Struvite Precipitation of Ammonia from Landfill Leachate

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ABSTRACT

The application of struvite (magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$) precipitation and its recycling use for the purpose of ammonia removal from both synthetic solutions and landfill leachate were investigated in this study. The results demonstrated that chemical precipitation by struvite formation is efficient for ammonia removal from aqueous solutions. In addition, by recycling the thermal residue of struvite, continuously removing ammonia can technically be achieved.

In the struvite precipitation, ammonia removal significantly depended on the pH and chemical molar ratios of $NH_4^+ : Mg^{2+} : PO_4^{3-}$. For synthetic solution (TAN=1,000 mg/L), remarkable TAN removal efficiency of over 98% has been reported when the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ equals 1.0:1.2:1.2, 1.0:1.3:1.3, 1.0:1.3:1.4 and 1.0:1.5:1.5 at optimum pH 9. The optimum combinations of reagents applied in landfill leachate (TAN=1,878 mg/L) were $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.3:1.3, 1.0:1.4:1.3, 1.0:1.5:1.4 and 1.0:1.5:1.5 at optimum pH 9.5, all of which displayed excellent TAN removal efficiencies of over 99%. Response surface method (RSM) helped to analyze the data and optimize the results.

The struvite pyrolysate provided best performance of removing ammonia in both simulated wastewater and landfill leachate at a dosage of 60 g/L, when struvite was previously heated at 105 ℃ by oven for 2.5 h**.** In the recycling phase, the struvite pyrolysate resulting from NaOH-mediated pyrolysis was more effective at continuously treating ammonia synthetic solution than was direct heating, with an initial mode of 87.4% at the beginning to 75.1% in the fifth round and direct heating of struvite from 80.9% in the first cycle and 60.6% in the final cycle. The struvite pyrolysate formed by NaOH-mediated pyrolysis performed with greater ability to continuously eliminate ammonia from landfill leachate (97.2% removal at the beginning and 72.3% in the fifth round), than did directly heated struvite (98.4% in the first cycle and 81.3% in the final cycle). Additionally, microwave irradiation could also dissociate struvite, which subsequently demonstrated moderate TAN removal in recycling phases.

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List of Abbreviations

AC: activated carbon;

AD: anaerobic digestion;

ANOVA: analysis of variance

AOXs: adsorbable organic halogens;

AS: activated sludge;

BOD: biochemical oxygen demand;

CEPA: Canadian Environmental Protection Agency

CI: confidence interval;

COD: chemical oxygen demand;

DF: degree of freedom;

DW: distilled water;

FA: free ammonia;

GAC: granular activated carbon

IER: ion-exchange resin;

LFG: landfill gas;

MAP: magnesium ammonium phosphate;

MBR: membrane bioreactor

MF: microfiltration;

MLSS: mixed liquor suspended solids;

MS: mean square

MWS: municipal solid waste;

MW: microwave;

NF: nanofiltration;

N:M:P=$NH_4^+ : Mg^{2+} : PO_4^{3-}$;

PAC: powdered activated carbon;

PAHs: polyarmatic hydrocarbons;

PCBs: polychlorinated biphenyls;

RO: reverse osmosis;

RSM: response surface methodology;

SBR: sequencing batch reactor;

SS: suspended solids

TAN: total ammonia nitrogen;

TKN: total Kjeldahl nitrogen;

UASB: up-flow anaerobic sludge blanket;

UF: ultrafiltration ;

USEPA: United State Environmental Protection Agency

VFA: volatile fatty acid ;

VSS: volatile suspended solid

CHAPTER I

INTRODUCTION

1.1 Background

Ammonia is recognized as one of the dominant inorganic contaminants in natural aquatic systems (Ip, 2010). Wastewater from municipal effluent discharges, metal industry, run-off from agricultural activities, petroleum and food-processing industries and landfill leachate contribute as the main source of ammonia in natural water environment (Metcalf and Eddy, 2003). In aqueous state, total ammonia (TAN) exists in two forms: the un-ionized ammonia (NH_3); and ionized ammonia (NH_4^+). The balance of these two types of ammonia in the aqueous phase depends on pH and temperature (Nair et al., 2014).

As containing one of the necessary elements (nitrogen, N) of life, low concentration of ammonia (50 to 200 mg/L), to some certain degree, can benefit the organisms' growth (Rajagopal et al., 2013). However, the presence of excessive ammonia can lead to accelerated eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water bodies (Du et al., 2005). The toxicity of ammonia can be illustrated as the inhibition to microorganisms due to un-ionized ammonia (Chen et al., 2008). Ammonia concentration is reported to be up to 13,000 mg/L in municipal landfill leachate (Renou et al., 2008), while the range from 1,500 to 5,000 mg/L is reported as the toxic levels resulting in inhibition (Lee et al. 2000; Liu et al., 2012). United States Environmental Protection Agency (USEPA) fresh water quality criteria for ammonia are 17 mg TAN/L (acute) and 1.9 mg TAN/L (chronic) under the circumstance of pH at 7 and temperature at 20 ℃ (Environmental Protection Agency, 2013). Canadian Environmental Protection Agency (CEPA) added ammonia to the list of toxic substances in 1999 (Environment Canada, 2001) and set the maximum concentration of un-ionized ammonia in the effluent (15±1℃): 1.25 mg/L as NH_3-N (Canada Gazette, 2012).

Different treatment methods for ammonia removal from aqueous environment include conventional processes such as biological nitrification/denitrification, air stripping, membrane filtration and ion-exchange (Ferraz et al., 2013; Hasar et al., 2009; Malekian et al., 2011; Sri et al., 2012). Developing feasible techniques and optimizing current methods for removing ammonia from highly contaminated wastewater as treatment or pre-treatment at reasonable cost has been one of the central research topic in water and wastewater in recent decades.

1.2 Objectives

The main aim of this project is to investigate the feasibility of the application of struvite (magnesium ammonium phosphate, MAP, $MgNH_4PO_4 \cdot 6H_2O$) precipitation for ammonia removal from the synthetic solution and municipal landfill leachate with high ammonium concentrations; thereby recovering struvite possible recycling use. First phase is to investigate the optimum operational parameters for ammonia removal from synthetic aqueous solution and landfill leahcate using chemical precipitation of struvite formation. Second phase is to study the performance of struvite pyrolysate on continuous ammonia removal from aqueous solutions. Objectives of this research include:

- To investigate ammonia removal by studying the effect of pH and molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ by the addition of magnesium and phosphate source
- To evaluate and optimize the results by the analysis of response surface methodology (RSM)
- To determine the optimum operation conditions (heating time, heating temperature, reaction pH, effect of struvite pyrolysate dosage, effect of NaOH addition in pyrolysis) for the regenerating and recycling of thermal-pretreated struvite to remove ammonia from liquid systems
- Study the application of microwave irradiation in dissociating struvite and the possible recycled use of struvite pyrolysate

1.3 Thesis Layout

This thesis is presented in the form of technical papers with six main chapters. Chapter I contains the background, introduction, the statement of the problem, the objectives of the research and the thesis organization. Chapter II is the literature review of the presence of high concentration ammonia in aqueous solution, especially in landfill leachate, and the current treatment approaches available. Chapter III presents the materials, equipment and methodology used in this study. Chapter IV is the first technical paper entitled: "Assessment and Optimization of Struvite Precipitation for Ammonia Removal from Aqueous Solution". Chapter V is the second technical paper entitled: "Assessment and Optimization of Struvite Precipitation of Ammonia from Landfill Leachate". Chapter VI summarizes the conclusions of this study and the future work recommendations. Taking into account that this thesis is prepared in a paper-based format, there could be some repeated information appearing in different chapters.

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CHAPTER II

LITERATURE REVIEW

2.1 Municipal Solid Waste Landfilling

Solid wastes management treatments, include waste sorting, recycling, composting, incineration and landfilling. Landfilling remains the main method for municipal solid waste (MSW) management in many countries and areas worldwide (Vigneron et al., 2007; Kheradmand et al., 2010). Landfilling of MSW is a very important method of the waste management system and up to 75% of such waste collected worldwide is disposed of in landfill sites (Abbas et al., 2009; Guo et al., 2010). A MSW landfill is regarded as a treatment facility whose objective is to obtain a residual solid of a "final storage quality", one which does not adversely affect the environment for long periods (Lubberding et al., 2012). Historically, landfills were operated in the "dry-tomb" method but now they are switching to bioreactor landfilling approach as it has many advantages over the conventional landfilling. They include: (1) it increases the effective density of waste and therefore increases the capacity of landfills, (2) it increases the potential for energy production and recovery of landfill gas, (3) in-situ treatment by recirculation of leachate in the bioreactors leads to reduced operational expenses, (4) it accelerates decompositions of waste with the effect of shortening the monitoring period and thereby reducing the overall cost, (5) it enhances the sustainability allowing possible reuse of the land (Fernandes et al., 2015; Mukherjee et al., 2014; Omar and Rohani, 2015; Warith, 2002). Currently, three types of bioreactor landfills (anaerobic, aerobic and semi-aerobic) are being widely employed and their potential advantages and disadvantages are displayed in Table 2.1 (Omar and Rohani, 2015). Solids wastes in the MSW landfill lead to two major environmental impacts. First, leachate, defined as the harmful liquid waste generated by water that has percolated through the landfilled waste material, which could migrate into groundwater; Second, gaseous emissions (Landfill gas or LGS) produced by the

fermentation of organic fractions, a source of air pollution and one of main contributing source for global warming (Ahmed and Lan, 2012).

Table 2. 1 Potential advantages and disadvantages of three types of bioreactor landfills (Adapted from Omar and Rohani, 2015)

	Advantages	Disadvantages
Anaerobic	(1) LFG has high methane concentration which can be used (2) Decreased waste stabilization times (3) Relatively low cost (4) In-situ treatment of leachate	(1) High VFA concentration can leach harmful constituents (2) Relatively high levels of ammonia in leachate (3) Production of hydrogen sulfide
Aerobic	(1) Decreased waste stabilization times (2) Little to no methane production decreases green house gas emissions (3) In-situ treatment of leachate (4) Removal of moisture by air stripping (5)Little to no ammonia production	(1) High cost for aeration (2) Produced air that can cause flammable/explosive mixture (3) Unknown gases may be produced
Semi-aerobic	(1) Decreased waste stabilization times (2) Little methane production decreases GHG emissions (3) In-situ treatment of leachate (4) Relatively low cost	(1) Unknown gases may be produced (2) Produced air that can cause flammable/explosive mixture

2.2 Landfill Leachate

As landfill leachate extracts several pollutants as it moves through the waste material, it is a very complex wastewater (Fernandes et al., 2015). Landfill leachate is a dark colored liquid (Figure 2.1), with a strong smell, which carries a high organic and inorganic load (Peng, 2013). The composition of leachate is complex and variable since it is influenced by surrounding conditions, features and composition of residual deposit, leachate age, operational manner of the landfill site and the dynamics of the decomposition process within the landfill cells and etc. (Aziz, 2004; El-Fadel et al., 2002; Thomas et al., 2009). According to a study by Paxéus (2000), more than two hundred individual organic compounds and classes of compounds were detected and some of them are extremely toxic to life. The understanding of leachate characteristics at a specific landfill site is the most crucial matter for designing management strategy for both old and new landfills (Rafizul and Alamgir, 2012).

Fig. 2. 1 Landfill Leachate (Fernandes et al. 2015)

Leachate composition can be characterized by several basic parameters: chemical oxygen demand (COD), biological oxygen demand (BOD), its associated ratio (BOD/COD), suspended solids (SS), total Kjeldahl nitrogen (TKN) and ammonia nitrogen (NH_3-N), heavy metals, etc. These parameters vary significantly from one landfill to another. An initial screening of leachate were conducted by El-Fadel et al.

(2013) displaying thirty-nine typical different parameters researchers commonly measured.

Table 2. 2 Initial screening of leachate (adapted from El-Fadel et al., 2013)

Parameter	Unit	Fresh Leachate 1	Fresh Leachate 2	Evaporation Pond
pH	pH units at 25 °C	7.26	7.91	7.56
EC	µ Simens/cm at 25°C	38,200	50,400	45,500
Turbidity	NTU	175	175	250
Apparent color	PtCo units	13,550	14,300	9,250
Total alkalinity	mg/L as $CaCO_3$	15,460	16,380	16,220
TDS	mg/L	19,100	25,200	22,800
TSS	mg/L	635	928	798
Total phosphorus	mg/L P	39.5	25	27
COD	mg/L	17,760	16,520	9,520
BOD	mg/L	10,935	9,720	4,890
Ammonia	mg/L NH_3	3,600	1,800	4,700
Total nitrogen	mg/L N	4,200	2,200	5,250
Chlorides	mg/L Cl^-	7,800	14,700	9,300
ortho-Phosphates	mg/L PO_4^{3-}	25.5	11	28
Total hardness	mg/L as $CaCO_3$	2,450	2,150	810
Fecal coliforms	CFU/50 ml	ND c	ND	ND
Total coliforms	CFU/50 ml	ND	ND	ND
Li	ppm	0.012	0.233	0.0215
Be	ppm	<0.002	<0.002	<0.002
Ti	ppm	0.707	0.526	0.934
V	ppm	0.258	0.323	0.361
Cr	ppm	0.461	0.685	0.481

Mn	ppm	0.193	0.329	0.234
Co	ppm	0.112	0.119	0.116
Ni	ppm	0.481	0.75	0.541
Cu	ppm	0.007	0.039	0.031
As	ppm	0.05	0.176	0.104
Se	ppm	0.042	0.086	0.029
Sr	ppm	0.516	0.675	0.438
Mo	ppm	0.027	0.116	0.035
Ag	ppm	<0.002	<0.002	<0.002
Cd	ppm	0.008	0.003	0.009
Sb	ppm	0.004	0.029	0.013
Ba	ppm	0.779	0.135	0.235
W	ppm	0.015	0.021	0.024
TI	ppm	<0.002	<0.002	<0.002
Pb	ppm	0.007	0.023	0.018
U	ppm	<0.002	<0.002	<0.002
Zn	ppm	0.05	0.007	0.053

Landfill leachate can cause enormous harm to ecosystem when released into the environment without suitable treatment (Mukherjee et al., 2014). In order to minimize its impact, regulatory limits of various leachate components (TAN, phosphorus, COD, BOD_5) in different countries are set, as summarized in Table 2.4. It can be observed that stricter limits are enforced in developed countries vs. developing countries. The stringent discharge limits for leachate demands advanced technologies and equipment that may lead to high operation and maintenance costs.

Table 2. 3 Regulatory limits of leachate contaminants (TAN, phosphorus, COD and BOD_5) (Adapted from Mukherjee et al. 2014)

Parameter/Country	NH_3-N (mg/L)	PO_4-P (mg/L)	COD (mg/L)	BOD_5 (mg/L)
Hong Kong	5	25	200	800
France	5	25	120	30
South Korea	50	-	50	-
Poland	10	-	125	30
Australia	0.5	0.1	-	10
China	15	0.5 (TP)	100	-
Bangladesh	50	-	200	50
India	50	-	250	30

Previous studies have found that average COD value lies in the range of 10,000 mg/L to 30,000 mg/L with approximately 100 mg/L reported as lowest and over 70,000 mg/L as the highest (Aziz et al., 2004; Duggan, 2005; Thomas et al., 2009). Some leachates have been reported to have neutral pH while others tend to lean to alkaline values over 7.5 (Abbas et al., 2009). The leachate has unique characteristics, such as high concentrations of ammonia nitrogen (NH_3 and NH_4^+), high COD, low potential for biological degradation, and the presence of metals and other organic and inorganic substances that confer a high toxicity to this type of waste, and hinder its treatment (Camargo et al., 2014). Among the leachate constituents, ammonia nitrogen is one of particular concern because its concentration could reach high levels (800 to 5,210 mg/L) (Ferraz et al., 2013) due to a process called ammonification (Berge et al., 2005). The leachate generated in landfills varies in strength and composition depending on several factors, but the most significant factor is the age of the landfill (Peng et al., 2008; Kheradman et al., 2010). Leachate types can be generally divided into young leachate and old (mature) leachate (Gao et al., 2014). Compared to old leachate, young leachate has extremely high concentrations of ammonia, VFAs and COD with a relatively low pH (Nair et al., 2014). Detailed characteristics of the mature and young leachate are

presented in Table 2.4. Young leachate have low molecular weight organic compounds characterized by linear chains, which are substituted through oxygenated functional groups such as carboxyl and alcoholic groups (Calace et al., 2001). Old leachate have organic compounds with a wide range of molecular weight fractions having complex structures with N, S, and O containing functional groups (Calace et al., 2001). Additionally, the concentration and biodegradability of leachate usually decrease with its age (El-Fadel et al., 2002). Ammonia concentration in leachate is also an important parameter to consider for the safe closure of landfill sites (Lubberding et al., 2012).

Table 2. 4 Classification of landfill leachate according to age (Adapted from Abbas et al., 2009; Mukherjee et al., 2014; Ren et al., 2010)

	Young (0-5)	Medium (5-20)	Old (>20)
Landfilling phase	Aerobic and acidic		Methanogenic
Age (year)	<1	1-5	>5
pH	<6.5	6.5-7.5	>7.5
TDS (mg/L)	10,000-25,000	2,000-10,000	<1,000
BOD_5 (mg/L)	10,000-25,000	50-1,000	<50
COD (mg/L)	>10,000	3,000-10,000	<1,000
BOD_5/COD	0.5-1.0	0.1-0.5	<0.1
TOC / COD	<0.3	0.3-0.5	>0.5
NH_3-N (mg/L)	500-1,500	300-500	<30
Kjeldahl nitrogen(mg/L)	100-200	400-600	<50
Heavey metals (mg/L)	>2	<2	<2
Cl^- (mg/L)	1,000-3,000	100-2,000	<100
Sulfate (mg/L)	500-2,000	50-1,000	<50
Phosphorus (mg/L)	100-300	10-100	<10
Ca (mg/L)	2,000-4,000	300-2,000	<300
Na, K (mg/L)	2,000-4,000	100-1,500	<100
Mg, Fe (mg/L)	500-1,500	50-1,000	<100

Zn, Al (mg/L)	100-200	50-100	<10
Organic compound	80% volatile fatty acids (VFA)	5-30% VFA + humic and fulvic acids	Humic and fulvic acids
Molecular size distribution	Over a broad range-high fraction of low MW organics	NA	Over a narrower range-high fraction of high MW organics
Biodegradability	Important	Medium	Low

2.3 Ammonia

2.3.1 Characteristics of Ammonia

Ammonia nitrogen contamination of groundwater has become an environmental and public health issue in developing and developed countries (Huang et al., 2015). In aquatic environment, ammonia is the most ordinarily encountered nitrogen compound in the liquid phase (Zhou et al., 2015). Depending on the pH and temperature, ammonia exists in two forms in aqueous solution: unionized 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 ammonia or total ammonia nitrogen (TAN) (Nair et al., 2014). The equilibrium of these two types of ammonia is derived and expressed in Eq. (2.1) and Eq. (2.2). K_a is defined as ionization constant, which varies due to the change of thermal condition; $[H^+]$ concentration represents the pH value. As a result, the portion of NH_3 increases as pH goes up.

$$\frac{[NH_3][H^+]}{[NH_4^+]} = K_a \quad \text{Eq. (2.1)}$$

$$NH_3(aq) + H^+ \leftrightarrow NH_4^+ \quad \text{Eq. (2.2)}$$

As displayed in the Fig. 2.2, at temperature 20 ℃, the distribution of NH_3 and NH_4^+ is approximately the same at pH 9.2. Unionized ammonia dominates when pH increases

over pH 9.2 and it becomes negligible when it is close to neutral pH condition. Overall, ammonia behaves as a moderately strong base with pK_a values to be within the range of approximately 9 to 10 depending on the temperature and ionic strength (Yenigün and Demirel, 2013). USEPA has upgraded fresh water quality criteria for ammonia of 17 mg TAN/L (acute) and 1.9 mg TAN/L (chronic) respectively under the circumstance of pH at 7 and temperature at 20 ℃ (USEPA, 2013). High concentration of ammonia should be treated before reaching surface water or ground water bodies, because it can accelerate algae growth due to its high nutrient content, deplete dissolved oxygen in the streams, and cause toxic effects in the surrounding water life (Hasar et al., 2009).

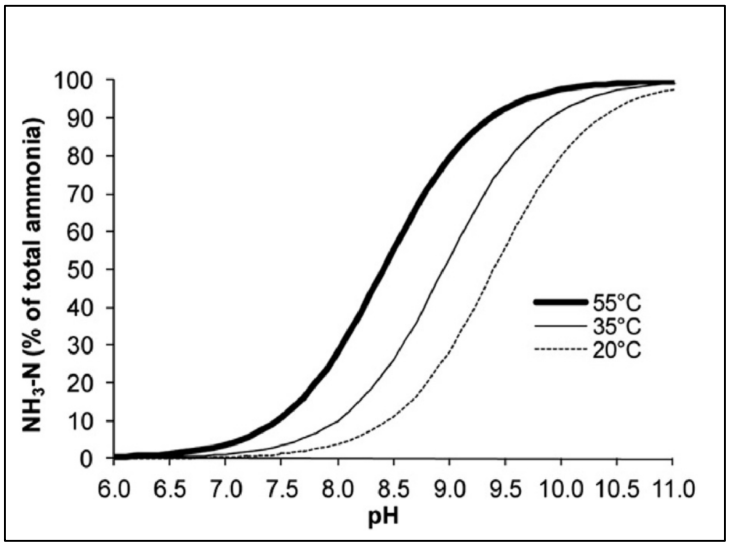

Fig. 2. 2 Free ammonia percentage in solution at 20, 35 and 55 ℃ and varying pH (Adapted from Fernandes et al., 2012)

2.3.2 Sources and concentrations of Ammonia

Ammonia, easily detected in the environment, is excreted by plants and animals, and produced as a result of the decomposition of organisms and sewage by micro-organisms, the release of fertilizers, industrial emissions, and volcanic activity (Randall and Tsui, 2002). Other sources of ammonia entering the environment include landfill leachate, construction residuals and wastewater leakage (Randall and Ip, 2006). The presence of

high concentration ammonia can contribute to eutrophication in rivers and lakes, and dissolved oxygen depletion in receiving water bodies (Nair et al., 2014). Its source can also be traced to the production process of agricultural fertilizer, coal gasification, metal manufacture, oil refining, animal husbandry, artificial fiber and glass products (Thomas et al., 2009). Total ammonia nitrogen concentration varies from low as 10 mg/L to high as 13,000 mg/L in landfills depending how long the landfills have been in service and for how long it has been closed (Ahmed and Lan, 2012). Lo (1996) found ammonia concentration of approximately 13,000 mg/L in a young landfill site, which is extremely high. The summary of the range of ammonia nitrogen concentration and pH from different landfill sites worldwide is displayed in Table 2.5.

Table 2. 5 Ammonia concentration and pH in different landfill sites (Adapted from Renou et al., 2008)

Age	Landfill Site	pH	NH_3-N(mg/L)	Reference
Y	Canada	5.8	42	(Henry et al., 1987)
Y	Canada	6.58	10	
Y	Hong Kong	7.7	2,260	(Lau et al., 2001)
Y	Hong Kong	7.0-8.3	3,000	(Lo, 1996)
Y		6.8-9.1	11,000	
Y		7.8-9.0	13,000	
Y	China, Mainland	7.4-8.5	630-1,800	(B. Wang and Shen, 2000)
Y	Greece	6.2	3,100	(Tatsi et al., 2003)
Y	Italy	8	3,917	(Di Palma et al., 2002)
Y	Italy	8.2	5,210	(Lopez et al., 2004)
Y	South Korea	7.3	1,682	(Im et al., 2001)
Y	Turkey	7.3-7.8	1,120-2,500	(Timur and Özturk, 1999)
Y	Turkey	5.6-7.0	2,020	(Özturk et al., 2003)
MA	Greece	7.9	940	(Tatsi et al., 2003)
MA	Italy	8.38	1,330	(Frascari et al., 2004)

MA	Poland	8	743	(Bohdziewicz et al., 2001)
MA	Taiwan	8.1	5,500	(Wu et al., 2004)
MA	Turkey	8.15	1,270	(Kargi and Pamukoglu, 2004)
O	Brazil	8.2	800	(Silva et al., 2004)
O	Finland	7.1-7.6	330-560	(Marttinen et al., 2002)
O	France	7.5	430	(Trebouet et al., 2001)
O	France	7.7	0.2	(Tabet et al., 2002)
O	France	7	295	(Gourdon et al., 1989)
O	South Korea	8.57	1,522	(Cho et al., 2002)
O	Turkey	8.6	1,590	(Uygur and Kargi, 2004)

Y: Young MA: Mature O: Old

2.3.3 Ammonia inhibition and toxicity

Ammonia toxicity can be a major issue to many fish species of ornamental, aqua-cultural and economical values, which leads to mass mortality under unfavorable conditions (Ip, 2010). This is because most biological membranes are permeable to free ammonia (NH_3) but relatively impermeable to ionized ammonia (NH_4^+) (D. J. Randall and Tsui, 2002). A variety of deleterious effects of having high levels of ammonia in the water body such as vulnerable tolerance of fish and mammals have been reported (Ip, 2010; Shingles et al., 2001).

Anaerobic digestion (AD) processes have gained significant attention within the last three decades, since biogas, a form of renewable energy, can be produced through biological treatment of wastes and wastewaters with different characteristics (Lauterböck et al., 2012). However, AD processes are vulnerable to inhibition by certain accumulating chemicals, among which ammonia being the most significant inhibitor (Yenigün and Demirel, 2013). McCarty and McKinney (2003) further proposed that the inhibition/toxicity was due to free ammonia (FA) in solution rather than the ammonium ions. The quantity of ammonia that will be generated from an anaerobic biodegradation of organic substrate can be estimated using the following stoichiometric relationship (Tchobanoglous et al., 1993):

$$C_aH_bO_cN_d + \frac{4a - b - 2c + 3d}{4} H_2O$$

$$\rightarrow \frac{4 + 2b - 2c - 3d}{8} CH_4 + \frac{4a - b + 2c + 3d}{8} CO_2 + dNH_3 \quad \text{Eq. (2.3)}$$

Among the four types of anaerobic microorganisms, the methanogens are the least tolerant and the most likely to cease growth due to ammonia inhibition (Kayhanian, 1994). There is conflicting information in the literature about the sensitivity of aceticlastic and hydrogenotrophic methanogens (Chen et al., 2008). Low concentration of total ammonia nitrogen (50-200 mg/L) was reported to be beneficial to the growth of bacteria as it can provide necessary nutrition (Calli et al., 2005). No significant inhibition phenomenon occurs when ammonia concentration is in the range of 200 to 1,500 mg/L (Chen et al., 2008). Unlike the importance of ammonia for bacterial growth at low concentrations, high concentration of ammonia may cause a severe disturbance in the anaerobic process performance resulting in the decline of microbial activities (Liu and Sung, 2002). Methanogenic bacteria activity declined by about 10% when TAN is higher than 1,500 mg/L but lower than 3,000 mg/L (Sheng et al., 2013). Some research found that when TAN concentration exceeds 3,000 mg/L, the AD processes are inhibited irrespective of pH (Procházka et al., 2012; Sung and Liu, 2003), not to mention the devastating consequence of ammonia concentration greater than 5,000 mg/L can bring.

Table 2. 6 Effect of ammonia concentration on anaerobic digestion process

Effect on AD process	Ammonia (mg NH_3-N/L)	References
Beneficial	50-200	(McCarty, 1964)
No anatagonistic effect	200-1,000	(Hobson and Shaw, 1976)
No significant adverse effect	200-1,500	(Chen et al., 2008; Sterling et al., 2001)

Inhibition (especially at higher pH values)	1,500-3,000	(Angelidaki et al., 1993)
Methanogenic activity dropped 10%	1,670-3,720	(Hafner et al., 2006; Strik et al., 2006)
Complete inhibition or toxic at any pH	>3,000	(Procházka et al., 2012; Sung and Liu, 2003)
Methanogenic concentration dropped by 50%	5,880-6,600	(Sung and Liu, 2003)

Temperature and pH are the two prominent factors, which affect the threshold of ammonia inhibition. Instability of AD that occurs at higher pH and it causes rapid conversion rate of ionized ammonia nitrogen into free ammonia nitrogen (Rajagopal et al., 2013). An increase in temperature during the AD process commonly leads to ammonia accumulation thus fails the process from satisfactory functioning with a lower methane yield (Angelidaki et al., 1993). These overall influences are expressed as (Hansen et al., 1998):

$$\mathrm{NH_3(Free)} = \mathrm{TAN} * \left(1 + \frac{10^{-\mathrm{pH}}}{10^{-(0.09018 + \frac{2729.92}{\mathrm{T(K)}})}}\right)^{-1} \quad \text{Eq. (2.4)}$$

Where NH_3, free ammonia nitrogen (FAN) mg/L; TAN, total ammonia nitrogen mg/L; T, temperature, K

2.4 Treatments for ammonia removal

During the recent decades, many simple biological and physiochemical treatment processes such as aerated lagoons, aerobic, and anaerobic digesters, adsorption and ion-exchange treatments, etc. have been considered ammonia removal from leachate. However, the knowledge of the impact of landfill leachate on the environment has forced authorities to apply more and more stringent standards for pollution control (Mukherjee et al., 2014). Based on the level of ammonia concentration in the landfill leachate, a

combination of physical, chemical and biological processes have been applied by some researchers (Hao et al., 2010; Nguyen and Tanner, 1998; Pirbazari et al., 1996; Sri Shalini and Joseph, 2012). Typically, wastewaters containing ammonia over 500 mg/L is considered as high concentration (Du et al., 2005; Liang and Liu, 2008). Unfortunately, a universal solution for ammonia treatment has not yet been established.

2.4.1 Biological treatment

Biological process is widely applied in removing ammonia in the relatively low concentrations (50 to 200 mg/L) because its simple operational setup and high removal effectiveness (70% to 95%) when BOD/COD ratio is greater than 0.5 (Renou et al., 2008). According to Barr and Robinson (1999), biological approaches applied in reactors include: upflow anaerobic sludge blanket reactor (USAB), membrane biological reactor (MBR), sequencing batch reactor (SBR), and anaerobic-aerobic combined reactor (Calli et al., 2005; Im et al., 2001; Liang and Liu, 2008; Pirbazari et al., 1996; Uygur and Kargi, 2004). The mechanisms involved in biological leachate treatment are illustrated below in Figure 2.3. The figure describes the potential nitrogen transformation that may occur in bioreactor landfills. Processes commonly include ammonification, sorption, volatilization, nitrification, denitrification, Anaerobic Ammonium Oxidation (ANAMMOX), and nitrate reduction, may all occur in landfill (Shalini and Joseph, 2012).

