

STRUVITE PRECIPITATION FOR THE RECOVERY OF AMMONIUM  
NITROGEN FROM LANDFILL LEACHATE

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A thesis submitted in fulfilment of the  
requirements for the award of the degree of  
Doctor of Philosophy (Civil Engineering)

Faculty of Civil Engineering  
Universiti Teknologi Malaysia

AUGUST 2017

*To my beloved parents, brother and sisters*

*To my elder brother Yahya ... Mercy of Allah be upon him*

*To my lovely wife, Dr. Shaymaa Mustafa, and sons, Yahya and Omar*

*To my country ... Palestine*

## ACKNOWLEDGEMENTS

First and above all, I am praise to Allah, The Almighty, for giving me strength and patience to complete this study. My deepest gratitude goes to my supervisor, Prof. Dr. Azmi bin Aris, who expertly guided me through my PhD study. His understanding, personal generosity and support made it possible for me to work on a topic that was of great interest to me. Also, I would like to express my sincere appreciation to my co-supervisors, Dr. Mohd Hafiz bin Puteh and Assoc. Prof. Dr. Aeslina binti Abdul Kadir, for giving many helpful advices that improved the quality of my study.

I would like to extend my sincerest thanks to Assoc. Prof. Dr. Zaiton Abdul Majid, Faculty of Science, for finding out time to share her experience and knowledge in XRD analysis results. Special thanks are also sent to SWM Environment SDN BHD for their cooperation in the collection of leachate samples from Seelong Landfill Site. I would like to acknowledge Universiti Teknologi Malaysia for supporting this study under Research University Grant Scheme (Vot No. Q.J130000.2509.12H27). Also, I would like to acknowledge with gratitude the Ministry of Higher Education, Malaysia for sponsoring me through the MIS scholarship.

Last but not least, I must express my most appreciations to my parents, Dr. Said Darwish and Mrs. Maha Darwish, my wife, Dr. Shaymaa Mustafa, and my children, Yahya and Omar, for their support and encouragement, which greatly helped me to accomplish this study.

## ABSTRACT

Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , MAP) precipitation is an effective method to recover ammonium nitrogen ( $\text{NH}_4\text{-N}$ ) from wastewater into a valuable and environmental friendly material. It is crystallized by a chemical reaction between  $\text{NH}_4\text{-N}$ , Mg and P, which is affected by several factors, mainly pH, molar ratios, foreign ions and mixing intensity ( $G$ ). Landfill leachate (LL) contains high concentration of  $\text{NH}_4\text{-N}$  that should be treated properly to avoid the environmental pollution problems. Therefore, the aim of this study is to develop a sustainable approach for  $\text{NH}_4\text{-N}$  recovery from municipal LL via MAP precipitation technology. The study investigated a low-cost P source, optimized  $\text{NH}_4\text{-N}$  recovery in terms of pH, Mg:N, K:N and  $G$ , studied the effect of organic matter and determined the effect and sorption mechanism of cadmium (Cd) and nickel (Ni) during MAP precipitation. Three types of waste bones were tested for low-cost P source; fish, chicken and cow waste bone ash. Fish bone ash contained the highest P content (17% wt.). The P extraction by acidic leaching was optimized by Response Surface Methodology (RSM) and the results showed that applying 2M  $\text{H}_2\text{SO}_4$  and 1.25 kg  $\text{H}_2\text{SO}_4/\text{kg}$  ash resulted with extracting 95% of P. The extracted P solution (150 g-P/L) was applied successfully in MAP precipitation. Recovery of  $\text{NH}_4\text{-N}$  in synthetic LL was optimized by RSM. Maximum  $\text{NH}_4\text{-N}$  recovery (90%) was achieved at pH 8.5, Mg:N = 1.25, K:N = 0.1 and  $G = 95 \text{ s}^{-1}$ . The effect of organic matter on MAP recovery was determined using synthetic and actual LL (filtered and unfiltered). Propionic, butyric and acetic acids formulated the organic content in synthetic LL, in which an insignificant effect was noticed with minor removal of total organic carbon (TOC) (6.30-13.96%). For actual LL,  $\text{NH}_4\text{-N}$  recovery efficiencies were 93%, 71% and 28% using  $\text{MgCl}_2 + \text{Na}_2\text{HPO}_4$ , MgO+P solution and MgO+ $\text{Na}_2\text{HPO}_4$ , respectively. It was also found that Cd and Ni were co-precipitated with MAP, forming struvite analogues, which could affect the purity of MAP. Sustainability of  $\text{NH}_4\text{-N}$  recovery has to be further improved to be efficient for large-scale applications of LL treatment.

