The water bath required a significantly longer period of time (>120s) to equalize the temperature between the sample and the water bath. This increased heating period would result in higher recorded removal efficiency, altering the outcome of the experiment. The sample temperature was constantly monitored to make sure the same temperature level was reached for the MW and WB process. The water adjustment and sampling process was identical to the MW process. The aeration process was applied after the first sampling process. Water loss was compensated again after the aeration process. The second measurement was taken after the second adjustment.

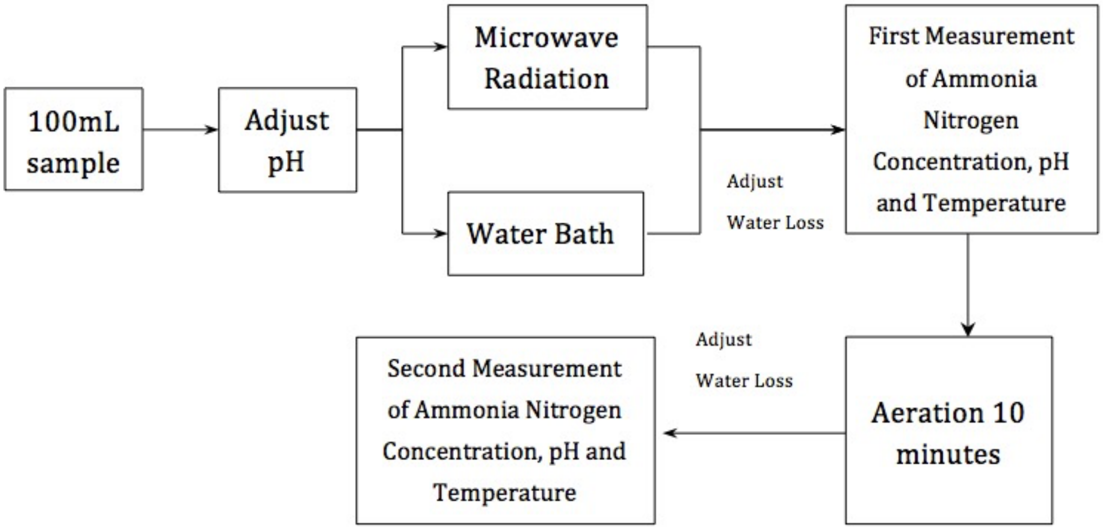


Fig. 4.1 Experimental flow chart

4.2.4 Statistical Methods

One-way ANOVA tests were performed to determine if significant differences ($p < 0.05$) existed among the ammonia removal efficiencies of the four different treatment methods with different MW radiation or WB thermal levels. When the ANOVA test showed a significant difference among all groups of data, several T-Tests ($p < 0.05$) of all were carried out for paired groups of data for further analysis.

4.3 Results and Discussion

4.3.1 Results of Preliminary Tests

The ammonia removal efficiency was calculated by the following Eq. (4.1):

$$\text{Ammonia removal efficiency} = \frac{\boldsymbol{C_1 - C_0}}{\boldsymbol{C_0}} \times \mathbf{100}\% \qquad (4.1)$$

Where $\boldsymbol{C_1}$ is the TAN concentration after treatment,

$\boldsymbol{C_0}$ is the initial TAN concentration.

The results of preliminary tests for determination of optimum aeration time are shown in Fig. 4.2 As shown in Fig.4.2, the ammonia removal efficiency rose as the aeration time increased from 0 minutes to 15 minutes. However, after 10 minutes, the increase in ammonia removal efficiency was negligible. For economic reasons, extending the aeration time beyond 10 minutes is not a cost-effective design. Thus, 10 minutes was chosen as the optimum aeration time and used for subsequent experiments.

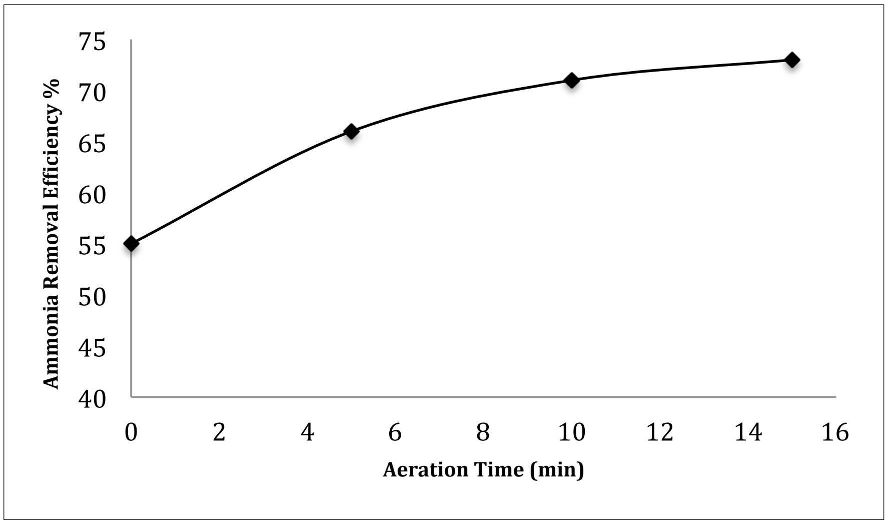


Fig. 4.2 Preliminary test result of aeration time, using pH=11, 60% of the total microwave output, 100 seconds of radiation time.

The results of preliminary tests for determination of optimum pH are shown in Figure 4.3. Ammonia removal efficiency increased sharply with pH until pH of 10.5 and dropped off after 10.5. Therefore, pH levels of 10, 10.5 and 11 were selected to be investigated in the following tests.

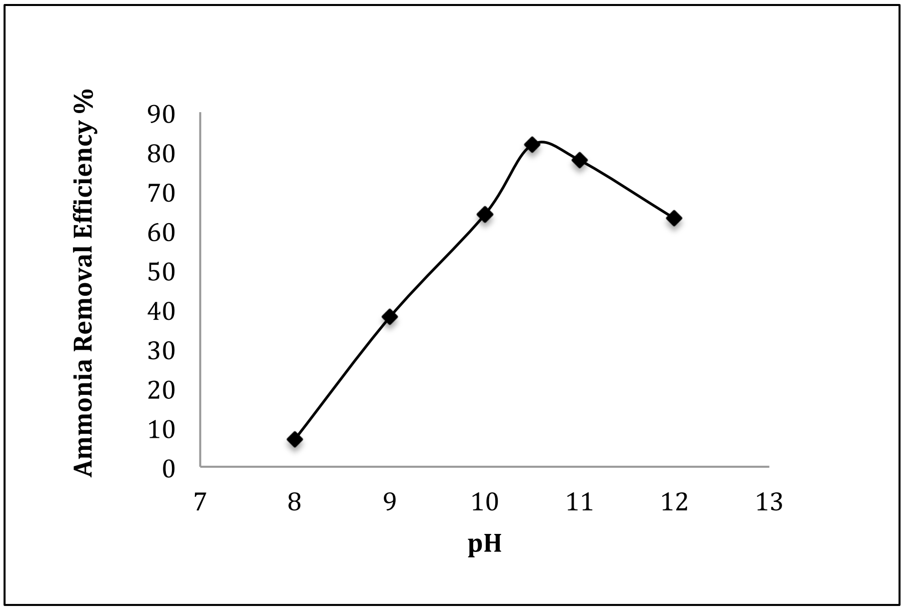


Fig. 4.3 Preliminary test result of pH, using 50% of the total MW power output, 120 seconds MW radiation time, and the aeration time was 10 minutes.

4.3.2 Effect of pH

All four sets of WB, MW, MW+A and WB+A tests were conducted at three different pH levels. As can be seen from Fig. 4.4, the general trend observed was that the ammonia removal efficiencies increased with the increase of pH from 10 to 10.5 and then increased or dropped as pH increased further to 11 for all three MW radiation (WB temperature) levels. For example in Fig. 4.4 c, when high MW radiation time of 120 s was applied, for both MW and M+A process, the ammonia removal efficiencies obtained at pH of 10.5 and 11 were relatively similar, but significantly higher than the values of pH 10. The WB and WB+A test results with high temperature levels of 95 °C showed the same trend. As such, it seems a pH of 10.5 is the optimum pH. The same trend was obtained in the combined MW and aeration conducted by Lin et al. (2009a).

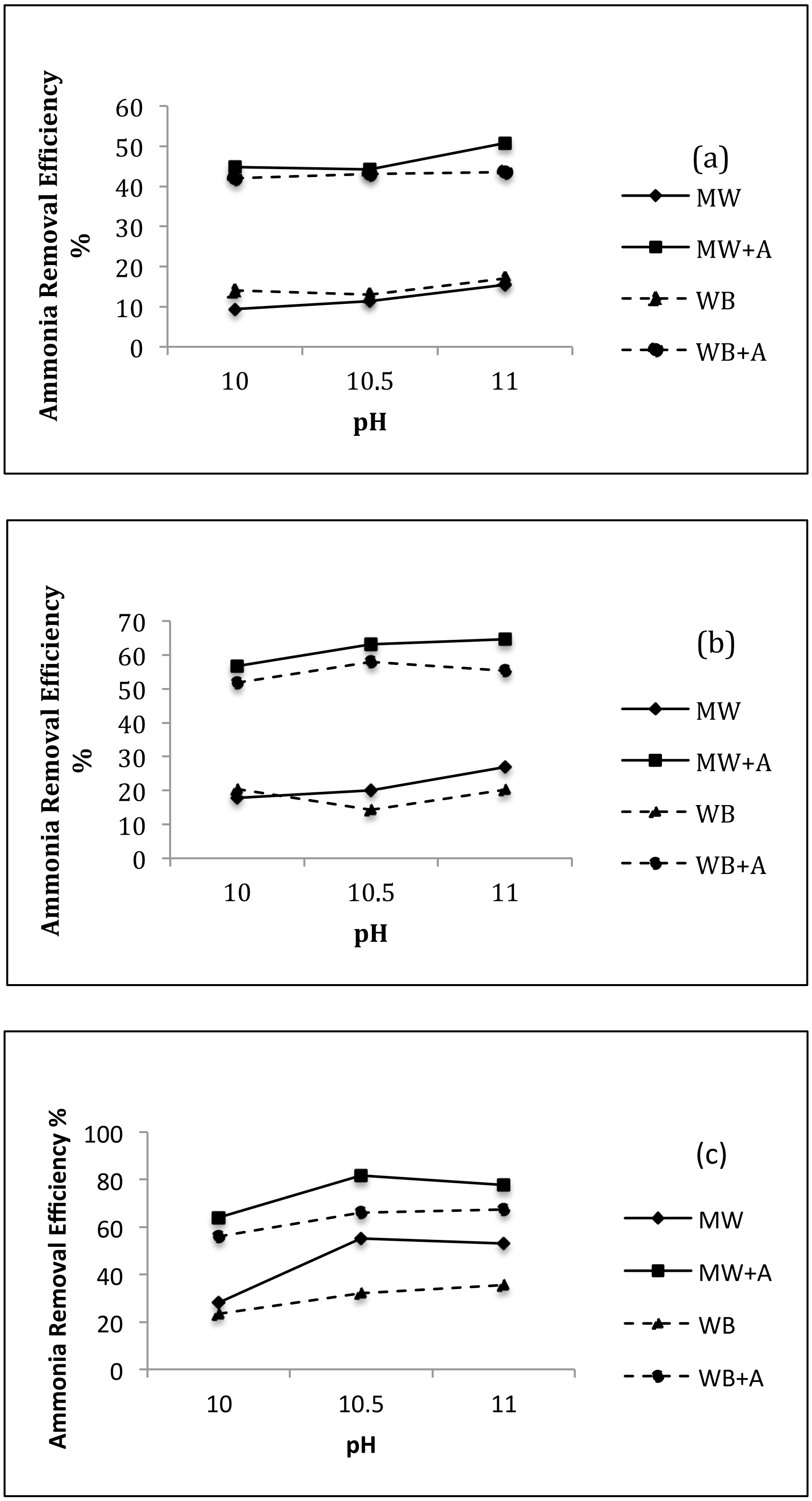


Fig. 4.4 Ammonia removal using MW and MW+A (WB and WB+A) processes with three MW irradiation time (corresponding final temperature) levels: (a) 60s(65°C), (b) 90s(85°C) and (c) 120s (95°C).