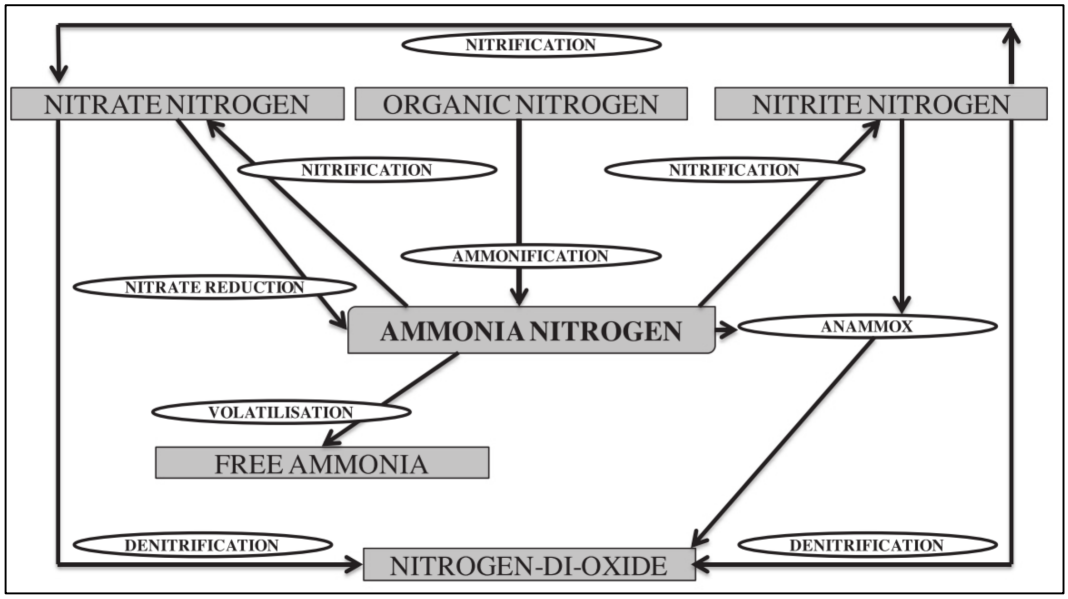

Fig. 2. 3 Nitrogen transformations in landfill environment

In nitrification, autotrophic bacteria (*Nitrosomonas)* initially oxidizes ammonia to nitrite followed by further oxidization of nitrite to nitrate occurring in the presence of another species of bacteria (*Nitrobacter*) (Metcalf and Eddy, 2003). As nitrification occurs in aerobic condition, it is almost non-existing in landfills with air infiltration blocked by landfill cover (Hao et al., 2010). In the second step, denitrification is available in anaerobic landfills and it requires anoxic condition, because oxygen is no longer electron acceptor, which is being taken placed by nitrate in the reaction. Nitrate is ultimately transformed into nitrogen gas by a great variety of bacteria called denitrifiers which includes Pseudomonas, Alcaligenes, Acinetobacter, Hyphomicrobium, Thiobacillus, Lactobacillus and Spirillum under anoxic condition (Metcalf and Eddy, 2003). Separate reaction equations are displayed:

Nitrification: $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H_2O$ Eq. (2.5)

Denitrification: $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2$ Eq. (2.6)

Although the biological nitrification and denitrification has high ammonia removal performance, it still has several disadvantages. Inhibition of microorganisms due to high

NH_3-N concentration is an evitable problem to the process (Berge et al., 2005). Furthermore, the high salinity and lack of sufficient electron donors (carbon sources), especially in stabilized leachates, are additional obstacles to nitrification-denitrification biological treatment (Di Iaconi et al., 2010). Therefore, innovative processes for NH_3-N removal have been developed such as CANON (Completely Autotrophic Nitrogen Removal Over Nitrite), OLAND (Oxygen Limited Autotrophic Nitrification and Denitrification), SHARON (Single reactor system for High activity Ammonia Removal Over Nitrite), ANAMMOX (Anaerobic Ammonium Oxidation) and Combined SHARON–ANAMMOX (Fudala-Ksiazek et al., 2014; Liang and Liu, 2008; Nhat et al., 2014; Spagni et al., 2014; Sri Shalini and Joseph, 2012). The comparison of conventional and innovative treatment process is given in Table 2.7.

In a previous study aimed at evaluating the effectiveness of biological nitrogen removal for treating a mature municipal landfill leachate, the authors obtained a low ammonia removal efficiency (i.e. 20%) even given a long hydraulic residence time (20 days) (Di Iaconi et al., 2006).

Table 2. 7 Comparison of conventional and novel ammonia nitrogen removal processes

System	Nitrification-Denitrification	OLAND	CANON	SHARON	ANAMMOX
Feed	Ammonium rich wastewater	Ammonium rich wastewater	Ammonium rich wastewater	Ammonium rich wastewater	Ammonium nitrite mixture
Discharge	N_2, NO_2^-, NO_3^-	NH_4^+, N_2	N_2, NO_3^-	NH_4^+, NO_2^-	N_2, NO_3^-
Conditions	Oxic, anoxic	Oxic, anoxic	Oxygen limited	Oxic	Anoxic
Oxygen requirements	High	Low	Low	Low	None
pH control	Yes	-	None	None	None

Biomass retention	None	Yes	Yes	Yes	Yes
COD requirement	Yes	None	None	None	None
Sludge production	High	Low	Low	Low	Low
Reactor capacity (kg N/m^3 day)	0.05-4	1	1-3	1	6-12
NH_4^+ loading (kg N/m^{-3} reactor day)	2-8	0.1	2-3	0.5-1.5	10-20
N-removal efficiency	95%	85%	90%	90%	90%
Application status	Established	Laboratory studies	Laboratory studies	Full scale plants	Full scale plants
Investment costs	Medium	Medium	Medium	Medium	Low
Operational costs	High	Unknown	Low	Low	Very low

2.4.2 Air stripping

Ammonia stripping or aeration has been successfully used for several wastewaters, such as pig slurry, mineral fertilizers, source-segregated food wastes, landfill leachate and anaerobically digested effluent since it provides satisfactory ammonia removal rate and the operation cost is relatively inexpensive (Campos et al., 2013; Ferraz et al., 2013). Air stripping is based on the principle of mass transfer, which involves large amount of air passing through the liquid, resulting the increase of gaseous ammonia in the aqueous

environment, thus forcing ammonia from liquid phase to an air stream (Eq. (2.7)) (Hao et al., 2010).

$$NH_4^+ \rightarrow NH_3(g) + H^+ \qquad \text{Eq. (2.7)}$$

Practically, air stripping process is normally operated in packed stripping tower (Marttinen et al., 2002). The efficiency of air stripping depends on several factors: pH, temperature, retention time, ratio of air to feed and feed characteristics (Zarebska et al., 2015). For leachate, a relatively high pH of 11 is recommended to favor ammonia removal by air stripping, and calcium hydroxide ($Ca(OH)_2$) is commonly used as the added alkali as it assists removal of heavy metals and colors caused by co-precipitation organic molecules (Ferraz et al., 2013). Previous research showed that this physical-chemical method for ammonia removal was able to get rid of up to 93% of ammonia from leachates with high initial ammonia concentration of 5,000 mg/L to 7,000 mg/L (Cheung et al., 1997). Marttinen et al. (2002) published 89% of ammonia elimination rate at pH 11 and 20 ℃ with a stripping duration of 24 hours. Stabilized leachate from Thessaloni landfill in Greece was treated by air stripping for 24 h with 11 g/L of $Ca(OH)_2$ for pH adjustment and the results demonstrated that ammonia concentration from 2,215 mg/L was reduced to 110 mg/L and ineffective COD removal of only 15%. Additionally, Dong and Sartaj (2015) used combined microwave/aeration application in treating ammonia from aqueous solution and a maximum ammonia removal of 81.7% was obtained. Other researches using sanitary landfill leachate were summarized as followed in Table 2.8. As a whole, ammonium stripping is remarkably effective for ammonia nitrogen removal (85% to 95%) but the reduction of COD is relatively low (<50%).

Despite the fact that ammonium stripping is powerful and economically appealing, the major drawback of such treatment is the atmosphere impact due to the release of NH_3 gas into the ambient environment if proper collection and treatment fail to implement (Kurniawan et al., 2006a). To prevent environmental pollution caused by the mass transfer from the liquid to gaseous phase, treatment of the stripped ammonia by absorption is recommended (Ferraz et al., 2013). Another operational issue is due to

calcium carbonate ($CaCO_3$) scaling when large amount of alkaline, e.g. lime, are needed to maintained high pH of 12 or higher (Zarebska et al., 2015).

Table 2. 8 Treatment performance of air stripping for removal of ammonia nitrogen (Adapted from Kurniawan et al., 2006a)

Location of landfill	Chemical for pH adjustment	Dose (g/L)	pH	Removal efficiency (%)		Reference
				COD	NH_3-N	
Thessaloniki (Greece)	$Ca(OH)_2$	3.1	11.5	NA	95	(Diamadopoulos, 1994)
Oyaderi (Turkey)	$Ca(OH)_2$	8	11	25	85	(Ozturk et al., 2003)
Komurcuoda (Turkey)	$Ca(OH)_2$	11	11	<15	94	(Calli et al., 2005)
Junk Bay (Hong Kong)	$Ca(OH)_2$	10	11	47	90	(Cheung et al., 1997)
Mustankorkea (Finland)	NA	NA	11	21	89	(Marttinen et al., 2002)

2.4.3 Adsorption by activated carbon

Activated carbon, which is generally presented in the forms of granular particles or powder, is widely employed for the removal of recalcitrant compounds from the landfill leachate (Park and Kim, 2005). Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions (Kurniawan et al., 2006a). Powder activated carbon (PAC), as well as granular activated carbon (GAC), tend to have large contact surface area, porous structure, low acid/base reactivity, thermal stability, inherent physical properties and high adsorption capacity, which makes significant contribution for pollutant removal in the pre-treatment of wastewater (Foo and Hameed, 2009). General granular activated carbon characteristics are presented in Table 2.9. Equilibrium

data for ammonium removal by activated carbon fitted well with both the Langmuir and the Freundlich adsorption isotherms (Aziz et al., 2011).

Table 2.10 presents some of the previous researches for the landfill leachate treatment (ammonia and COD) via activated carbon adsorption process for the last two decades. In most cases, activated carbon has revealed the prominence in removal an essential portion of organic fractions and ammonia nitrogen from leachates. In particular, stabilized leachate from the Goslar landfill, Germany was firstly evaluated using a granular activated carbon (GAC) column in 1995, it showed a COD removal of 91% with an initial concentration of 940 mg/L (Morawe et al., 1995). Another observation was reported showing that about 40% of the ammonia nitrogen with initial concentration of more than 1,000 mg/L was removed by the addition of activated carbon (Aziz et al., 2004). Horan et al. proved possible to reach 85% to 90% ammonia reduction and 60-81% COD. However, although the ability of activated carbon in terms of ammonia removal is usually reasonable, it is still considered to remove COD and organic molecules more efficiently than ammonia.

Table 2. 9 Granular activated carbon characteristics (Adapted from Aziz et al., 2004)

Specification	Value
Grade	KI5060
Particle size	12
Distribution	12-40
Lodine	1,000 mg/(g·min)
pH	9-10
Ash content	5% max
Moisture	5% max
Hardness	90 min

Table 2. 10 Lists of researches for the landfill leachate treatment via activated carbon adsorption process during the last 15 years (Adapted from Foo and Hameed, 2009)

Activated carbon	Adsorbate	Leachate	Removal(%)	Reference
Commercial PAC	COD	Synthetic	87	(Kargi et al., 2004)
	Ammonia	Synthetic	16	
DARCO	COD	Stabilized	38	(Gotvajn et al., 2009)
Commercial PAC	COD	Intermediate	24.6	(Liyan et al., 2009)
Commercial GAC	COD	Stabilized	60	(Kurniawan et al., 2006b)
	Ammonia	Stabilized	95	
PAC	COD	Intermediate	75	(Uygur and Kargi, 2004)
	Ammonia	Intermediate	44	
Oil Palm shell	COD	Stabilized	50	(Lim et al., 2009)
Norit 0.8	COD	Intermediate	68	(F. J. Rivas et al., 2006)
Commercial GAC	Ammonia	Intermediate	40	(Aziz et al. 2004)
Chemviron	COD	Intermediate	55	(F. J. Rivas et al., 2006)
Picacarb	COD	Intermediate	48	(F. J. Rivas et al., 2006)
Commercial PAC	COD	Intermediate	49	(Kargi et al., 2003)
	Ammonia	Intermediate	16	
Commercial PAC	COD	Stabilized	38	(Morawe et al., 1995)
Commercial PAC	COD	Young	49	(Aghamohammadi et al.,2007)
	Ammonia	Young	78	
Rice husk	COD	Young	70	(Kalderis et al., 2008)
Norit 0.8	COD	Stabilized	90	(Rivas et al., 2003)

2.4.4 Ion-exchange by Zeolite

Recently, materials with ion-exchange capacity such as zeolite have been tested for ammonia removal, and treatment performances close to those obtained with activated

carbon have been observed (Jorgensen and Weatherle, 2003). Possible applications of natural, synthetic and modified zeolite for removal ammonia, heavy metal, volatile organic compound (VOC) from contaminated solutions are extensively studied (Lei et al., 2008; Lind et al., 2000; Malekian et al., 2011; Nguyen and Tanner, 1998). Zeolite is a porous material with large surface area, high cation exchange capacity and cation selectivity (Saltali et al., 2007). Natural zeolites are ubiquitous minerals, which are found worldwide in massive deposits with volcanic and sedimentary origins (Delkash et al., 2015). The general formula of a zeolite is as follows (Saltali et al., 2007):

$$\left(M_x^+, M_y^{2+}\right)\left(Al_{(x+2y)}Si_{n-(x+2y)}O_{2n}\right)\cdot mH_2O$$

where Al^{3+} and Si^{4+} are known as the structural cations, and they make up the framework if the structure with O, M^+ and M^{2+}; the latter are monovalent and divalent cations such as Na^+, K^+, Ca^{2+}, Mg^{2+}, and Ba^{2+}, respectively. They are called exchangeable cations and can be easily replaced by same equivalent amount of other cations such as ammonium (NH_4^+) (Saltali et al. 2007).

The ion exchange behavior of the zeolites is dependent on many factors such as the size of the exchanging ions, ions concentrations and presence of competitive ions, structure of the zeolite, etc. (Delkash et al. 2015). Clinoptilolite, one general form of zeolite, shows a high preference of ammonia as it can be seen from the selectivity series it exhibits for the following ions (Papadopoulos et al., 1996):

$$Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^+ > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$$

It was found that lower removal rate was obtained at lower pH values (Karadag et al., 2006) and highest performance for ammonia adsorption performance at neutral pH solution (Malekian et al., 2011). Ding and Sartaj (2015) has investigated the application of both zeolite and ion-exchange resin for ammonia removal and found that up to 87% removal can be obtained at a neutral pH level. For ammonia aqueous solution with initial TAN concentration of 3,000 mg/L, the optimal adsorption capacity of zeolite was

reported 22.9 mg/g at pH 7 while the maximum adsorption ability of 28.78 mg/g of ion-exchange resin was achieved at pH 6. Generally, modifying of zeolite, may remarkably enhance the adsorption ability of the zeolite (Delkash et al., 2015). It was reported that a natural raw clinoptilolite demonstrated 2.7 to 3.2 mg/g for ammonia at 20 ℃ (Wang et al., 2006) and a remarkable increase of 10 to 14 mg/g for ammonia adsorption was observed at 20 to 60 ℃ and pH varying (4 to 9) using calcium modified form of the same zeolite (Ji et al., 2007). However, presence of competitive cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, and Ba^{2+}) in the wastewater with complex matrices will negatively influence the zeolite capacity for adsorbing NH_4^+ (Wang et al., 2006) and the regeneration of such material could be another issue.

2.4.5 Membrane processes

In recent decades, advance treatment techniques like membrane filtrations, which were originally employed for drinking water purification, are being applied for leachate treatment (Mukherjee et al., 2014). Microfiltration (0.1 to 10 μm), ultrafiltration (2 to 100 nm), nanofiltration (1 to 2 nm) and reverse osmosis (<1 nm) are primary membrane filtration processes for leachate treatment (Petersen, 1993; Tabet et al., 2002).

Microfiltration (MF) is a low-pressure process economically expensive but it can only applied to remove colloids and suspended solids in aqueous solutions (Silva et al. 2004). Ameen et al. (2011) reported that MF decreased the turbidity, color, total suspended solids (TSS), total dissolved solids (TDS) and volatile suspended solids (VFA) in the leachate by 98, 90, 99, 14 and 20 %, respectively.

Ultrafiltration (UF) is a selective fractionation process boosted by pressures up to 10 bar (Piatkiewicz et al., 2001). UF can be used to remove the large molecular weight components of leachate that tend to foul reverse osmosis (RO) membranes (Gao et al., 2014). The study of Pi et al. (2009) presented that COD of the leachate steadily decreased from 20,000 to < 3,000 mg/L, and ammonium (NH_4^+) decreased from 368 to 259 mg/L in the UF process. COD removal varied from 10 to 75 % by applying ultrafiltration depending on the operational conditions and the material of membrane (Brockmeyer and Spitzy, 2013).

Nanofiltration (NF) displays unique characteristics between ultrafiltration and reverse osmosis, which makes it found a place in the removal of recalcitrant organic compounds and heavy metals from leachate (Ozturk et al., 2003; Tatsi et al., 2003). Unlike reverse osmosis membranes, nanofiltration membranes have a looser structure, enabling higher fluxes and lower operating pressures (Kuusik et al., 2014). Compared to ultrafiltration membranes, nanofiltration membranes have a tighter structure and are therefore able to reject small organic molecules, they can reject molecules as small as 200 to 300 Da in size (Trebouet et al., 2001). Physical methods were in combination with nanofiltration and it was found that satisfactory removal (70-80%) of refractory COD from the leachate was obtained (Abbas et al., 2009; Zarebska et al., 2015). Ozkaya et al. (2004) has obtained a removal rate of about 89% COD and 72% NH_3-N with initial concentration of 3,000 mg/L for COD and 950 mg/L for NH_3-N, respectively in Odayeri landfill, Turkey. When NF was applied in combination with other physical process, and they are able to provide moderate ammonia removal of 50 to 60 % (Trebouet et al., 2001).

With high fluxes and the ability to operate over wide temperature and pH range, RO is considered to be the most promising treatment technique in treating stabilized leachate due to its high removal pollutant efficiency (Chan et al., 2007; Hasar et al., 2009; Kim et al., 2003; Kurniawan et al., 2006a). Composite reverse osmosis membranes typically consist of a thick, porous, nonselective layer formed in a first process step, which is subsequently overcoated with an ultrathin barrier layer on its top surface in a second process (Petersen 1993). In RO application in industrial landfill leachate, the contemporaneous presence of both high concentration of organic compounds, ammonia and heavy metals in the solvent could be reduced significantly (Ushikoshi et al., 2002). Several studies were performed, both at lab and industrial scale, to investigate RO performances on the separation of pollutants from landfill leachate. Previous studies demonstrated that over 98% and 99% of COD and heavy metal removal, respectively were achieved (Bohdziewicz et al., 2001). As for ammonia, comparable reductions of over 97% were observed in the optimal conditions of pH=6.4 using two different RO membranes (Di Palma et al., 2002). At the Yachiyo landfill in Japan has witnessed an

outstanding complete removal of ammonia nitrogen and 98% for COD using RO membranes (Ushikoshi et al., 2002). Table 2.11 shows the removal of ammonia nitrogen and COD using membrane filtration in different landfills site worldwide. Overall, RO has been found to be highly effective for the removal of both COD and NH_3-N.

In spite of many advantages, when dealing with wastewater or leachate, the widespread application of membrane filtration is still restricted by membrane fouling (Mallia et al., 2001). Uncontrolled membrane fouling leads to rapid decrease in membrane permeate flux (MPF) and/or increase in trans-membrane pressure (TMP), resulting in decrease of lifecycle of membrane productivity, high energy consumption and operating costs (Skouteris et al., 2015). High trans-membrane pressure (120 to 200 bars) is another major drawback for most pressure-driven processes and especially for RO process, taking account for 60 to 80% treatment energy (Gong et al., 2013). Thus, a number of techniques have been explored for fouling control: these techniques either target at adopting suitable aeration strategies or optimization of other operating conditions. These include sub-critical flux operation, periodic air/permeate back-flushing and/or intermittent suction allowing a relaxation period for back diffusion of loosely attached foulants from membrane surface (Skouteris et al., 2015).

Table 2. 11 Removal of NH_3-N and COD using NF/ RO (Adapted from Kurniawan et al., 2006a)

Location of landfill	Type	Pressure (bar)	NH_3-N Removal (%)	COD Removal (%)	Reference
Odayeri (Turkey)	NF	25	72	89	Ozturk et al., 2003
Mustankorkea (Finland)	NF	6-8	50	66	Marttinen et al., 2002
Chung Nam (Korea)	RO	NA	96	97	Ahn et al., 2002
Yachiyo (Japan)	RO	9-11	98	100	Ushikoshi et al., 2002
Hedeskoga (Sweden)	RO	40	82	95	Thorneby et al., 2003
Spillepeng (Sweden)	RO	30	98	98	Linde et al., 1995
Wijster (Holland)	-	40	98	98	Linde et al., 1995

Ihlenberg (Germany)	RO	36-60	100	99	Peters et al., 1999
Lipówka (Poland)	RO	27.6	NA	97	Bohdziewics et al., 2001

2.4.6 Chemical precipitation

Struvite precipitation was reported as a valid alternative for the removal of high ammonia concentrations from the anaerobically digested liquor of piggery wastes due to its high removal effectiveness, reaction rate, and solid–liquid separation capability (Huang et al., 2011). Struvite (magnesium ammonium phosphate, MAP, $MgNH_4PO_4 \cdot 6H_2O$) is a white crystalline compound composed of magnesium, ammonium, and phosphate in an equal molar ratio (Di Iaconi et al. 2010). Struvite produced from lagoon wastewater is displayed in Figure. 2.4.

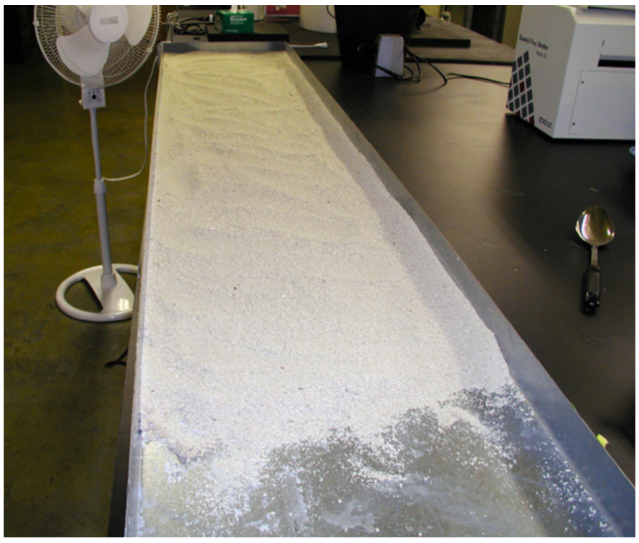

Fig. 2. 4 Struvite crystal produced from lagoon wastewater (Westerman, 2009)

Application of struvite for removal of ammonia has been investigated for the treatment of wastewaters that is rich in ammonia, such as landfill leachate (Di Iaconi et al., 2010), coking wastewater (Chen et al., 2009), semiconductor wastewater (Kim et al., 2009), and human urine (Ganrot et al., 2007). MAP (magnesium ammonium phosphate) precipitation demonstrated multiple advantages taking into account the economic impact

of growing energy and dosage costs as it is identified and utilized as a slow release fertilizer, and as a raw material to the phosphate industry for making fire resistant panels, or as a binding material in cements in several potential markets (Ali and Rajshahi, 2005; Stratful et al., 2001). Particularly, struvite precipitation from landfill leachate rich in NH_3-N proceeded by addition of excess magnesium and phosphate sources followed by addition of the buffering reagent, providing the optimum condition to reach the thermodynamic equilibrium of struvite via precipitation (Kim et al., 2007). By adding magnesium and phosphate to wastewater containing ammonium, the main chemical reaction occurs as follows (Zhou and Wu, 2012):

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow \qquad \text{Eq. (2.8)}$$

Generally, in order to achieve high ammonia removal, additional sources of Mg^{2+} (e.g., $Mg(OH)_2$, $MgCl_2 \cdot 6H_2O$, MgO, $MgSO_4$), and phosphate (e.g., KH_2PO_4, H_3PO_4 and Na_2HPO_4), have to be added to wastewater to balance the high ammonium concentrations (Galbraith and Schneider, 2014; He et al. 2007; Jaafarzadeh et al., 2010; Korchef et al., 2011; Santinelli et al., 2013; Xavier et al., 2014). Most of the previous researchers favored $MgCl_2 \cdot 6H_2O$ as a source of magnesium for struvite precipitation, and only few of them used other chemicals like $MgSO_4$, $Mg(OH)_2$ and MgO. No significantly different performance of $MgCl_2 \cdot 6H_2O$ and of $MgSO_4$ was found by Yetilmezsoy and Sapci-Zengin (2009) in the case of ammonia removal. However, a relatively poor ammonia removal efficiency (67%) was reported by Di Iaconi et al. (2010) using MgO as additional magnesium reagent due to its low solubility. Kim et al. (2007) claimed that $Mg(OH)_2$ was not ideal for struvite precipitation based on a low ammonia removal efficiency of 60%. Similar result (62% removal) was found because magnesium hydroxide has a lower solubility in aqueous medium compared to magnesium chloride (Xavier et al. 2014). In terms of the phosphorus source, phosphoric acid (H_3PO_4) was commonly used since it is inexpensive compared to other phosphorus salts such as Na_2HPO_4, KH_2PO_4 and $Ca(H_2PO_4)_2$ and will not increase salinity concerns by introducing other ions (Kochany et al., 2009; Ren et al., 2010; Türker and

Çelen, 2007). Interestingly, Huang et al. (2014) proposed to use waste phosphoric acid as alternate phosphate source, along with MgO, to form struvite and obtained 83% ammonia removal by saving 68% chemical costs in comparison with pure reagents.

The main factors influencing the formation of struvite are molar ratios of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ and pH (Doyle and Parsons, 2002; Kumar and Pal, 2015; Rahman et al., 2014). Zhang et al. (2012) found the highest removal efficiency (87%) under $NH_4^+ : Mg^{2+} : PO_4^{3-}$ ratio of 1.2:1.0:1.0. With $NH_4^+ : Mg^{2+} : PO_4^{3-}$ molar ratio of 1.0:1.5:1.0 and pH 9.0, the removal efficiency of NH_3-N was 89.4% for sewage sludge effluent (Uysal et al. 2010). However, Stratful et al. (2001) obtained only 18% TAN removal by maintaining $NH_4^+ : Mg^{2+} : PO_4^{3-}$ ratio at 1.9:1.0:1.0 and pH 7.5; it could be probably due to the lower pH value of the wastewater. Li et al. (2012) found that the $NH_4^+ : Mg^{2+} : PO_4^{3-}$ at a molar ratio of 1.0:1.0:1.1 ($MgCl_2 \cdot 6H_2O$ and H_3PO_4) effectively removed ammonium and avoided creating a higher concentration of phosphorus in the effluent. Yetilmezsoy and Sapci-Zengin (2009) conducted a series of experiments to see the effect of ammonia nitrogen, magnesium and phosphate ratio on struvite precipitation and TAN removal efficiency. They found a lower TAN and COD removal under dose conditions of molar ratios of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ (1.0:0.5:1.0, 1.0:0.5:1.0, 1.0:1.0:0.5, 1.0:1.0:0.8) compared to higher molar concentrations (1.0:1.2:1.0, 1.0:1.5:1.0, 1.0:1.0:1.2, 1.0:1.0:1.5). Most researches up to date have indicated the optimum ratio is between 1.0:1.0:1.0 and 1.0:1.6:1.6 (Cusick et al., 2014; El Diwani et al., 2007; Doyle and Parsons, 2002; Jeong and Hwang, 2005).

Various researchers have investigated the effect of pH on the removal efficiency of ammonia nitrogen (Khaodhiar et al., 2014; Korchef et al., 2011; Kumar and Pal, 2013; Siciliano et al., 2013; Yu et al., 2012). All these investigations have found a higher ammonia removal with the increasing pH value and this might due to the fact that solubility of struvite decreases with the increasing pH. The optimum pH for struvite precipitation has been reported as 8.5–10 at stoichiometric magnesium and phosphate dosages (Kabdaşlı et al., 2008; Kabdaşlı et al., 2009). A lab-scale study was performed to investigate the efficiency of struvite precipitation using bittern at different pH from 7–11 at two different molar ratios of N:M:P (1:1:1) and (0.6:1.6:1) on synthetic struvite in

distilled water and found the optimal pH to be 9.6 (El Diwani et al., 2007). In another study, the ammonia removal from stabilized leachate was reported to be up to 98% with an initial concentration of 5,618 mg/L at a pH 9.0 for a 15 minutes reaction time (Patel and Desai, 2014). Huang et al. (2009) also obtained a maximum ammonia removal rate from wastewater at pH 9.0, they observed an ammonia concentration decrease from 5,460 mg/l to 327.6 mg/L. Li and Zhao (2001) also demonstrated that TAN concentration was reduced reduced (5618 to 112 mg/L) within a 15 minutes reaction time in the pH range of 8.5 to 9.0.

Temperature can have an impact on the ion activity and product solubility (Le Corre et al., 2007), hence it has impact on the MAP process and crystal formation. However, some previous studies have found that operation temperatures in the 25 to 35 ℃ range had no significant influence on the removal of TAN (Jia, 2013) and this maybe because the temperature was not very high and there was no significant difference in ions activity except contributing to the volatilization of NH_3. Similar results has been seen in the research of Türker and Çelen (2007), who conducted a series of experiments at 25 ℃ and 40 ℃ and no obvious differences of temperature on TAN removal was noted. Table 2.12 summarized the truvite precipitation for ammonia removal from wastewater.

Table 2. 12 Magnesium ammonium phosphate precipitation for ammonia removal from wastewater (Adapted from Guo, 2010; Li et al., 2012; Rahman et al., 2014)

Type of the waste	Chemicals added	Chemicals N:M:P	NH_4^+-N Initial Concentration (mg/L)	NH_4^+-N Removal (%)	Optimal pH	Reference
Landfill leachates	$MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O$	1.0:1.0:1.0	2750	92	9	(Li and Zhao, 2003)
Industrial wastewater	Bittern + KH_2PO_4	0.6:1.6:1.0	110	91	9.6	(El Diwani et al., 2007)
Effluent of a sewage sludge anaerobic digester	$MgCl_2 \cdot 6H2O + 85\% H_3PO_4$	1.0:1.5:1.0	749	89.35	9	(Munch and Barr, 2001)
Cooking waste water	$MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O$	1.0:1.0:1.0	500	88	9.5	(Zhang et al., 2009)
Effluent of UASB treating poultry manure wastewater	$MgCl_2 \cdot 6H_2O + KH_2PO_4$	1.0:1.0:1.0	1318	85.4	9	(Yetilmezsoy and Sapci-Zengin, 2009)

Effluent from the anaerobic treatment of the baker's yeast	$MgCl_2 \cdot 6H_2O + Na_2HPO_4$	1.0:1.1:1.1	735	83	9.2	(Ozturk et al., 2003)
Swine wastewater	$MgCl_2 \cdot 6H_2O + K_2HPO_4$	1.0:1.0:1.0	844.5	88	9	(Ryu and Lee, 2010)
Synthetic wastewater	Seawater	1.1:1.3:1.0	-	54	10	(Lee et al., 2003)
Synthetic wastewater	Bittern	1.1:1.3:1.0	-	39	9.6	(Lee et al., 2003)
Side-streams from AD treating sludge	$Mg(OH)_2$	1.3:1.1:1.0	790	6	8.5	(Munch and Barr, 2001)
Wastewater from cochineal insect processing	Low grade MgO	1.0:1.0:1.0	2320	89	8.5-9.0	(Chimenos et al., 2003)
Anaerobic treatment effluent from baker's yeast industry	$MgCl_2 \cdot 6H_2O$	1.0:1.0:1.0	735	84	9.2	(Ozturk et al., 2003)
Landfill leachate	$MgCO_3$	1.0:1.0:1.0	2100	91	8.6	(Gunay et al., 2008)
Landfill leachate	$MgSO_4 \cdot 7H_2O$	1.0:1.0:1.0	2750	70	9	(Li and Zhao, 2003)
Landfill leachate	$MgCl2 \cdot 6H_2O$	1.0:1.0:1.0	2750	92	9	(Li and Zhao, 2003)
Landfill leachate	Bittern	1.0:1.0:1.0	2900	80	8.38	(Li and Zhao, 2003)

Swine water	$MgCl_2$	1.0:1.2:1.0	-	31	8.0-9.0	(Rahman et al., 2014)
Swine water	$MgCl_2$	1.0:0.8:1.0	-	65	7.82-8.92	(Liu et al., 2012)
Synthetic wastewater	$MgCl_2$	1.0:1.0:2.0	-	45	8.5-10.5	(Le Corre et al., 2007)
MAP containing slurry	$MgCl_2$, K_2HPO_4	1.0:1.0:1.0	-	40	8.0-9.0	(Cho et al., 2009)
Slurry-type swine wastewater	MgO, H_3PO_4	1.0:1.5:1.0	-	20	8.0-11.0	(Lee and Rim, 2004)
Digested swine wastewater	Bittern	1.0:0.6:1.0	-	23-29	8.0-11.0	(Ye et al., 2011)

Although struvite precipitation was proven a powerful and efficient method to deal with wastewater containing high concentrations of ammonia, it was still hampered by some drawbacks. To achieve satisfactory ammonia removal from heavily contaminated solutions, such as landfill leachate, large quantities of magnesium and phosphate salts need to be added, because landfill leachate generally lacks Mg^{2+} and PO_4^{3-} used for struvite precipitation. This leads eventually to high treatment costs and deters the widespread application of this process (Huang et al., 2014). To solve this problem, some attempts have been made including using low-grade magnesium and phosphate source such as MgO (Chimenos et al. 2003; Quintana et al. 2008), brine and bittern (Lee et al., 2003) and the pyrolysate of magnesite (Huang et al. 2011). To better manage reagent consumption and costs, one potential approach is the recycling of struvite (He et al., 2007; Huang et al., 2011; Türker and Çelen, 2007). This involves acidolysis, electrolysis, chlorination decomposition and pyrolysis were reported as feasible techniques for disintegrating struvite (Huang et al., 2015; Liu et al., 2011; Yu et al., 2013; Zhang et al., 2004). Thermal treatments of the MAP sludge by applying frequent use of oven heating and microwave (MW) irradiation with much less exposure in MW were reported previously (Cho et al., 2009; Yu et al., 2013). Additionally, the process of reusing the thermally decomposed struvite was investigated by scholars to both maintain high total ammonia nitrogen removal and reduce costs of operation (He et al., 2007; Huang et al., 2009; Sugiyama et al., 2005; Türker and Çelen, 2007; Yu et al., 2013; Zhang et al., 2009). Huang et al. (2009) introduced recycling of MAP by dry pyrolysis, which could achieve an ammonia removal of 99%. Up to 96% of the ammonia in struvite powder could be released with sodium hydroxide addition and 84% TAN removal from synthetic wastewater under the following conditions: molar concentration ratio $NH_4^+:OH^- = 1.0:1.0$; heating temperature of 90 ℃; heating time of 2 hour (He et al. 2007). Microwave irradiation was applied as an alternative for dissociating struvite into Mg, NH_4 and PO_4, which were recycled again to the influent swine wastewaters for struvite precipitation (Cho et al., 2009). The dry pyrolysis of magnesium ammonium phosphate (MAP) with the addition of sodium hydroxide powder for ammonia gas release, combined with MAP pyrolysate recycling, was investigated by Yu et al. (2013).