## ABSTRAK

Pemendakan struvit ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , MAP) merupakan satu kaedah yang berkesan untuk perolehan semula nitrogen ammonia ( $\text{NH}_4\text{-N}$ ) daripada air sisa kepada bahan yang berharga dan mesra alam. Ia membentuk kristal melalui tindak balas kimia di antara  $\text{NH}_4\text{-N}$ , Mg dan P, yang dipengaruhi oleh beberapa faktor, terutamanya pH, nisbah molar, ion-ion luaran dan keamatan pembauran ( $G$ ). Air larut lesap daripada tapak pelupusan sisa pepejal (LL) mengandungi  $\text{NH}_4\text{-N}$  pada kepekatan tinggi yang perlu dirawat dengan baik untuk mengelakkan masalah pencemaran alam sekitar. Oleh itu, tujuan kajian ini adalah untuk membentuk satu kaedah mampan bagi memperolehi  $\text{NH}_4\text{-N}$  daripada LL menggunakan teknologi pemendakan MAP. Kajian ini mengkaji satu sumber P berkos rendah, mengoptimumkan perolehan  $\text{NH}_4\text{-N}$  dari aspek pH, Mg:N, K:N dan  $G$ , mengkaji kesan bahan organik dan menentukan kesan dan mekanisma jerapan kadmium (Cd) dan nikel (Ni) semasa pemendakan MAP. Tiga jenis sisa tulang telah diuji bagi sumber P berkos rendah, iaitu abu sisa tulang ikan, ayam dan lembu. Abu tulang ikan mempunyai kandungan P tertinggi (17% berat). Pengekstrakan P oleh larut lesapan asid telah dioptimumkan dengan Kaedah Permukaan Tindak Balas (RSM) dan hasil kajian menunjukkan bahawa penggunaan 2M  $\text{H}_2\text{SO}_4$  dan 1.25 kg  $\text{H}_2\text{SO}_4/\text{kg}$  abu menghasilkan pengestrakan 95% P. Larutan P yang diekstrak (150 g-P/L) telah berjaya digunakan dalam pemendakan MAP. Perolehan  $\text{NH}_4\text{-N}$  dalam sintetik LL telah dioptimumkan menggunakan RSM. Perolehan maksimum  $\text{NH}_4\text{-N}$  (90%) dicapai pada pH 8.5, Mg:N = 1.25, K:N = 0.1 dan  $G = 95 \text{ s}^{-1}$ . Kesan bahan organik terhadap perolehan MAP ditentukan dengan menggunakan LL sintetik dan sebenar (dituras dan tidak dituras). Asid propionik, butirik dan asetik dirumuskan untuk kandungan organik dalam LL sintetik, yakni kesan yang tidak ketara didapati dengan penyingkiran kecil jumlah karbon organik (TOC) (6.30-13.96%). Bagi LL sebenar, masing-masing perolehan  $\text{NH}_4\text{-N}$  sekitar 93%, 71% dan 28% telah dicapai dengan menggunakan  $\text{MgCl}_2 + \text{Na}_2\text{HPO}_4$ , larutan MgO+P dan MgO+ $\text{Na}_2\text{HPO}_4$ . Juga didapati Cd dan Ni mendak bersama dengan MAP, membentuk analog struvit yang boleh menjejaskan keaslian MAP. Kemampunan perolehan  $\text{NH}_4\text{-N}$  perlu dipertingkatkan lagi supaya lebih berkesan untuk penggunaan rawatan LL pada skala yang lebih besar.