The increase of ammonia removal efficiency with increasing pH could be explained by the equilibrium distribution between NH_3 and NH_4^+, which is heavily dependent on the pH value and temperature of the aqueous solution. The percentage of NH_3 and NH_4^+ can be derived by the following equation containing the acid ionization constant, K_a:

$$\frac{[NH_3][H^+]}{[NH_4^+]} = K_a \qquad (4.2)$$

Where $[NH_3]$ is the concentration of NH_3, and $[NH_4^+]$ stands for the concentration of NH_4^+. $[H^+]$ is the concentration of H^+ (pH). K_a is the acid ionization constant, which changes with respect to temperature. Fig.4.5 shows the distribution of NH_3 and NH_4^+ as a function of pH at a temperature of 20°C. The pKa (acid dissociation constant at logarithmic scale) value at this temperature is approximately 9.2, which means that at pH = 9.2, the ratio of NH_3 to NH_4^+ is about 1:1. For pH values lower than 7, the majority of ammonia exists as NH_4^+. At low pH conditions, the concentration of un-ionized ammonia is negligible. As pH increases over 7, the concentration of NH_3 rises and it becomes the dominant form.

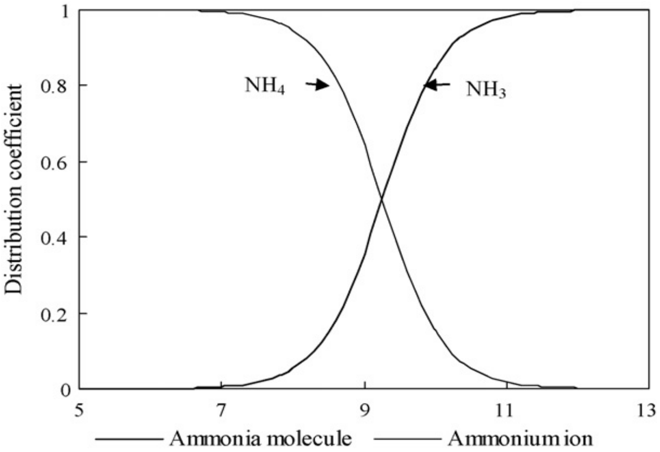
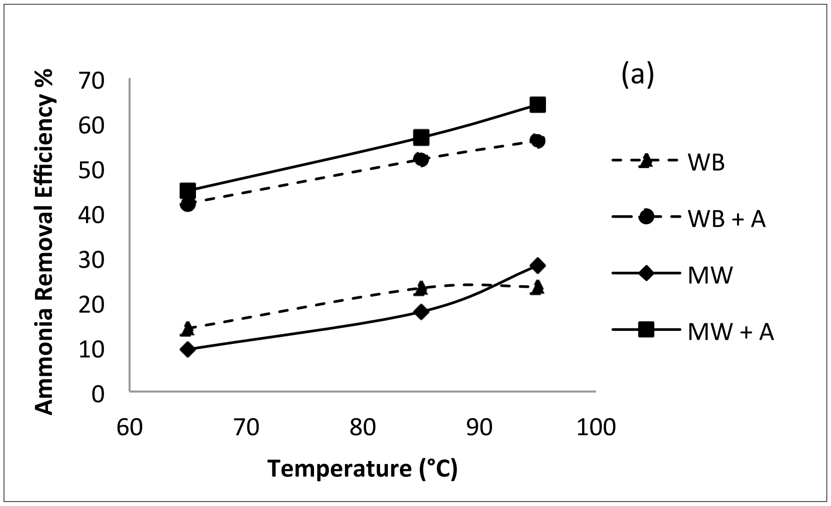


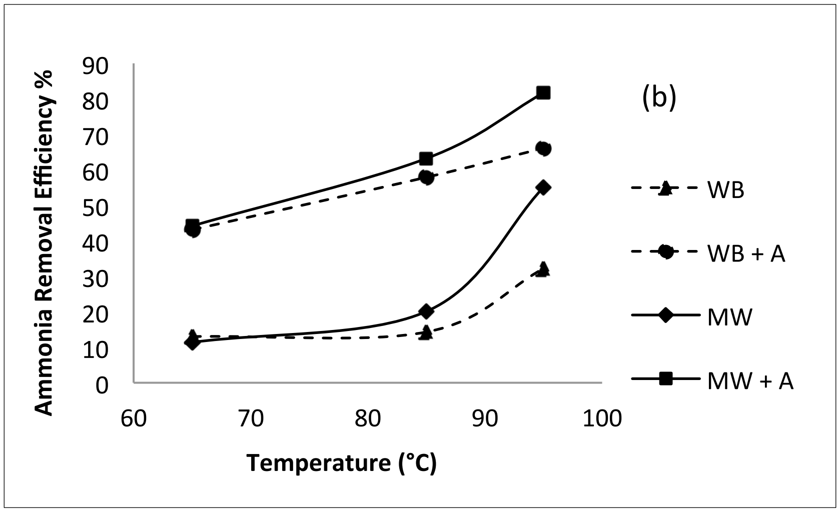
Fig. 4.5 Distribution coefficients of NH_3 and NH_4^+ at different pH levels (20°C). (Adapted from Lin et al, 2009a)

4.3.3 Effect of Temperature

The ammonia removal results for WB, WB+A, MW, and MW+A as a function of temperature at pH of 10, 10.5 and 11 are shown in Fig.4.6. For the MW and MW+A methods, both thermal and non-thermal effects exist during the ammonia removal process. There are three main contributing factors to the ammonia removal for the MW+A process: the thermal effect (increased temperature), the electromagnetic field (EMF) generated by MW radiation, and the aeration process. Therefore, WB and WB+A tests were conducted as controls to determine the effect of temperature and EMF for the MW and MW+A processes.

Fig.4.6 shows that the removal efficiencies of all four different methods increased with time (and temperature). This is in agreement with previous research (Rabah et al., 2012; Lin et al., 2009a.). For the shortest MW radiation time (60s), the differences in ammonia removal efficiencies between the MW/WB processes and the corresponding processes with aeration were not significant under all three pH levels. For tests with longer radiation time, the ammonia removal efficiencies obtained from approaches involving the MW process were higher than those using WB with the exception of those conducted under pH level of 10. This can be explained by Henry's law, which expresses that the gas solubility of an aqueous system decreases with the increase of temperature. The excess volatile NH_3 would dissipate from the aqueous solution. The high temperature also increases the molecular movement for both water and NH_3. More ammonia nitrogen would leave the system during the heating process in the form of volatile ammonia nitrogen gas (NH_3) than at lower temperatures due to the increased kinetic energy.





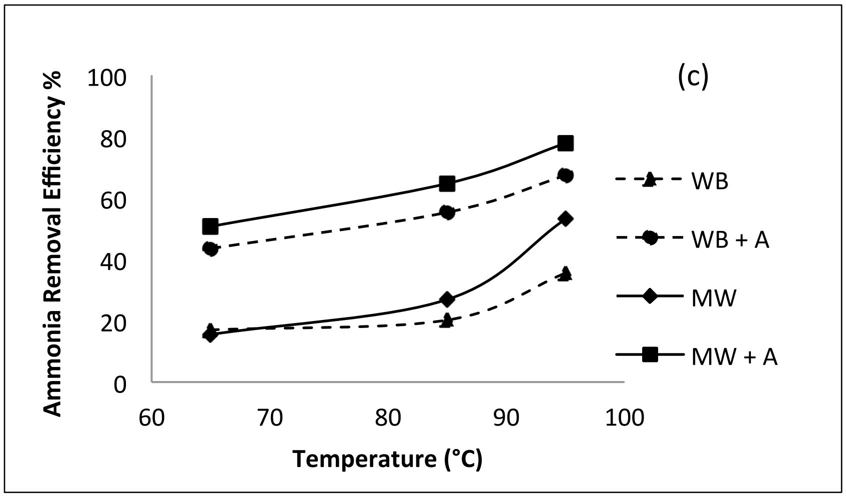


Fig. 4.6 Ammonia removal using WB and WB+A (MW and MW+A) processes with three final temperature (corresponding MW irradiation time) levels: 65°C (60 s), 85°C (90 s) and 95°C (120 s) under pH of (a) 10, (b) 10.5 and (c) 11.

4.3.4 Effect of Microwave Radiation

As shown in Fig. 4.6, the ammonia removal efficiencies of WB tests were referred as the thermal contributions of the thermal during the MW process. When the shortest MW radiation period of 60 s was applied, the contribution of the thermal process to ammonia removal was quite significant, but decreased as the MW irradiation time increased. The contribution of the EMF became significant at high MW radiation levels (temperature) with the exception at a low pH level of 10. The contributions of the EMF during the MW and MW+A test showed a similar trend at the operational pH of 10.5 and 11.

The ANOVA test result for all data (ammonia removal efficiencies) collected from different methods under different MW radiation time or WB temperature at pH of 10.5 is shown in table 4.3. Similar trends were observed for other pH values with the exception of pH 10 with MW (WB) only; however, to avoid repetition and limit the number of figures, only tests results from pH 10.5 are presented and discussed below. According to the ANOVA test (Table 4.3), the P value was 1.40E-18, which is lower than 0.05, indicating there were significant differences between the removal efficiencies using different treatment methods and/or conditions.

Table 4.3 Single factor ANOVA test among all collected data

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F cr.*
Between Groups	17890.91	11	1626.45	129.18	1.40E-18	2.22
Within Groups	302.18	24	12.59			
Total	18193.09	35				

One-way ANOVA tests for four methods (MW, MW+A, WB and WB+A) for each MW radiation period or corresponding final temperature levels were conducted to investigate if the removal efficiencies of each methods are significantly different within one MW radiation power level and the corresponding WB temperature level. As shown in Table 4.4 the P values for all three one-way ANOVA tests are 0.00, indicating that there are significant differences between methods within one MW radiation power level and the corresponding WB temperature level.

Table 4.4 One-way ANOVA tests for four methods (MW, MW+A, WB and WB+A) under three different MW radiation periods (WB temperature): (a) 60 s (65°C), (b) 90 s (85°C) and (c) 120 s (95°C).

(a)

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F cr.*
Between Groups	2920.79	3	973.60	94.68	0.00	4.35
Within Groups	71.98	7	10.28			
Total	2992.77	10				

(b)

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F cr.*
Between Groups	5068.74	3	1689.58	215.42	0.00	4.35
Within Groups	54.90	7	7.84			
Total	5123.65	10				

(c)

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F cr.*
Between Groups	3898.38	3	1299.46	85.38	0.00	4.07
Within Groups	121.77	8	15.22			
Total	4020.14	11				

Fig.4.7 shows the ammonia removal efficiencies of different methods at three different MW radiation periods or corresponding final temperature levels. T-Tests were performed based on Two-Sample Assuming Unequal Variance. Results are shown in Table 4.5. For the T-test of both MW versus WB and MW+A versus WB+A, when under low radiation time (60 s) and temperature (65°C), the P values were larger than 0.05, which showed that there was no significant difference between them. Thus, the contribution of the electromagnetic field generated by microwave is not significant at low radiation levels. For the same two sets of T-test, under high radiation time (120 s) and temperature (95°C), the P value was lower than 0.05, indicating that the contribution of the EMF under high radiation level was significant.