Their experimental results demonstrated that this process was able to maintain over 80% ammonia removal with struvite pyrolysate recycling by heating the struvite at 110 ℃ for 180 minutes with a $NaOH : NH_4^+ = 1.0.1.0$ molar ratio.

The theoretical mass loss for the formula ($MgNH_4PO_4 \cdot 6H_2O$) is 51.42%, and is made up of a mass loss for water of 44.08% and for ammonia of 7.34% (Frost et al., 2004). It has been reported that heating MAP results in the expulsion of all of the water due to hydration from $MgNH_4PO_4 \cdot 6H_2O$ (MAP), and of the chemically bound ammonia, leading to the formation of magnesium hydrogen phosphate ($MgHPO_4$), commonly known as newberyite (Frost et al., 2004; Wang et al., 2006). Sugiyama et al. (2005), used X-ray diffraction analysis of the thermal disintegration of MAP, and confirmed the composition of the residual as a mixture of $MgHPO_4$ (MHP) and $Mg_2P_2O_7$. Bhuiyan et al. (2008) suggested that MAP can be thermally decomposed into a mixture of $MgHPO_4$, $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$. Possible reactions can be expressed as in Eq. (2.9), (2.10), (2.11), and (2.12) during the pyrolysis process (Chen et al. 2015). When the pyrolysis temperature is within the range of 80 ℃ to 227 ℃, the dominant component of struvite pyrolysate is MHP (Sugiyama et al. 2005). When struvite encounters higher temperatures, magnesium pyrophosphate (Eq. (2.11)) is likely to form in the residuals (Sugiyama et al. 2005).

$$MgNH_4PO_4 \cdot 6H_2O \xrightarrow{heat} MgNH_4PO_4 \cdot H_2O + 5H_2O \uparrow \quad \text{Eq. (2.9)}$$

$$MgNH_4PO_4 \cdot 6H_2O \xrightarrow{heat} MgHPO_4 \cdot 3H_2O + 3H_2O \uparrow + NH_3 \uparrow \quad \text{Eq. (2.10)}$$

$$3MgNH_4PO_4 \cdot 6H_2O \xrightarrow{heat} Mg_2P_2O_7 + MgHPO_4 + 18H_2O \uparrow + 3NH_3 \uparrow \quad \text{Eq. (2.11)}$$

$$2MgHPO_4 \xrightarrow{heat} Mg_2P_2O_7 + H_2O \uparrow \quad \text{Eq. (2.12)}$$

$MgHPO_4$ (MPH) is also reported as the principle component of MAP pyrolysates for further ammonia removal from an aqueous system, as compared to $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$, based on the research of Sugiyama et al. (2005). They explained that MHP has

a greater solubility (0.3 g/100 mL) than $Mg_3(PO_4)_2$ (0.02 g/100 mL) and $Mg_2P_2O_7$, which barely dissolves in water. The reaction of these three possible pyrolysates of struvite in a synthetic ammonia solution are shown to be as follows (Sugiyama et al. 2005; Yu et al. 2012):

$$MgHPO_4 \cdot 3H_2O(s) + NH_4^+(aq) + 3H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + H^+ \quad \text{Eq. (2.13)}$$

$$Mg_3(PO_4)_2 + 2NH_3 + 14H_2O \rightarrow 2MgNH_4PO_4 \cdot 6H_2O + Mg(OH)_2 \quad \text{Eq. (2.14)}$$

$$Mg_2P_2O_7 + 2NH_3 + 13H_2O \rightarrow 2MgNH_4PO_4 \cdot 6H_2O \quad \text{Eq. (2.15)}$$

Recently, in order to enhance the ammonia release from struvite and the TAN removal from an aqueous solution, struvite was heated with an alkaline addition, such as sodium hydroxide (NaOH) or magnesium hydroxide ($Mg(OH)_2$) powders (Türker and Celen, 2007; Yu et al., 2013; Yu et al., 2013). Higher ammonia-removal efficiency by the alkaline pyrolysis of struvite rather than direct heating has been reported in previous studies. He et al. (2007) has suggested that struvite regeneration under alkaline conditions could be expressed as in the Eq. (2.16) and Eq. (2.17), which could solve the problem of precipitant costs in recycling struvite and could help create suitable pH conditions for struvite reformation. The active product of the NaOH pyrolysis of struvite is magnesium sodium phosphate ($MgNaPO_4$), which can react with NH_4^+ to form struvite (Huang et al., 2015). Up to 96% of ammonia in struvite powder could be released with sodium hydroxide addition, and 84% TAN removal from synthetic wastewater could occur under the following conditions: a molar concentration ratio for $NH_4^+ : OH^- = 1.0:1.0$; a heating temperature of 90 ℃; and a heating time of 2 hour (He et al. 2007).

$$MgNH_4PO_4 \cdot 6H_2O + NaOH(s) \xrightarrow{heat} MgNaPO_4\,(s) + 7H_2O \uparrow + NH_3 \uparrow \quad \text{Eq. (2.16)}$$

$$MgNaPO_4 + NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O\,(s) \downarrow + Na^+ \quad \text{Eq. (2.17)}$$

The X-ray diffraction analysis, studies of Bhuiyan et al. (2008) and Sugiyama et al. (2005) demonstrated that MAP can be thermally decomposed into a mixture of $MgHPO_4$, $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$. Zhang et al. (2004) reported that struvite could be decomposed by direct heating at 300 ℃, and he also revealed that MAP disintegrated with acid dipping. However, He et al. (2007) found that MAP residues that were collected at high temperature led to a low ammonia removal. Thermal decomposition of MAP under certain conditions can produce highly concentrated ammonia gas (NH_3), but also a pyrolysis product that may be applied to treat wastewater, which reduces the consumption of chemical precipitation reagents (Chen et al. 2015). From the thermogravimetric analysis (TGA) curve in Fig. 2.5, it can be seen that the mass of MAP gradually drops with increasing temperature, and a sharp decline occurs between approximately 60 ℃ and 120 ℃. Such a phenomenon can be explained by dehydration and ammonia release (Bhuiyan et al. 2008; Chen et al. 2015; He et al. 2007; Sugiyama et al. 2005). In order to maximize the amount of MHP instead of $Mg_2P_2O_7$, the MAP decomposition temperature should be controlled within the range of 60 ℃ to 180 ℃ (Chen et al. 2015).

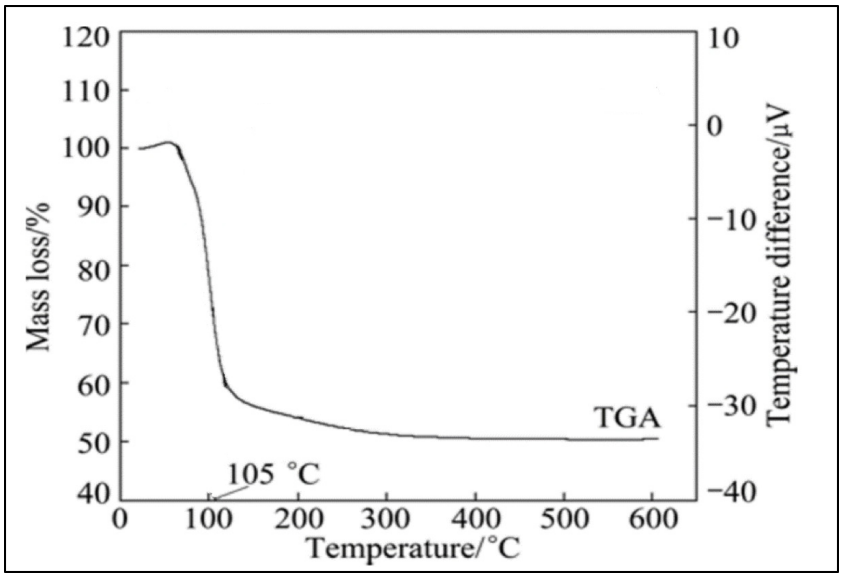

Fig. 2. 5 TGA-DTA curve of struvite (Adapted from Chen et al., 2015)

2.5 Summary

Conventional methods for ammonia removal from aqueous solution include biological treatment, air stripping, ion-exchange and adsorption (Wang et al., 2008). Biological processes incorporate nitrification and denitrification and are widely applied in removing low concentration of ammonia (50 to 200 mg /L) with satisfactory removal (75 to 95 %). However, they perform poorly when they encounter solutions with high levels of ammonia like landfill leachate (Karadag et al., 2006; Mohanty et al., 2013). Air stripping provides remarkable results in high pH conditions where most ammonia is transformed to NH_3 but the installation difficulty and managing costs remained problematic issues (Ferraz et al., 2013; Marttinen et al., 2002). Ion-exchange and adsorption processes incorporating resins and activated carbon or combined as reagents and absorbents have received more attentions as possible treatments due to relatively simply operation and high removal efficiency (Bashir et al., 2010; Du et al., 2005). However, the need for frequent regeneration of the sorbents may limit its application for the treatment of landfill leachate (Kurniawan et al., 2006). In addition, due to high concentration of solids in leachate, the application of these methods might be problematic because of potential clogging. To seek efficient and feasible methods for ammonia removal for wastewaters with high ammonia concentrations has became one of the centre research interests in wastewater treatment.

Among the alternative processes, struvite (magnesium ammonium phosphate, MAP, $MgNH_4PO_4 \cdot 6H_2O$) precipitation has been shown to be a promising method for the removal of ammonia nitrogen from wastewater because of the high reaction rate and removal ratio (Kochany and Lipczynska-Kochany, 2009). To better manage reagent consumption, one potential approach is the recycling of struvite decomposition residues (He et al., 2007; Huang et al., 2011; Türker and Çelen, 2007). Thermal treatments of the MAP sludge were previously reported by applying oven heating and MW (Cho et al., 2009; Yu et al. 2013). The main objective of this study is to evaluate the effect of different parameters (pH and molar ratio of NH_4^+: Mg^{2+}: PO_4^{3-}) in the process of struvite precipitation for ammonia removal in liquid systems (synthetic solution and landfill leachate). A secondary objective is to investigate the impact of the operational parameters

of struvite recycling and reuse. In terms of struvite recycled use for ammonia removal, different parameters (heating temperature, heating time, heating method, the dosage of thermally decomposed struvite, reaction pH, the addition of sodium hydroxide) were investigated. Microwave irradiation was also introduced to dissociate struvite, which is further used in ammonia removal from aqueous environment.

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CHAPTER III

MATERIAL AND METHODOLOGY

3.1 Materials and Equipment

3.1.1 Synthetic Ammonia Solution and Landfill Leachate

Synthetic solution containing 1,000 mg TAN /L was prepared by dissolving 3.81 g analytical grade of ammonia chloride into distilled water to form 1,000 mL solution. Other combination of NH_4Cl and deionized water was similarly applied to achieve desired TAN concentration. Landfill leachate was obtained from a local landfill in Casseleman, Ontario with an initial pH 8.9±0.2 and TAN concentration of approximately 1,878 mg/L, see Table 3.1. The leachate was stored in the lab fridge at temperature of 4 ℃. For every test, 100 ml of leachate sample was placed in the fume hood for approximately 2 hours to reach room temperature of 25±2 ℃ before any other further treatment process.

Table 3. 1 Leachate characteristics

Parameters	Concentration (mg/L)
TAN	1878
PO_4^{3-}	368.8
Mg^{2+}	35
K^+	386
Na^+	137
Ca^{2+}	311
COD	4,425
VFA	549
Alkalinity	6,725
pH	8.9±0.2

3.1.2 Chemical Reagents

All reactions and tests were carried out at room temperature (25℃). Analytical grade of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) from Fisher Chemical and crystalized phosphoric acid (H_3PO_4) from by Sigma-Aldrich were used as a source of Mg^{2+} and PO_4^{3-} to form struvite.

The pH was controlled by addition of 2N sodium hydroxide (NaOH) and 2N hydrochloric acid (HCl). In the thermal treatment of struvite under alkaline condition, sodium hydroxide pellets were mixed with struvite powder.

3.1.3 Lists of Equipment

The following table shows the main equipment used in this study.

Table 3. 2 Lists of equipment

Equipment	Description
Microwave Oven	CEM Microwave Accelerated Reaction System (MARS 5) with power consumption of 300 W, 600 W and 1200 W. All power can be adjusted from 10% to 100% heating power in 10% intervals. MARS 5 can also provide thermostatic heating by automatically adjusting power output. UltraPrep Vessels designed specially for ultra high-temperature digestions with operational parameters over 300 ℃ and a temperature sensor (RTP-300 Plus) are also attached for use
Mechanical Convection Oven	PRECISION Mechanical Convection Oven with adjustable temperature
Magnetic Stirrer	Magnetic Stirrer HI190 from HANNA Instrument with adjustable speed
Balance	Mettler PC 4400
pH meter	Fisher Accumet® Model XL25 dual channel pH/ion meter
Filtration Kit	Filtration Kit with 0.1 μm filter paper

Fig. 3. 1 CEM Microwave Accelerated Reaction System (MARS 5)

Fig. 3. 2 PRECISION mechanical convection oven

Fig. 3. 3 Filtration kit

Fig. 3. 4 Dry struvite generated from synthetic solution (left) and landfill leachate (right)

3.1.4 Analytical Techniques

For each tests, initial and final pH were measured with a glass electrode in combination with a Fisher Accumet® Model XL25 dual channel pH/ion meter. The

concentration of TAN in the liquid phase was determined by Salicylate method (Method 10205) TNTplus 832 test using a DR6000 spectrophotometer from HACH Company, see Figure 3.5 and 3.6. Samples were measured at a wavelength of 690 nm. Additionally, 10 mg/L ammonia nitrogen standard solution from the same company was used to calibrate the spectrophotometer. Liquid-phase ammonia removal efficiency was obtained by Eq. 3.1.

$$\text{TAN removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100\ \% \qquad \text{Eq. (3.1)}$$

Where C_0 is the initial concentrations of ammonia nitrogen, (mg/L)

C_e is the concentration of ammonia nitrogen after treatment, (mg/L)

Fig. 3. 5 HACH TNTplus832 Ammonia vial

Fig. 3. 6 HACH DR6000 spectrophotometer

3.2 Methodology

In this study, experiments were separated mainly into two series of tests. The first phase introduced magnesium and phosphate into the ammonia synthetic solution/landfill leachate to precipitate struvite and to investigate the effects of pH and molar ratio on the removal of TAN. The second phase dealt with the possible recycled use of the thermal decomposition product of struvite under different conditions for TAN removal in both simulated solutions and landfill leachate. These conditions included: heating method (oven convection heating and microwave irradiation), heating temperature, heating duration, pH, struvite pyrolysate dosage, and the addition of sodium hydroxide in the pyrolysis of struvite.

The first set of experiments were conducted in batch mode with the pH of the solution varying from 7 to 10.5 at intervals of 0.5, and with a molar ratio for $NH_4^+ : Mg^{2+} : PO_4^{3-}$ prepared at 1.0:1.0:1.0 and 1.0:1.2:1.2. Based on the results the optimum pH was determined and the subsequent tests were carried out under the optimum pH conditions. Different combinations of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ were set as shown in the following table, and tests were conducted with the solution pH stabilized at the optimum value obtained above and then total ammonia nitrogen concentration was

measured. All samples (100 mL) were prepared and mixed for 20 minutes and settled for another 10 minutes at room temperature (25 ℃). Subsequently, the supernatant was separated by filtering from the solution and the concentration of total ammonia nitrogen was measured. All tests were duplicate.

Table 3. 3 Different combinations of $NH_4^+ : Mg^{2+} : PO_4^{3-}$

Change in Mg^{2+}	Change in PO_4^{3-}	Change in NH_4^+:Mg^{2+}:PO_4^{3-}	
N:M:P	N:M:P	N:M:P	N:M:P
1.0:0.8:1.0	1.0:1.0:0.8	1.0:1.0:1.0	1.0:1.1:1.1
1.0:0.9:1.0	1.0:1.0:0.9	1.0:1.1:1.0	1.0:1.2:1.1
1.0:1.0:1.0	1.0:1.0:1.0	1.0:1.2:1.0	1.0:1.0:1.2
1.0:1.1:1.0	1.0:1.0:1.1	1.0:1.0:1.1	1.0:1.1:1.2
1.0:1.2:1.0	1.0:1.0:1.2	1.0:1.1:1.1	1.0:1.2:1.2
1.0:1.3:1.0	1.0:1.0:1.3	1.0:1.2:1.1	1.0:1.3:1.3
1.0:1.4:1.0	1.0:1.0:1.4	1.0:1.0:1.2	1.0:1.4:1.3
		1.0:1.1:1.2	1.0:1.4:1.4
		1.0:1.2:1.2	1.0:1.5:1.4
		1.0:1.1:1.0	1.0:1.5:1.5
		1.0:1.2:1.0	1.0:2.0:1.5
		1.0:1.0:1.1	1.0:2.0:2.0

The second phase of the study is to investigate the several parameters that affect the performance of thermally decomposed struvite on the TAN removal in simulated solutions. These parameters included: heating method (oven heating and microwave irradiation), heating temperature, heating duration, pH, struvite pyrolysate dosage, and the addition of sodium hydroxide in the pyrolysis of struvite. Before any tests, struvite generated from synthetic solution/landfill leachate was prepared as follows: (1) Struvite precipitate was generated by adding $MgCl_2 \cdot 6H_2O$ and H_3PO_4 to the synthetic solution with 1,000 mg/L TAN, so as to make the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.2:1.2 .The solution was agitated for 20 min at pH 9; (2) The precipitate was collected using a

0.1 μm filter paper and washed twice with deionized water before it was dried at room temperature (25 ℃) for 48 h.

Dry struvite powder was first heated in an oven (105 ℃) for a certain period of time varied from 0.5 to 3 h with 30 min increments and then was added (40 g/L) into the ammonia synthetic solution containing 1,000 mg TAN/L at pH 9. Based on the results the optimum heating duration was determined, synthetic struvite was thermally treated at temperatures ranging 75 ℃ and 140 ℃ (specifically, 75, 90, 105, 120 and 140 ℃) under the optimum pyrolysis time. Subsequently, the removal of total ammonia nitrogen from simulated wastewater by using the residues (60 g/L) generated from the struvite pyrolysis was performed at pH 9. After optimum heating duration and heating temperature were determined, struvite pyrolysate was added from 10 to 60 g/L into the synthetic solution containing 1,000 mg/L TAN at pH 9. To determine the optimum pH for the reuse of the struvite pyrolysate under the optimum conditions above, experiments were performed at a pH range of 8.5–10.5. All samples (100 mL) were prepared and mixed for 20 minutes and settled for another 10 minutes at room temperature (25 ℃). Subsequently, the supernatant was separated by filtering from the solution and the concentration of total ammonia nitrogen was measured. All tests were duplicate.

During the multiple recycling processes of struvite decomposition product, struvite was thermally treated under the optimum conditions obtained from previous results. Two recycling modes were conducted. In the first mode, the decomposition product of struvite was used at 60 g/L directly and repeatedly. (1) Struvite precipitate was generated by adding $MgCl_2 \cdot 6H_2O$ and H_3PO_4 to the synthetic solution with 1,000 mg/L TAN, so as to make the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.2:1.2. The solution was agitated for 20 min at pH 9. (2) The precipitate was collected using a 0.1 μm filter paper and washed twice with deionized water before it was dried at room temperature (25 ℃) for 48 h. (3) The collected solids (MAP) then were treated at optimum heating time and temperature. (4) The recycled MAP residue was added at 60 g/L to 100 ml of simulated wastewater containing 1,000 mg/L TAN, and were agitated for 20 min at pH 9.0. After that, the TAN concentration from the supernatant was measured. Steps 2, 3 and 4 were repeated for five times. All tests were duplicate.

In the second mode of reclycing, sodium hydroxide (NaOH) was added in the pyrolysis proess of struvite. The decomposition product of NaOH-mediated struvite pyrolysis was dosed at 60 g/L into the synthetic solution. (1) Struvite precipitate was generated by adding $MgCl_2 \cdot 6H_2O$ and H_3PO_4 to the synthetic solution with 1,000 mg/L TAN, so as to make the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.2:1.2. The solution was agitated for 20 min at pH 9. (2) The precipitate was collected using a 0.1 μm filter paper and washed twice with deionized water before it was dried at room temperature (25 ℃) for 48 h. (3) In the alkaline pyrolysis of struvite, sodium hydroxide (NaOH) pellets were added with struvite powder to make the molar ratio of $NH_4^+ : OH^-$= 1.0:1.0 before it was treated in the heating equipment. (4) The recycled MAP residue was added to 100 ml of simulated wastewater containing 1,000 mg/L TAN, and were agitated for 20 min at pH 9.0. After that, the TAN concentration from the supernatant was measured. Steps 2, 3 and 4 were repeated for five times. All tests were duplicate.

A CEM Microwave Accelerated Reactions System (MARS 5) was used to treat dry struvite generated from synthetic solutions. An UltraPrep Vessel designed especially for ultra high-temperature digestions with operational temperature greater than 300 ℃ was used to contain struvite powders during the heating process. A temperature sensor for monitoring the temperature change was inserted into the vessel tube. Synthetic struvite powders were thermally treated by MW at two power levels (600 W and 1200 W) for five different heating times (1, 5, 10, 20 and 30 min). After each process, struvite powders were cooled and then dosed at 60 g/L into 100 mL of synthetic solution containing 1,000 mg/L of TAN. The reaction took place under the following conditions: pH = 9.0, stirring time = 20 min, settling time = 15 min and reaction temperature = 25 ℃. After that, the TAN concentration from the supernatant was measured. In the recycling phase, similar to the previous steps, struvite powders were thermally treated by MW irradiation at two power levels (600 W and 1200 W) and a heating time of 30 min in each run. Struvite residues were dosed at 60 g/L back into the synthetic solution to absorb ammonium at pH = 9 for five times. All tests were tested in duplicate.

Similar to the experiments with synthetic solution, landfill leachate were treated in a same procedure except that the recycling use of struvite from leachate was using pH 9.5. Experimental flow chart was shown in Fig. 3.7.

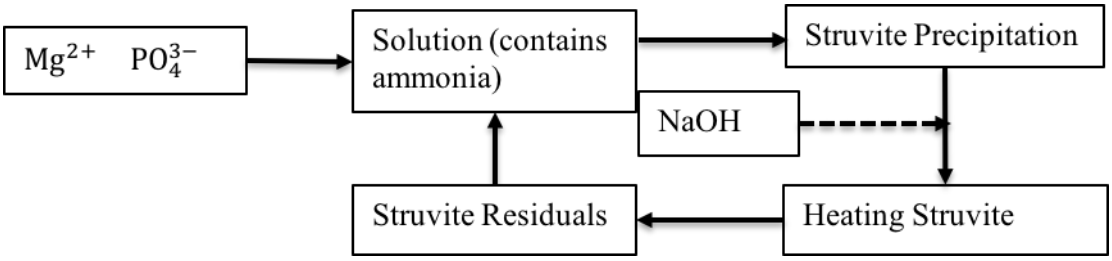

Fig. 3. 7 Experimental Flow Chart

3.3 Response surface methodology

Response surface methodology (RSM) is a combination of mathematical and statistical techniques generally used in the optimization of chemical reactions and industrial processes (Zhou and Wu, 2012). RSM utilizes its statistical tools for analysis of experimental data obtained from definite experimental design to model and optimize any process in which several variables influence the desired response (Bashir et al. 2010).

An empirical model can be built to find out the true relationship between the dependent variable and set of independent variables (where the single-response modeled using the RSM corresponds to an independent variable) (Kumar and Pal 2013). The following quadratic equation (Eq. (3.2)) indicates the behavior of the system:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_{ii}^2 + \sum b_{ij} x_i x_j \qquad \text{Eq. (3.2)}$$

Y is the predicted response; b_0, b_i, b_{ii} and b_{ij} are the offset terms, the linear effect, the squared effect, and the interaction effect, respectively; and x_i and x_j represent the coded independent variables. The accuracy of the mode presented above was evaluated by the correlation coefficient (R^2). The F−value (Fisher variation ratio) and probability value (Prob > F) were applied (Kumar and Pal, 2012).

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CHAPTER IV

TECHNICAL PAPER I

Assessment and Optimization of Stuvite Precipitation of Ammonia from Aqueous Solution

Chi Zhang, Majid Sartaj

Abstract

Struvite precipitation has a great deal of appeal to those interested in removing ammonia from highly contaminated wastewater, such as municipal landfill leachate. Synthetic ammonia solution was treated by such a method to investigate the effect under several operational conditions. The experimental data demonstrated that a slightly alkaline pH of 9 was preferred in aqueous ammonia removal. Remarkable TAN removal efficiency of over 98% has been reported when the stoichiometric molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ equals 1.0:1.2:1.2, 1.0:1.3:1.3, 1.0:1.3:1.4 and 1.0:1.5:1.5 at the optimum pH condition. The response surface method (RSM) was introduced to optimize the three factors (pH, dosage of Mg^{2+} and dosage of PO_4^{3-}). To tackle the issue of high reagent consumptions in continuous ammonia removal, struvite samples that were thermally treated by oven heating and microwave irradiation were recycled. The thermally treated struvite provided best performance of removing ammonia in simulated wastewater at a dosage of 60 g/L and pH 9, when struvite was previously heated at 105 ℃ for 2.5 h**.** The struvite pyrolysate resulting from NaOH-mediated pyrolysis was more effective at treating ammonia solution continuously than was direct heating, with an initial mode of 87.4% at the beginning to 75.1% in the fifth round and direct heating of struvite from 80.9% in the first cycle and 60.6% in the final cycle. Additionally, with shorter heating time compared

to conventional oven heating, microwave irradiation could also dissociate struvite, which demonstrated subsequently a moderate TAN removal efficiency.

Keywords: Ammonia; Struvite precipitation; Recycling struvite; Ammonia synthetic solution

4.1 Introduction

Ammonia is one of the main water quality parameters of concern. In addition to being toxic for fish, it contributes to eutrophication of lakes, estuaries and other aquatic environments (Korchef et al., 2011). Ammonia toxicity, even at low concentrations (5 to 20 mg/L), can be a major problem for many fish species of ornamental, aqua-cultural and economic values, and may lead to mass mortality under unfavorable conditions (Ip, 2010). Extremely high ammonia concentrations (1,500 to 5,000 mg/L) from wastewater, such as municipal landfill leachate, can cause failure in further wastewater treatment processing due to the inhibition effect (Lee et al., 2000; Uygur and Kargi, 2004). A complete inhibition effect of ammonia in the anaerobic digestion process was reported to occur, irrespective of pH, when ammonia concentrations exceed 3,000 mg/L (Procházka et al., 2012; Sung and Liu, 2003). Ammonia can exist in the liquid phase in either the un-ionized (NH_3) or the ionized forms (NH_4^+), depending on pH and temperature. These two forms of ammonia are normally combined and expressed as one term - total ammonia nitrogen (TAN) (Nair et al., 2014). Most biological membranes are permeable to free ammonia (NH_3) but impermeable to ionized ammonia (NH_4^+), which in many cases makes un-ionized ammonia toxic (Randall and Tsui, 2002). Considering the above, there is a need for controlling and regulating the concentration of ammonia prior to its disposal into the natural environment.

Conventional methods for ammonia removal from aqueous solution include biological treatment, air stripping, ion-exchange and adsorption (Ding and Sartaj, 2015; Wang et al., 2008). Biological processes incorporate nitrification and denitrification, and are widely applied in removing low concentrations of ammonia (50 to 200 mg/L) with satisfactory removal rates (75% to 95%). However, they perform poorly when they encounter solutions, such as landfill leachates, with high levels of ammonia (Karadag et al., 2006; Mohanty et al., 2013). Air stripping provides remarkable results for ammonia removal in high pH conditions, where most ammonia is transformed to NH_3, but the potential ambient air pollution by ammonia gas and the managing costs have remained problematic issues (Ferraz et al., 2013; Marttinen et al., 2002). Ion-exchange and adsorption processes, either by adding zeolite, resin or activated carbon as reagents and

absorbents have received significant attention as possible treatments, due to their relatively simple operation and high removal efficiency (Mohammed J. K. Bashir et al., 2010; Du et al., 2005). However, the need for frequent regeneration of reagents may limit their application for the treatment of landfill leachate (Kurniawan et al., 2006). The search for an efficient and feasible method for ammonia removal has become one of the principle research interests in the treatment of highly contaminated water.

Among the alternative processes, struvite (magnesium ammonium phosphate, MAP, $MgNH_4PO_4 \cdot 6H_2O$) precipitation has been shown to be a promising method for the treatment of high-strength ammonia wastewaters. These include rear-earth wastewater (Huang et al., 2009), human urine (Ganrot et al., 2007), and landfill leachate (Di Iaconi et al., 2011). It is promising because of the high reaction rate and removal rates (Kochany and Lipczynska-Kochany, 2009). Struvite, a white, sparingly soluble, crystalline compound, precipitates in an equimolecular concentration with NH_4^+, Mg^{2+} and PO_4^{3-} at slightly alkaline conditions and can occur naturally (Li and Zhao, 2001; Rahman et al., 2014). In recent decades, researchers have tried to identify the factors that influence struvite precipitation, including types of chemicals added ($NH_4^+ : Mg^{2+} : PO_4^{3-}$), molar ratios, pH, reaction time, and temperature (Ali et al., 2003; Etter et al., 2011; Ozturk et al., 2003; Ryu et al., 2008; Xavier et al., 2014; Xiu et al., 2011). Optimization of process parameters during struvite crystallization can maximize nitrogen recovery from ammonia-rich wastewater and minimize ammonia concentration in the treated effluent (Ahmad and Idris, 2013). About 98% removal of NH_3-N in leachate with an initial concentration ranging from 3,260 mg/L to 5,618 mg/L has been achieved by using struvite precipitation (Kurniawan et al. 2006). Zhang et al. (2012) found the lowest concentration (22 mg/L) of ammonia nitrogen in the effluent of treated swine wastewater indicating that the highest removal efficiency (87%) under an N:M:P ratio of 1.2:1.0:1.0. With a molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$=1.0:1.5:1.0 and a pH of 9.0, the removal efficiency of NH_3-N from sewage sludge effluent was 89.4% (Uysal et al., 2010). Most previous researchers used $MgCl_2$ as a source of magnesium for struvite precipitation, but only a few of them used $MgSO_4$, MgO and $Mg(OH)_2$ (Jaafarzadeh et al., 2010; Rahman et al., 2014). As for phosphate sources, KH_2PO_4, H_3PO_4 and Na_2HPO_4 are the

most popular reagents found in the literature review (He et al., 2007; Kabdaşlı et al., 2008; Kim et al., 2007; Zhou and Wu, 2012).