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## LIST OF ABBREVIATIONS

AAS	-	Atomic absorption spectrometry
ANOVA	-	Analysis of variance
BOD	-	Biological oxygen demand
COD	-	Chemical oxygen demand
EBPR	-	Enhanced Biological Phosphorus Removal
Eqn.	-	Equation
FBA	-	Fish bone ash
HRT	-	Hydraulic retention time
ICP-OES	-	Inductively coupled plasma-optical emission spectroscopy
LL	-	Landfill leachate
MAP	-	Magnesium ammonium phosphate (Struvite)
MPP	-	Magnesium potassium phosphate (Struvite-K)
SEM-EDX	-	Scanning electron microscopy-Energy dispersive X ray
SS	-	Suspended solids
TC	-	Total carbon
TOC	-	Total organic carbon
TSS	-	Total suspended solids
WWTP	-	Wastewater Treatment Plant



**LIST OF SYMBOLS**

Al	-	Aluminum
As	-	Arsenic
°C	-	Celsius
Ca	-	Calcium
CaHPO <sub>4</sub> ·2H <sub>2</sub> O	-	Dicalcium phosphate
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	-	Monocalcium phosphate
Cd	-	Cadmium
CH <sub>3</sub> COOH	-	Acetic acid
Cl	-	Chloride
Cr	-	Chromium
Cu	-	Copper
<i>G</i>	-	Mixing intensity
h	-	Hour
H <sub>2</sub> SO <sub>4</sub>	-	Sulfuric acid
H <sub>3</sub> PO <sub>4</sub>	-	Phosphoric acid
HCl	-	Hydrochloric acid
K	-	Potassium
M	-	Mole
Mg	-	Magnesium
MgCl <sub>2</sub> ·6H <sub>2</sub> O	-	Magnesium chloride hexahydrate
MgO	-	Magnesium oxide

Mg(OH) <sub>2</sub>	-	Magnesium hydroxide (Brucite)
N	-	Nitrogen
Na <sub>2</sub> HPO <sub>4</sub> ·2H <sub>2</sub> O	-	Disodium phosphate dihydrate
NaClO	-	Sodium hypochlorite
NaOH	-	Sodium hydroxide
NH <sub>4</sub> -N	-	Ammonium nitrogen
Ni	-	Nickel
P	-	Phosphorus
PO <sub>4</sub>	-	Phosphate
<i>t</i> <sub>d</sub>	-	Mixing duration
Zn	-	Zinc

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Overview

Landfilling is a common method applied for solid waste disposal, especially in low- and middle-income countries. It is recognized as an important option both now and in the near future. In Malaysia, 95% of the collected solid wastes are landfilled, with roughly 5% being recycled (Johari et al., 2014). Such situation has several consequences on the environment around the landfills, as the huge amounts of wastes produce different by-products, such as biogas and leachate.

Landfill leachate (LL) is the liquid produced as a result of different chemical and biochemical reactions that took place when water percolates through the disposed landfill waste components. Landfill leachate is a high strength waste stream that contains high concentrations of organics, suspended solids (SS) and nitrogen (N), namely ammonium nitrogen ( $\text{NH}_4\text{-N}$ ) (Ismail and Manaf, 2013). High-ammonium from LL has been known to cause eutrophication to surface water bodies and result in pollution to groundwater and aquaculture (Taha et al., 2011; Marañón et al., 2006).

Biological treatment methods (aerobic or anaerobic) have the capability to reduce organic loads from wastewater. However, they are less efficient when applied

to LL (Zhang et al., 2009a), especially when it is in the methanogenic (mature) phase (Di Iaconi et al., 2010). The reason is that mature LL holds large amounts of recalcitrant organics and very high concentrations of  $\text{NH}_4\text{-N}$  that has toxic inhibition to microorganisms responsible for the biological degradation. Moreover, the ratio of biological oxygen demand/chemical oxygen demand ( $\text{BOD}_5/\text{COD}$ ) in this phase of LL is frequently much lower than required for efficient biological processes (Siciliano et al., 2013), making the application of such conventional methods more expensive and difficult.

Several techniques have been applied for LL treatment such as ammonia stripping (Leite et al., 2013), ion exchange (Boyer et al., 2011) and electrochemical oxidation (Bashir et al., 2009). The cost of ammonia stripping method is considered high, as huge stripping towers have to be built, as well as large amounts of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is needed to recover ammonia ( $\text{NH}_3$ ) in the form of ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ) (See section 2.3). The main constraint that hinders the development of an effective  $\text{NH}_4\text{-N}$  treatment by ion exchange method is the high cost of resins that are needed to be changed frequently, while the major problem in achieving large-scale application of electro-oxidation is the high electricity consumption together with the high cost of electrodes.