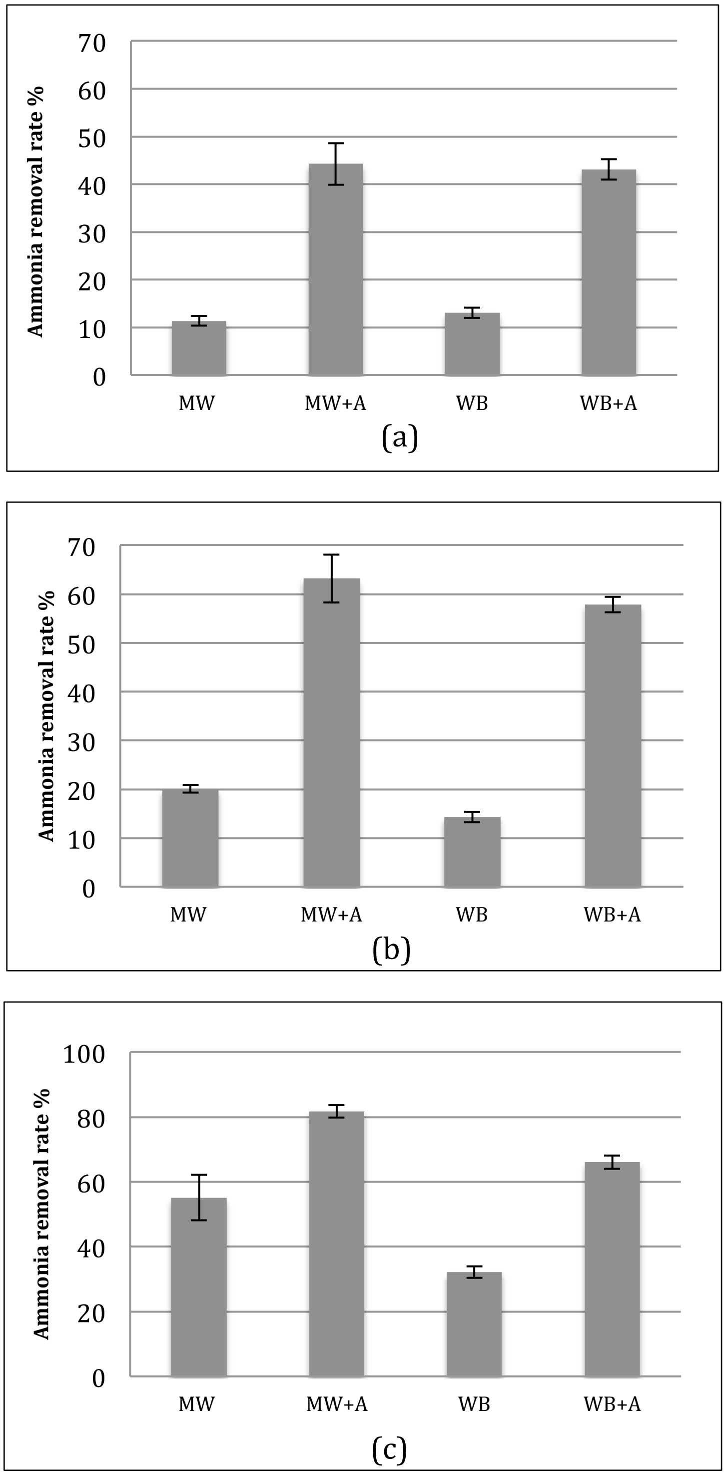


Fig. 4.7 Ammonia removal using MW and MW+A (WB and WB+A) processes with three MW irradiation time (corresponding final temperature) levels: (a) 60 s(65°C), (b) 90 s(85°C) and (c) 120 s (95°C).

The contribution of EMF can be explained by the heating mechanism of MW. MWs are a type of electromagnetic wave, with a frequency range from 300 MHz to 300 GHz. When applying MW radiation to a material, it causes polarized chains of molecules to align with the direction of the electrical field and make the dipoles change their orientation in phase with the electromagnetic field at high rotating speeds. However, the intermolecular bonds restrict the movements between the dipoles, causing the delay of rotation. This resistance converts part of the radiation energy into heat (Coelho, 2012). Three types of interactions of microwave with three different types of materials as shown in Fig. 4.8.

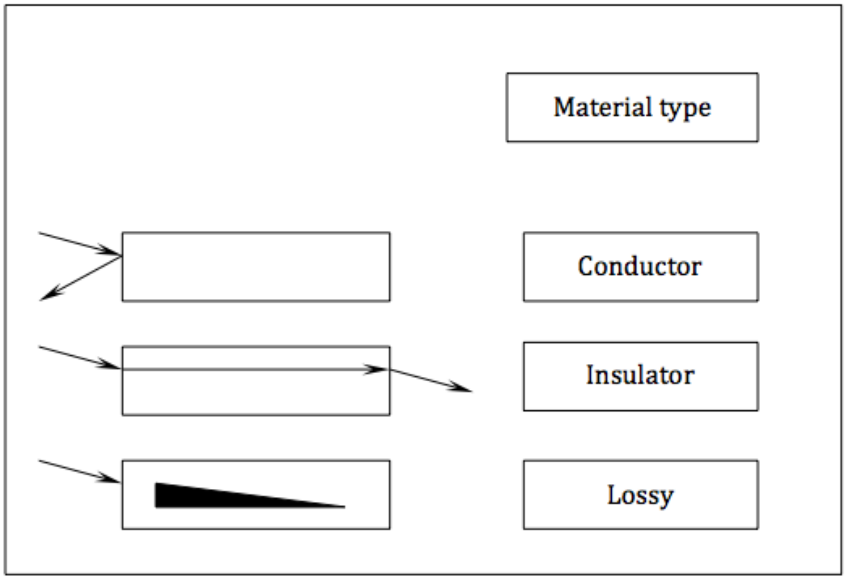


Fig. 4.8 The interaction of MW with different materials (Chan & Reader, 2000)

Table 4.5 T-Test results for different treatment methods under three different MW radiation time (WB temperature): (a) 60 s (65°C), (b) 90 s (85°C) and (c) 120 s (95°C).

(a) 60s (65°C)

	MW	*WB*	*MW +A*	*WB+A*	*MW*	*MW +A*	*WB*	*WB+A*
Mean	11.40	13.00	44.20	45.20	11.40	44.20	13.00	45.20
Variance	1.09	1.17	19.60	14.80	1.09	19.60	1.17	14.80
Observations	3.00	2.00	3.00	3.00	3.00	3.00	2.00	3.00
Hypothesized Mean Difference	0.00		0.00		0.00		0.00	
df	2.00		4.00		2.00		2.00	
t Stat	-1.67		-0.27		-12.50		-13.70	
P(T<=t) two-tail	0.24		0.80		0.01		0.01	
t Critical two-tail	4.30		2.78		4.30		4.30	

(b) 90s (85°C)

	MW	*WB*	*MW+A*	*WB+A*	*MW*	*MW+A*	*WB*	*WB+A*
Mean	20.10	14.30	63.20	58.80	20.10	63.20	14.30	57.90
Variance	0.60	1.07	23.80	0.07	0.60	23.80	1.07	2.55
Observations	3.00	2.00	3.00	2.00	3.00	3.00	2.00	3.00
Hypothesized Mean Difference	0.00		0.00		0.00		0.00	
df	2.00		2.00		2.00		3.00	
t Stat	6.75		1.55		-15.10		-37.00	
P(T<=t) two-tail	0.02		0.26		0.00		0.00	
t Critical two-tail	4.30		4.30		4.30		3.18	

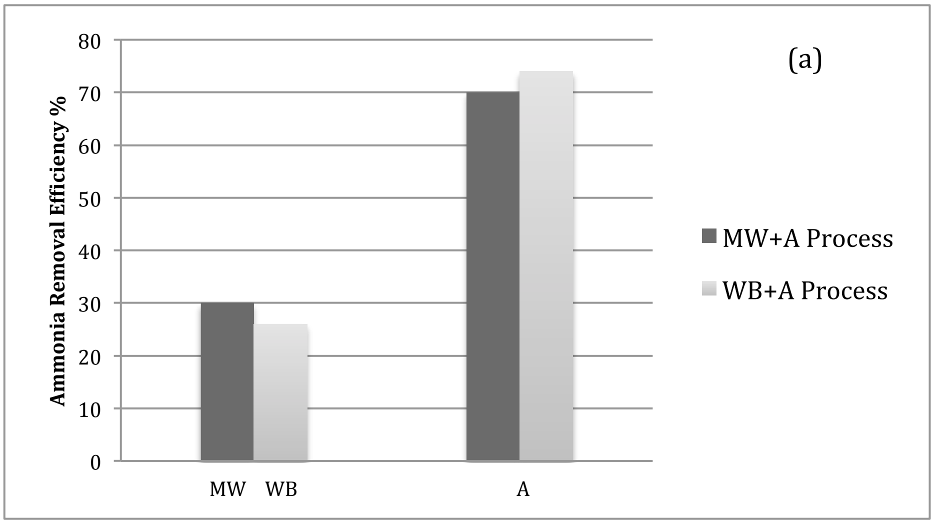
(c) 120s (95°C)

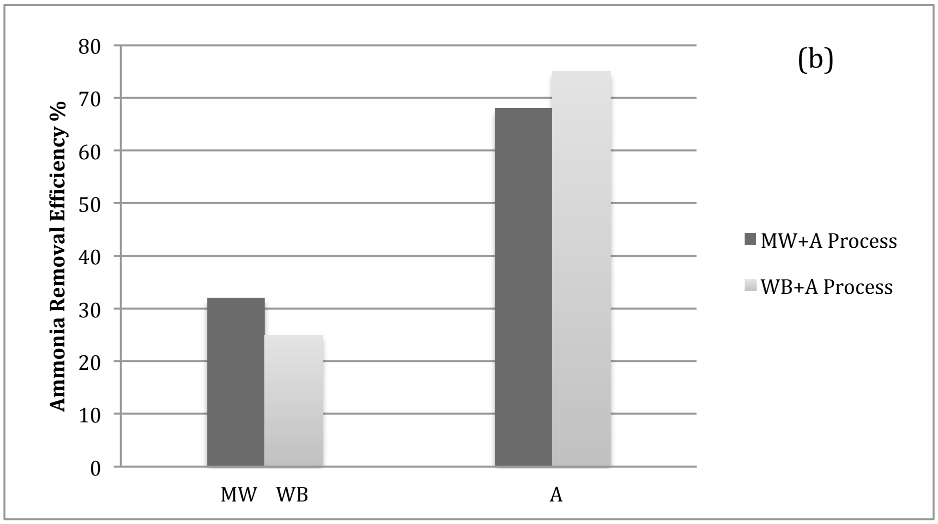
	MW	*WB*	*MW+A*	*WB+A*	*MW*	*MW+A*	*WB*	*WB+A*
Mean	55.10	32.20	81.70	66.10	55.10	81.70	32.20	66.10
Variance	49.60	3.39	3.62	4.29	49.60	3.62	3.39	4.29
Observations	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Hypothesized Mean Difference	0.00		0.00		0.00		0.00	
df	2.00		4.00		2.00		4.00	
t Stat	5.47		9.63		-6.31		-21.20	
P(T<=t) two-tail	0.03		0.00		0.02		0.00	
t Critical two-tail	4.30		2.78		4.30		2.78	

When applying microwaves to a conductor, the radiation can be reflected from the surface of the material such as in the case of metals. Insulators are transparent to microwave radiation: the radiation can pass directly through the material without interference. The third type is lossy material, which can adsorb the microwave radiation. The energy that is dissipated in the material turns into heat. The ammonia aqueous solution is a lossy material that adsorbs microwave energy (Chan & Reader, 2000). The heating mechanism of the microwave is dipole polarization: the dipoles are rotating under the electromagnetic field created by the microwave radiation. In this case, both NH_3 and water molecules are dipoles. One potential explanation for the ammonia removal of the MW process is that during this dipole rotation under the radiation process, the molecular bonds between the NH_3 and water molecules could get weakened, which makes it easier for the ammonia molecules to leave the aqueous system. Thus, during the microwave radiation process, some NH_3 is dissipated through thermal processes (increased temperature); the rest escapes the system as a result of the weaker molecular bounds and increased molecular movement caused by the electromagnetic field.