To achieve satisfactory ammonia removal from heavily contaminated solutions, such as landfill leachate, large quantities of magnesium and phosphate salts need to be added, because landfill leachate generally has Mg^{2+} and PO_4^{3-} concentrations much lower than required for struvite precipitation. This leads eventually to high treatment costs and deters the widespread application of this process (Huang et al., 2014). To better manage reagent consumption and costs, one potential approach is the recycled use of struvite decomposition residues (He et al., 2007; Huang et al., 2011; Türker and Çelen, 2007). Acidolysis, electrolysis, chlorination decomposition and pyrolysis were reported as feasible techniques for disintegrating struvite (Huang et al., 2015; Liu et al., 2011; Yu et al., 2013; Zhang et al., 2004). Thermal treatments of the MAP sludge mainly by oven heating were reported previously (Yu et al., 2013). The dominant component of MAP pyrolysates was reported to be magnesium hydrogen phosphate ($MgHPO_4$), with possible magnesium pyrophosphate ($Mg_2P_2O_7$) and magnesium phosphate ($Mg_3(PO_4)_2$) by-products (Sugiyama et al. 2005). Microwave irradiation was applied as another alternative for dissociating struvite into Mg, NH_4 and PO_4, which were recycled again to the influent swine wastewaters for struvite precipitation (Cho et al. 2009). The dry pyrolysis of magnesium ammonium phosphate with the addition of sodium hydroxide powder for ammonia release, combined with MAP pyrolysate recycling, was investigated by Yu et al. (2013). Their experimental results demonstrated that this process was able to maintain over 80% ammonia removal with struvite pyrolysate recycling by heating at 110℃ for 180 minutes with a molar ratio of NaOH : NH_4^+ =1.0:1.0. However, very limited research has been conducted with recycled struvite for the treatment of high strength landfill leachate using microwave irradiation to enhance the struvite decomposition.

The main objective of this study is to evaluate the application of struvite precipitation for removal of ammonia from liquid systems, and determine the optimal operation parameters, such as pH and reagent dose. The recycled use of struvite accompanied with

thermal treatment to perform efficient ammonia removal in aqueous solution will be investigated as well.

4.2 Materials and Methodology

In this study, experiments were separated mainly into two series of tests. The first phase introduced magnesium and phosphate into a high strength ammonia synthetic solution to precipitate struvite and to investigate the effects of pH and molar ratio on the removal of TAN. The second phase dealt with the possible recycling use of the thermal decomposition product of struvite under different conditions for TAN removal in simulated solutions. These struvite processing conditions included: heating method (oven convection heating and microwave irradiation), heating temperature, heating duration, pH, struvite pyrolysate dosage, and the addition of sodium hydroxide in the pyrolysis of struvite.

The first series of tests was divided into two parts. In the first part, the pH was varied from 7 to 10.5 to identify the optimum pH for two N:M:P ratios. The synthetic solution containing 1,000 mg/L TAN used for experiments was prepared by dissolving 3.81 g of analytical grade ammonia chloride in distilled water to form a 1,000 mL solution. All reactions and tests were carried out at room temperature (25 ℃). Analytical grade magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) from Fisher Chemical and crystalized phosphoric acid (H_3PO_4), produced by Sigma-Aldrich, were used as a source of Mg^{2+} and PO_4^{3-} to form struvite. The pH was controlled by the addition of 2N sodium hydroxide ($NaOH$) and 2N hydrochloric acid (HCl).

The first set of experiments were conducted in batch mode with the pH of the solution varying from 7 to 10.5 at intervals of 0.5, and with a molar ratio for $NH_4^+ : Mg^{2+} : PO_4^{3-}$ prepared at 1.0:1.0:1.0 and 1.0:1.2:1.2. Based on the results the optimum pH was determined and the subsequent tests were carried out under the optimum pH conditions. Different combinations of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ were set as shown in the following table, and tests were conducted with the solution pH stabilized at the optimum value obtained above and then total ammonia nitrogen concentration was measured. All samples (100 mL) were prepared and mixed for 20 minutes and settled for

another 10 minutes at room temperature (25 ℃). Subsequently, the supernatant was separated by filtering from the solution and the concentration of total ammonia nitrogen was measured. All tests were duplicate.

Table 4. 1 Different combinations of $NH_4^+ : Mg^{2+} : PO_4^{3-}$

Change in Mg^{2+}	Change in PO_4^{3-}	Change in NH_4^+:Mg^{2+}:PO_4^{3-}	
N:M:P	N:M:P	N:M:P	N:M:P
1.0:0.8:1.0	1.0:1.0:0.8	1.0:1.0:1.0	1.0:1.1:1.1
1.0:0.9:1.0	1.0:1.0:0.9	1.0:1.1:1.0	1.0:1.2:1.1
1.0:1.0:1.0	1.0:1.0:1.0	1.0:1.2:1.0	1.0:1.0:1.2
1.0:1.1:1.0	1.0:1.0:1.1	1.0:1.0:1.1	1.0:1.1:1.2
1.0:1.2:1.0	1.0:1.0:1.2	1.0:1.1:1.1	1.0:1.2:1.2
1.0:1.3:1.0	1.0:1.0:1.3	1.0:1.2:1.1	1.0:1.3:1.3
1.0:1.4:1.0	1.0:1.0:1.4	1.0:1.0:1.2	1.0:1.4:1.3
		1.0:1.1:1.2	1.0:1.4:1.4
		1.0:1.2:1.2	1.0:1.5:1.4
		1.0:1.1:1.0	1.0:1.5:1.5
		1.0:1.2:1.0	1.0:2.0:1.5
		1.0:1.0:1.1	1.0:2.0:2.0

The second phase of the study is to investigate the several parameters that affect the performance of thermally decomposed struvite on the TAN removal in simulated solutions. These parameters included: heating method (oven heating and microwave irradiation), heating temperature, heating duration, pH, struvite pyrolysate dosage, and the addition of sodium hydroxide in the pyrolysis of struvite. Before any tests, struvite was prepared as follows: (1) Struvite precipitate was generated by adding $MgCl_2 \cdot 6H_2O$ and H_3PO_4 to the synthetic solution with 1,000 mg TAN/L, so as to make the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.2:1.2 .The solution was agitated for 20 min at pH 9. (2) The precipitate was collected using a 0.1 μm filter paper and washed twice with deionized water before it was dried at room temperature (25 ℃) for 48 h.

Dry struvite powder was first heated in an oven (105 ℃) for a certain period of time varied from 0.5 to 3 h with 30 min increments and then was added (40 g/L) into the ammonia synthetic solution containing 1,000 mg TAN/L at pH 9. Based on the results the optimum heating duration was determined, synthetic struvite was thermally treated at temperatures ranging 75 ℃ and 140 ℃ (specifically, 75, 90, 105, 120 and 140 ℃) under the optimum pyrolysis time. Subsequently, the removal of total ammonia nitrogen from simulated wastewater by using the residues (60 g/L) generated from the struvite pyrolysis was performed at pH 9. After optimum heating duration and heating temperature were determined, struvite pyrolysate was added from 10 to 60 g/L into the synthetic solution containing 1,000 mg TAN/L at pH 9. To determine the optimum pH for the reuse of the struvite pyrolysate under the optimum conditions above, experiments were performed at a pH range of 8.5–10.5. All samples (100 mL) were prepared and mixed for 20 minutes and settled for another 10 minutes at room temperature (25 ℃). Subsequently, the supernatant was separated by filtering from the solution and the concentration of total ammonia nitrogen was measured. All tests were duplicate.

During the multiple recycling processes of struvite decomposition product, struvite was thermally treated under the optimum conditions obtained from previous results. Two recycling modes were conducted. In the first mode, the decomposition product of struvite was used at 60 g/L directly and repeatedly. (1) Struvite precipitate was generated by adding $MgCl_2 \cdot 6H_2O$ and H_3PO_4 to the synthetic solution with 1,000 mg TAN/L, so as to make the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.2:1.2. The solution was agitated for 20 min at pH 9. (2) The precipitate was collected using a 0.1 μm filter paper and washed twice with deionized water before it was dried at room temperature (25 ℃) for 48 h. (3) The collected solids (MAP) then were treated at optimum heating time and temperature. (4) The recycled MAP residue was added at 60 g/L to 100 ml of simulated wastewater and were agitated for 20 min at pH 9.0. After that, the TAN concentration from the supernatant was measured. Steps 2, 3 and 4 were repeated for five times. All tests were duplicate.

In the second mode of reclycing, sodium hydroxide (NaOH) was added in the pyrolysis process of struvite. The decomposition product of NaOH-mediated struvite

pyrolysis was dosed at 60 g/L into the synthetic solution. (1) Struvite precipitate was generated by adding $MgCl_2 \cdot 6H_2O$ and H_3PO_4 to the synthetic solution with 1,000 mg TAN/L, so as to make the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.2:1.2. The solution was agitated for 20 min at pH 9. (2) The precipitate was collected using a 0.1 μm filter paper and washed twice with deionized water before it was dried at room temperature (25 ℃) for 48 h. (3) In the alkaline pyrolysis of struvite, sodium hydroxide (NaOH) pellets were added with struvite powder to make the molar ratio of $NH_4^+ : OH^-$= 1.0:1.0 before it was treated in the heating equipment. (4) The recycled MAP residue was added to 100 ml of simulated wastewater, and were agitated for 20 min at pH 9.0. After that, the TAN concentration from the supernatant was measured. Steps 2, 3 and 4 were repeated for five times. All tests were duplicate.

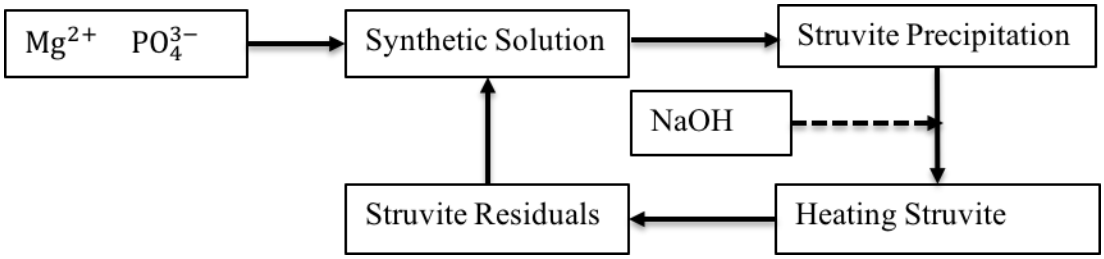

Fig. 4. 1 Experimental Flow Chart (Synthetic Solution)

A CEM Microwave Accelerated Reactions System (MARS 5) was used to treat dry struvite generated from synthetic solutions. An UltraPrep Vessel designed especially for ultra high-temperature digestions with operational temperature greater than 300 ℃ was used to contain struvite powders during the heating process. A temperature sensor for monitoring the temperature change was inserted into the vessel tube. Synthetic struvite powders were thermally treated by MW at two power levels (600 W and 1200 W) for five different heating times (1, 5, 10, 20 and 30 min). After each process, struvite powders were cooled and then dosed at 60 g/L into 100 mL of synthetic solution containing 1,000 mg TAN/L. The reaction took place under the following conditions: pH = 9.0, stirring time = 20 min, settling time = 15 min and reaction temperature = 25 ℃. After that, the TAN concentration from the supernatant was measured. In the recycling phase, similar to

the previous steps, struvite powders were thermally treated by MW irradiation at two power levels (600 W and 1200 W) and a heating time of 30 min in each run. Struvite residues were dosed at 60 g/L back into the synthetic solution to absorb ammonium at pH = 9 for five times. All tests were duplicate.

For each test, initial and final pH were measured with a glass electrode in combination with a Fisher Accumet® Model XL25 dual channel pH/ion meter. The concentration of TAN in the liquid phase was determined by the salicylate method (Method 10205) TNTplus 832 test using a DR6000 spectrophotometer from the HACH Company. Samples were measured at a wavelength of 690 nm. Additionally, 10 mg/L ammonia nitrogen standard solution from the same company was used to check the spectrophotometer. Liquid-phase ammonia removal efficiency was calculated using Eq. (4.1):

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

Where C_0 is the initial concentrations of ammonia nitrogen, (mg/L)

C_e is the concentration of ammonia nitrogen after treatment, (mg/L)

Response surface methodology (RSM) is a combination of mathematical and statistical techniques generally used in the optimization of chemical reactions and industrial processes (Zhou and Wu, 2012). RSM utilizes its statistical tools for analysis of experimental data obtained from definite experimental design to model and optimize any process in which several variables influence the desired response (Bashir et al. 2010).

An empirical model can be built to find out the relationship between the dependent variable and the set of independent variables (Kumar and Pal, 2013). The following quadratic equation (Eq. (4.2)) indicates the behavior of the system:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_{ii}^2 + \sum b_{ij} x_i x_j \qquad \text{Eq. (4.2)}$$

Y is the predicted response; b_0, b_i, b_{ii} and b_{ij} are the offset terms, the linear effect, the squared effect, and the interaction effect, respectively; and x_i and x_j represent the coded independent variables. The performance of the mode presented above was evaluated by the correlation coefficient (R^2), the F–value (Fisher variation ratio) and probability value (Prob > F) (Kumar and Pal, 2012).

4.3 Results and Discussion

4.3.1 Effect of pH

Generally, pH is a predominant factor that has a significant impact on driving the precipitation reaction and, importantly, precipitate formation efficiency, crystallization and purity (Rahman et al. 2014). MAP can be precipitated over a wide range of pH (7.0 to 11.5), but the appropriate pH range is reported to be between 7.5 to 9.0 (Hao et al., 2013). As seen in Figure 4.2, for a molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.0:1.0, the greatest total ammonia removal (90.29%) was obtained at pH = 9, while a 98.65% TAN removal rate (shown as solid lines) was obtained at the same pH for $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.2:1.2. For the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.0:1.0 ammonia removal increased from 81.53% at an initial pH = 7 to a peak value of 90.29% at pH=9 and dropped to 87.5% at pH=10.5. For the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.2:1.2 ammonia removal increased from 92.3% at an initial pH = 7 to a peak value of 98.65% at pH=9 and dropped to 94.2% at pH=10.5. By increasing magnesium and phosphate concentration from $NH_4^+ : Mg^{2+} : PO_4^{3-}$ = 1.0:1.0:1.0 and 1.0:1.2:1.2, an average improvement of 8% in total ammonia removal was obtained. These results demonstrated that the optimal pH for removing ammonia from synthetic solutions is around 9. Although for pH range of 9-10 comparable results were obtained, a pH of 9 will be favorable when taking into account the cost of chemicals required for pH adjustment (alkali consumption). The above is in agreement with the previous investigations which found greater ammonia removal with increasing pH (Khaodhiar et al., 2014; Korchef et al., 2011; Kumar and Pal, 2013; Siciliano et al., 2013); this might be due to the fact that struvite solubility decreases with increasing pH. Additionally, lower pH values (≤ 7) favors increased formation of ionized ammonia, while pH ≥ 11

strongly promotes NH_3 volatilization (Philippe et al., 2011). At a solution pH lower than 8, although the majority of the TAN in solution is present in the form of the NH_4^+ species, a high concentration of H^+ may inhibit the formation of struvite, resulting in reduced ammonia removal efficiency (Huang et al., 2014). On the other hand, when solution pH rises above 10.0, the following reactions (Eq. (4.3) and Eq. (4.4)) can take place (Maekawa et al., 1995). This also lowers the chance of producing struvite.

$$Mg^{2+} + PO_4^{3-} \rightarrow Mg_3(PO_4)_2 \qquad \text{Eq. (4.3)}$$

$$Mg^{2+} + H_2O \leftrightarrow Mg(OH)_2 \downarrow + 2H^+ \qquad \text{Eq. (4.4)}$$

This study also conforms the high TAN removal efficiency (89.4%) from sewage sludge effluent at pH 9, reported by Uysal et al. (2010) and 98% removal of ammonia from stabilized leachate (initial TAN=5,618 mg/L) at pH 9.0 for 15 minutes reaction time reported by Patel and Desai (2014).

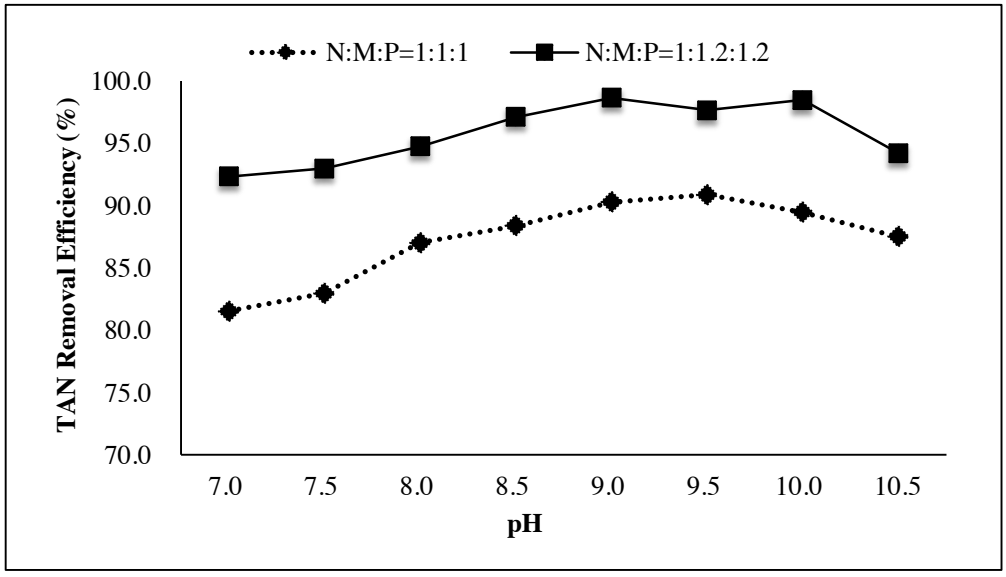

Fig. 4. 2 Effect of pH on TAN removal by struvite precipitation ($NH_4^+ : Mg^{2+} : PO_4^{3-}$ ==1.0:1.0:1.0 and 1.0:1.2:1.2) (at 1,000 mg TAN/L)

4.3.2 Effect of molar ratio

According to Eq. 4.5, struvite precipitation occurs in solution at an equimolecular condition for NH_4^+, Mg^{2+} and PO_4^{3-}. Theoretically, with a stoichiometric ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.0:1.0, the struvite crystallization process is able to occur. However, magnesium and phosphate might be consumed by the presence of other ions in the solution.

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O = MgNH_4PO_4 \cdot 6H_2O \downarrow \quad \text{Eq. (4.5)}$$

As discussed above, the optimum pH was determined to be 9. Also, higher molar ratios of $Mg^{2+} : PO_4^{3-}$ resulted in higher ammonia removal rates. Therefore, in order to evaluate the impact of the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ on ammonia removal from a synthetic solution, different combinations (molar ratios shown in Table 4.1) were tested under the following conditions: pH = 9, stirring duration = 20 minutes, settling time = 10 minutes. The average removal rates are presented in Fig. 4.2 and Fig. 4.3.

Fig. 4.3 shows the effect of individual variation of magnesium and phosphate molar concentration separately, which was obtained by keeping one at a molar ratio equal to ammonia (equal to 1) and changing the other one and revers the order. Results indicate that the additional amounts of Mg^{2+} and PO_4^{3-} in excess to a mole ratio of 1 with respect to ammonia will results in higher ammonia removals. Magnesium concentration was increased from a molar ratio $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:0.8:1.0 to 1.0:1.4:1.0, which resulted in an increase in TAN removal from 84% to 92%. A slightly different situation was found by raising the concentration of phosphate from $NH_4^+ : Mg^{2+} : PO_4^{3-}$ = 1.0:1.0:0.8 to 1.0:1.0:1.4; TAN removal efficiency gradually increased from 87% to 96%. Thus, addition of excess phosphate was slightly more effective (4% additional removal) than addition of the same quantity of excess magnesium.

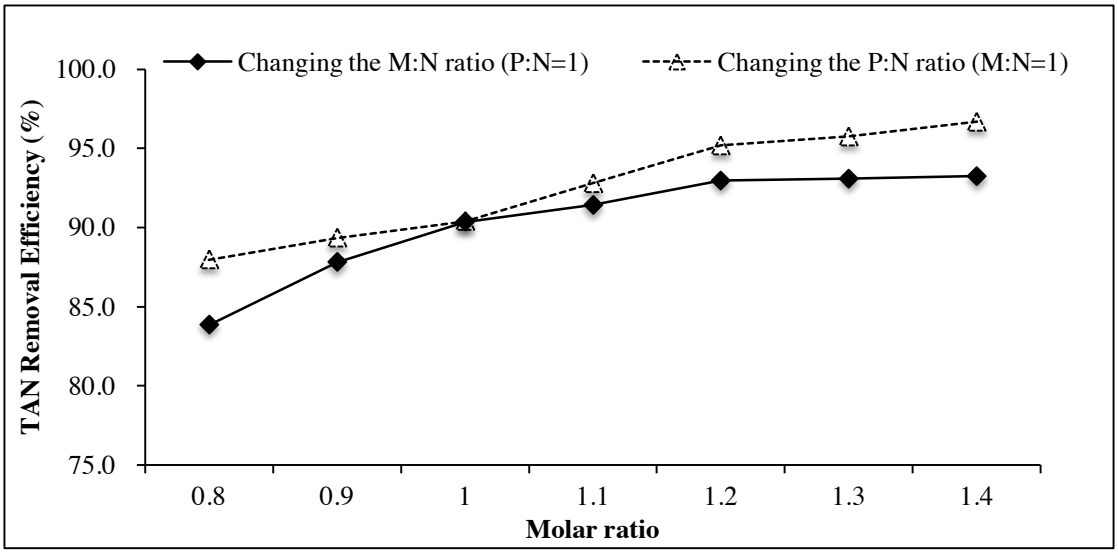

Fig. 4. 3 Effect of the individual variation of magnesium/phosphate levels on the TAN removal efficiency from synthetic solution (at 1,000 mg TAN/L and pH of 9)

Fig. 4.4 shows that chemical precipitation by struvite formation was effective in removing ammonia inform the aqueous solution as removal rates from 89.7% to 98.9% were observed. Among different molar ratios considered, the molar ratios of $NH_4^+ : Mg^{2+} : PO_4^{3-}$= 1.0:1.2:1.2, 1.0:1.3:1.3, 1.0:1.3:1.4 and 1.0:1.5:1.5, resulted in at least 98% TAN removal rate. The lowest TAN removal efficiency (approximately 90%) was obtained for reagents at a molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$= 1.0:1.0:1.0.

No significant improvement was observed in ammonia removal with increasing magnesium concentration when the N:P ratio was fixed at 1.0:1.0, especially when $Mg^{2+} : NH_4^+$ exceeded 1.2:1.0. This may have been due to the formation of magnesium hydroxide ($Mg(OH)_2$) and magnesium phosphate ($Mg_3(PO_4)_2$) when excessive Mg^{2+} appeared in the solution at alkaline conditions, which eventually would lead to the reduction of ammonia removal (Li et al., 2012). Put another way, struvite is more abundant in the system with high NH_4^+ and PO_4^{3-} concentrations, compared to Mg^{2+} levels (Ramaru, 2009). This result is in agreement with other researchers (Huang et al., 2009; Jia, 2013; Korchef et al., 2011). However, in contrast to this study, Zhang et al. (2009) published results showing that enhancing magnesium concentration would result in higher ammonia removal efficiency, and Le Corre et al. (2007) found that better

struvite crystal characteristics are obtained with higher magnesium dosage. Li et al. (2012) found that the $NH_4^+ : Mg^{2+} : PO_4^{3-}$ molar ratio was readily controlled at a ratio of 1.0:1.0:1.1 by adding $MgCl_2 \cdot 6H_2O$ and H_3PO_4, so as to both effectively remove ammonium and avoid creating a higher concentration of phosphorus in the effluent. In general, introducing additional amounts of phosphate increases the TAN removal, but this could also lead to higher phosphate concentration in the effluent, which demands subsequent biological treatment.

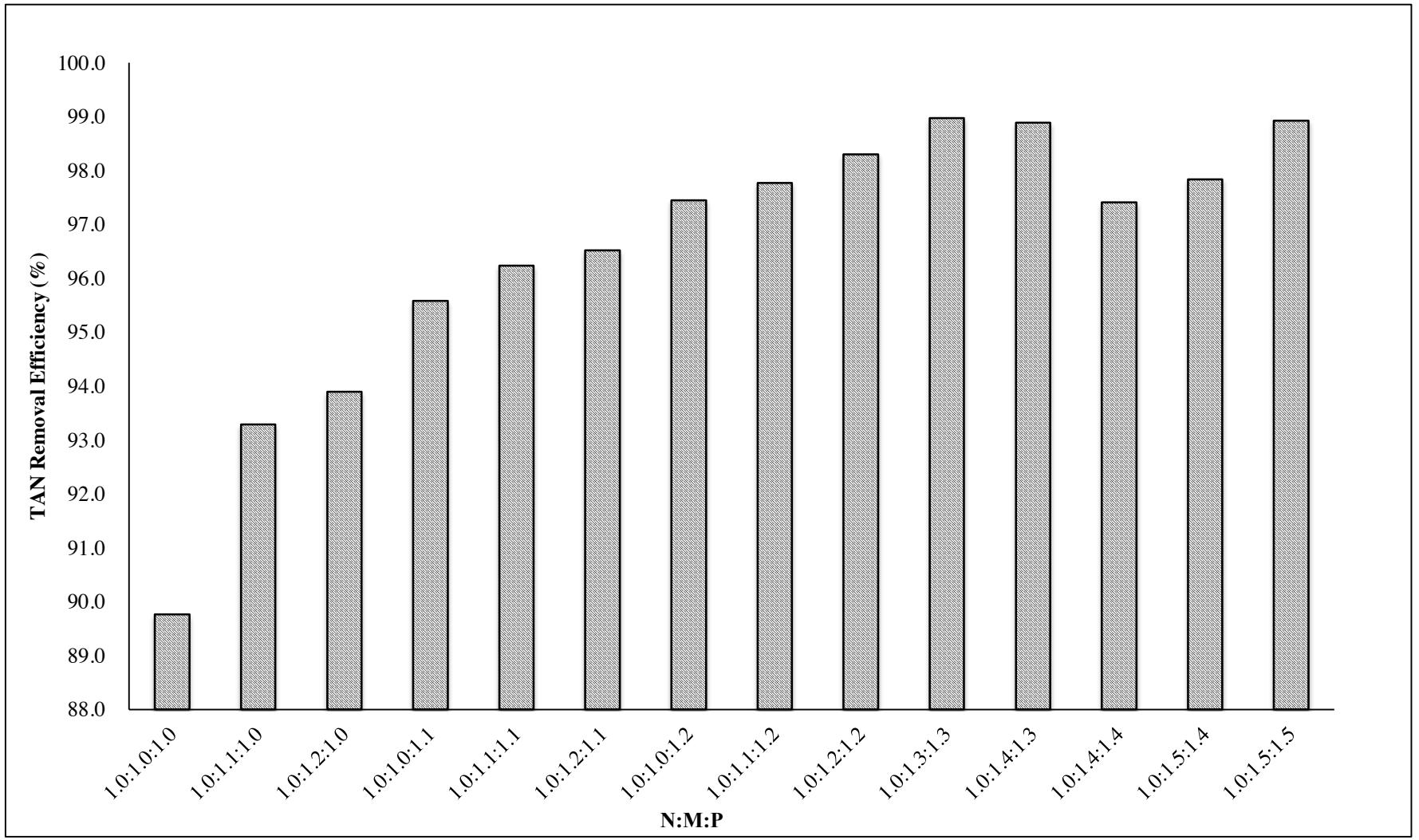

Fig. 4. 4 Effect of the different molar ratios of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ on the TAN removal efficiency (at 1,000 mg TAN/L and pH of 9)

4.3.3 Response surface optimization and statistical analysis

The chemical process of conversion of ammonia nitrogen into struvite with the addition of magnesium and phosphate salts was optimized using response surface methodology (RSM) with Design-Expert software for the batch experiments results. After performing 72 runs, based on design of three independent variables, the experimental results for ammonia removal were obtained. The quadratic equation given in section 4.2.4 describes the behavior of the system. In the present work, a second-order polynomial equation was used to analyze the data.

F-test was conducted for the analysis of variance (ANOVA) to evaluate the statistical significance of the quadratic model. The ANOVA testes results are shown in Table 4.2 and 4.3. The obtained F-value of 148.45 and the "Prob>F" value of <0.0001 implies that the model was statistically significant for ammonia removal. The value of "Prob>F" (<0.0001), being less than 0.05, indicated that model terms were significant. "Prof>F" values are larger than 0.05, which implies these parameters are insignificant and can be eliminated. In this case, pH, $n(Mg^{2+}:NH_4^+)$, $n(PO_4^{3-}:NH_4^+)$, pH^2 and $[n(Mg^{2+}:NH_4^+)]^2$ are significant terms, which are kept in the reduced model. As can be see, the reduced model with F value of 199.26 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 56.221 indicates an adequate signal since it is larger than the boundary value of 4. The final regression equation (Eq. 4.6), developed through analysis of variance (ANOVA), showed the empirical relationship among the target response (denotes total ammonia nitrogen removal, %) and the operating variables (pH, $n(Mg^{2+}:NH_4^+)$ and $n(PO_4^{3-}:NH_4^+)$).

$$Y = -197.04 + 41.21pH + 134.67[n(Mg^{2+}:NH_4^+)] + 17.52[n(PO_4^{3-}:NH_4^+)] - 2.23pH^2 - 54.52[n(Mg^{2+}:NH_4^+)]^2 \quad \text{Eq. (4.6)}$$

The performance of the developed model was assessed based on the correlation coefficient R^2, adjust R^2, predicted $R^2$and the value of the standard deviation (Zhang et al., 2011). The closer the value of R^2 is to unity, the smaller is the standard deviation

and the more accurate is the response. Adjust 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. The predicted R^2 suggests how well a regression model predicts responses for new observations. The R^2 value of 0.938 (R^2_{adj}=0.933) indicates that the predicted values obtained from the model is a good fit of the experimental data. The lack-of-fit compares the residual error to the pure error from triplicated experimental design points. A relatively low R^2 value and the significant lack-of-fit value can suggest that the regression model fails to describe the the functional relationship between the experimental factors and the response adequately. However, a model with reasonable R^2 is acceptable (Kumar and Pal, 2013). Compared the two models, the difference in R^2 is not considerable, and the reduced model is simpler with less terms. As a result, the reduced quadratic model was considered to be appropriate to describe the design because it has a high R^2 value of 0.938 and adequate precision ratio of 56.221.

Table 4. 2 Analysis of variance (ANOVA) for RSM full quadratic model parameters

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1469.5	7	209.93	148.45	< 0.0001	significant
pH	105.88	1	105.88	74.87	< 0.0001	
n(M:N)	121.35	1	121.35	85.81	< 0.0001	
n(P:N)	327.99	1	327.99	231.94	< 0.0001	
n(M:N)*n(P:N)	0.49	1	0.49	0.35	0.5586	
pH^2	182.78	1	182.78	129.25	< 0.0001	
$n(M:N)^2$	89.26	1	89.26	63.12	< 0.0001	
$n(P:N)^2$	6.12	1	6.12	4.33	0.0415	
Residual	90.5	64	1.41			
Lack of Fit	73.44	21	3.5	8.81	< 0.0001	significant
Pure Error	17.06	43	0.4			
Total	1560.01	71				
R^2=0.942	R^2_{adj}=0.936	R^2_{pred}=0.926		Adequate Precision=49.342		

Table 4. 3 Analysis of variance (ANOVA) for RSM reduced quadratic model parameters

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1469.02	6	244.84	174.9	< 0.0001	significant
pH	105.55	1	105.55	75.4	< 0.0001	
n(M:N)	121.32	1	121.32	86.66	< 0.0001	
n(P:N)	327.64	1	327.64	234.04	< 0.0001	
pH^2	185.67	1	185.67	132.63	< 0.0001	
$n(M:N)^2$	121.3	1	121.3	86.65	< 0.0001	
Residual	90.99	65	1.4			
Lack of Fit	73.93	22	3.36	8.47	< 0.0001	significant
Pure Error	17.06	43	0.4			
Total	1560.01	71				
R^2=0.938	R^2_{adj}=0.933	R^2_{pred}=0.927		Adequate Precision=56.221		

A three-dimensional surface plot are illustrated in Fig. 4.5, 4.6 and 4.7, as to provide a better visualization of the statically significant factors derived from the statistical analysis.