The process of chemical precipitation of  $\text{NH}_4\text{-N}$ , forming magnesium ammonium phosphate hexahydrate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , MAP), known as struvite, has been thoroughly investigated for different types of wastewater (Huang et al., 2016c; Chen et al., 2013; Ryu and Lee, 2010; Warmadewanthi and Liu, 2009; Liu et al., 2008), which showed high efficacy in nutrients' recovery. The process of  $\text{NH}_4\text{-N}$  recovery by struvite precipitation has unique benefits; it has the ability to treat high concentrations of  $\text{NH}_4\text{-N}$ , as well as recovering it into valuable material, which is not available in other nitrogen treatment methods. In addition, struvite has significant benefits for the agronomic field; it is an effective fertilizer as its nutrients are released slowly, causing

no adverse effects on plants roots (Rahman et al., 2014). Moreover, MAP precipitation technology had shown an effectiveness higher than many other methods such as the biological treatment methods (Akkaya et al., 2010), ammonia stripping (Hidalgo et al., 2016) and fenton oxidation (Kochany and Lipczynska-Kochany, 2009).

However, LL is usually poor in magnesium (Mg) and phosphorus (P), which makes struvite precipitation costly, due to the required addition of Mg and P. Therefore, using low-cost sources of Mg and P could significantly reduce the operational costs of the process (Liu et al., 2013a; Siciliano et al., 2013; Borjovich et al., 2010; Di Iaconi et al., 2010). Fundamentally, struvite precipitation is influenced by several factors, mainly pH, molar ratios of Mg:N and P:N, initial  $\text{NH}_4\text{-N}$  concentration and mixing intensity ( $G$ ). The presence of foreign ions, mainly calcium (Ca) and potassium (K), could lower the efficiency of  $\text{NH}_4\text{-N}$ . Calcium ions has the ability to react with phosphate, while the presence of K could result with the formation of magnesium potassium phosphate hexahydrate ( $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ ), which competes with MAP. Besides, recovery of pure MAP could be impeded by the presence of organic matter in the stream (Gunay et al., 2008b).

During the process of  $\text{NH}_4\text{-N}$  recovery from LL, heavy metals may contaminate the produced struvite. Several studies illustrated that heavy metals could be incorporated into struvite's crystal network, or sorbed onto its surface (Ronteltap et al., 2007). Thereafter, if struvite would be used as a fertilizer, the incorporated heavy metals might cause hazardous impacts on humans and plants. Different heavy metals, like Ni & Cd, were found in quite high concentrations in leachates of different landfills in Malaysia (Yusof et al., 2009) and Palestine (Alslaibi et al., 2011). However, their sorption mechanisms during MAP precipitation are still undefined.

## 1.2 Problem statement

Landfill leachate is a high-strength waste stream, containing high concentration of  $\text{NH}_4\text{-N}$  that is difficult to be treated by traditional biological methods. Disposing LL without a proper treatment causes significant pollution for surface and groundwater, consequently affecting human health and aquatic life.

Struvite precipitation is a promising solution that has been investigated for  $\text{NH}_4\text{-N}$  and P recovery. However, the high cost of raw Mg and P reagents is still the main obstacle in sustainable application of struvite precipitation. Whilst most of researches tended to investigate alternative sources of Mg (Ye et al., 2011; Gunay et al., 2008b; Chimenos et al., 2003), little efforts have been carried out to investigate the alternative low-cost sources of P (Siciliano et al., 2013) despite the fact that P is more expensive and rare as compared to Mg (Di Iaconi et al., 2010).

As LL has a complex nature, there are many elements that could have negative effects on MAP precipitation, thus inhibiting  $\text{NH}_4\text{-N}$  removal. The presence of Potassium ( $\text{K}^+$ ) has been proven to affect the purity of MAP by forming a different struvite analogue. In the same context, high concentration of  $\text{K}^+$  has been found in different LLs in Malaysia. However, the interaction effect of K with pH, Mg:N and *G* has not been determined before.