4.3.5 Effect of Aeration

For both WB+A and MW+A processes, all tests were carried out immediately after the WB or MW test. To determine the effect of aeration, tests were carried out without neither microwave nor water bath processes. 100 mL synthetic solution was adjusted to a pH of 10.5 first, then aerated for 10 minutes. At room temperature (25°C), the ammonia nitrogen removal efficiency was about 20% during this treatment process.


(a)
Ammonia Removal Efficiency %
80
70
60
50
40
30
20
10
0
MW WB
A
MW+A Process
WB+A Process


(b)
Ammonia Removal Efficiency %
80
70
60
50
40
30
20
10
0
MW WB
A
MW+A Process
WB+A Process

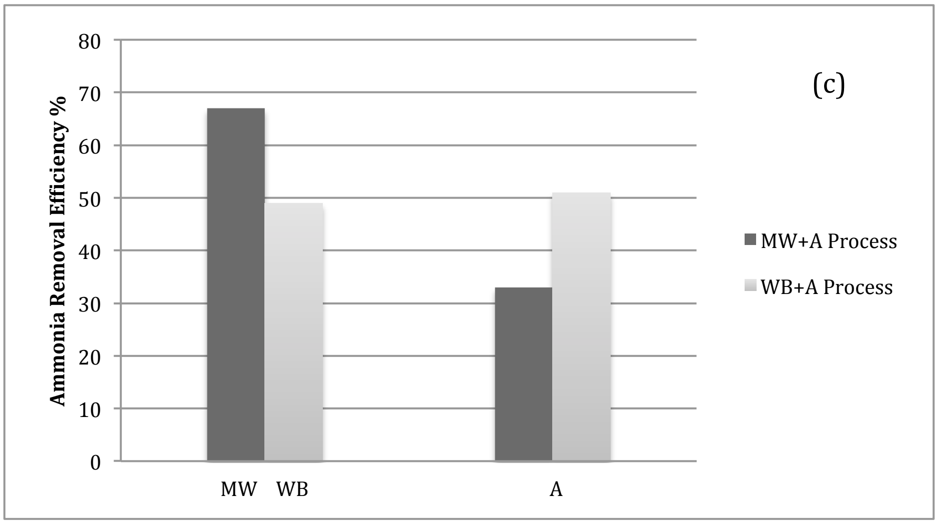


Fig. 4.9 Contribution of MW WB and aeration (A) during the MW+A and WB+A process under MW different radiation time (WB temperature) (a) 60 s (65°C), (b) 90 s (85°C) and (c) 120 s (95°C).

According to Fig. 4.9, at low radiation time periods, most of the ammonia was removed due to the aeration process. For the 60 s MW+A process, 74% of the total removal was due to the aeration process. For the 65°C WB+A process, 70% of the total ammonia removal was a result of the aeration process. At low radiation time periods the contribution from aeration of the MW+A and WB+A process were almost identical. For the MW+A process, at the longest irradiation period (120 s), only 33% of the total ammonia removal was due to the aeration process, which is significantly lower than the value at 60s. For the WB+A process, when the final temperature was 95°C, the contribution of the aeration process was 51%. The aeration process contributed significantly to ammonia removal for both MW+A and WB+A process at lower thermal conditions. With longer radiation time, the contribution of the aeration process decreases relative to the effects of the MW radiation process. When reduced the aeration rate to half of the initial value, the ammonia removal efficiency decreased by 10%.

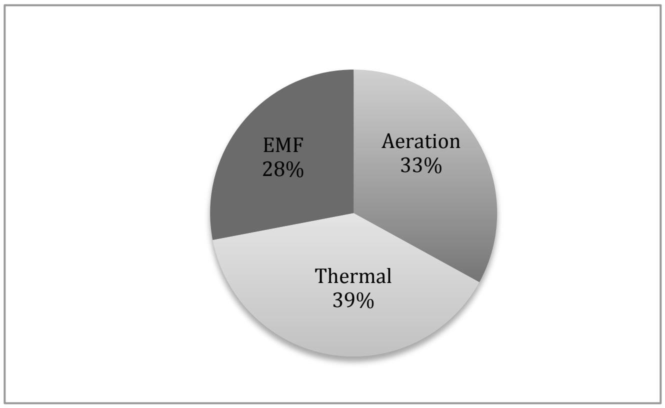


Fig. 4.10 Contribution of electromagnetic field (EMF), aeration and thermal for the MW+A process with the highest removal efficiency achieved at pH of 10.5, with 120s microwave radiation and 10 minutes aeration.

For all four methods under different thermal conditions, the MW+A method attained the highest removal efficiency using 120s radiation time. As shown in Fig. 4.10, 39% percent of the total ammonia removal was due to the thermal effect, 61% was due to the non-thermal process. The two main non-thermal affects are the aeration and electromagnetic field. In previous research (Lin et al., 2009), when the aeration was applied during the microwave process, the effects of the aeration process were limited at longer radiation periods. In this study, the contribution of aeration was 33% when reaching the maximum ammonia removal efficiency.

4.4 Conclusion

The thermal and non-thermal effect of the MW+A process for removal of ammonia from the aqueous solution was researched. Four different ammonia removal methods (MW, MW+A, WB, WB+A) were used specify the effect of thermal and non-thermal process. The conclusions are as follow:

1. There was significant removal of ammonia nitrogen during the sequential microwave/aeration process. For 100 mL synthetic solution, the maximum removal efficiency of 81.7% was achieved at pH 10.5; by applying 650 W microwave radiation (50% of the total MW power output) over 120 seconds MW irradiation time followed by 10 minutes aeration.

2. Under the optimum removal conditions, 39% of the total ammonia removed was a result of the thermal processes, while 61% of the total ammonia removal was from non-thermal processes.

3. The non-thermal effects during the MW+A process were aeration and EMF, the contributions of aeration and EMF were 33% and 28% respectively at maximum ammonia removal conditions.

4. At a pH of 10 during the shortest irradiation periods, the EMF contribution to total ammonia removal was negligible. As the MW radiation power level and irradiation period was increased, the contribution of microwave EMF also increased correspondingly, ultimately accounting for approximately 28% of the total ammonia removal during the MW+A process.

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CHAPTER V

TECHNICAL PAPER II

Statistical Analysis and Optimization of Ammonia Removal from Landfill Leachate by Sequential Microwave/Aeration Process Using Factorial Design and Response Surface

Sainan Dong, Majid Sartaj

Abstract

The application of microwave (MW) radiation followed by aeration (A) for the purpose of ammonia removal from both synthetic solutions and landfill leachate was investigated in this study. Results confirmed that the sequential microwave/aeration process was an effective approach for removal of ammonia from aqueous systems. Maximum ammonia removal of 81.7 % for synthetic solution and 70% for landfill leachate was achieved by applying 7.8 KJ MW energy output/L sample and 10 minutes aeration. Factorial design and response surface methodology were applied to evaluate and optimize the effects of pH, MW energy level and microwave power output. When applying the same energy output to the batch tests, the effect of varying MW power output is negligible. For 100 mL synthetic ammonia solution, the optimum pH and MW energy output level for ammonia removal were 11 and 7.8 KJ MW energy output/L sample and the maximum ammonia removal efficiency predicted for the synthetic solution is 76.3%. R^2 of 0.941 indicates that the observed results fitted well with the model prediction.

Keywords: Ammonia; microwave; aeration; leachate; factorial design; response surface methodology

5.1 Introduction

As one of the major inorganic pollutants in surface water, ammonia exists in aqueous solution in two forms: un-ionized ammonia (NH_3) and ionized ammonia (NH_4^+) (Ding and Sartaj, 2015). It is common in aquatic chemistry to refer to and express the sum of NH_3 and NH_4^+ as simply ammonia or total ammonia nitrogen (TAN) (Nair et al., 2014). Previous research has shown that toxicity is mainly due to NH_3 form (Clément and Merlin, 1995; Rutherford et al., 2000). The concentration distribution of the ionized and un-ionized ammonia depends on pH, temperature, and total ammonia concentration. Under low pH conditions, the majority of TAN is in the form of NH_4^+, while under high pH conditions, NH_3 becomes the dominant species (Ding and Sartaj, 2015). Agricultural drainage and wastewaters from steel, fertilizer, petroleum, and meat-processing industries and landfill leachate are the main sources of ammonia in natural water bodies (Metcalf and Eddy, 2003). According to the EPA's fresh water criteria (2013), ammonia is toxic to aquatic organisms even at low levels (1.9 mg/L as TAN at 20 °C and pH of 7). Also, discharge of wastewater with high ammonia concentration can increase nitrogen levels in natural aqueous systems, thus causing eutrophication (Dachs et al, 2000).

With the increase of population and life quality globally, the generation of municipal solid waste (MSW) has increased rapidly over the past 30 years. EPA data shows that the total MSW generation in the US in 1980 was 151.6 million tons; this increased to 253.7 tons by the year 2005, and remained approximately at the same level until 2012 (USEPA, 2014). The most common MSW management approach is landfilling due to easy operation procedures and low cost. One of the main concerns associated with landfilling process is leachate generation, which is one kind of hazardous and severely polluted wastewater that contains large amounts of organic matters, ammonia nitrogen, heavy metals, chlorinated organic and inorganic salts (Wang et al., 2008). Mature landfill leachate is usually characterized by a low BOD/COD ratio as low as 0.04, and high NH_3-N level up to 13,000 mg/L (Renou et al., 2008). Ward et al. (2000) reported that the significant toxicity of leachate from a landfill in Florida was due to the presence of ammonia.

Traditional biological processes for treatment of ammonia incorporate nitrification and denitrification and they do not perform well to high concentration of ammonia in the landfill leachate, which could inhibit microbial activities including the nitrification process. The inhibition of the nitrification process is reported to be due to un-ionized (NH_3) form while the presence of NH_4-N in the aqueous solution is reported to inhibit the NO_2-N oxidation process at concentrations of 20 mg/L, and also begins to inhibit the NH_4-N oxidation process at concentrations of 100 mg/L of [NH_4-N] (Metcalf and Eddy, 2003). Ammonia inhibition effects on microorganisms in biological treatments have been reported in the range of 1500 to 5000 mg/L as TAN by other researchers (Lee et al., 2000; Liu et al., 2012).

For wastewaters with high ammonia concentration, physical and chemical methods have reported to exhibit high removal efficiencies. However, physical and chemical methods usually come with high cost and some other issues such as the large volume of contaminated sludge generated from the flocculation and coagulation approach, as well as the long contact time during the stripping process (Ozturk et al., 2003; Hasar et al., 2009).