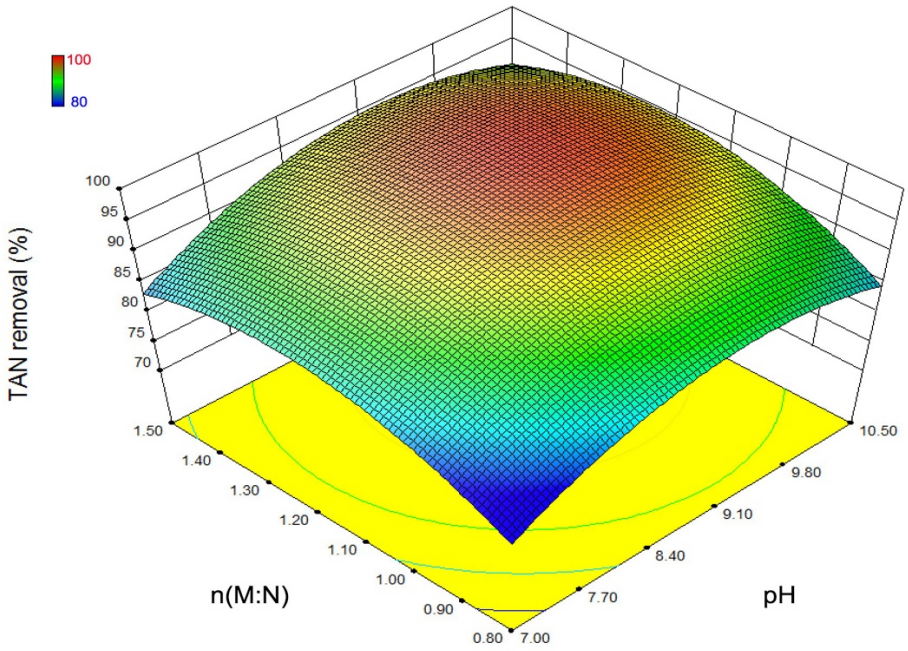

Fig. 4. 5 RSM model of TAN removal by struvite formation at n(P:N) = 1.25

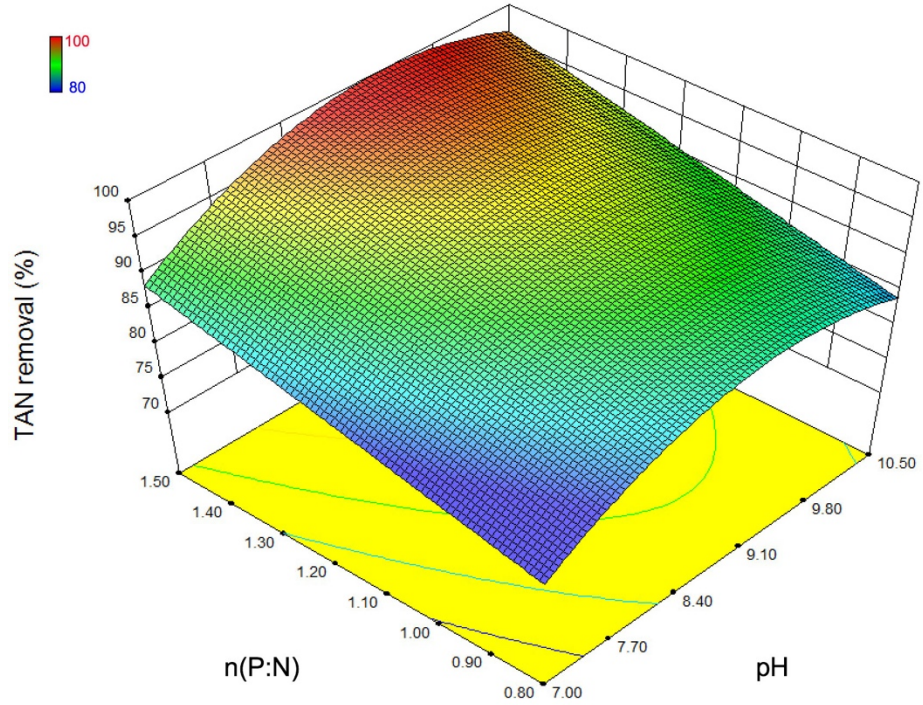

Fig. 4. 6 RSM model of TAN removal by struvite formation at n(M:N) = 1.0

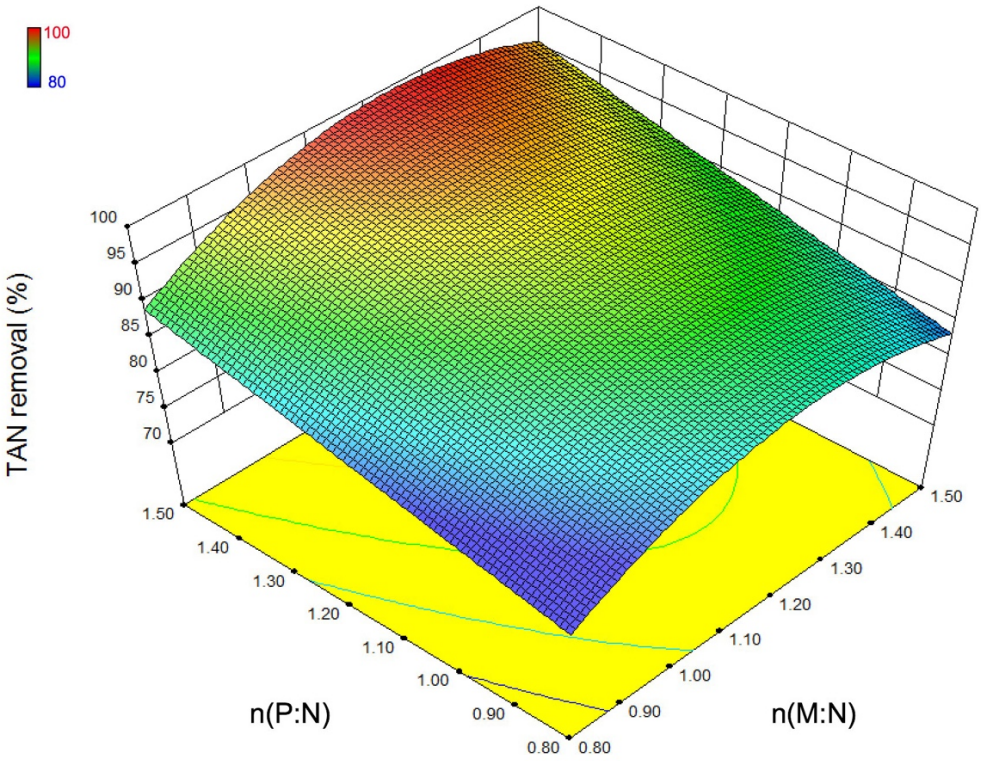

Fig. 4. 7 RSM model of TAN removal by struvite formation at pH = 8

4.3.4 Thermal treatment of struvite by oven heating

Although struvite precipitation has been shown to be a powerful and efficient method for dealing with wastewater containing a high concentration of ammonia, it is still hampered by some drawbacks, including the high dose and costs of precipitants and the further disposal of the sludge (Kurniawan et al., 2006). These drawbacks also explain the lack of practical application of magnesium ammonium phosphate (MAP) chemical precipitation worldwide (Yu et al., 2013). Some attempts have been made to address this issue, including the use of low-grade magnesium and phosphate sources, such as MgO (Chimenos et al., 2003; Quintana et al., 2008), brine and bittern (Lee et al., 2003) and the pyrolysate of magnesite (Huang et al., 2011). Additionally, the process of reusing the decomposition product of struvite has been investigated by scholars to both maintain high total ammonia nitrogen removal and reduce costs of operation (He et al., 2007; Huang et al., 2009; Türker and Çelen, 2007; Yu et al., 2013; Zhang et al., 2009). Huang et al. (2009) introduced recycling of MAP by dry pyrolysis, which could achieve an ammonia removal efficiency of 99%.

The theoretical mass loss for the formula ($MgNH_4PO_4 \cdot 6H_2O$) is 51.42%, and is made up of a mass loss for water of 44.08% and for ammonia of 7.34% (Frost et al., 2004). It has been reported that heating MAP results in the expulsion of all of the water due to hydration from $MgNH_4PO_4 \cdot 6H_2O$ (MAP), and of the chemically bound ammonia, leading to the formation of magnesium hydrogen phosphate ($MgHPO_4$), commonly known as newberyite (Frost et al., 2004; Wang et al., 2006). Sugiyama et al. (2005), using X-ray diffraction analysis of the thermal disintegration of MAP, confirmed the possible residual composition as a mixture of $MgHPO_4$ (MHP) and $Mg_2P_2O_7$. The study of Bhuiyan et al. (2008) suggested that MAP can be thermally decomposed into a mixture of $MgHPO_4$, $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$. Possible reactions can be expressed as in Eq. (4.7), (4.8), (4.9), and (4.10) during the pyrolysis process (Chen et al., 2015). When the pyrolysis temperature is within the range of 80 ℃ to 227 ℃, the dominant component of struvite pyrolysate is MHP (Sugiyama et al., 2005). When struvite encounters higher temperatures, magnesium pyrophosphate is likely to form in the residuals (Sugiyama et al., 2005).

$$MgNH_4PO_4 \cdot 6H_2O \xrightarrow{heat} MgNH_4PO_4 \cdot H_2O + 5H_2O \uparrow \quad \text{Eq. (4.7)}$$

$$MgNH_4PO_4 \cdot 6H_2O \xrightarrow{heat} MgHPO_4 \cdot 3H_2O + 3H_2O \uparrow + NH_3 \uparrow \quad \text{Eq. (4.8)}$$

$$3MgNH_4PO_4 \cdot 6H_2O \xrightarrow{heat} Mg_2P_2O_7 + MgHPO_4 + 18H_2O \uparrow + 3NH_3 \uparrow \quad \text{Eq. (4.9)}$$

$$2MgHPO_4 \xrightarrow{heat} Mg_2P_2O_7 + H_2O \uparrow \quad \text{Eq. (4.10)}$$

MHP is also reported as the principle component of MAP pyrolysates for further ammonia removal from an aqueous system, as compared to $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$, based on the research of Sugiyama et al. (2005). They explained that MHP has a greater solubility (0.3 g/100 mL) than $Mg_3(PO_4)_2$ (0.02 g/100 mL) and $Mg_2P_2O_7$, which barely dissolves in water. The reaction of these three possible pyrolysates of struvite in a synthetic ammonia solution were shown to be as follows in Eq. (4.11), (4.12) and (4.13):

$$MgHPO_4 \cdot 3H_2O(s) + NH_4^+(aq) + 3H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + H^+ \quad \text{Eq. (4.11)}$$

$$Mg_3(PO_4)_2 + 2NH_3 + 14H_2O \rightarrow 2MgNH_4PO_4 \cdot 6H_2O + Mg(OH)_2 \quad \text{Eq. (4.12)}$$

$$Mg_2P_2O_7 + 2NH_3 + 13H_2O \rightarrow 2MgNH_4PO_4 \cdot 6H_2O \quad \text{Eq. (4.13)}$$

In order to enhance the ammonia release from struvite and the TAN removal from an aqueous solution, struvite was heated with an alkaline addition, such as sodium hydroxide (NaOH) or magnesium hydroxide ($Mg(OH)_2$) powders (Türker et al., 2007; Yu et al., 2013). Higher ammonia-removal efficiency by the alkaline pyrolysis of struvite rather than direct heating has been reported in previous studies. He et al. (2007) has suggested that struvite regeneration under alkaline conditions could be expressed as Eq. (4.14) and Eq. (4.15), which could solve the problem of precipitant costs in recycling struvite and could help create suitable pH conditions for struvite reformation. The active product of

the NaOH pyrolysis of struvite is magnesium sodium phosphate ($MgNaPO_4$) , which can react with NH_4^+ to form struvite (Huang et al., 2015). Up to 96% of ammonia in struvite powder could be released with sodium hydroxide addition, and 84% TAN removal from synthetic wastewater could occur under the following conditions: a molar concentration ratio for $NH_4^+ : OH^-$ =1.0:1.0; a heating temperature of 90 ℃; and a heating time of 2 hour (He et al. 2007).

$$MgNH_4PO_4 \cdot 6H_2O + NaOH(s) \xrightarrow{heat} MgNaPO_4\,(s) + 7H_2O \uparrow + NH_3 \uparrow \quad \text{Eq. (4.14)}$$

$$MgNaPO_4 + NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O\,(s) \downarrow + Na^+ \quad \text{Eq. (4.15)}$$

From the TGA curve in Fig. 4.8, it may be seen that the mass of MAP gradually drops with increasing temperature, and a sharp decline occurs between approximately 60 ℃ and 120 ℃. Such a phenomenon can be explained by dehydration and ammonia release (Bhuiyan et al., 2008; Chen et al., 2015; He et al., 2007; Sugiyama et al., 2005). In order to maximize the amount of MHP instead of $Mg_2P_2O_7$, the MAP decomposition temperature should be controlled within the range of 60 ℃ to 180 ℃ (Chen et al., 2015).

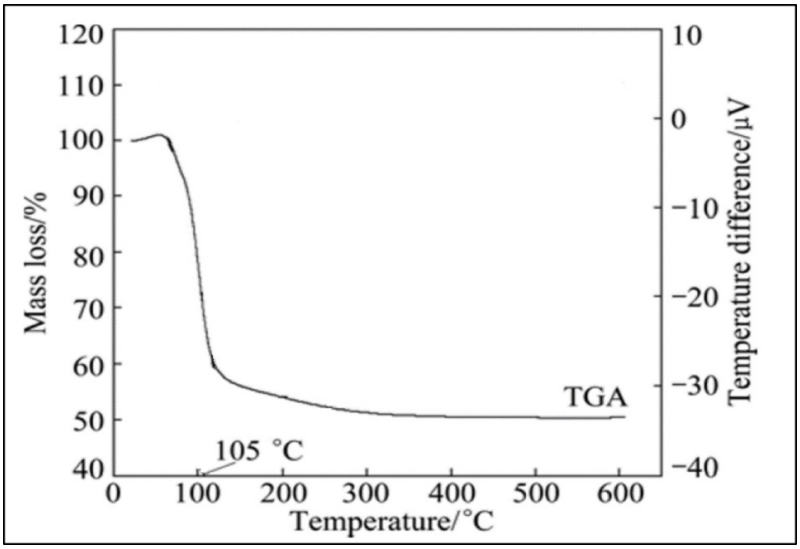

Fig. 4. 8 Thermogravimetric analysis (TGA)-Differential thermal analysis (DTA) curve of struvite (Adapted from Chen et al., 2015)

4.3.4.1 Effect of heating time

To investigate the effect of struvite heating time in the recycling processing on the subsequent ammonia removal performance, dry struvite powder was first heated in an oven (105 ℃) for a certain period of time and then was added (40 g/L) into the ammonia synthetic solution. The heating duration was changed from 0.5 to 3 hours at 30 min increments. The results shown in Fig. 4.9 indicates that TAN removal efficiency was enhanced the pyrolysis time increased from 0.5 to 2.5 hours, but dropped afterwards. Initially, after 0.5 hour, oven-treated struvite did not provide satisfactory ammonia removal (32.4%). Nevertheless, the TAN removal ratio jumped to 63.3% at 1 hour, and gradually climbed to a peak value of around 75% at 2.5 hours. At a temperature of 105 ℃, as the heating time was prolonged, struvite dissociated and a growing amount of $MgHPO_4$, which has a moderate solubility in water and can react with NH_4^+ to precipitate struvite, was likely to occur. This could explain the increasing TAN removal by residues of thermally-treated struvite in the first 2.5 hours. A slight drop in TAN removal rate was observed when heating duration reached 3 hours, which could be due to the production of $Mg_2P_2O_7$ and $Mg_3(PO_4)_2$ and their slight effects on TAN removal, as mentioned previously. Optimum heating time for struvite in this study is 2.5 h.

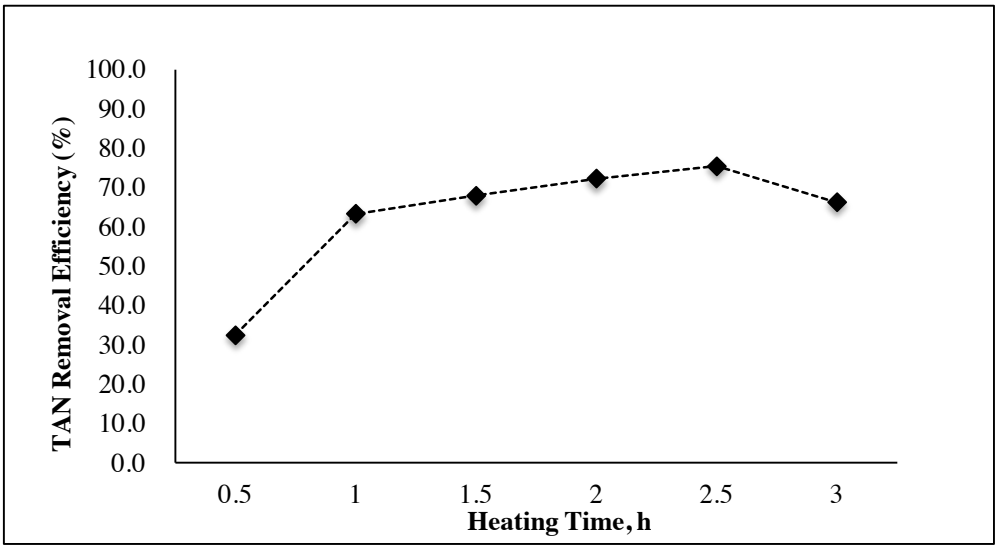

Fig. 4. 9 TAN removal efficiency by the use of struvite pyrolysate generated at different heating times at 105℃ (at 1,000 mg TAN/L and pH of 9)

4.3.4.2 Effect of heating temperature

To study the impact of struvite heating on its effectivenesss when it is recycled, synthetic struvite was thermally treated by convection oven heating at temperatures ranging between 75 ℃ and 140 ℃ (specifically, 75, 90, 105, 120 and 140 ℃) and a pyrolysis time of 2.5 hours. Subsequently, the removal of total ammonia nitrogen from the simulated wastewater using the residues (60 g/L) generated from the struvite pyrolysis as a magnesium and phosphate source was performed at pH 9 and a reaction time of 20 min. As may be noted from Fig. 4.10, when the temperature increased from 75 ℃ to 105 ℃, the TAN removal efficiency increased progressively from approximately 65% to over 80%. However, when the pyrolysis temperature continued to rise, a downward trend in TAN removal was observed, from 80.9% at 105 ℃ and 78.7% at 130 ℃ to 72.1% at 140 ℃. When struvite was pyrolyzed at 105 ℃ for 2.5 hours, it is presumed that the amount of $Mg_2P_2O_7$ and $Mg_3(PO_4)_2$ started to accumulate with increasing temperature. In particular, $Mg_2P_2O_7$ and $Mg_3(PO_4)_2$ make almost no contribution to the removal of ammonium because of their poor solubility (Sugiyama et al., 2005). Based on the results discussed above, 105 ℃ could be assumed to be the optimum temperature for struvite decomposition for further aqueous ammonia elimination. Thermal decomposition of MAP under certain conditions can produce highly concentrated ammonia gas (NH_3), but also a pyrolysis product that may be applied to treat wastewater, which reduces the consumption of chemical precipitation reagents (Chen et al., 2015).

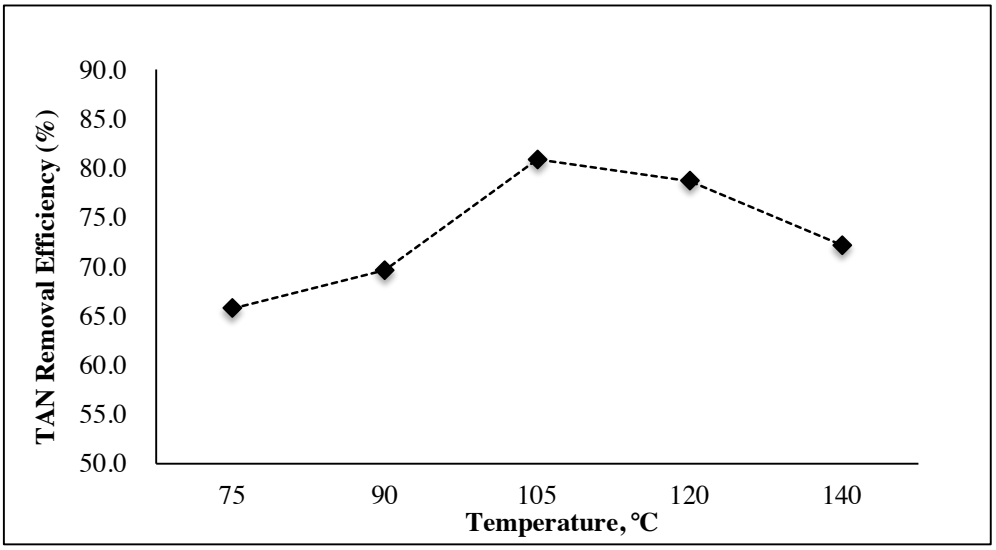

Fig. 4. 10 TAN removal efficiency by the use of struvite pyrolysate generated at different pyrolysis temperatures for a heating duration of 2.5h (at 1,000 mg TAN/L and pH of 9)

4.3.4.3 Effect of struvite pyrolysate dosage

The effect of the struvite pyrolysate dosage on the TAN removal was investigated by adding struvite residues of 10 g/L to 60 g/L into the synthetic solution containing 1,000 mg TAN/L. The experimental data are given in Fig. 4.11. The results reveal that the TAN removal efficiency increases progressively with increasing amounts of pyrolyzed struvite. Relatively low TAN removal of 10% and 30.5% for 10 g/L and 20 g/L were observed, respectively. When oven-treated struvite residues were dosed at 30 g/L into the synthetic solution, the TAN removal rate leaped to 61%. Elimination percentages of TAN continued to increase gradually from 40 g/L (79%) to 60 g/L, with the best value (80.9%) occurring for 60 g/L. Furthermore, the results indicated that the increase in TAN removal was negligible when the concentration of pyrolyzed struvite was greater than 40 g/L. This may be attributed to the achievement of equilibrium in the struvite dissolution–precipitation in the solution. In this case, to reduce struvite pyrolysate consumption, the optimum dosage concentration should be 40 g/L.

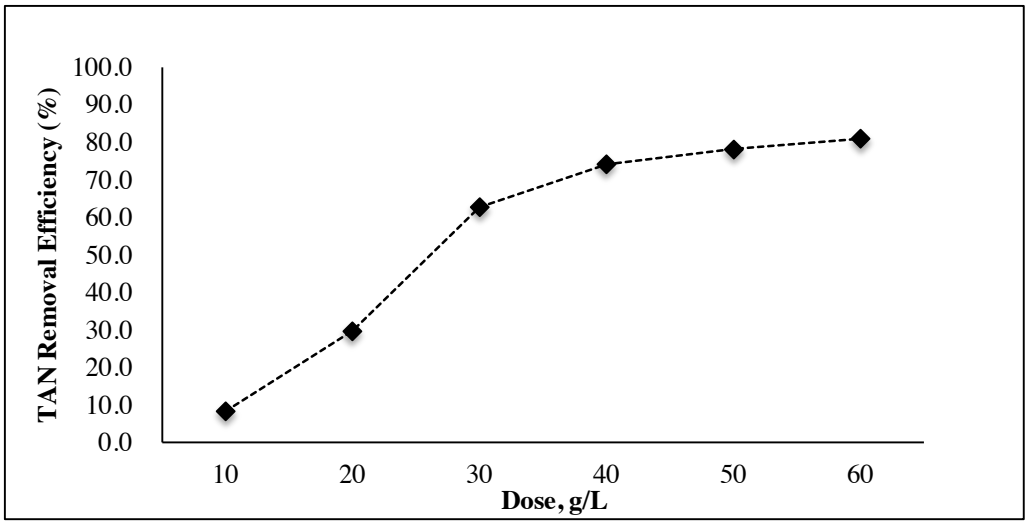

Fig. 4. 11 Effect of the dosage of struvite pyrolysate (heating time=2.5h and heating temperature=105 ℃) on the removal of TAN from synthetic solution (at 1,000 mg TAN/L and pH of 9)

4.3.4.4 Effect of pH

Similar to the previous phase, to determine the optimum pH for ammonia removal were now conducted using the recycled struvite pyrolysate, the experiments were performed at a pH range of 8.5–10.5, with a reaction time of 20 min. The experimental results are shown in Fig. 4.11. As expected, the pH value of the solution was found to be an important factor for TAN removal by the pyrolysate. TAN removal efficiency increased from around 70% to 77% with pH value rising from 8.5 to 9. However, when the pH continued to increase further, TAN removal showed an obvious downward trend, from 74% at pH = 9.5 and 70% at pH = 10 to 67% at a final pH of 10.5. As the pH rises from 9 to 10, the conversion of NH_4^+ to NH_3, which cannot be precipitated as struvite, accelerates, and $Mg_3(PO_4)_2$ begins to form instead of struvite. With increasing formation of $Mg_3(PO_4)_2$, struvite precipitation is blocked, resulting in the decrease of the NH_4-N elimination. When pH is lower than the optimum point (pH = 9), the formation of struvite is inhibited by rising levels of hydrogen ions (Huang et al., 2015). Therefore, as shown in this study, the optimum pH for ammonia nitrogen removal efficiency is 9.

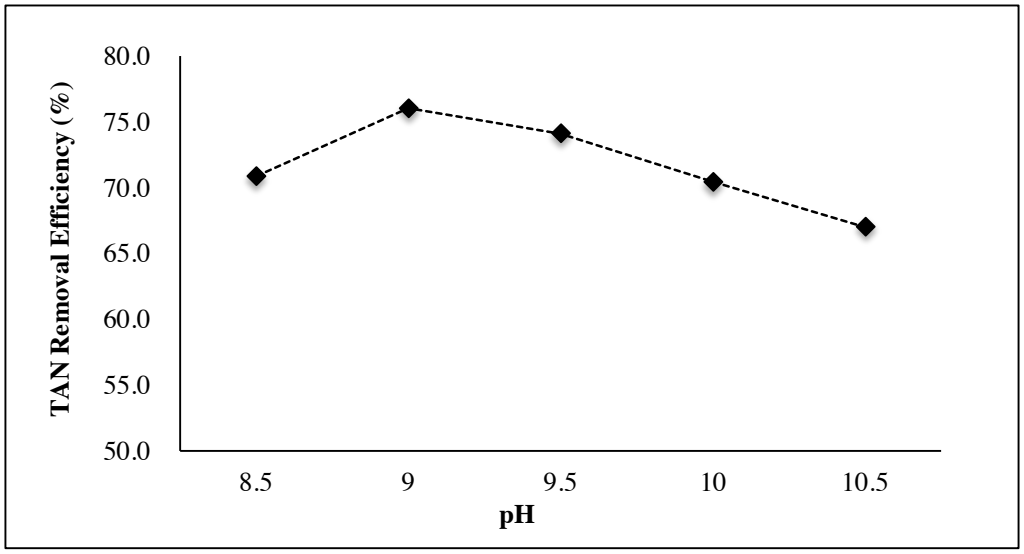

Fig. 4. 12 Effect of pH on TAN removal from synthetic solution with 40 g/L of struvite pyrolysate heated for 2.5 h at 105 ℃ (at 1,000 mg TAN/L)

4.3.4.5 Effect of multiple struvite pyrolysate resue cycles

As previously mentioned, to reduce reagent consumption, the recycling of struvite decomposition residues was investigated. However, gradual decline in TAN removal efficiency with increasing number of recycling cycles needs to be investigated further. This was mainly caused by the accumulation of magnesium pyrophosphate ($Mg_2P_2O_7$) and magnesium phosphate ($Mg_3(PO_4)_2$), which have a negative impact on ammonium removal.

During the multiple recycling processes of struvite decomposition product, two recycling modes were conducted to investigate the performance of the decomposition product as a source for magnesium and phosphate in TAN removal from simulated wastewater. First, the decomposition product was used at 60 g/L directly and repeatedly at a pH of 9. Second, the decomposition product of NaOH-mediated struvite pyrolysis was dosed at 60 g/L into the synthetic solution, also at a pH of 9. Both modes were without any further supplement of magnesium and phosphate salts. Experimental results (Fig. 4.13) show that TAN removal efficiencies decreased as the number of recycling periods increased from 1 to 5 times for both modes. The TAN removal with direct heating of struvite was 80.9% in the first cycle and 60.6% in the fifth cycle. For the

second mode, the TAN removal ratio did not decrease significantly with increased recycling numbers during the struvite decomposition recycling with NaOH pyrolysis. The TAN removal with sodium hydroxide-adjusted struvite was 87% in the first cycle and 75% in the final cycle, with a removal loss of approximately 3% in each cycle. The reason why TAN elimination efficiency dropped may be attributed to the growing amount of inactive amorphous $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$ in the regenerated pyrolysate, as they have poor solubility and hardly react with NH_4^+ to further precipitate struvite. In addition, the losses of Mg^{2+} and PO_4^{3-} in the supernatant per cycle time could also be responsible for the declining TAN removal rate.

Türker and Çelen (2007) reported that the TAN removal was initially 92%, and that it decreased progressively to 77% in the fifth cycle. Huang et al. (2009) recycled the pyrolysis product of struvite five times and discovered that the TAN removal percentages decreased from 80% in the first cycle to 67% in the fifth cycle. He et al. (2007) investigated TAN removal from landfill leachate by recycling the NaOH-mediated pyrolysate of struvite, and reported that it rapidly decreased from > 90% in the first cycle to < 65% in the sixth cycle. Yu et al. (2013) reported that, when fertilizer wastewater was treated by recycling struvite pyrolysate by acidolysis, TAN removal levels of 90.7% in the first cycle and 79.4% in the sixth cycle were achieved. Similar research reinforces the results of this study. Therefore, the multiple recycling of the struvite decomposition product, the proposed process demonstrated a moderate performance on TAN removal, with NaOH-adjusted pyrolysate of struvite having a better ability for absorbing ammonia.

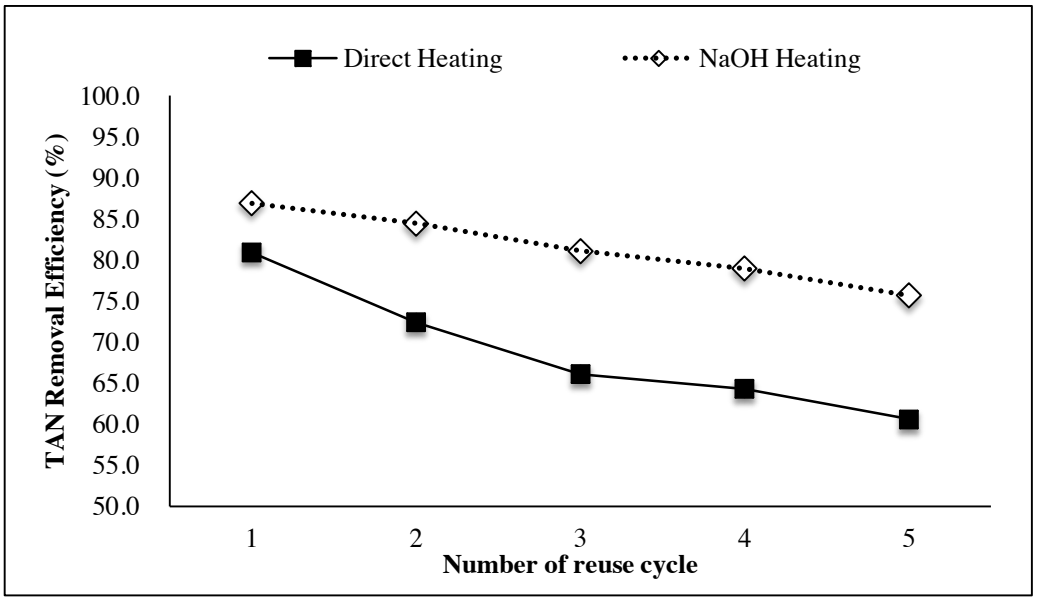

Fig. 4. 13 Repeat use of the struvite pyrolysate (heating time=2.5h and heating temperature=105 ℃) by direct heating and NaOH-mediated heating as a precipitator in TAN removal from synthetic solution (1,000 mg TAN/L, pH = 9, struvite pyrolysate dosage = 60 g/L)

4.3.5 Struvite decomposition by microwave irradiation

Microwave (MW) irradiation is an alternative to conventional heating methods, such as convection oven heating. MW reduce the reaction time dramatically by using the longer wavelengths and lower frequencies in the electromagnetic spectrum (Saha et al., 2011). Microwaves produce homogeneous and quick thermal reactions due to molecular-level heating, which saves considerable time and energy for a similar degree of heating as compared to conventional heating methods (Menéndez et al., 2002). In the published studies, microwave irradiation has been reported to be a powerful tool in the degradation of various organic compounds, including pesticides, ammonia nitrogen and organic dyes in domestic, industrial and medical wastewater (Remya and Lin, 2011). High removal efficiencies of ammonia have been achieved by microwave radiation of strucite in bench-scale experiments (Zhang et al., 2007). The mechanism for ammonia removal was proposed by Lin et al. (2009) as the evaporation of NH_3 by MW irradiation. Other advantages of MW technology for wastewater treatment based on

pollutant degradation may involve selective heating, friendly operational controls and increasing the yield and purity of products (Chou et al., 2015; Lei et al., 2008; Tyagi and Lo, 2013).