Organic matter can cause mutual effects with  $\text{NH}_4\text{-N}$ , which may affect  $\text{NH}_4\text{-N}$  removal and struvite purity as well. In particular, propionic, butyric and acetic acids are the main carboxylic acids that formulate the organic matter of LL. However, their potential influence on  $\text{NH}_4\text{-N}$  recovery has not been reported in the literature. In addition, the efficiency of applying the alternative P (P extraction) has to be determined.

High concentrations of Cd and Ni have been found in LL in some countries like Malaysia and Palestine. These heavy metals could drastically influence the purity of struvite as a fertilizer. A comprehensive explanation of Cd and Ni effect and behaviour during MAP precipitation is still lacking, which should be discussed in detail.

### 1.3 Objectives

The main goal of this study is to develop a sustainable approach for  $\text{NH}_4\text{-N}$  recovery from municipal LL by means of struvite precipitation method. The following objectives are proposed to be achieved:

1. To choose the best type of waste bone ash to be used as a low-cost source of phosphorus required for struvite precipitation.
2. To optimize  $\text{NH}_4\text{-N}$  recovery and struvite purity in terms of  $\text{K}^+$ , pH, Mg:N molar ratio and  $G$ .
3. To investigate the potential effect of organic matter in synthetic LL on  $\text{NH}_4\text{-N}$  recovery, as well as the efficiency of P extraction for  $\text{NH}_4\text{-N}$  recovery from actual LL.
4. To study the effect and sorption mechanisms of Cd and Ni during struvite precipitation.



#### 1.4 Scope of study

This study investigates the recovery of  $\text{NH}_4\text{-N}$  from LL via struvite crystallization technology. Three types of waste bones, produced from fish, chicken and cow were characterized to choose the best alternative P source among them to apply it in MAP formation. Consequently, P extraction from the best wasted bone ash (fish wasted bone ash) was optimized by Response Surface Methodology (RSM). The interaction effects of pH, Mg:N and K:N molar ratios and  $G$  on  $\text{NH}_4\text{-N}$  removal from synthetic LL were also optimized using RSM. The influences of three organic acids (propionic, butyric and acetic acids) on struvite recovery was also studied. The efficiency of P extraction in MAP recovery from actual LL was determined. Furthermore, the effect and sorption mechanisms of Cd and Ni during struvite precipitation process was defined.

#### 1.5 Limitation of study

This study discussed some aspects related to  $\text{NH}_4\text{-N}$  recovery from LL by MAP precipitation. However, some other aspects could not be covered such as:

1. The alternative source of Mg, as the main purpose was to discover a new alternative P source, and study its efficiency in MAP precipitation.
2. Not all influencing factors that affect MAP recovery were investigated. Instead, based on the literature, the most influential factors were considered.
3. A combination of only three organic acids was applied to represent the organic content in the synthetic leachate. This was because the sole parameter that measured the organic content was TOC, as the other indicators, according to literature, are either does not represent the organic carbon alone such as COD, or not affected by the chemical precipitation process such as BOD.

## 1.6 Significance of study

MAP precipitation is a promising approach to remove and recover  $\text{NH}_4\text{-N}$  from LL. On the whole, this study will contribute to the environment protection, through the attainment of sustainable removal of  $\text{NH}_4\text{-N}$  from LL, and production of valuable materials.

In particular, extracting P from wasted bones ash and using it in MAP recovery has several benefits:

1. Decreasing the consumption of natural sources of P (phosphate rocks), which are threatened to be depleted in the next coming 50 years.
2. Contributing to minimize organic wastes disposal and recover the contained nutrients.

Additionally, considering the influential factors and the different levels of LL pollution, determining the optimum condition of struvite precipitation will explain the potential interferences that may inhibit the efficient recovery of  $\text{NH}_4\text{-N}$ . Furthermore, this can be considered as a milestone for large-scale applications of struvite recovery. Moreover, focusing on heavy metals and their impact on struvite purity will benefit in estimating the level of potential contamination with heavy metals, as well as assessing the feasibility of using struvite, recovered from LL, as a fertilizer.

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