Considering cost and removal efficiency, the application of chemical/physical methods as a pretreatment for the high ammonia concentration before biological processes could be an effective option. The biological processes require a proper C:N ration around 20:1 for the aerobic treatment and 40:1 for the anaerobic process. Since high ammonia levels in the leachate usually result in a low C:N ration in the system, the pretreatment could reduce the ammonia concentration while still retaining enough carbon sources for the biological process (Gray, 1999).

Microwave (MW) radiation has been widely applied in the environmental field for the sludge and wastewater treatments (Alslaibi, et al., 2013; Toreci et al., 2009; Veksha et al., 2015; Zalat & Elsayed, 2013). MW enhanced oxidation processes with oxidants such as hydrogen peroxide (H_2O_2) and persulfate ($S_2O_8^{2-}$) increased the degradation rate of COD and some micro-pollutants such as acid orange 7 (AO7), bromophenol blue, phenol and pharmaceutical wastewater (Remya and Lin, 2011).

MW radiation under high pH levels was reported to reduce ammonia significantly without affecting the organic compounds (Lin et al., 2009a). It was observed that, when applying 350W microwave irradiation, the MW radiation process (below the boiling point, without thermal contributions) was responsible for 40% of the ammonia removal. The remaining portion of the dissipated ammonia was removed in the following two minutes after the solution reached the boiling point, by a combination of MW and thermal processes. Meanwhile, when aeration process was applied concurrently with MW radiation process, the contribution of aeration decreased with longer radiation time. However, the continuous boiling process employed in the research by Lin et al. (2009a) could be a safety concern due to the high operation temperatures and may possibly generate unknown secondary pollutants when applied to real landfill leachate. Moreover, when MW radiation has been used as a pretreatment approach, the high effluent temperature can have a negative effect on the subsequent biological treatment processes.

Aeration is another effective physical treatment for the removal of ammonia without affecting carbon sources in the aqueous system. The main drawback of the aeration process is the energy expenditure, the need to raise pH and the contact time required (Quan et al., 2014). Mattinen et al. (2002) reported 89% ammonia reduction at pH 11 with 24 hours contact time. In a similar research, the maximum ammonia removal efficiency was found at 85% for a landfill leachate with approximately 1000 mg/L ammonium nitrogen, at pH of 12 with 17 hours contact time (Ozturk et al., 2003).

In this study, a sequential MW radiation followed by aeration process was systematically applied for ammonia removal from aqueous phase under different MW power output, pH and radiation time based on a factorial experimental design. Response surface methodology (RSM) was also applied to evaluate and optimize the effect of pH, MW power output, and radiation time. For both safety and economic concerns, the samples were maintained below the boiling point. The temperature of the samples was significantly increased during the MW radiation stage, and then decreased through subsequent aeration process. And lastly, the MW treatments with and without aeration processes were applied for the ammonia removal from a real landfill leachate.

5.2 Material and Methods

5.2.1 Materials and Equipment

The synthetic solution which contained 2,700 mg/L total TAN was prepared by dissolving ammonia chloride in distilled water. In each test, 100 mL of the fresh synthetic solution were prepared. The initial pH was 5.5± 0.3. The pH was adjusted to the desired value using 10 mol/L NaOH. The landfill leachate was obtained from a local landfill in Ottawa with the initial pH 9.0±0.2 and TAN concentration of approximately 4000 mg/L.

The MW process was carried out by a Panasonic microwave oven (Model NN-S 750) with an operating frequency of 2450 MHz and power consumption of 1320 W. The maximum power output is 1300 W and can be adjusted from 10% to 100% in 10% intervals.

The aeration process was performed using a Model 200 MARINA pump with a total aeration rate of 110 L/h with 2 air diffusers. In each test, only one diffuser was placed in the batch reactor. For the tests carried out with the synthetic solution, a 150 mL beaker was used as the batch reactor for all MW with and without aeration processes. For the landfill leachate, a 1 L beaker was used as the batch reactor for the microwave process and a 4 L glass container was used for the aeration process.

5.2.2 Analytical Methods

TNT 832 ammonia vials from HACH Company were used to test ammonia concentrations based on the Salicylate Method using a HACH DR5000 Spectrophotometer. The 10 mg/L ammonia nitrogen standard solution from HACH Company was used to calibrate the spectrophotometer. The pH was measured using a glass electrode in combination with a Fisher Accumet® Model XL25 dual channel pH/ion meter (Alqaralleh, 2012).

5.2.3 Experimental Design

For this study microwave (MW) and aeration were performed in sequence. Experimental conditions for the tests conducted are summarized in Table 5.1. The pH range was selected based on the results of a preliminary set of experiments, which was conducted to evaluate the effect of pH on process efficiency. At a 100% power, MW radiation times greater than 90 s resulted in boiling of the samples and hence they were not carried out. For MW+A, the aeration time was kept at 10 minutes for all samples. The aeration time was selected based on another preliminary set of tests.

MW with and without aeration process for landfill leachate was conducted using 50 % power output with 120 seconds radiation time under three pH levels of 10, 10.5, 11 and 10 minutes of aeration if applicable.

Table 5.1 Experimental design of MW processes for the synthetic solution.

MW time, Sec		30		45		60		90		120	
Power Output Level (%)		50	100	50	100	50	100	50	100	50	100
pH	10	✓	✓	—	✓	✓	✓	✓	—	✓	—
	10.5	✓	✓	—	✓	✓	✓	✓	—	✓	—
	11	✓	✓	—	✓	✓	✓	✓	—	✓	—

Fig. 5.1 presents the order of tests carried out. For the each test, 100 mL of either synthetic solution or leachate was used. pH was adjusted to desired level using 10 mol/L NaOH solution. The sample was then exposed to MW radiation for the desired radiation time according to the conditions presented in Table 5.1. The sample temperature was measured immediately after the MW treatment. Distilled water was used to compensate any water loss. Then, TAN, pH and temperature of the sample were measured. The sample was aerated 10 minutes and TAN, pH and temperature was measured for the second time after another adjustment for water loss.

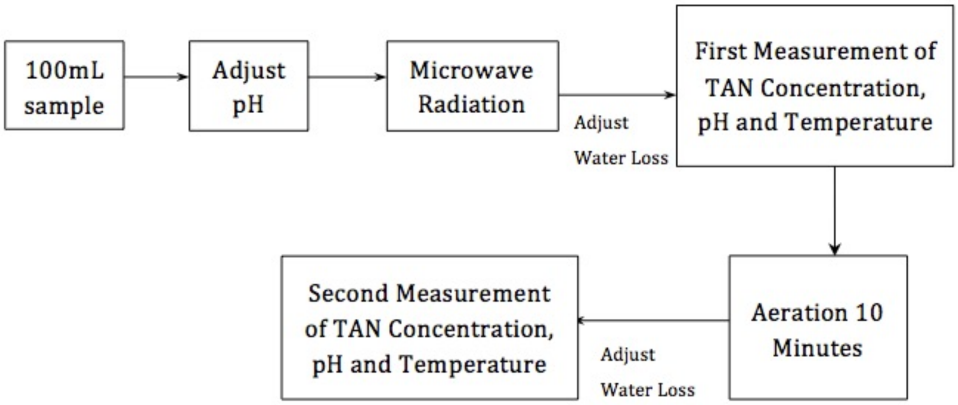


Fig. 5.1 Experimental flow chart

5.2.4 Statistical Method and Data Analysis

Factorial design and response surface methodology (RSM) were applied to evaluate and optimize the pH and MW energy output for ammonia removal from aqueous systems. MW energy output was used to investigate the combined effect of MW power output and radiation time. Two independent variables X_1 (MW energy output) and X_2 (pH) were used for the response surface model and the outcome response was Y (ammonia removal rate). As shown in Table 5.2, X_1 was coded at four levels from -1 to 1. X_2 was coded at three levels between -1 to 1. The ranges of the individual factors were chosen from the preliminary test. All tests were carried out in triplicates, with the purpose of obtaining a reliable estimate of the random error, and to reduce the noise and bias for the outcome response.

Table 5.2 Experimental design and the levels of independent process variables.

Independent variable		Coded levels				
	Symbol	-1	-0.33	0	0.33	1
MW Energy Output (KJ)	X_1	19.5	39	--	58.5	78
pH	X_2	10	--	10.5	--	11

Statistical analysis was performed using DesignExpert® software. Ammonia removal efficiency (Y) was calculated using the following equation:

$$Y\ (\%) = \frac{C-C_0}{C_0}\times 100\% \qquad (5.1)$$

Where C is the ammonia nitrogen concentration after treatment,

C_0 is the initial ammonia nitrogen concentration.

As a combination of mathematical and statistical techniques, response surface methodology (RSM) has been widely used to acquire the optimal operation conditions for both laboratory and industrial processes (Sharma et al., 2009). In this study, the optimum operation conditions for ammonia removal were obtained by analysing the relationships between the variables (pH and MW energy output) and the response (ammonia removal). The behaviour of the RSM in this study was expressed by the following second-order polynomial equation:

$$Y = A_0 + \sum_{i=1}^{n} A_i X_i + \sum_{i=1}^{n} A_{ii} X_i^2 + \sum_{i\neq 1,j=1}^{n} A_{ij} X_i X_j + \varepsilon \qquad (5.2)$$

Where Y is the response variable, A_0 is the value of the fixed response at the center point of the design; A_i, A_{ii}, A_{ij}, represents the linear, quadratic and second order effect regression terms; *n* is the number of independent variable; and ε is the random error.

Coefficient of determination (R^2) was used to describe the accuracy of the model; Fvalue (Fisher variation ratio) and probability value (Prob > F) were applied to evaluate the significance of the model terms (Montgomery, 2008; Ding & Sartaj, 2015).

5.3 Results and Discussion

5.3.1 Effect of Power Output

Based on a preliminary set of tests, a pH of 10.5 was identified as the optimum pH for the ammonia removal by MW from synthetic solution. As mentioned above, three pH levels of 10, 10.5, and 11 were investigated in this study. Two power output levels used in this test were 100% (1300 W) and 50% (650 W) of the total MW power output. As shown in Eq. (5.3) the energy output was calculated according to the corresponding MW irradiation time.

$$E = P \times t \, / \, 1000 \qquad (5.3)$$

Where E is the MW energy output, KJ;

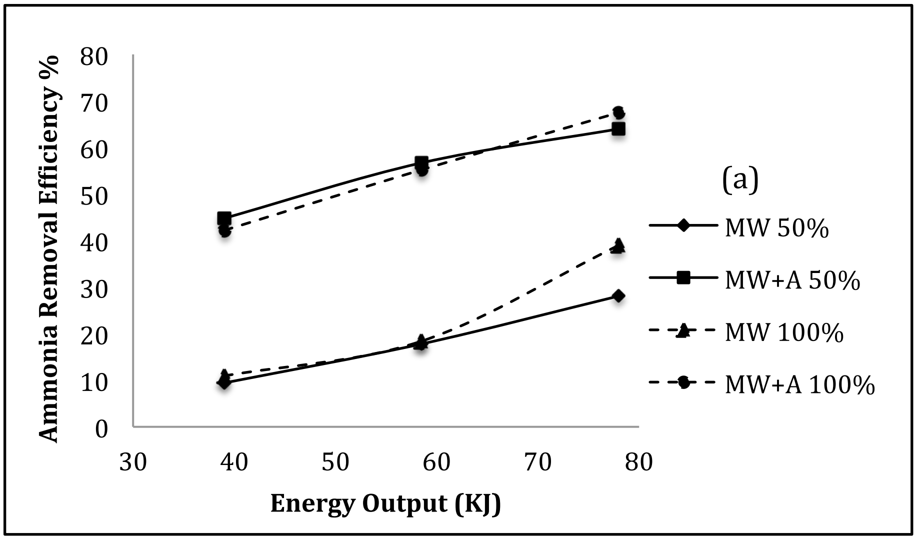
P is the power output, W;

T is the MW irradiation time.