However, to the best of our knowledge, reseach on thermal treatment of struvite by microwave irradiation has been reported rarely up to this date. Only Cho et al. (2009) have demonstrated that microwave-treated struvite can be recycled again to the influent wastewaters for further struvite precipitation, so as to reduce the treatment costs. Taking account of MW's advantages, it might be an efficient way to decompose struvite and increase its recycling application in ammonia removal from landfill leachate.

Synthetic struvite powders were thermally treated by MW at two power levels (600 W and 1200 W) and five different heating times (1, 5, 10, 20 and 30 min). After each process, struvite powders were cooled and then dosed at 60 g/L into 100 mL of synthetic solution containing 1,000 mg/L of TAN. The ammonia removal reaction by struvite precipitation took place under the following conditions: pH = 9.0, stirring time = 20 min, settling time = 15 min and reaction temperature = 25 ℃. Total ammonia nitrogen concentration was then measured from the supernatant of the treated solutions. As may be seen from the results displayed in Fig. 4.14, low TAN removal efficiencies (< 21%) were found for both microwave power outputs when the heating time was no longer than 5 min. This could be the result of incomplete decomposition of struvite, so that its pyrolysates can hardly dissolve in the solution. After ten minutes of microwaving time, the MWs with 1200 W demonstrated slightly over 10% more TAN elimination (63.9%) than MWs with 600 W (52.2%), despite the former power output being double the latter one. TAN removal continued to rise to 73.3% for 1200 W and 61.4% for 600 W at a heating time of 20 min before it reached the peaks of 90.2% and 73.1% after 30 min of irradiation, respectively. Through these series of experiments, microwave irradiation, especially at a high power level, has shown to be efficient in dissociating struvite that eventually recycles back to treat aqueous ammonia, based on the relatively high TAN removal. However, to the best of authors' knowledge, no supportive studies have been published.

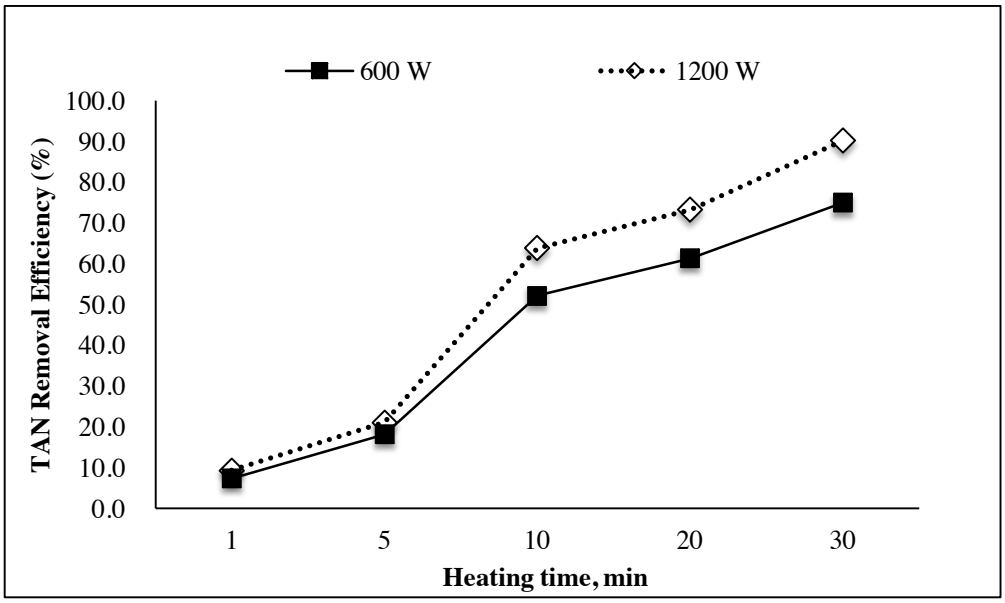

Fig. 4. 14 TAN removal efficiency in synthetic solution by the use of struvite pyrolysate generated at different heating time by microwave irradiation (pH = 9, pyrolysate dosage = 60 g/L)

Similar to the previous steps, struvite powders were thermally treated by MW irradiation at two power levels (600 W and 1200 W) and a heating time of 30 min in each run. Struvite residues were dosed at 60 g/L back into the synthetic solution to absorb ammonium at pH = 9. The results (Fig. 4.15) displayed that, after struvite had been recycled for five times, the TAN removal declined remarkably from 90.3% to 63.8% for 1200 W, and 72.5% to 57.3% for 600 W, respectively. As mentioned previously, the decrease in TAN elimination efficiency may be due to the accumulation of inactive $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$ in the regenerated pyrolysate. The losses of Mg^{2+} and PO_4^{3-} in the supernatant with each cycle time were not measured but they could also be responsible for the declining TAN removal.

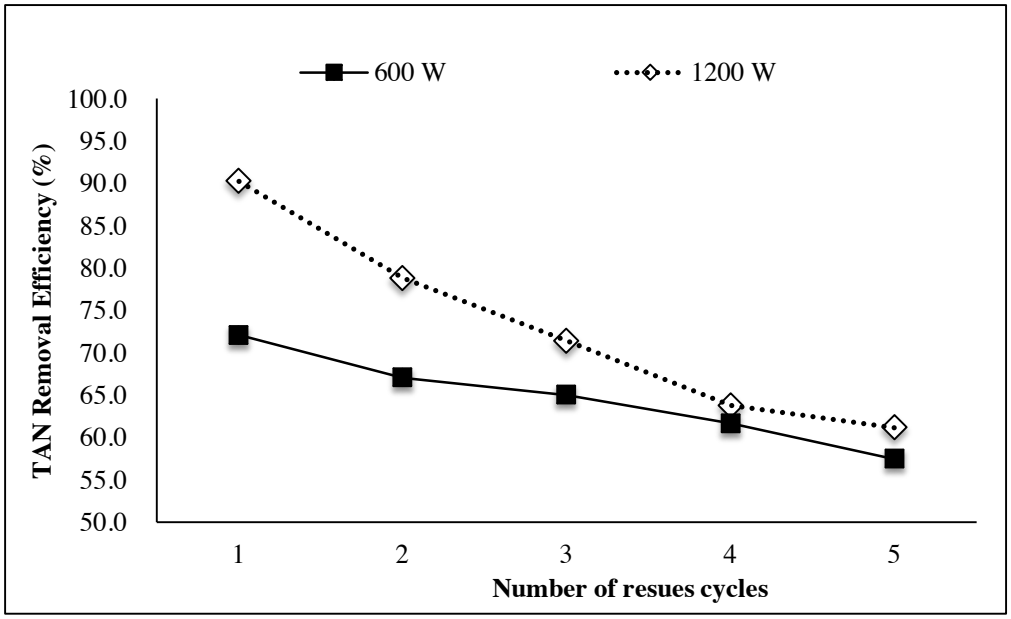

Fig. 4. 15 Repeated use of the struvite pyrolysate from microwave irradiation with two different power outputs, as a precipitator in TAN removal from synthetic solution (pH = 9, pyrolysate dosage = 60g/L, heating time= 30 min)

4.4 Conclusion

Experimental results indicated that chemical precipitation by struvite formation can be an effective method for ammonia removal from aqueous solution. By recycling the thermally decomposed struvite, continuous removal of ammonia can be achieved, which can be applied toward treatment of any wastewater containing high ammonia concentrations, such as landfill leachate. In the struvite precipitation, ammonia removal significantly depended on the reaction pH and molar ratios of $NH_4^+ : Mg^{2+} : PO_4^{3-}$. Optimum pH was reported in this study to be 9. Remarkable TAN removal efficiencies of over 98% can be achieved when excessive magnesium and phosphate are added. Response surface methodology (RSM) helped to analyze the data and optimize the results. The struvite pyrolysate provided the best performance in removing ammonia from simulated wastewater at a dosage of 60 g/L and pH 9, when struvite was previously heated at 105 ℃ for 2.5 h**.** In the recycling phase, the struvite pyrolysate formed by NaOH-mediated pyrolysis performed better than did directly heated struvite. Additionally, microwave irradiation could also dissociate struvite, which subsequently demonstrated moderate TAN removal in each run.

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CHAPTER V

TECHNICAL PAPER II

Assessment and Optimization of Struvite Precipitation of Ammonia from Landfill Leachate

Chi Zhang, Majid Sartaj

Abstract

Municipal landfill leachate was treated by struvite precipitation to investigate the effect of operational parameters of the process and struvite recycling parameters. The experimental data demonstrated that a slightly alkaline pH (9.0-9.5) was preferred for aqueous ammonia removal. Remarkable TAN removal efficiency of over 99% has been reported when the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ equals 1.0:1.3:1.3, 1.0:1.4:1.3, 1.0:1.5:1.4 and 1.0:1.5:1.5 at the optimum pH condition. The response surface method (RSM) was introduced to optimize the three factors (pH, dosage of magnesium, and dosage of phosphate) while avoiding the tedious repetition of experiments. To reduce high reagent consumptions in continuous ammonia removal, struvite samples that were thermally treated by oven heating and microwave irradiation were recycled. The struvite pyrolysate resulting from NaOH-mediated pyrolysis was more effective at treating ammonia solution continuously than was direct heating, with an initial mode of 98.4% at the beginning to 81.3% in the fifth round and direct heating of struvite from 97.2% in the first cycle and 72.3% in the final cycle. Additionally, with shorter heating time compared to conventional oven heating, microwave irradiation could also dissociate struvite, which demonstrated subsequently a moderate TAN removal efficiency.

Keywords: Ammonia; Struvite precipitation; Recycling struvite; Landfill leachate

5.1 Introduction

As environmental protection agencies impose ever stricter nutrients effluent standards related to the removal of nutrient contents, such as for ammonia, which can lead to eutrophication in aquatic system when present in excess (Xavier et al., 2014). As one of the major inorganic pollutants in surface water, ammonia can exist in liquid phase in either un-ionized (NH_3) or ionized forms (NH_4^+), depending on pH and temperature (Ding and Sartaj, 2015). These two forms of ammonia are normally combined and expressed as one term - total ammonia nitrogen (TAN) (Nair et al., 2014). Free ammonia (NH_3) is toxic because most biological membranes are permeable to un-ionized ammonia but impermeable to ionized ammonia (NH_4^+) (Randall and Tsui, 2002). Ammonia toxicity, even at low concentrations (0.53 to 22.8 mg/L), can be a fatal issue for many fish species of ornamental, aqua-cultural and economic values, and may lead to mass mortality under unfavourable conditions (Ip, 2010). Extremely high ammonia concentrations (1,500 to 5,000 mg/L) from wastewater, such as municipal landfill leachate, can cause failure in biological wastewater treatment process due to the inhibition effect on microorganism (Lee et al., 2000; Uygur and Kargi, 2004). A complete inhibition effect of ammonia in the anaerobic digestion process was reported to occur, irrespective of pH, when ammonia concentration exceeds 3,000 mg/L (Procházka et al., 2012; Sung, 2003). Consequently, it is crucial to treat ammonia in the wastewater before it is discharged to a natural environment.

Municipal landfill leachate, resulting from the water percolation through solid wastes, is considered one of the most contaminated wastewater to the environment because of high concentrations of ammonia, salts, heavy metals and organic matter, which make its treatment a challenge (Di Iaconi et al., 2010). Recirculating leachate, as practiced in many modern landfills operated as bioreactor landfill, increases the rate of ammonification, resulting in accumulation of higher levels of ammonia, which intensifies the toxicity of the leachate. This is due to the fact that there is no degradation pathway for ammonia in anaerobic systems (Nair et al., 2014). High concentrations of ammonia in recirculated leachate could undermine the anaerobic digestion process performance by inhibiting microorganisms and result in low methane production.

Conventional biological processes incorporate nitrification and denitrification, and are widely applied in removing low concentrations of ammonia (50 to 200 mg/L) with satisfactory removal rates (75% to 95%), but perform poorly when they encounter landfill leachates with high levels of ammonia (Karadag et al., 2006; Mohanty et al.c 2013). Air stripping provides remarkable results for ammonia removal from landfill leachate at high pH, where most ammonia is transformed to NH_3, but the potential ambient air pollution by ammonia gas and the high consumption of alkali have remained problematic issues (Ferraz et al., 2013; Marttinen et al., 2002). Ion-exchange and adsorption processes, either by adding zeolite, resin and activated carbon or by combining these materials as reagents and absorbents, have received more attention as possible treatments to eliminate ammonia from landfill leachate, due to their relatively simple operation and high removal efficiency (Mohammed et al., 2010; Du et al., 2005). However, the need for frequent regeneration of reagents may limit their application for the treatment of landfill leachate (Kurniawan et al., 2006). The search for efficient and feasible methods for ammonia removal from landfill leachate has become one of the principal research interests in the treatment of municipal landfill leachate.

Recently, struvite (magnesium ammonium phosphate, MAP, $MgNH_4PO_4 \cdot 6H_2O$) precipitation has been shown to be an effective method for the removal of ammonia nitrogen from wastewater, such as rear-earth wastewater (Huang et al., 2009), human urine (Ganrot et al., 2007), piggery effluents (Ali et al., 2003) and landfill leachate (Di Iaconi et al., 2011) because of the high reaction rate and removal efficiencies (Kochany and Lipczynska-Kochany, 2009). Struvite, a white, sparingly soluble, crystalline compound, precipitates in an equimolecular concentration with NH_4^+, Mg^{2+} and PO_4^{3-} at slightly alkaline conditions (Li and Zhao, 2001; Rahman et al., 2014). In fact, landfill leachate is characterized by low concentration of magnesium and phosphate and therefore external sources of these compounds are required to force struvite formation. In recent years, researchers have tried to identify the factors that influence struvite precipitation, including types of chemicals added molar ratios of ($NH_4^+ : Mg^{2+} : PO_4^{3-}$), pH, reaction time, and temperature (Etter et al., 2011; Ozturk et al., 2003; Ryu et al., 2008; Xavier et al., 2014; Xiu et al., 2011). Optimization of process parameters during struvite

crystallization can maximize nitrogen recovery from ammonia-rich wastewater and minimize ammonia concentration in the treated effluent (Ahmad and Idris, 2013). About 98% removal of NH_3-N in leachate with an initial concentration ranging from 3,260 mg/L to 5,618 mg/L was achieved by using struvite precipitation (Kurniawan et al., 2006). Zhang et al. (2012) found the lowest concentration (22 mg/L) of ammonia nitrogen in the effluent of treated swine wastewater indicating the highest removal efficiency (87%) under a N:M:P ratio of 1.2:1.0:1.0. With a N:M:P molar ratio of 1.0:1.5:1.0 and a pH of 9.0, the removal efficiency of NH_3-N from sewage sludge effluent was 89.4% (Uysal et al., 2010).

To achieve satisfactory ammonia removal from heavily contaminated solutions, such as landfill leachate, large quantities of magnesium and phosphate salts need to be added, because landfill leachate generally lacks Mg^{2+} and PO_4^{3-} used for struvite precipitation. This leads eventually to high treatment costs and deters the widespread application of this process (Huang et al., 2014). To better manage reagent consumption and costs, one potential approach is the recycled use of struvite decomposition residues (He et al., 2007; Huang et al., 2011; Türker and Çelen, 2007). Acidolysis, electrolysis, chlorination decomposition and pyrolysis were reported as feasible techniques for disintegrating struvite (Huang et al., 2015; Liu et al., 2011; Yu et al., 2013; Zhang et al., 2004). Thermal treatments of the MAP sludge mainly by oven heating were reported previously (Yu et al., 2013). The dominant component of MAP pyrolysates was reported to be magnesium hydrogen phosphate ($MgHPO_4$), with possible magnesium pyrophosphate ($Mg_2P_2O_7$) and magnesium phosphate ($Mg_3(PO_4)_2$) by-products (Sugiyama et al. 2005). Microwave irradiation was applied as another alternative for dissociating struvite into Mg, NH_4 and PO_4, which were recycled again to the influent swine wastewaters for struvite precipitation (Cho et al. 2009). The dry pyrolysis of magnesium ammonium phosphate (MAP) with the addition of sodium hydroxide powder for ammonia release, combined with MAP pyrolysate recycling, was investigated by Yu et al. (2013). Their experimental results demonstrated that this process was able to maintain over 80% ammonia removal with struvite pyrolysate recycling under the conditions of heating at 110 ℃ for 180 minutes with a molar ratio of NaOH :

NH_4^+ =1.0:1.0. In addition, very limited research has been conducted with recycled struvite for the removal of high ammonia concentrations from landfill leachate using microwave irradiation to enhance the struvite decomposition.

The main objective of this study is to optimize the application struvite precipitation for removal of ammonia from landfill leachate. This is achieved using the response surface methodology (RSM) to determine the optimum conditions for operation parameters, such as pH and reagent dose. The recycled use of struvite through thermal treatment by convection oven heating and microwave heatingto perform efficient and continuous ammonia removal is investigated as well.

5.2 Materials and Methodology

In this study, experiments were separated mainly into two series of tests. The first phase introduced magnesium and phosphate into the landfill leachate to precipitate struvite and to investigate the effects of pH and molar ratio on the removal of TAN. The second phase dealt with the possible recycled use of the thermal decomposition product of struvite under different conditions and its impact on subsequent for TAN removal in leachate solutions. The conditions included: heating method (oven convection heating and microwave irradiation), heating temperature, heating duration, pH, struvite pyrolysate dosage, and the addition of sodium hydroxide (NaOH) in the pyrolysis of struvite.

Landfill leachate was obtained from a local landfill in Casseleman, Ontario with an initial pH 8.9±0.2 and TAN concentration approximately 1,878 mg/L. The leachate was stored in the lab fridge at an operational temperature of 4 ℃. For every test, 100 ml of leachate sample was placed in the fume hood for approximately 2 hours to reach room temperature of 25±2 ℃. Leachate water quality characteristics are presented in Table 5.1. All reactions and tests were carried out at room temperature (25 ℃). Analytical grade of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) from Fisher Chemical and crystalized phosphoric acid (H_3PO_4), produced by Sigma-Aldrich, were used as the source of Mg^{2+} and PO_4^{3-} to form struvite. The pH was controlled by the addition of 2N sodium hydroxide (NaOH) and 2N hydrochloric acid (HCl).

Table 5. 1 Leachate characteristics

Parameters	Concentration (mg/L)
TAN	1,878
PO_4^{3-}	368.8
Mg^{2+}	35
K^+	386
Na^+	137
Ca^{2+}	311
COD	4,425
VFA	549
Alkalinity	6,725
pH	8.9±0.2

The first set of experiments were conducted in batch mode with the pH of the solution varying from 7 to 10.5 at intervals of 0.5, and with a molar ratio for $NH_4^+ : Mg^{2+} : PO_4^{3-}$ of 1.0:1.0:1.0. Based on the results the optimum pH was determined and the subsequent tests were carried out under the optimum pH conditions. Different combinations of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ were shown in Table 5.2 were tests with the solution pH stabilized at the optimum value obtained above and then total ammonia nitrogen concentration was measured. All samples (100 mL) were prepared in 200 mL beakers and mixed for 20 minutes and allowed to settled for 10 minutes at room temperature (25 ℃). Subsequently, the supernatant was separated by filtering from the solution and the filtrate concentration of total ammonia nitrogen was measured. All tests were duplicate.

Table 5. 2 Different combinations of NH_4^+: Mg^{2+}: PO_4^{3-}

Change in Mg^{2+}	Change in PO_4^{3-}	Change in NH_4^+:Mg^{2+}:PO_4^{3-}	
N:M:P	N:M:P	N:M:P	N:M:P
1.0:0.8:1.0	1.0:1.0:0.8	1.0:1.0:1.0	1.0:1.1:1.1
1.0:0.9:1.0	1.0:1.0:0.9	1.0:1.1:1.0	1.0:1.2:1.1
1.0:1.0:1.0	1.0:1.0:1.0	1.0:1.2:1.0	1.0:1.0:1.2
1.0:1.1:1.0	1.0:1.0:1.1	1.0:1.0:1.1	1.0:1.1:1.2
1.0:1.2:1.0	1.0:1.0:1.2	1.0:1.1:1.1	1.0:1.2:1.2
1.0:1.3:1.0	1.0:1.0:1.3	1.0:1.2:1.1	1.0:1.3:1.3
1.0:1.4:1.0	1.0:1.0:1.4	1.0:1.0:1.2	1.0:1.4:1.3
		1.0:1.1:1.2	1.0:1.4:1.4
		1.0:1.2:1.2	1.0:1.5:1.4
		1.0:1.1:1.0	1.0:1.5:1.5
		1.0:1.2:1.0	1.0:2.0:1.5
		1.0:1.0:1.1	1.0:2.0:2.0

The second phase of the study investigated the several parameters that affect the performance of thermally decomposed struvite on the TAN removal in landfill leachate. These parameters included: heating method (oven heating and microwave irradiation), heating temperature, heating duration, pH, struvite pyrolysate dosage, and the addition of sodium hydroxide in the pyrolysis of struvite. Before any tests, struvite was prepared as follows: (1) Struvite precipitate was generated by adding $MgCl_2 \cdot 6H_2O$ and H_3PO_4 to the landfill leachate containing 1,878 mg TAN/L, so as to make the molar ratio of NH_4^+: Mg^{2+}: PO_4^{3-} =1.0:1.2:1.2. The solution was agitated for 20 min at pH 9. (2) The precipitate was collected using a 0.1 μm filter paper and washed twice with deionized water before it was dried at room temperature (25 ℃) for 48 h.

Dry struvite powder was first heated in an oven (105 ℃) for a different period of time ranging from 0.5 to 3h (at 30 min increments) and then it was added (at a dosage of 40 g/L) into the leachate at pH 9. Based on the results the optimum heating duration was determined, struvite was thermally treated at temperatures ranging 75 ℃ and 140 ℃

(specifically, 75, 90, 105, 120 and 140 ℃). Subsequently, the removal of total ammonia nitrogen from landfill leachate by using the residues (60 g/L) generated from the struvite pyrolysis was performed at pH 9.5. After optimum heating duration and heating temperature were determined, struvite pyrolysate was added from 10 to 60 g/L into the leachate at pH 9.5. To determine the optimum pH for the reuse of the struvite pyrolysate under the optimum conditions above, experiments were performed at a pH range of 8.5–10.5. All samples (100 mL) were prepared in 200 mL beakers and mixed for 20 minutes and settled for another 10 minutes at room temperature (25 ℃). Subsequently, the supernatant was separated by filtering from the solution and the concentration of total ammonia nitrogen was measured. All tests were duplicate.

During the multiple cycle of struvite decomposition product reuse, struvite was thermally treated under the optimum conditions obtained from previous results. Two recycling modes were conducted. In the first mode, the decomposition product of struvite was used at 60 g/L directly and repeatedly. The procedure was as follows: (1) Struvite precipitate was generated by adding $MgCl_2 \cdot 6H_2O$ and H_3PO_4 to the leachate containing 1,878 mg TAN/L, so as to make the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.2:1.2. The solution was agitated for 20 min at pH 9. (2) The precipitate was collected by vaccum filtering through a 0.1 μm filter paper and washed twice with deionized water before it was dried at room temperature (25 ℃) for 48 h. (3) The collected solids (MAP) then were treated at optimum heating time and temperature. (4) The recycled MAP residue was added at 60 g/L to 100 ml of leachate and were agitated for 20 min at pH 9.5. After that, the TAN concentration from the supernatant was measured. Steps 2, 3 and 4 were repeated for five times. All tests were performed in duplicate.

In the second mode of reclycing, sodium hydroxide (NaOH) was added in the pyrolysis process of struvite. The decomposition product of NaOH-mediated struvite pyrolysis was dosed at 60 g/L into the synthetic solution. The procedure was as follows: (1) Struvite precipitate was generated by adding $MgCl_2 \cdot 6H_2O$ and H_3PO_4 to the landfill leachate containing 1,878 mg TAN/L, so as to make the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.2:1.2. The solution was agitated for 20 min at pH 9.5. (2) The

precipitate was collected using a 0.1 μm filter paper and washed twice with deionized water before it was dried at room temperature (25 ℃) for 48 h. (3) In the alkaline pyrolysis of struvite, sodium hydroxide (NaOH) pellets were added with struvite powder to make the molar ratio of $NH_4^+ : OH^-$= 1.0:1.0 before it was treated in the heating equipment. (4) The recycled MAP residue was added to 100 ml of the leachate, and were agitated for 20 min at pH 9.5. After that, the TAN concentration from the supernatant was measured. Steps 2, 3 and 4 were repeated for five times. All tests were conducted in duplicate.

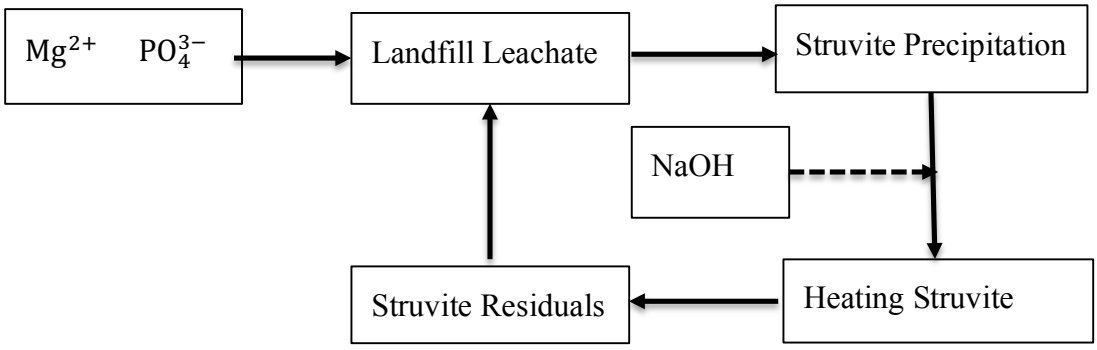

Fig. 5. 1 Experimental Flow Chart (Landfill Leachate)

A CEM Microwave Accelerated Reactions System (MARS 5) was used to treat dry struvite generated from landfill leachate. An UltraPrep Vessel designed especially for ultra high-temperature digestions with operational temperature greater than 300 ℃ was used to contain struvite powders during the heating process. A temperature sensor for monitoring the temperature change was inserted into the vessel tube. Synthetic struvite powders were thermally treated by MW at two power levels (600 W and 1200 W) for five different heating times (1, 5, 10, 20 and 30 min). After each processing, the struvite powders were cooled and then dosed at 60 g/L into 100 mL of the leachate. The reaction took place under the following conditions: pH = 9.0, stirring time = 20 min, settling time = 15 min and reaction temperature = 25 ℃. After that, the TAN concentration from the supernatant was measured. In the recycling phase, similar to the previous steps, struvite powders were thermally treated by MW irradiation at two power levels (600 W and 1200

W) and a heating time of 30 min in each run. Struvite residues were dosed at 60 g/L back into the leachate to react with ammonium at pH = 9.5 for both power levels for five times. All tests were conducted in duplicate.

For each test, initial and final pH were measured with a glass electrode in combination with a Fisher Accumet® Model XL25 dual channel pH/ion meter. The concentration of TAN in the liquid phase was determined by the salicylate method (Method 10205) TNTplus 832 test using a DR6000 spectrophotometer from the HACH Company. Samples were measured at a wavelength of 690 nm. Additionally, 10 mg/L ammonia nitrogen standard solution from the same company was used to check the spectrophotometer. Liquid-phase ammonia removal efficiency was calculated using Eq. (5.1):

$$\text{TAN removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \qquad \text{Eq. (5.1)}$$

Where C_0 is the initial concentrations of total ammonia nitrogen, (mg/L)

C_e is the concentration of total ammonia nitrogen after treatment, (mg/L)

Response surface methodology (RSM) is a combination of mathematical and statistical techniques generally used in the optimization of chemical reactions and industrial processes (Zhou and Wu, 2012). RSM utilizes its statistical tools for analysis of experimental data obtained from definite experimental design to model and optimize any process in which several variables influence the desired response (Bashir et al., 2010). An empirical model can be built to find out the true relationship between the dependent variable and set of independent variables (where the single-response modeled using the RSM corresponds to an independent variable) (Kumar and Pal, 2013). The following quadratic equation (Eq. (5.2)) indicates the behavior of the system:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_{ii}^2 + \sum b_{ij} x_i x_j \qquad \text{Eq. (5.2)}$$

Y is the predicted response; b_0, b_i, b_{ii} and b_{ij} are the offset terms, the linear effect, the squared effect, and the interaction effect, respectively; and x_i and x_j represent the coded independent variables. The performance of the mode presented above was evaluated by the correlation coefficient (R^2), the F−value (Fisher variation ratio) and probability value (Prob > F) (Kumar and Pal, 2012).

5.3 Results and Discussion

5.3.1 Effect of pH

Generally, pH is a predominant factor that has a significant impact on driving the precipitation reaction and, importantly, precipitate formation efficiency, crystallization and purity (Rahman et al., 2014). Magnesium ammonium phosphate can be precipitated over a wide range of pH (7.0 to 11.5). During the optimization of struvite precipitation for the landfill leachate, a series of tests were carried out at different pH levels (7.5 to 10.5) to determine the optimum pH under which the highest removal of TAN could be obtained at the theoretical stoichiometric ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$=1.0:1.0:1.0. In Figure 5.2, the TAN removal efficiency was at least 84.7% (pH=7), reaching to the peak of 94.1% when the pH was adjusted to 9.5. There was a slight decline in TAN removal ratio from 94.1% to 90.9% when pH value drops from 9.5 to 10.5. These results demonstrated that the optimum pH for removing ammonia from landfill leachate lies in a range of 8.5 to 9.5, and pH=9 should be considered more suitable when taking into account the most promising removal. The above results are consistent with the results of Khaodhiar et al. (2014), Korchef et al. 2011 and Siciliano et al. 2013.

At solution pH lower than 8, although the majority of the ammonia in solution is present in the form of the NH_4^+ species, a high concentration of H^+ may inhibit struvite crystallization, resulting in reduced ammonia removal efficiency (Huang et al., 2014). At pH >9.2, NH_4^+ is easily converted into NH_3, which cannot be removed by the formation of struvite. In particular, when solution pH rises above 10.0, the following reactions (Eq. (5.3) and (5.4)) can easily take place (Maekawa et al., 1995). This also lowers the chance of producing struvite. Additionally, lower pH values (≤ 7) favor increased formation of ionized ammonia, and pH ≥ 11 strongly promotes NH_3 formation and its volatilization

(Philippe et al., 2011). Possible formation of calcium phosphate species between pH 9 and 10.5, which consumes PO_4^{3-} in the solution, could also hampers struvite precipitation.

$$Mg^{2+} + PO_4^{3-} \rightarrow Mg_3(PO_4)_2 \quad \text{Eq. (5.3)}$$

$$Mg^{2+} + H_2O \leftrightarrow Mg(OH)_2 \downarrow + 2H^+ \quad \text{Eq. (5.4)}$$

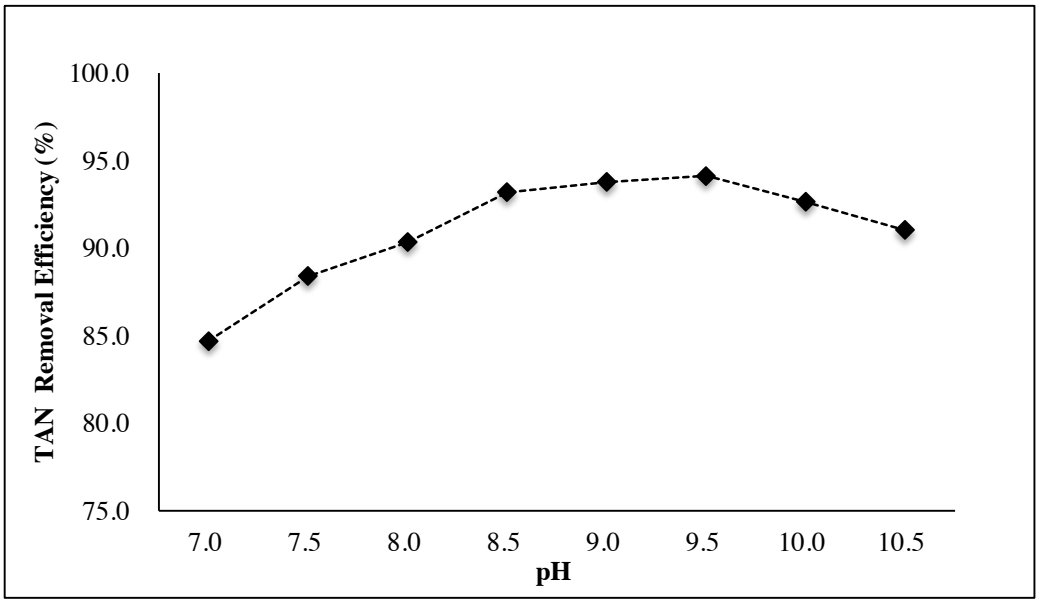

Fig. 5. 2 Effect of pH on TAN removal from landfill leachate by struvite precipitation (NH_4^+: Mg^{2+}: PO_4^{3-}=1.0: 1.0:1.0) (at 1,878 mg TAN/L)

5.3.2 Effect of molar ratio

Landfill leachate generally contains high concentration of ammonia, but have inadequate sources of magnesium and phosphate (Birnhack et al., 2015). In order to remove and/or recover ammonia, an addition of external magnesium and phosphate sources must be involved. Most of the previous researchers favored $MgCl_2 \cdot 6H_2O$ as a source of magnesium for struvite precipitation, whereas only a few applied other chemicals, such as $MgSO_4$, $Mg(OH)_2$ and MgO. No significant difference between the performances of $MgCl_2 \cdot 6H_2O$ and of $MgSO_4$ in the case of ammonia removal was found by Yetilmezsoy et al. (2009). However, a relatively poor ammonia removal

efficiency (67%) was reported by Di Iaconi et al. (2010) using MgO as the magnesium reagent because of its low solubility. Kim et al. (2007) claimed that $Mg(OH)_2$ was not ideal for struvite precipitation, based on a low removal efficiency of 60%. A similar result (62%) was found for magnesium hydroxide; compared to magnesium chloride it has a lower solubility in aqueous media (Xavier et al., 2014). In terms of the phosphorus source, phosphoric acid (H_3PO_4) has been commonly used because it is inexpensive compared to other phosphorus salts, such as Na_2HPO_4, KH_2PO_4, and $Ca(H_2PO_4)_2$, and will not increase salinity concerns by introducing other ions (Ren et al., 2010). Interestingly, Huang et al. (2014) proposed to use waste phosphoric acid as an alternate phosphate source, along with MgO, to form struvite, and obtained 83% ammonia removal while saving 68% of the chemical costs in comparison with pure reagents.

According to Eq. 5.5, struvite precipitation occurs in solution at an equimolecular condition for NH_4^+, Mg^{2+} and PO_4^{3-}. Theoretically, with a stoichiometric ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-} = 1.0:1.0:1.0$, the struvite crystallization process is able to occur. However, magnesium and phosphate might be consumed by the presence of other ions in the landfill leachate.

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O = MgNH_4PO_4 \cdot 6H_2O \downarrow \qquad \text{Eq. (5.5)}$$

As discussed above, the optimum pH was determined to be 9.5. Also, higher molar ratios of $Mg^{2+} : PO_4^{3-}$ resulted in higher ammonia removal rates. Therefore, in order to evaluate the impact of the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ on ammonia removal from a synthetic solutions, different combinations (molar ratios shown in Table 5.1) were tested under the following conditions: pH = 9, stirring duration = 20 minutes, settling time = 10 minutes. The average removal rates are presented in Fig. 5.2 and Fig. 5.3.

Fig. 5.3 shows the effect of individual variation of magnesium and phosphate molar concentration separately, which was obtained by keeping one at a molar ratio equal to ammonia (equal to 1) and changing the other one and revers the order. Results indicate that the additional amounts of Mg^{2+} and PO_4^{3-} in excess to a mole ratio of 1 with respect to ammonia will result in percent higher ammonia removals. Magnesium

concentration was increased from a molar ratio $NH_4^+: Mg^{2+}: PO_4^{3-} = 1.0:0.8:1.0$ to 1.0:1.4:1.0, which resulted in an increased in TAN removal from 89.3% to 95.5%. However, a slight drop (1.5%) in TAN removal was observed in the following combinations when Mg^{2+}molar concentration keeps increasing. Regarding phosphate ratios, it was discovered by raising the concentration of PO_4^{3-} from $NH_4^+: Mg^{2+}: PO_4^{3-} = 1.0:1.0:0.8$ to 1.0:1.0:1.4, TAN removal efficiency gradually increased from 89.9% to 98.6%. Thus, addition of excess phosphate was slightly more effective (2% additional removal) than addition of the same quantity of excess magnesium.

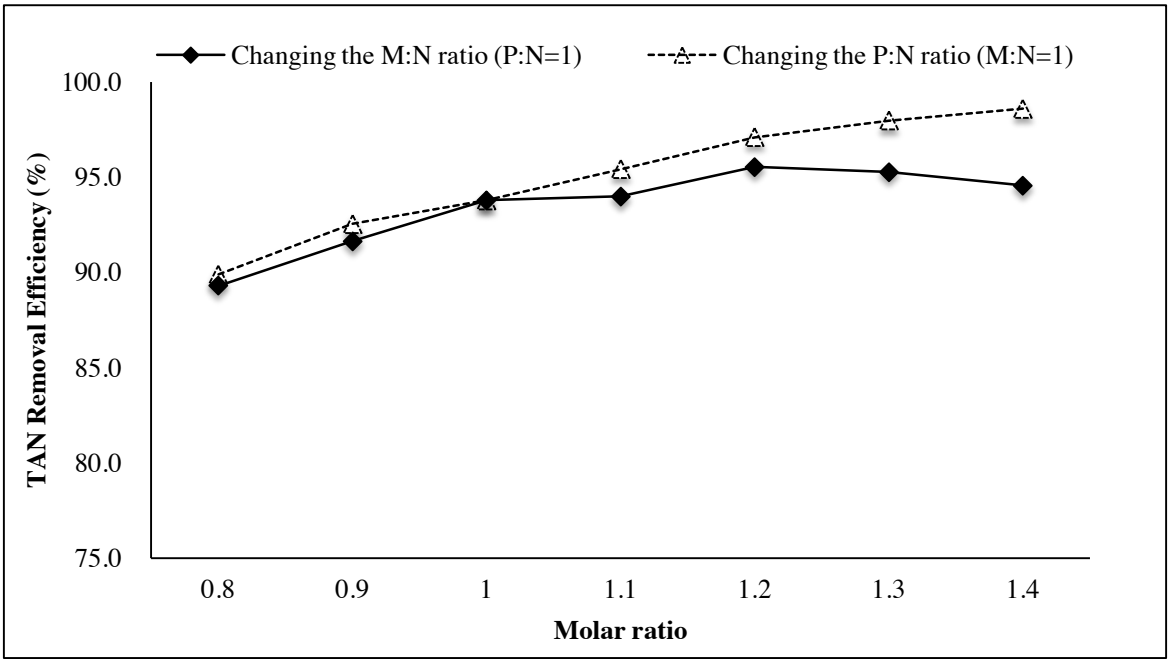

Fig. 5. 3 Effect of the individual variation of magnesium/phosphate levels on the TAN removal efficiency from landfill leachate (at 1,878 mg TAN/L and pH of 9)

Fig. 5.4 shows that chemical precipitation by struvite formation was effective in removing ammonia inform the aqueous solution as removal rates from 93.7% to 99.5% were observed. Among different molar ratios considered, the molar ratios of $NH_4^+: Mg^{2+}: PO_4^{3-}$= 1.0:1.3:1.3, 1.0:1.4:1.3, 1.0:1.5:1.4 and 1.0:1.5:1.5 resulted in at least 99% TAN removal rate. The lowest tow TAN removal efficiency (both slightly below

94%) were obtained for reagents at molar ratios of $NH_4^+ : Mg^{2+} : PO_4^{3-}$= 1.0:1.0:1.0 and 1.0:1.1:1.0.

No striking improvement was observed in ammonia removal with increasing magnesium concentration when the N:P ratio was fixed at 1.0:1.0, especially when $Mg^{2+} : NH_4^+$ exceeded 1.2:1.0. This may have been due to the formation of magnesium hydroxide ($Mg(OH)_2$) and magnesium phosphate ($Mg_3(PO_4)_2$) when excessive Mg^{2+} appeared in the solution at alkaline conditions, which eventually would lead to the reduction of ammonia removal (Li et al., 2012). Put another way, struvite is more abundant in the system with high NH_4^+ and PO_4^{3-} concentrations, compared to Mg^{2+} levels (Ramaru, 2009). This result is in agreement with other researchers (Huang et al., 2009; Jia, 2013; Korchef et al., 2011). However, in contrast to this study, Zhang et al. (2009) published results showing that enhancing magnesium concentration would result in higher ammonia removal efficiency, and Le Corre et al. (2007) found that better struvite crystal characteristics are obtained with higher magnesium dosage. Li et al. (2012) found that the $NH_4^+ : Mg^{2+} : PO_4^{3-}$ molar ratio was readily controlled at a ratio of 1.0:1.0:1.1 by adding $MgCl_2 \cdot 6H_2O$ and H_3PO_4, so as to both effectively remove ammonium and avoid creating a higher concentration of phosphorus in the effluent. In general, introducing additional amounts of phosphate increases the TAN removal, but this could also lead to higher phosphate concentration in the effluent, which demands subsequent biological treatment. Some metal ions such as K^+, Ca^{2+}, Fe^{3+} and Al^{3+} in the leachate may be an important factor toward inhibiting the formation of struvite and higher reagents dosage are required (Huang et al., 2011). For example, the presence of K^+ in the leachate could compete with NH_4^+ to form K-struvite ($MgKPO_4 \cdot 6H_2O$) and Ca^{2+} could consume some of the PO_4^{3-} to precipitate calcium phosphate ($Ca_3(PO_4)_2$), which inhibited the crystallization of struvite and consumed Mg^{2+} and PO_4^{3-} (Di Iaconi et al., 2010).

A computer program called Visual Minteq was used to predict the possible compounds formation and ammonia removal from aqueous solution (Çelen et al., 2007; Crutchik et al., 2013; Lee et al., 2013; Wahal, 2010). Their findings include: From solutions containing Mg^{2+}, NH_4^+ and PO_4^{3-}, possible magnesium species can

crystalize: magnesium ammonium phosphate or struvite ($MgNH_4PO_4 \cdot 6H_2O$), magnesium hydrogen phosphate trihydrate or newberyite ($MgHPO_4 \cdot 3H_2O$), magnesium hydroxide or brucite [$Mg(OH)_2$], magnesite ($MgCO_3$), bobierrite [$Mg_3(PO_4)_2 \cdot 8H_2O$], [$Mg_3(PO_4)_2 \cdot 22H_2O$], [$CaMg(CO_3)_2$] and [$CaMg_3(CO_3)_4$]. In the presence of PO_4^{3-} and Ca^{2+} in the solution, possible calcium species are considered in this study: calcium hydroxide [$Ca(OH)_2$], calcite ($CaCO_3$), brushite ($CaHPO_4 \cdot 2H_2O$), monetite ($CaHPO_4$), tricalcium phosphate [$Ca_3(PO_4)_2$, [$Ca_5(PO_4)_3OH$] and [$Ca_8(HPO_4)_2(PO_4) \cdot 5H_2O$]. Higher dosage of magnesium and phosphate is demanded because some of them could be consumed by the formation of abovementioned compounds.

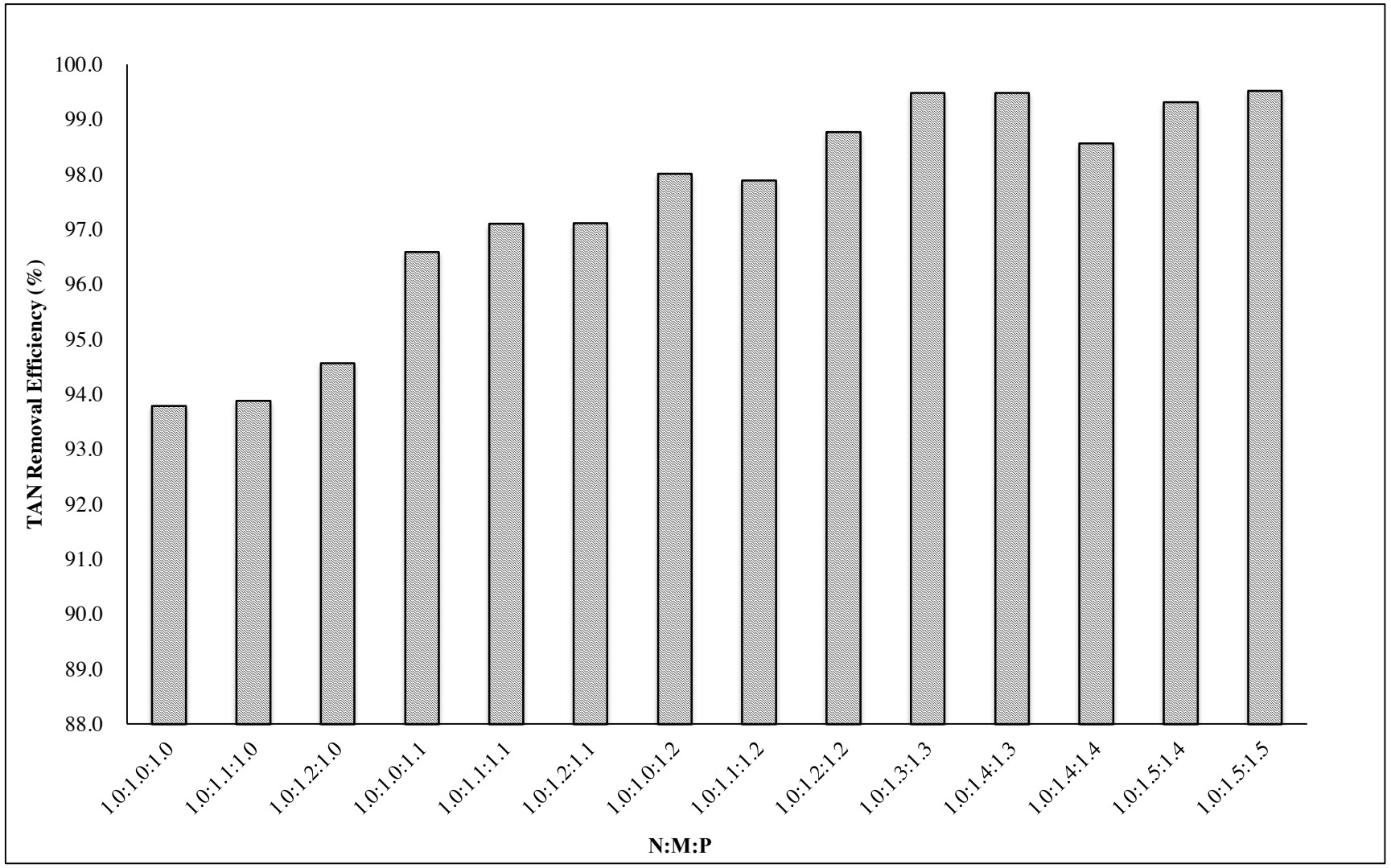

Fig. 5. 4 Effect of the different molar ratios of NH_4^+: Mg^{2+}: PO_4^{3-} on the TAN removal from leachate (at 1,878 mg TAN/L and pH 9)

5.3.3 Response surface optimization and statistical analysis

The chemical process of conversion of ammonia nitrogen into struvite with the addition of magnesium and phosphate salts was optimized using response surface methodology (RSM) with Design-Expert software for the batch experiments results. After performing 72 runs, based on design of three independent variables, the experimental results for ammonia removal were obtained. The quadratic equation given in section 5.2.4 describes the behavior of the system.

F-test was conducted for the analysis of variance (ANOVA) to evaluate the statistical significance of the quadratic model. The ANOVA testes results are shown in Table 5.3 and 5.4. The obtained F-value of 246.33 and the "Prob>F" value of <0.0001 implies that the model was statistically significant for ammonia removal. The value of "Prob>F" (<0.0001), being less than 0.05, indicated that model terms were significant. "Prof>F" values are larger than 0.05, which implies these parameters are insignificant and can be eliminated. In this case, $n(Mg^{2+}:NH_4^+)$, $n(PO_4^{3-}:NH_4^+)$, pH^2, $[n(Mg^{2+}:NH_4^+)]^2$ and $[n(PO_4^{3-}:NH_4^+)]^2$ are significant terms, which are kept in the reduced model. As can be see, the reduced model with F value of 349.82 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 63.096 indicates an adequate signal since it is larger than the boundary value of 4. The final regression equation (Eq. 5.6), developed through analysis of variance (ANOVA), showed the empirical relationship among the target response (denotes total ammonia nitrogen removal, %) and the operating variables (pH, $n(Mg^{2+}:NH_4^+)$ and $n(PO_4^{3-}:NH_4^+)$).

$$Y = -46.89 + 71.04[n(Mg^{2+}:NH_4^+)] + 46.17[n(PO_4^{3-}:NH_4^+)] - 0.86pH^2 - 28.7[n(Mg^{2+}:NH_4^+)]^2 - 13.72[n(PO_4^{3-}:NH_4^+)]^2 \quad \text{Eq. (5.6)}$$

The performance of the developed model was assessed based on the correlation coefficient R^2, adjust R^2, predicted $R^2$and the value of the standard deviation (Zhang et al., 2011). The closer the value of R^2 is to unity, the smaller is the standard deviation and the more accurate is the response. Adjust 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. The predicted R^2 suggests how well a regression model predicts responses for new observations. The R^2 value of 0.964 (R^2_{adj}=0.961) indicates that the predicted values obtained from the model is a good fit of the experimental data. The lack-of-fit compares the residual error to the pure error from triplicated experimental design points. A relatively low R^2 value and the significant lack-of-fit value can suggest that the regression model fails to describe the the functional relationship between the experimental factors and the response adequately. However, a model with reasonable R^2 is acceptable (Kumar and Pal, 2013). Compared the two models, the difference in R^2 is not considerable, and the reduced model is simpler with less terms. As a result, the reduced quadratic model was considered to be appropriate to describe the design because it has a high R^2 value of 0.964 and adequate precision ratio of 63.096.

Table 5. 3 Analysis of variance (ANOVA) for RSM full quadratic model parameters

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	576.92	7	82.42	246.33	< 0.0001	significant
pH	0.043	1	0.043	0.13	0.7209	
n(M:N)	32.48	1	32.48	97.07	< 0.0001	
n(P:N)	235.27	1	235.27	703.16	< 0.0001	
n(M:N)*n(P:N)	0.31	1	0.31	0.91	0.3426	
pH^2	27.43	1	27.43	81.97	< 0.0001	
$n(M:N)^2$	30.56	1	30.56	91.33	< 0.0001	
$n(P:N)^2$	7.5	1	7.5	22.41	< 0.0001	
Resid. Error	21.41	64	0.33			
Lack of Fit	18.48	21	0.88	12.9	< 0.0001	significant
Pure Error	2.93	43	0.068			
Total	598.33	71				
R^2=0.964	R^2_{adj}=0.960	R^2_{pred}=0.956		Adequate Precision=54.588		

Table 5. 4 Analysis of variance (ANOVA) for RSM reduced quadratic model parameters

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	576.57	5	115.31	349.82	< 0.0001	significant
n(M:N)	32.51	1	32.51	98.63	< 0.0001	
n(P:N)	235.27	1	235.27	713.72	< 0.0001	
pH^2	27.92	1	27.92	84.7	< 0.0001	
$n(M:N)^2$	40.26	1	40.26	122.13	< 0.0001	
$n(P:N)^2$	7.92	1	7.92	24.01	< 0.0001	
Residual	21.76	66	0.33			
Lack of Fit	18.82	23	0.82	12	< 0.0001	significant
Pure Error	2.93	43	0.068			
Cor Total	598.33	71				
R^2=0.964	R^2_{adj}=0.961	R^2_{pred}=0.956		Adequate Precision=63.096		

A three-dimensional surface plot are illustrated in Fig. 5.5, 5.6 and 5.7, as to provide a better visualization of the statically significant factors derived from the statistical analysis.

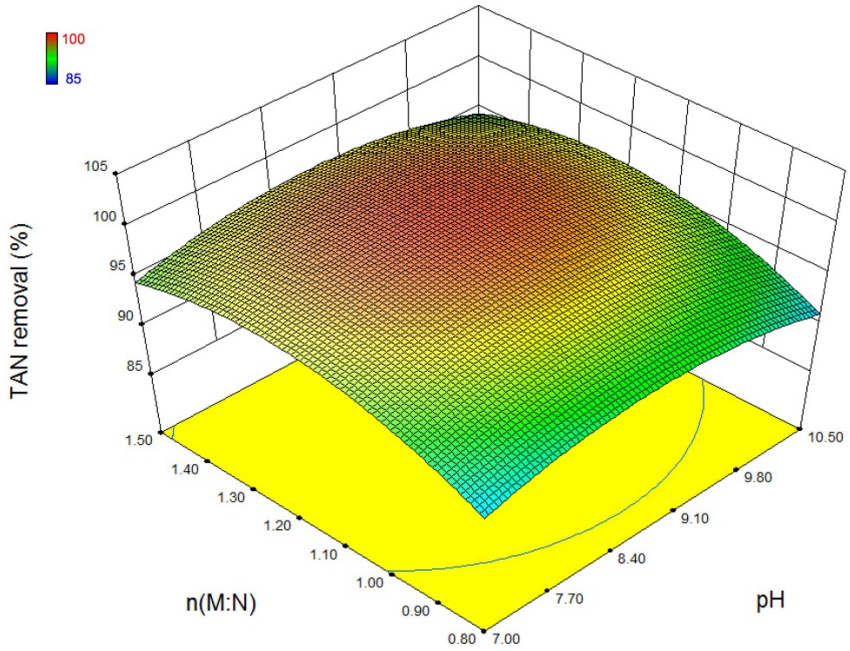

Fig. 5. 5 RSM model of TAN removal by struvite formation at n(P:N) = 1.25

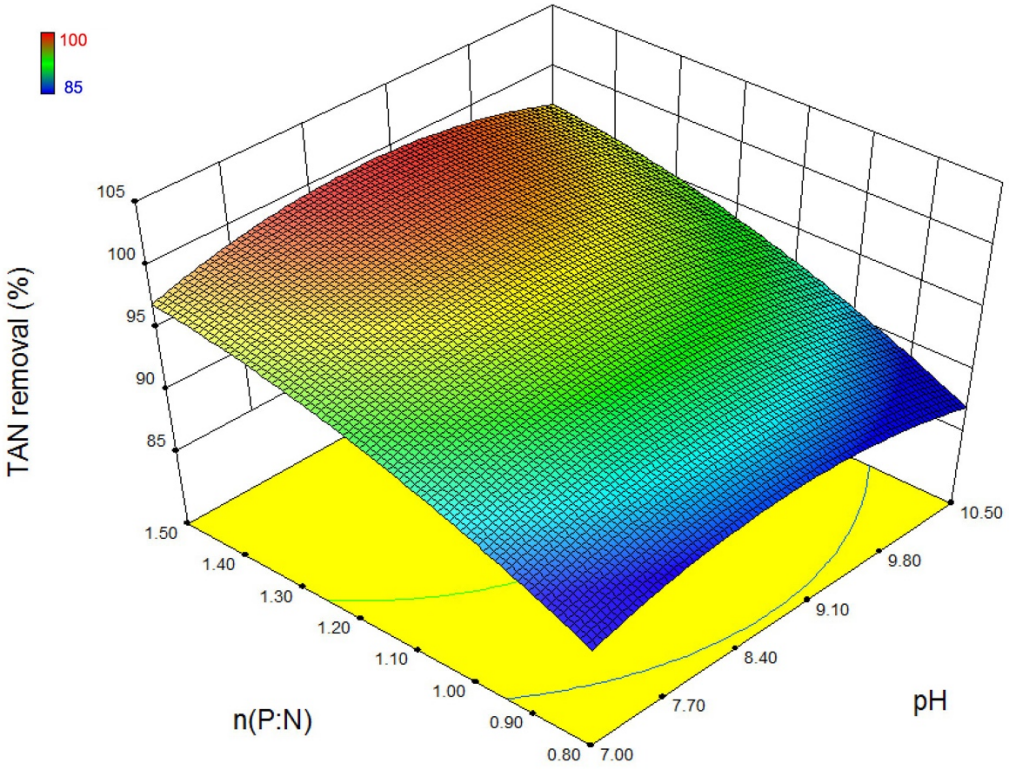

Fig. 5. 6 RSM model of TAN removal by struvite formation at n(M:N) = 1.0

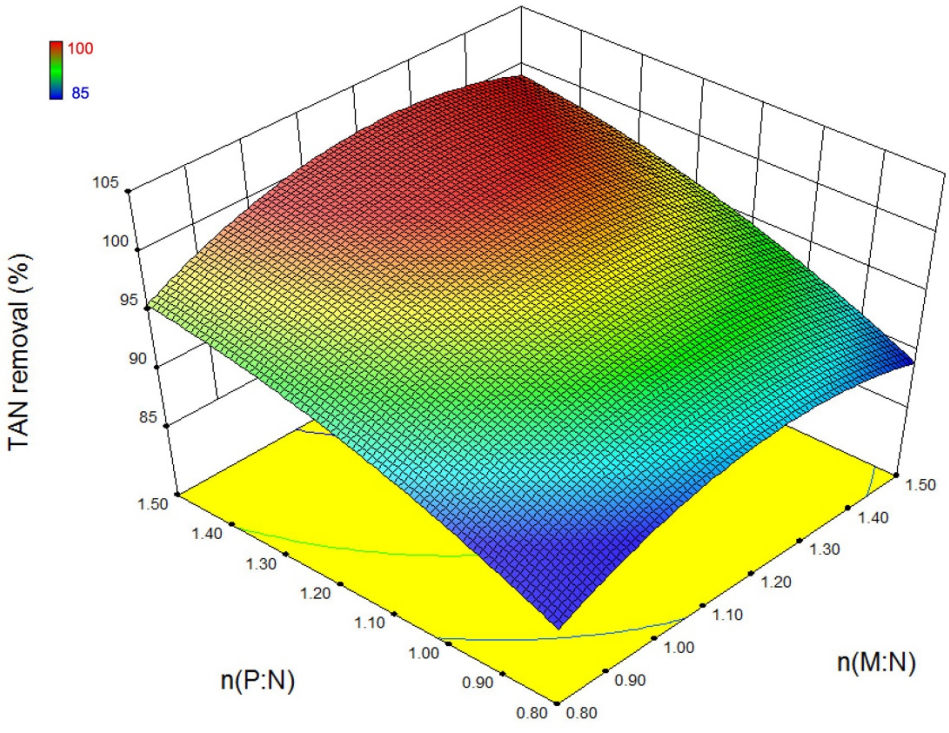

Fig. 5. 7 RSM model of TAN removal by struvite formation at pH = 9

5.3.4 Thermal treatment of struvite by oven heating

Although struvite precipitation has been shown to be a powerful and efficient method for dealing with wastewater containing a high concentration of ammonia, it is still hampered by some drawbacks, including the high dose and costs of precipitants and the further disposal of the sludge (Kurniawan et al., 2006). These drawbacks also explain the lack of practical application of magnesium ammonium phosphate (MAP) chemical precipitation worldwide (Yu et al., 2013). Some attempts have been made to address this issue, including the use of low-grade magnesium and phosphate sources, such as MgO (Chimenos et al. 2003; Quintana et al. 2008), brine and bittern (Lee et al., 2003) and the pyrolysate of magnesite (Huang et al., 2011). Additionally, the process of reusing the decomposition product of struvite has been investigated by scholars to both maintain high total ammonia nitrogen removal and reduce costs of operation (He et al., 2007; Huang et al., 2009; Türker and Çelen, 2007; Yu et al., 2013; Zhang et al., 2009). Huang et al. (2009) introduced recycling of MAP by dry pyrolysis, which could achieve an ammonia removal efficiency of 99%.

The theoretical mass loss for the formula ($MgNH_4PO_4 \cdot 6H_2O$) is 51.42%, and is made up of a mass loss for water of 44.08% and for ammonia of 7.34% (Frost et al., 2004). It has been reported that heating MAP results in the expulsion of all of the water due to hydration from $MgNH_4PO_4 \cdot 6H_2O$ (MAP), and of the chemically bound ammonia, leading to the formation of magnesium hydrogen phosphate ($MgHPO_4$), commonly known as newberyite (Frost et al., 2004; Wang et al., 2006). Sugiyama et al. (2005), using X-ray diffraction analysis of the thermal disintegration of MAP, confirmed the possible residual composition as a mixture of $MgHPO_4$ (MHP) and $Mg_2P_2O_7$. The study of Bhuiyan et al. (2008) suggested that MAP can be thermally decomposed into a mixture of $MgHPO_4$, $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$. Possible reactions can be expressed as in Eq. (5.7), (5.8), (5.9), and (5.10) during the pyrolysis process (Chen et al., 2015). When the pyrolysis temperature is within the range of 80 ℃ to 227 ℃, the dominant component of struvite pyrolysate is MHP (Sugiyama et al., 2005). When struvite encounters higher temperatures, magnesium pyrophosphate is likely to form in the residuals (Sugiyama et al., 2005).

$$MgNH_4PO_4 \cdot 6H_2O \xrightarrow{heat} MgNH_4PO_4 \cdot H_2O + 5H_2O \uparrow \quad \text{Eq. (5.7)}$$

$$MgNH_4PO_4 \cdot 6H_2O \xrightarrow{heat} MgHPO_4 \cdot 3H_2O + 3H_2O \uparrow + NH_3 \uparrow \quad \text{Eq. (5.8)}$$

$$3MgNH_4PO_4 \cdot 6H_2O \xrightarrow{heat} Mg_2P_2O_7 + MgHPO_4 + 18H_2O \uparrow + 3NH_3 \uparrow \quad \text{Eq. (5.9)}$$

$$2MgHPO_4 \xrightarrow{heat} Mg_2P_2O_7 + H_2O \uparrow \quad \text{Eq. (5.10)}$$

MHP is also reported as the principle component of MAP pyrolysates for further ammonia removal from an aqueous system, as compared to $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$, based on the research of Sugiyama et al. (2005). They explained that MHP has a greater solubility (0.3 g/100 mL) than $Mg_3(PO_4)_2$ (0.02 g/100 mL) and $Mg_2P_2O_7$, which barely dissolves in water. The reaction of these three possible pyrolysates of struvite in a synthetic ammonia solution were shown to be as follows in Eq. (5.11), (5.12) and (5.13):

$$MgHPO_4 \cdot 3H_2O(s) + NH_4^+(aq) + 3H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + H^+ \quad \text{Eq. (5.11)}$$

$$Mg_3(PO_4)_2 + 2NH_3 + 14H_2O \rightarrow 2MgNH_4PO_4 \cdot 6H_2O + Mg(OH)_2 \quad \text{Eq. (5.12)}$$

$$Mg_2P_2O_7 + 2NH_3 + 13H_2O \rightarrow 2MgNH_4PO_4 \cdot 6H_2O \quad \text{Eq. (5.13)}$$

In order to enhance the ammonia release from struvite and the TAN removal from an aqueous solution, struvite was heated with an alkaline addition, such as sodium hydroxide (NaOH) or magnesium hydroxide ($Mg(OH)_2$) powders (Türker and Celen, 2007; Yu et al., 2013). Higher ammonia-removal efficiency by the alkaline pyrolysis of struvite produced than direct heating has been reported in previous studies. He et al. (2007) has suggested that struvite regeneration under alkaline conditions could be expressed as Eq. (5.14) and Eq. (5.15), which could solve the problem of precipitant costs in recycling struvite and could help create suitable pH conditions for struvite reformation. The active

product of the NaOH pyrolysis of struvite is magnesium sodium phosphate ($MgNaPO_4$), which can react with NH_4^+ to form struvite (Huang et al., 2015). Up to 96% of the ammonia in struvite powder could be released with sodium hydroxide addition, and 84% TAN removal from synthetic wastewater could occur under the following conditions: a molar concentration ratio for $NH_4^+ : OH^- = 1.0:1.0$; a heating temperature of 90 ℃; and a heating time of 2 hour (He et al. 2007).

$$MgNH_4PO_4 \cdot 6H_2O + NaOH(s) \xrightarrow{heat} MgNaPO_4\,(s) + 7H_2O \uparrow + NH_3 \uparrow \quad \text{Eq. (5.14)}$$

$$MgNaPO_4 + NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O\,(s) \downarrow + Na^+ \quad \text{Eq. (5.15)}$$

From the TGA curve in Fig. 5.8, it may be seen that the mass of MAP gradually drops with increasing temperature, and a sharp decline occurs between approximately 60 ℃ and 120 ℃. Such a phenomenon can be explained by dehydration and ammonia release (Bhuiyan et al., 2008; Chen et al., 2015; He et al., 2007; Sugiyama et al., 2005). In order to maximize the amount of MHP instead of $Mg_2P_2O_7$, the MAP decomposition temperature should be controlled within the range of 60 ℃ to 180 ℃ (Chen et al., 2015).