In order to test the ammonia removal efficiencies at two power output levels while maintaining the same energy output, the radiation time used for 100% power output level was half the radiation time for 50% of the power output level.

As shown in Fig. 5.2, ammonia removal efficiency increased with increasing MW energy output under all three pH levels. Similar results were obtained by Rabah & Darwish (2012) and Lin et al., (2009a). Moreover, under the lower energy output values, the difference for ammonia removal efficiencies obtained from 50% and 100% MW power output were not considerable. The difference in ammonia removal efficiencies for 50% and 100% MW power output increases for higher energy output levels, and it is dependent on pH. At a pH of 10, higher ammonia removal of 67.5% was obtained using 100% of the total MW power output than the value of 64% using 50% MW power output. At pH levels of 10.5 and 11, the 50% power output groups had slightly higher removal efficiencies than the 100% groups. Thus, for the MW+A method, the differences of ammonia removal efficiencies obtained from 50% and 100% MW power output tests were negligible. Therefore, in the modeling process, the ammonia removal data were catalogued by the MW energy output level instead MW radiation time and power output level.

Depending on the energy output and pH levels, the MW process can remove between 10.9% - 53.1% TAN in the synthetic solution. When applying the sequential aeration process, an additional 20.5% - 45.2% TAN removal can be achieved depending on the operation parameters.



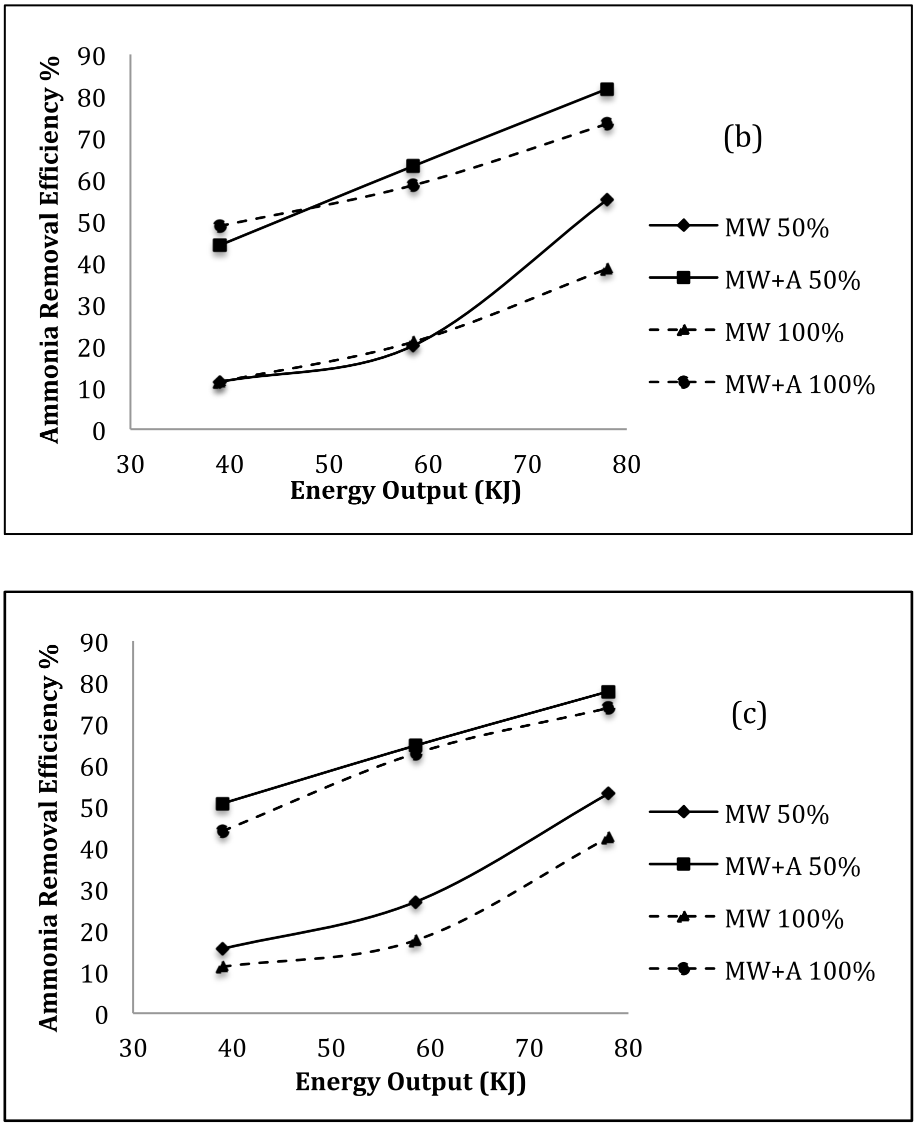


Fig. 5.2 Ammonia removal using the same energy output with 50% and 100% of the total power output under pH of 10 (a), 10.5 (b), 11(c).

5.3.2 Statistical Analysis and Modeling

After performing 63 runs, based on a factorial design of two independent variables, the experimental results for ammonia percent removal (Y) were obtained. All the data was evaluated by DesignExpert® to detect any outlier and unreliable result. External studentized residuals were calculated to eliminate the outliers. All collected data was in the acceptable range to be used to develop the model. Regression analysis was applied to develop the best-fit model using the collected data. The response ammonia removal percentage (Y) was predicted by a second-order polynomial equation shown as Eq. (5.4) below.

$$Y = 54.49 + 21.11X_1 + 3.20X_2 + 1.65X_1X_2 - 1.12X_1^2 - 2.07\,X_2^2 \tag{5.4}$$

Where, Y is the ammonia removal efficiency,

X_1 is the MW energy output,

X_2 is the adjusted pH value of the sample.

F-test was conducted for the analysis of variance (ANOVA) to evaluate the statistical significance of the quadratic model. The ANOVA tests results are as shown in Table 5.3 (a). The F-value of 197.22 and the “Prob > F” value of < 0.0001 suggests that the model was statistically significant for ammonia removal. Values of "Prob > F" less than 0.05 indicate model terms are significant. In this case, $X_1, X_2, and\ X_2^2$ are significant model terms. For terms X_1X_2 and X_1^2 the corresponding "Prob > F" values are larger than 0.05, which implies these are insignificant terms and can be eliminated. The ANVOA test results of the reduced form are as shown in Table 5.3 (b). As can be seen, the reduced model with F value of 311.57 and “Prob > F” value of < 0.0001 indicate that the reduced model is significant. There is only a 0.01% chance that the large F-value is a result of noise. The adequate precision ratio of 50.82 indicates an adequate signal since it is larger than the Boundary value of 4 (Bashir et al., 2010; Beg et al., 2003). The reduced model of ammonia removal percentage is shown as Eq. (5.5) below:

$$Y = 53.97 + 20.94X_1 + 3.44X_2 - 2.07\,X_2^2 \qquad (5.5)$$

Table 5.3 Analysis of variance (ANOVA) for RSM (a) full and (b) reduced quadratic model parameters

(a)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	13614.64	5	2722.93	197.22	<0.0001	Significant
X_1	12442.30	1	12442.30	901.18	<0.0001	
X_2	412.49	1	412.49	29.88	<0.0001	
X_1X_2	53.64	1	53.64	3.88	0.054	
X_1^2	14.45	1	14.45	1.05	0.311	
X_2^2	59.90	1	59.90	4.34	0.042	
Residual	786.98	57	13.81			
Lack-of-Fit	165.56	6	27.60	2.26	0.052	Not Significant
Pure Error	621.42	51	12.18			
Total	14401.62	62				

$R^2 = 0.945$ $R_{adj}^2 = 0.941$ $R_{pred}^2 = 0.933$ Adequate Precision = 42.402

(b)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	13546.55	3	4515.512	311.57	<0.0001	Significant
X_1	12990.65	1	12990.65	896.36	<0.0001	
X_2	496.009	1	496.01	34.23	<0.0001	
X_2^2	59.90	1	59.90	4.13	0.047	
Residual	855.06	59	14.49			
Lack-of-Fit	233.64	8	29.21	2.40	0.028	Significant
Pure Error	621.42	51	12.18			
Total	14401.62	62				

$R^2 = 0.941$ $R^2_{adj} = 0.937$ $R^2_{pred} = 0.932$ Adequate Precision = 50.82

Coefficient of determination (R^2), adjusted R^2 and predicted R^2 values were used to evaluate the fitness of the model. Adjusted R^2 is a modification of R^2 , which adjusts for the number of explanatory terms in a model relative to the number of data points (Anderson & Whitcomb, 2005). The predicted R^2 indicates how well a regression model predicts responses for new observations (Myers, et al., 2012). The R^2 value of 0.941 (R^2_{adj} = 0.937) indicates that the predicted values obtained from the model is a good fit of the experimental data (Rabah & Darwish, 2012). The lack-of-fit compares the residual error to the pure error from triplicated experimental design points (Gomez & Sartaj, 2014). In the full model, the p-value for lack-of-fit is 0.052, which is greater than 0.05, indicating that the lack-of-fit is insignificant relative to the pure error. There is a 5.4% chance that the lack-of-fit occurs due to noise or random error, which means there was no lack-of-fit of the model. However in the reduced model the lack-of-fit value is 0.028, which implies the lack-of-fit is significant in the reduced model. This could due to the systematic variations unaccounted for in the model (Khamis et al., 2015). Another possible reason is that the large numbers (up to 6) of close replicate values that used to provide an estimate of pure error (Ding & Sartaj, 2015; Bashir et al., 2010). A relatively low R^2 value and the significant lack-of-fit value can suggest that regression model fails to adequately describe the functional relationship between the experimental factors and the response variable adequately (Ryan & Joiner, 2001). However, a model with reasonable R^2 value is acceptable with significant lack-of-fit (Benyahia et al., 2014; Jabeen, et al., 2015; Palaniandy et al., 2015). Compared with the reduced model, the difference between R^2 values is not considerable, and the reduced model is more simple, i.e. has less terms. The reduced quadratic model was considered to be appropriate to describe the design due with a high R^2 value of 0.941, and adequate precision ratio of 50.82.

Fig. 5.3 illustrates the predicted versus observed values for ammonia removal. Actual values are collected from each specific run, and predicted values are produced by the model of Eq. (5.2). The linear distribution of the points along the idealized trend indicates the predicted values are good approximations of the corresponding observed values. The R^2 value of 0.964 indicates a high correlation between the actual and predicted values for this model.

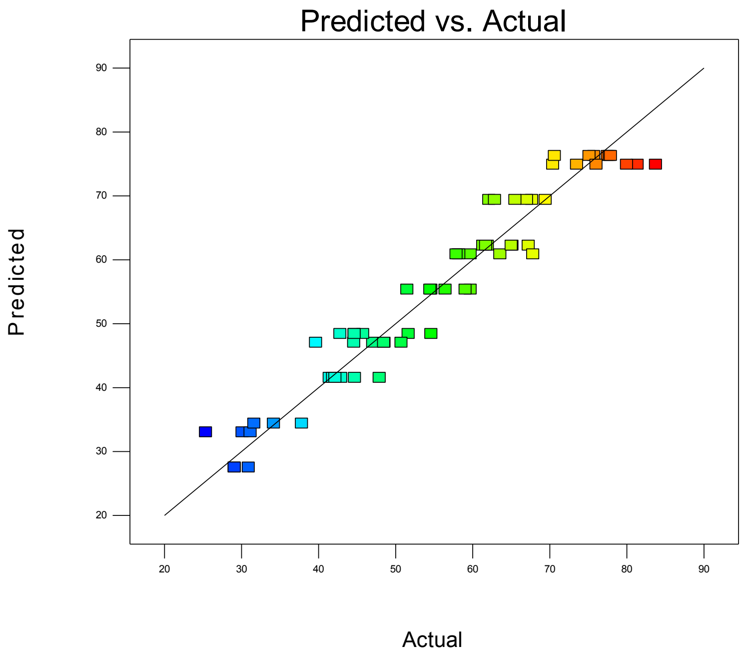


Fig. 5.3 Predicted versus actual values for ammonia percent removal.

Fig. 5.4 shows the diagnostics plots of externally studentized residual versus predicted value, run, pH and time. Outliers in the diagnostics plots simply indicate the magnitude of the residuals, determining if any of the data had particularly large residuals (Salahi et al., 2013). As shown in the diagnostics plots, the red line was produced by the software based on the externally studentized to define outliers. No outlier exists in the plot indicating that the model is consistent with all the data. Furthermore, there is no significant distribution pattern for all the diagnostics plots graphs and all the externally studentized residual were randomly scattered across the graph. Thus there is no violation of the independence or constant variance assumption for all runs (Montgomery, 2008). Fig. 5.5 presents an adequate fit of the externally studentized residuals versus normal probability percentage, confirming that the statistical assumptions suit the analytical data.

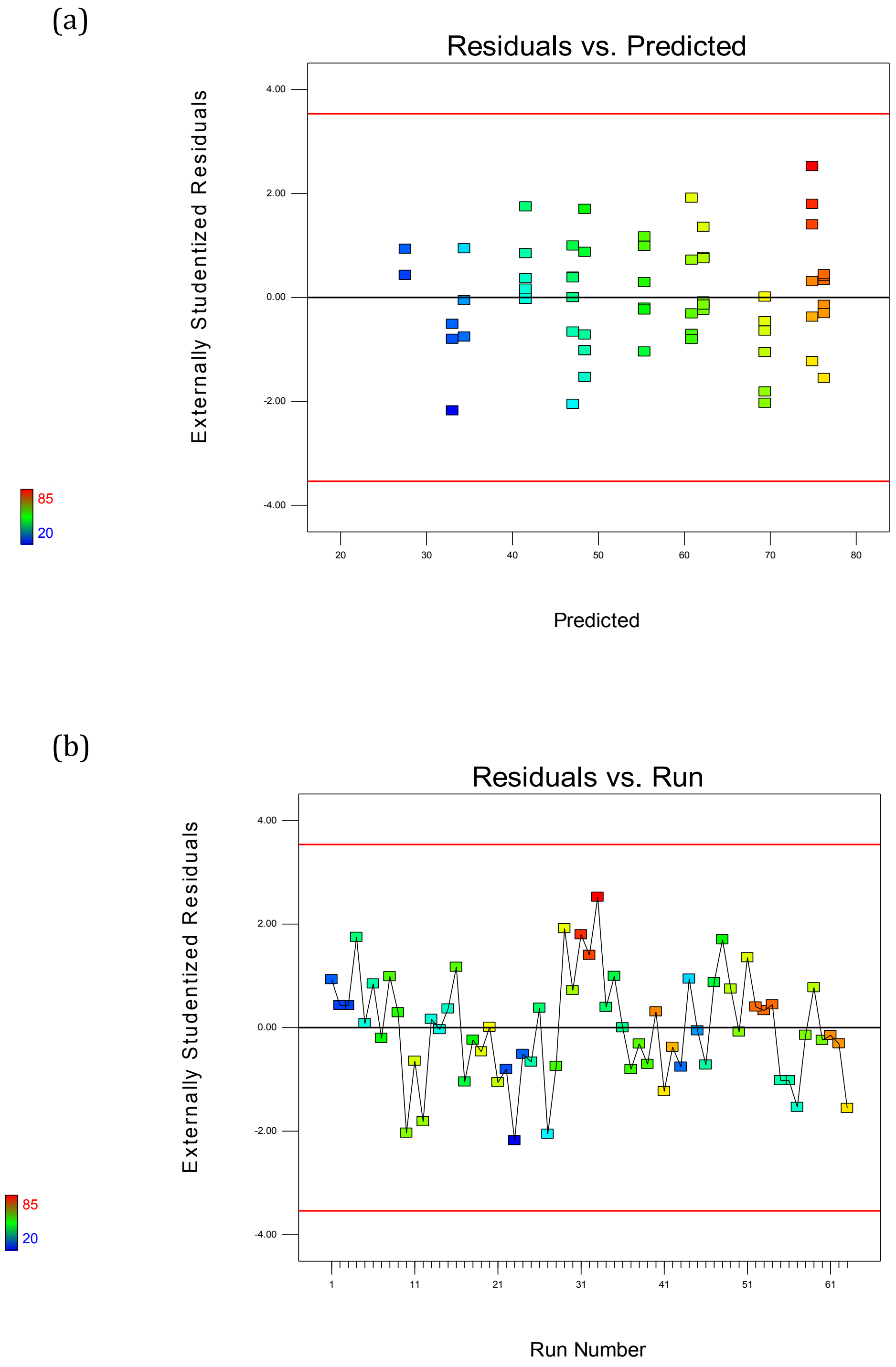


Fig. 5.4 Diagnostics plots for ammonia removal (a) externally studentized residual versus predicted values, (b) externally studentized residual versus run values

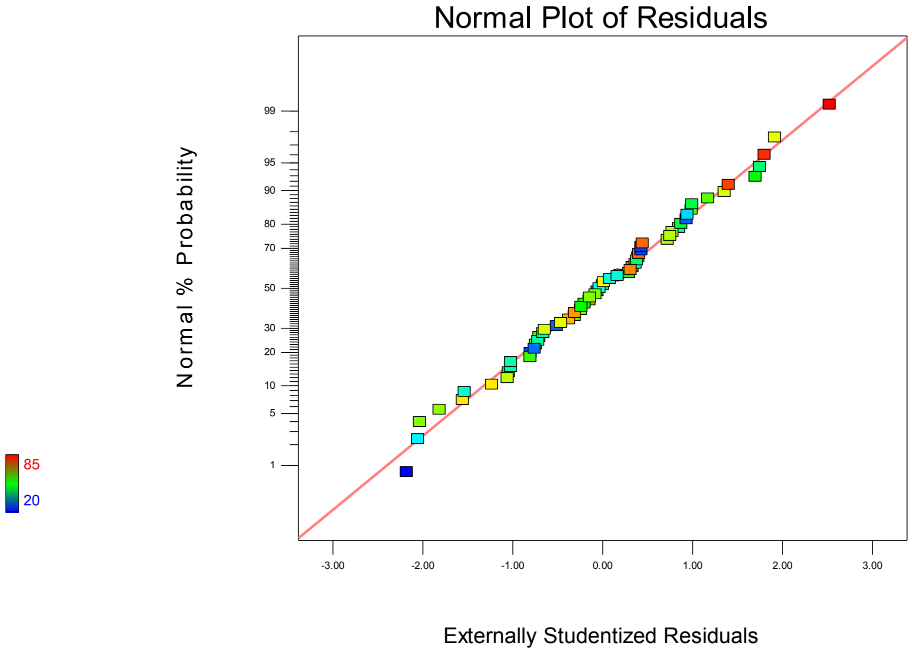


Fig. 5.5 Normal probability of externally studentized residuals for ammonia removal

5.3.3 Response Surface Methodology

A three-dimensional surface plot and a two-dimensional contour plot are illustrated in Figs 5.6 and 5.7, respectively, to provide a better visualization of the statistically significant factors derived from the statistical analysis. The effects and interactions of MW energy output and different pH levels on the removal of ammonia are illustrated in both figures. It can be seen that the MW energy output had a positive effect for the ammonia removal all the time. Since samples in batch tests were maintained under the boiling point, the maximum ammonia removal was achieved at the highest MW energy output level. The effect of pH was significant at low MW energy output level as the ammonia removal efficiencies were increased with higher pH. With high MW energy output, the ammonia removal efficiencies of pH of 10.5 and 11 were relatively close but significantly higher than that of pH of 10. For synthetic solution, the optimum pH and MW energy output for ammonia removal were found to be 11 and 7.8 KJ MW energy output/L sample and the maximum ammonia removal efficiency predicted is 76.3%.

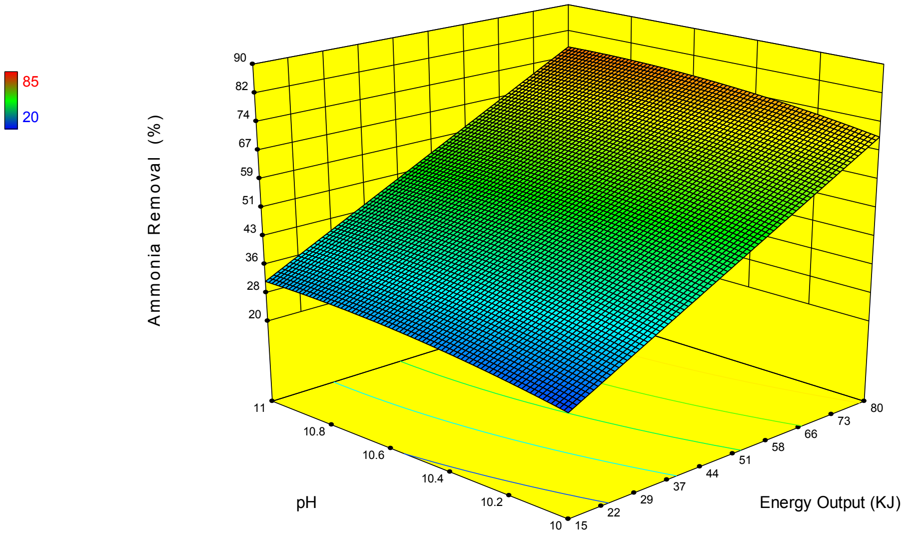


Fig. 5.6 Three-dimensional surface plot by response surface methodology.

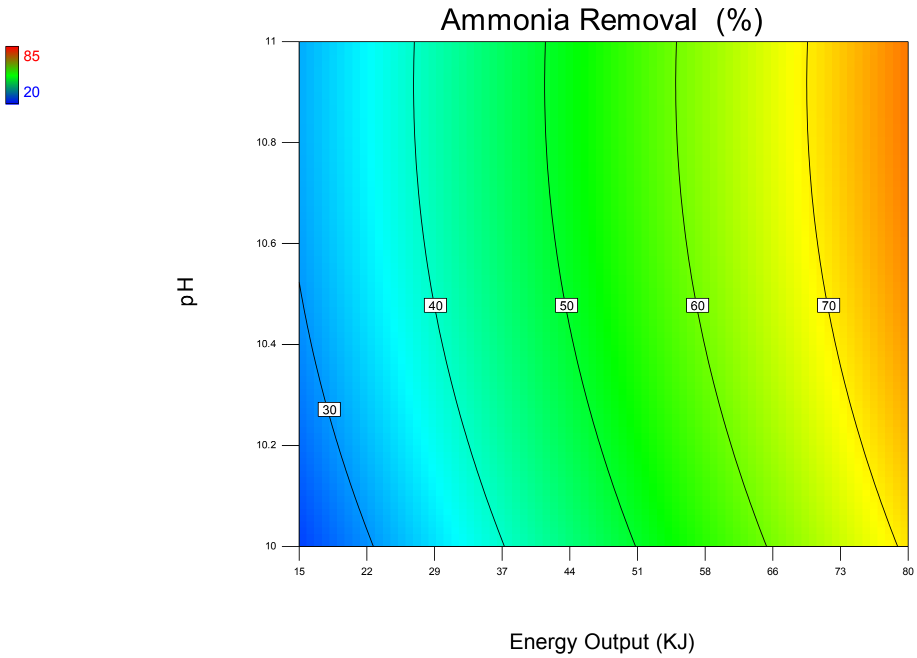


Fig. 5.7 Two-dimensional contour plot by response surface methodology.