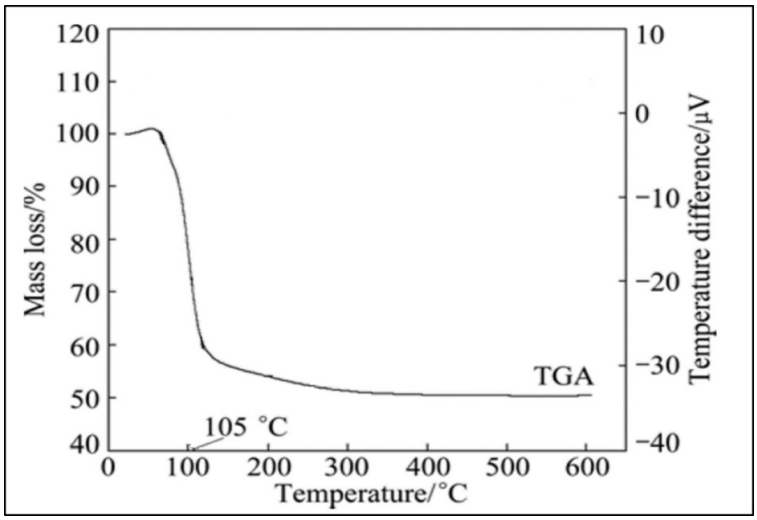

Fig. 5. 8 Thermogravimetric analysis (TGA)-Differential thermal analysis (DTA) curve of struvite (Adapted from Chen et al. 2015)

5.3.4.1 Effect of heating time

To investigate the effect of heating time on the ammonia removal performance of struvite pyrolysate, dry struvite powder was first heated in an oven (105 ℃) for a certain period of time and then dosed (40 g/L) into the landfill leachate. Heating duration was changed from 0.5 to 3 hours with 30 min increments. The results shown in Fig. 5.9 indicate that TAN removal efficiency was significantly enhanced as the pyrolysis time increased from 0.5 to 2.5 hours, but dropped slightly at 3 hours. Initially, after 0.5 hour, oven-treated struvite did not provide satisfactory ammonia removal (37.4%). Nevertheless, the TAN removal ratio jumped to approximately 67% at 1 hour, and gradually climbed to 81.2% at 1.5 hour and then stabilized from 1.5 to 2.5 hours. At a temperature of 105 ℃, as the heating time was prolonged, struvite dissociated and presumably produced a growing amount of $MgHPO_4$, which has a moderate solubility in water and can react with NH_4^+ to precipitate struvite, was likely to occur. This could explain the increasing TAN removal by residues of thermally-treated struvite in the first 2.5 hours. A slight drop in TAN removal rate was observed when heating duration reached 3 hours, which could be due to the presence of $Mg_2P_2O_7$ and $Mg_3(PO_4)_2$ in the thermally treated struvite. Optimum heating time for struvite decomposition is between 1.5 and 2.5 hour in this study.

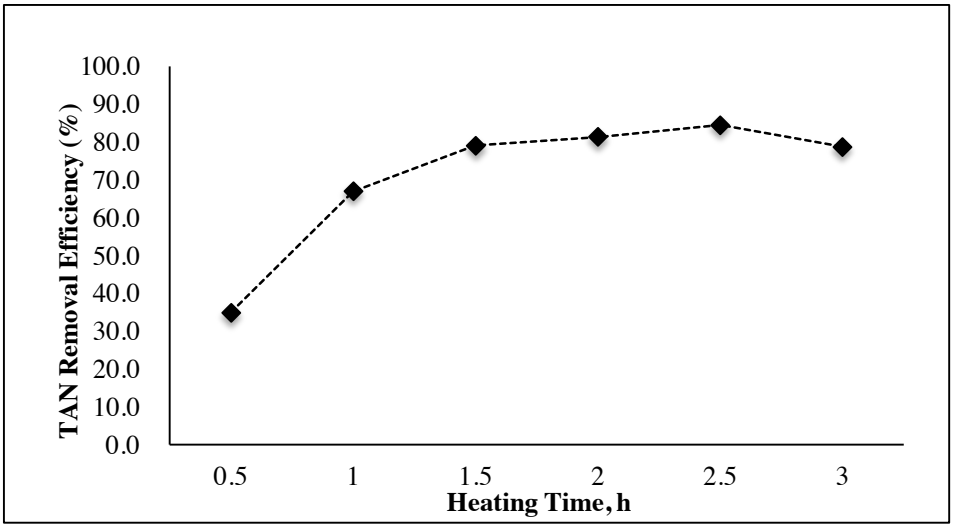

Fig. 5. 9 TAN removal efficiency in landfill leachate by the use of struvite pyrolysate generated at different heating times at 105℃ (at 1,878 mg TAN/L and pH of 9)

5.3.4.2 Effect of heating temperature

In this study, struvite generated from the landfill leachate was thermally treated by oven heating at temperatures ranging between 75 ℃ and 140 ℃ (specifically, 75, 90, 105, 120 and 140 ℃) and a pyrolysis time of 2.5 hours. Subsequently, the removal of total ammonia nitrogen from simulated wastewater by using the residues (60 g/L) generated from the struvite pyrolysis as magnesium and phosphate source was performed at pH 9.5 and a reaction time of 20 min. As may be noted from Fig. 5.10, when the temperature increased from 75 ℃ to 105 ℃, it was observed that TAN removal efficiency increased progressively from approximately 73.2% to over 97%. However, when the pyrolysis temperature continued to rise, a downward trend in TAN removal was observed, from 97.2% at 105 ℃ and 78.7% at 130 ℃ to 92.5% at 140 ℃. When struvite was pyrolyzed at 105 ℃ for more than 2.5 hours, the amount of $Mg_2P_2O_7$ and $Mg_3(PO_4)_2$ started to accumulate with increasing temperature. In particular, $Mg_2P_2O_7$ and $Mg_3(PO_4)_2$ make almost no contribution to the removal of ammonium because of their poor solubility. Based on the results discussed above, 105 ℃ could be assumed to be the optimum temperature for struvite decomposition for further used in aqueous ammonia elimination.

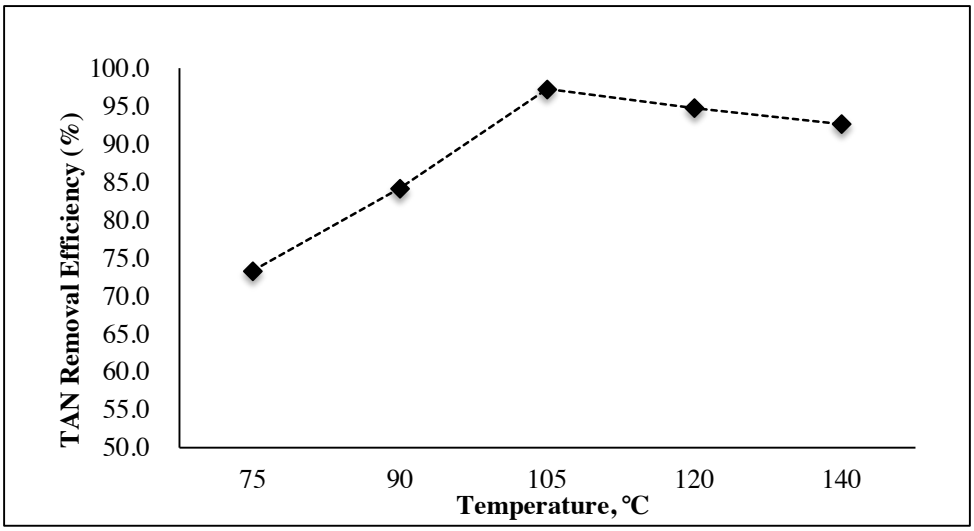

Fig. 5. 10 TAN removal from landfill leachate by the use of struvite pyrolysate generated at different pyrolysis temperatures for a heating duration of 2.5h (at 1,878 mg TAN/L and pH of 9)

5.3.4.3 Effect of dosage

The effect of the struvite pyrolysate dosage on the TAN removal was investigated by adding struvite residues of 10 g/L to 60 g/L into the landfill leachate containing 1,878 mg/L TAN. The experimental data are given in Fig. 5.11. The results reveal that the TAN removal efficiency increases progressively with increasing amounts of pyrolyzed struvite. Relatively low TAN removals were observed of 24.2% and 39.4% for 10 g/L and 20 g/L, respectively. When oven-treated struvite residues were dosed at 30 g/L into the synthetic solution, the TAN removal rate leaped to 77.6%. Elimination percentages of TAN continued to increase gradually from 40 g/L (87.5%) to 60 g/L, with the best value (97.2%) occurring for 60 g/L. Although higher dosage of the struvite pyrolysate results in better performance on TAN removal from the leachate, this could result excessive phosphate in the effluent, which would require further treatment.

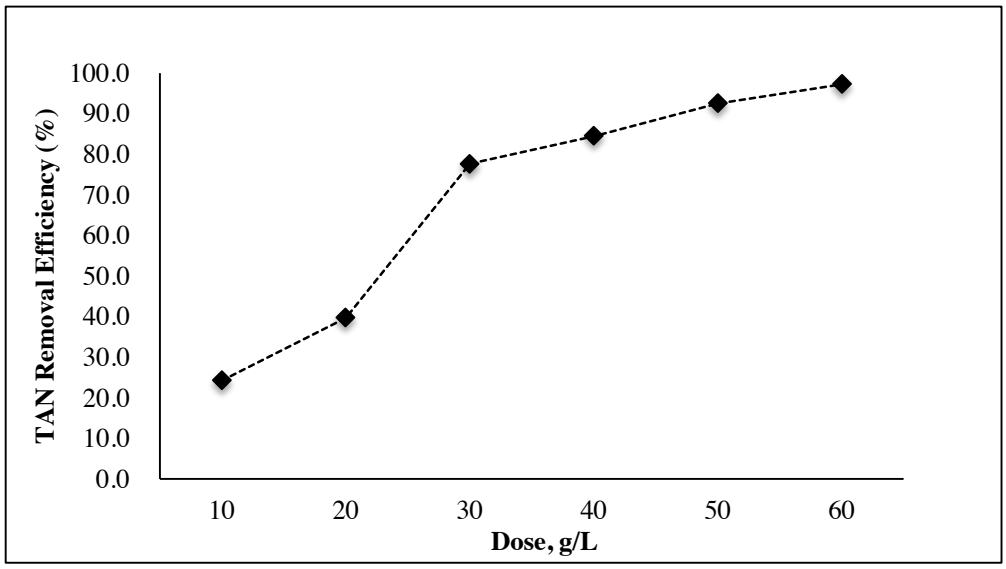

Fig. 5. 11 Effect of the dosage of struvite pyrolysate (heating time=2.5h and heating temperature=105 ℃) on the removal of TAN from landfill leachate (at 1,878 mg TAN/L and pH of 9)

5.3.4.4 Effect of pH

Similar to the previous study, to determine the optimum pH for the reuse of the struvite pyrolysate, experiments were performed at pHs in the 8.5–10.5 range, with a dose of 40 g/L and a reaction time of 20 min. The experimental results are shown in Fig. 5.12. The pH value of the solution was discovered to be an important factor for TAN removal by the pyrolysate. TAN removal efficiency increased slightly from 80.9% to 84.5% with pH value rising from 8.5 to 9.5. However, when the pH continued to increase further, TAN removal showed an obvious downward trend, from 84.5% at pH = 9.5 and 76.7% at pH = 10 to 72.9% at a final pH of 10.5. As the pH rises from 9 to 10, the conversion of NH_4^+ to NH_3, which cannot be precipitated as struvite, accelerates, and magnesium phosphate ($Mg_3(PO_4)_2$) begins to form instead of struvite. With increasing formation of $Mg_3(PO_4)_2$, struvite precipitation is blocked, resulting in the decrease of the NH_4-N elimination. When pH is lower than the optimum point (pH = 9.5), the formation of struvite is inhibited by rising levels of hydrogen ions (Huang et al., 2015). Therefore, as shown in this study, the optimum pH for ammonia nitrogen removal efficiency is 9.5.

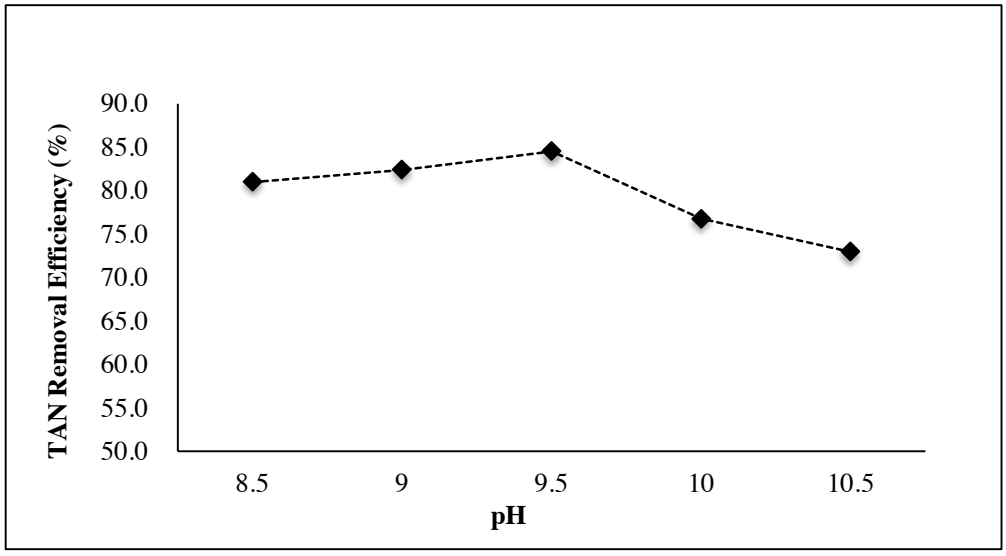

Fig. 5. 12 Effect of pH on TAN removal from landfill leachate with 40 g/L of struvite pyrolysate heated for 2.5 h at 105 ℃(at 1,878 mg TAN/L)

5.3.4.5 Effect of multiple cycles of treated struvite reuse

As previously mentioned, to reduce reagent consumption, the recycling of struvite decomposition residues was investigated. However, gradual decline in TAN removal efficiency with increasing recycling times needs to be investigated. This was mainly caused by the accumulation of magnesium pyrophosphate ($Mg_2P_2O_7$) and magnesium phosphate ($Mg_3(PO_4)_2$), which have negative impact on ammonium removal.

During the multiple recycling processes of struvite decomposition product, two recycling modes were conducted to investigate the performance of the decomposition product as a source for magnesium and phosphate in TAN removal from landfill leachate. First, the decomposition product was used at 60 g/L directly and repeatedly at a pH of 9.5. Second, the decomposition product of NaOH-mediated struvite pyrolysis was dosed at 60 g/L into the leachate, also at a pH of 9.5. Both modes were without any further supplement of magnesium and phosphate salts. Experimental results (Fig. 5.13) show that TAN removal efficiencies decreased as the number of recycling periods increased from 1 to 5 times for both modes. The TAN removal rate with direct heating of struvite was 97.2% in the first cycle and 72.3% in the fifth cycle. For the second mode, compared to direct heating, the TAN removal ratio decreased less significantly with increased recycling numbers during the struvite decomposition recycling with NaOH pyrolysis. The TAN removal with sodium hydroxide-adjusted struvite was 98.4% in the first cycle and 81.3% in the final cycle. The reason why TAN elimination efficiency dropped may be attributed to the growing amount of inactive amorphous $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$ in the regenerated pyrolysate, as they have poor solubility and hardly react with NH_4^+ to further precipitate struvite. The losses of Mg^{2+} and PO_4^{3-} in the supernatant per cycle time could also be responsible for the declining TAN removal rate. In addition, the accumulation of some metal ions such as K^+, Ca^{2+}, Fe^{3+} and Al^{3+} in the leachate may also be an important factor toward inhibiting the formation of struvite (Huang et al., 2011). For example, the presence of K^+ in the leachate could compete with NH_4^+ to form K-struvite ($MgKPO_4 \cdot 6H_2O$) and Ca^{2+} could consume some of the PO_4^{3-} to precipitate calcium phosphate ($Ca_3(PO_4)_2$), which inhibited the crystallization of struvite, resulting in the potential impurity of the sludge (Di Iaconi et al., 2010).

In the published literature, Türker and Çelen (2007) reported that the TAN removal was initially 92%, and that it decreased progressively to 77% in the fifth cycle. Huang et al. (2009) recycled the pyrolysis product of struvite five times and discovered that the TAN removal percentages decreased from 80% in the first cycle to 67% in the fifth cycle. He et al. (2007) investigated TAN removal from landfill leachate by recycling the NaOH-mediated pyrolysate of struvite, and reported that it rapidly decreased from > 90% in the first cycle to < 65% in the sixth cycle. Yu et al. (2013) reported that, when fertilizer wastewater was treated by recycling struvite pyrolysate by acidolysis, TAN removal levels of 90.7% in the first cycle and 79.4% in the sixth cycle were achieved. Similar research reinforces the results of this study. Therefore, with regard to the multiple recycling of the struvite decomposition product, the proposed process demonstrated a moderate performance on TAN removal, with NaOH-adjusted pyrolysate of struvite having a better ability for absorbing ammonia from landfill leachate.

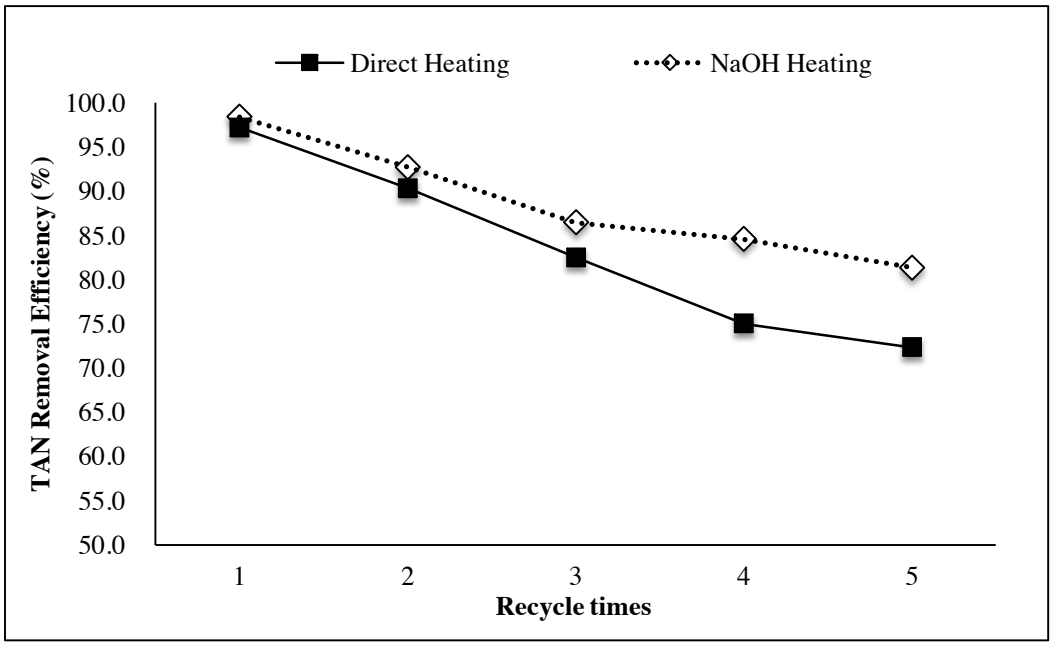

Fig. 5. 13 Repeat use of the struvite pyrolysate (heating time=2.5h and heating temperature=105 ℃) by direct heating and NaOH-mediated heating as a precipitator in TAN removal from landfill leachate (1,878 mg TAN/L, pH = 9, struvite pyrolysate dosage = 60 g/L)

5.3.5 Struvite decomposition by microwave irradiation

Microwave (MW) irradiation is an alternative to conventional heating methods, such as oven convection heating. They reduce the reaction time dramatically by using the longer wavelengths and lower frequencies in the electromagnetic spectrum (Eskicioglu et al., 2011). Microwaves produce homogeneous and quick thermal reactions due to molecular-level heating, which saves considerable time and energy for a similar degree of heating as compared to conventional heating methods (Menéndez et al., 2002). In the published studies, microwave irradiation has been reported to be a powerful tool in the degradation of various organic compounds, including pesticides, ammonia nitrogen and organic dyes in domestic, industrial and medical wastewater (Remya and Lin, 2011). High removal efficiencies of ammonia have been achieved by microwave radiation in bench-scale experiments (Zhang et al., 2007). The mechanism for ammonia removal was proposed as the evaporation of NH_3 by MW irradiation (Lin et al. 2009). Other advantages of MW technology for wastewater treatment based on pollutant degradation may involve selective heating, friendly operational controls and increasing the yield and purity of products (Chou et al., 2015; Lei et al., 2008; Tyagi and Lo, 2013).

However, to the best of our knowledge, thermal treatment of struvite by microwave irradiation has been reported rarely up to this date. Only Cho et al. (2009) have demonstrated that microwave-treated struvite can be recycled again to the influent wastewaters for further struvite precipitation, so as to reduce the treatment costs. Taking account of MW's advantages, it might be an efficient way to decompose struvite and increase its recycling application in ammonia removal from landfill leachate.

Struvite powders were thermally treated by MW at two power levels (600 W and 1200 W) for five different heating times (1 min, 5 min, 10 min, 20 min and 30 min). After each process, struvite powders were cooled and then dosed at 60 g/L into 100 mL of landfill leachate containing 1,878 mg/L of TAN. The reaction took place under the following conditions: pH = 9.5, stirring time = 20 min, settling time = 15 min and reaction temperature = 25 ℃. Total ammonia nitrogen concentration was then measured from the supernatant of the treated solutions. As may be seen from the results displayed in Fig. 5.14, low TAN removal efficiencies (< 30%) were found for both microwave

power outputs when the heating time was no longer than 5 min. This could be the result of incomplete decomposition of struvite, so that its pyrolysates can hardly dissolve in the solution. After ten minutes of microwaving time, the MWs with 1200 W demonstrated merely 1.4% more TAN elimination (69.2%) than MWs with 600 W (71.6%), despite the former power output being double the latter one. TAN removal continued to rise to 88.9% for 1200 W and 85.4% for 600 W at a heating time of 20 min before it reached the peaks of 99.0% and 92.0% after 30 min of irradiation, respectively. Through these series of experiments, microwave irradiation, especially at a high power level, has shown to be efficient in dissociating struvite that eventually recycles back to treat aqueous ammonia, based on the relatively high TAN removal. However, to the best of our knowledge, no supportive studies have been published.

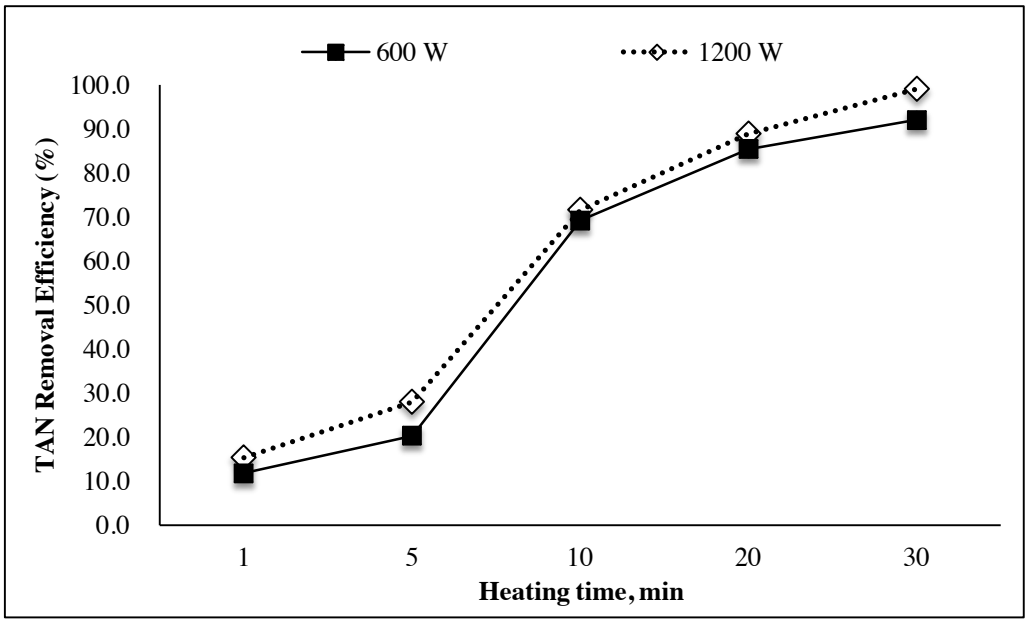

Fig. 5. 14 TAN removal efficiency in landfill leachate by the use of struvite pyrolysate generated at different heating time by microwave irradiation (pH = 9.5, pyrolysate dosage = 60 g/L)

Similar to the previous steps, struvite powders were thermally treated by MW irradiation at two power levels (600 W and 1200 W) and a heating time of 30 min in each run. Struvite residues were dosed at 60 g/L back into the landfill leachate to absorb

ammonium at pH = 9.5. The results (Fig. 5.15) displayed that, after struvite had been recycled for five times, the TAN removal declined remarkably from 99.0% to 69.2% for 1200 W, and 92.0% to 66.5% for 600 W, respectively. As mentioned previously, the decrease in TAN elimination efficiency may be due to the accumulation of inactive $Mg_3(PO_4)_2$ and $Mg_2P_2O_7$ in the regenerated pyrolysate. The losses of Mg^{2+} and PO_4^{3-} in the supernatant with each cycle time could also be responsible for the declining TAN removal. Besides, the accumulation of some component (calcium, potassium) from landfill leachate might inhibit the formation of struvite and hamper its recycling use in later runs.

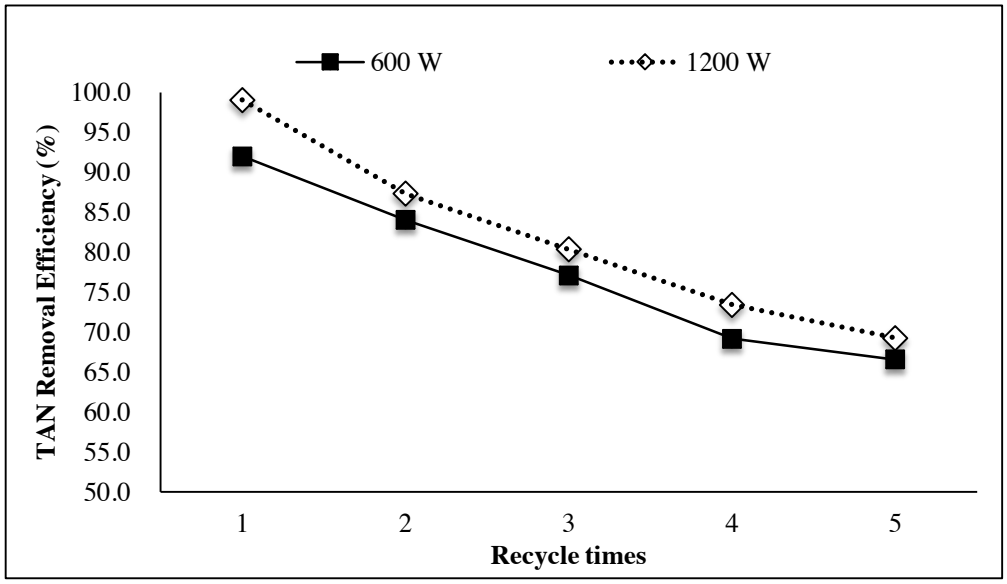

Fig. 5. 15 Repeated use of the struvite pyrolysate from microwave irradiation with two different power outputs, as a precipitator in TAN removal from landfill leachate (pH = 9, pyrolysate dosage = 60g/L)

5.4 Conclusion

Experimental results indicated that chemical precipitation by struvite formation can be a promising method for ammonia removal from landfill leachate. By recycling the thermal residue of struvite, continuously removing ammonia can technically be achieved.

In the struvite precipitation, ammonia removal significantly depended on the reaction pH and molar ratios of $NH_4^+ : Mg^{2+} : PO_4^{3-}$. Optimum pH was reported to be in the range of 9 to 9.5. The best combinations of added reagents were $NH_4^+ : Mg^{2+} : PO_4^{3-}$ = 1.0:1.3:1.3, 1.0:1.4:1.3, 1.0:1.5:1.4 and 1.0:1.5:1.5, all of which displayed remarkable TAN removal efficiencies of over 99%. Response surface methodology (RSM) helps to analyze the data and optimize the results. In the recycling phase, the struvite pyrolysate formed by NaOH-mediated pyrolysis performed with greater ability to continuously treat ammonia solution (97.2% removal at the beginning and 72.3% in the fifth round), than did directly heated struvite (98.4% in the first cycle and 81.3% in the final cycle). Additionally, microwave irradiation could also dissociate struvite, which subsequently demonstrated moderate TAN removal in each run.

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CHAPTER VI

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

The results demonstrated that chemical precipitation by struvite formation is an efficient method for ammonia removal from aqueous solutions and landfill leachate. In addition, by recycling the thermal residue of struvite, continuously removing ammonia can technically be achieved and the reagent consumption could be saved.

Excessive magnesium and phosphate sources are necessary to force struvite to form. In the struvite precipitation, ammonia removal significantly depended on the pH and chemical molar ratios of $NH_4^+ : Mg^{2+} : PO_4^{3-}$. The optimum pH was found to be in the range of 9 to 9.5. For synthetic solution with initial total ammonia nitrogen (TAN) concentration of 1,000 mg/L, remarkable TAN removal efficiency of over 98% has been reported when the molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$ equaled 1.0:1.2:1.2, 1.0:1.3:1.3, 1.0:1.3:1.4 and 1.0:1.5:1.5. The optimum combinations of reagents applied in landfill leachate (TAN=1,878 mg/L) were $NH_4^+ : Mg^{2+} : PO_4^{3-}$ =1.0:1.3:1.3, 1.0:1.4:1.3, 1.0:1.5:1.4 and 1.0:1.5:1.5, all of which displayed over 99% TAN removal efficiencies. However, in order to both achieve satisfactory ammonia removal and to reduce chemical consumption, pH should controlled at 9 with less alkali addition and molar ratio of $NH_4^+ : Mg^{2+} : PO_4^{3-}$= 1.0:1.2:1.3 and 1.0:1.3:1.3 should be considered. Response surface method (RSM) helped to analyze the date and optimize the results.

The struvite pyrolysate provided best performance of removing ammonia in both simulated wastewater and landfill leachate at a dosage of 60 g/L and pH in the range of 9 to 9.5, when struvite was previously heated at 105 ℃ for 2.5 h**.** In the recycling phase, the struvite pyrolysate resulting from NaOH-mediated pyrolysis was more effective at continuously treating ammonia synthetic solution than was direct heating, with an initial mode of 87.4% at the beginning to 75.1% in the fifth round and direct heating of struvite

from 80.9% in the first cycle and 60.6% in the final cycle. The struvite pyrolysate formed by NaOH-mediated pyrolysis performed with greater ability to continuously eliminate ammonia from landfill leachate (97.2% removal at the beginning and 72.3% in the fifth round), than did directly heated struvite (98.4% in the first cycle and 81.3% in the final cycle). Therefore, recycling thermal-pretreated struvite to treat landfill leachate containing high concentration of ammonia is feasible and operation costs could be reduced.

Microwave irradiation could also dissociate struvite, which subsequently demonstrated moderate TAN removal in recycling phases. Considering microwave can shorten the heating time to dissociate struvite at high power output, it should be considered as primary heating method in the future research.

6.2 Future work

It is costly and cumbersome to determine that how much additional magnesium source and phosphate source are needed because leachate composition can vary from one site to another. To tackle the problem, a computer program such as Visual Minteq might be used to predict struvite precipitation for ammonia removal in leachate and other possible compounds formation.

As explained in previous chapters, struvite can precipitate with other chemicals in the leachate. To produce as pure struvite as possible becomes a new challenge for the application of this process. Future research could involve purification of struvite, which could enhance its recycling use.

Since $MgCl_2 \cdot 6H_2O$ could release huge amounts of salts (chlorides) and excessive phosphate could be observed in the effluent if $MgCl_2 \cdot 6H_2O$ and H_3PO_4 are dosed with large quantity, potential subsequent biological treatment is needed.

APPENDIX

Temperature profile of using microwave at 600W and 1200W power output with different irradiation time