5.3.4 Ammonia Removal from Landfill Leachate

To achieve the optimum MW energy output level, the MW process with and without aeration using 50% of the total power output with 120 seconds radiation time was applied to the leachate sample. Three pH levels of 10, 10.5, and 11 were investigated in the course of this research. Fig. 5.8 shows the ammonia removal efficiency for landfill leachate at three different pH levels of 10, 10.5 and 11 using 50% of total MW output for 120s MW radiation time. The ammonia removal efficiencies for both MW and MW+A methods increased with the increase of pH. This is a similar trend to the result obtained from the synthetic solution test. However, the maximum ammonia removal of 70% in the leachate was achieved under conditions of pH of 11 and 120 s MW radiation time, which is lower than the 77.8% ammonia removal from the synthetic solution test using the same pH and energy output level. This can be explained by the complex composition of the landfill leachate. During the generation of landfill leachate, water percolates through solid wastes that are undergoing decomposition; both biological materials and chemical constituents are leached into solution (Tchobanoglous et al., 1993). Most water-soluble organic and inorganic compounds in the leachate are dipoles, due to the high polarity of water molecules. Comparing with the synthetic solution the landfill leachate has more dipoles other than the ammonia molecule. When the sample is treated by MW radiation, these dipoles adsorb part of the MW energy at the same time. Thus the degasification process of the ammonia is less effective in the leachate test.

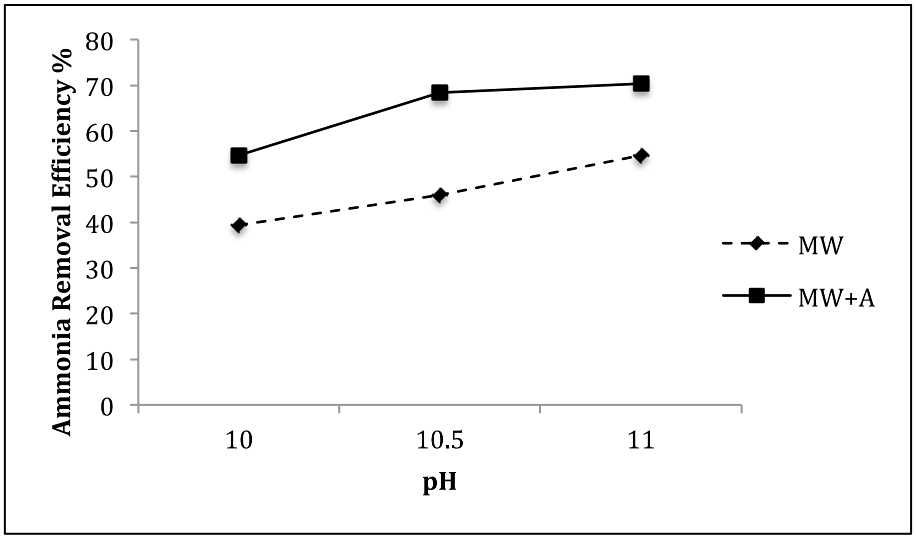


Fig. 5.8 Ammonia removal from landfill leachate under three different pH levels of 10, 10.5 and 11 using 50% of total MW output for 120 s MW irradiation time.

5.4 Conclusion

Sequential microwave/aeration process is confirmed to be an effective approach for the ammonia removal from both synthetic solution and landfill leachate. Maximum ammonia removal of 81.7 % for the synthetic solution and 70% for the landfill leachate was achieved, respectively.

Statistical analysis of experimental data showed that ammonia removal efficiency strongly depended on pH and MW energy output. Applying the same MW energy output to the batch tests, the effect of MW power output and corresponding radiation time is negligible. The R^2 of 0.941 indicates that the observed results fitted well with the model prediction. Surface and contour plot showed that the optimum pH and MW energy output level for ammonia removal were 11 and 7.8 KJ MW energy output/L sample and the maximum ammonia removal efficiency predicted for the synthetic solution is 76.3%.

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CHAPTER VI

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

The application of sequential microwave/aeration process for the purpose of ammonia removal from both synthetic solutions and landfill leachate was investigated in this study. Results confirmed that the sequential microwave/aeration process was an effective approach for removal of ammonia from aqueous systems. Maximum ammonia removal of 81.7 % for synthetic solution and 70% for landfill leachate was achieved by applying 7.8 KJ MW energy output/L sample and 10 minutes aeration.

Three main contributors for ammonia removal using the sequential microwave/aeration process (thermal effects, EMF generated by MW radiation, and aeration processes) were investigated. Similar ammonia removal trends for all four approaches were observed at all pH values with the exception of pH 10 with MW (WB) only. At a pH of 10 during the shortest irradiation periods, the EMF contribution to total ammonia removal was negligible. The contribution of EMF becomes increasingly significant with the increase of MW irradiation time, except at a pH of 10. Under the optimum operation conditions of 7.8 KJ MW energy output/L sample and a pH 0f 10.5, for the sequential microwave/aeration process, 39% of the total ammonia removed was a result of the thermal processes, while 61% of the total ammonia removal was from non-thermal processes (33%aeration contribution and 28% EMF contribution).

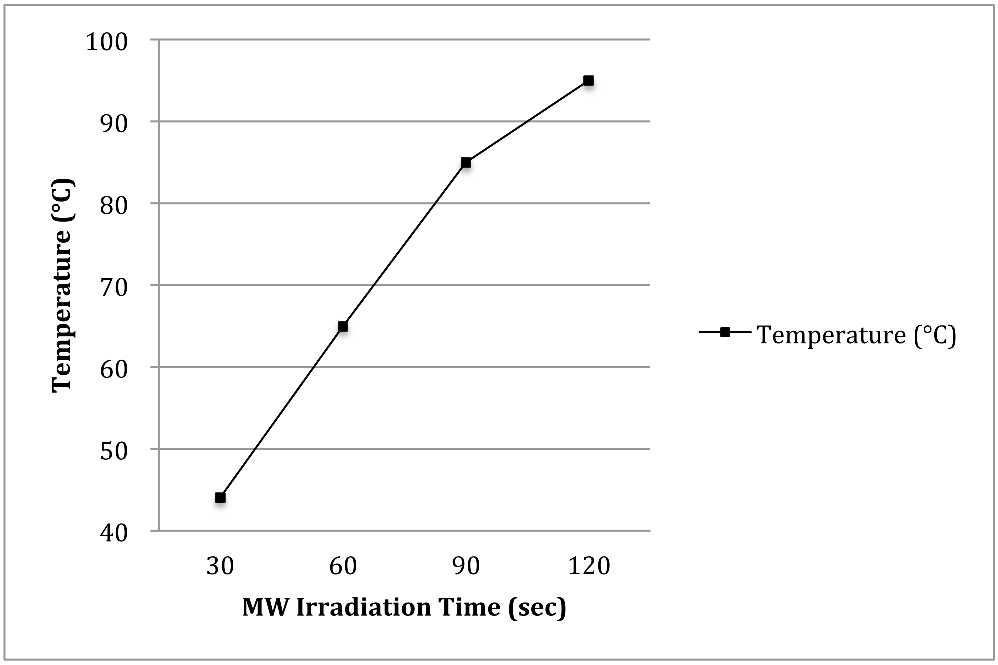
Statistical analysis of experimental data showed that ammonia removal efficiency strongly depended on pH and MW energy output. Applying the same MW energy output to the batch tests, the effect of MW power output and corresponding radiation time is negligible. The R^2 of 0.941 suggests that the observed results fitted well with the model prediction. Surface and contour plot showed that for aqueous solution, the optimum pH and MW energy output levels for ammonia removal were 11 and 7.8 KJ/L respectively, and the maximum ammonia removal efficiency predicted for the synthetic solution is 76.3%.

6.2 Future Work

This study confirmed the viability of sequential microwave/aeration process as an effective ammonia removal approach for both synthetic solution and landfill leachate. Since only batch tests were conducted in this stage, future research could focus on continuous sequential microwave/aeration reactors. The system could be constructed by either installing a reactor inside a microwave oven or attaching microwave generator to the outside of a reactor, then connecting the microwave reactor to a sequential aeration reactor. Using a pre-existing microwave oven is the simpler option, but the size of the MW reactor is limited by the capacity of the microwave oven. For the second option of installing microwave generators around the reactor, the main concern is controlling MW leakage, but the capacity of the reactor can be designed to necessary specifications. This is most likely the more viable option when applying the sequential microwave/aeration process on an industrial scale.

Appendix A

Temperature profile of using 50% MW power output with different irradiation time

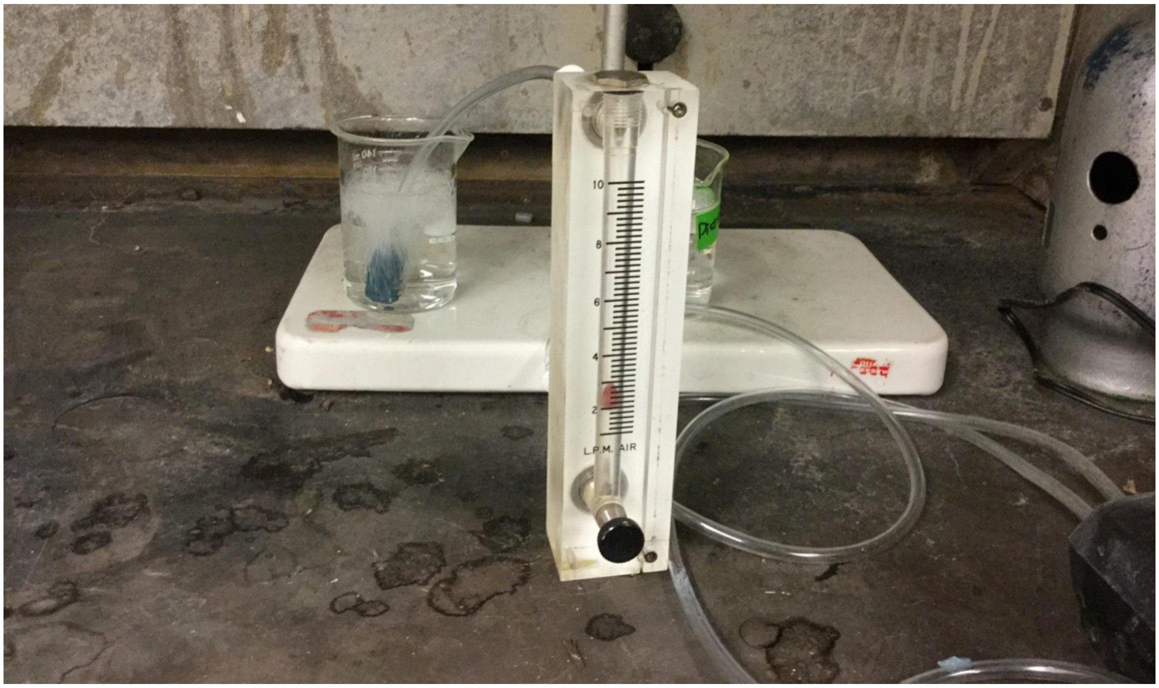


Appendix B

Experimental Setup and Measurement

B.1 Microwave Setup

B.2 Aeration Setup



B.3 Ammonia Measurement: HACH TNT 832 Ammonia Vials

B.4 Ammonia Measurement: HACH DR 5000 Spectrophotometer