

Application of Recycled Fish Wastes for the Recovery of Struvite Fertilizer From Actual Landfill Leachate

Nur Zulaikha Yaakub¹ Mohamad Darwish^{1*} Khalida Muda¹ Azmi Aris^{1,2}
Mohamed Zuhaili Mohamed Najib¹

¹*School of Civil Engineering, Faculty of Engineering, Universiti Teknologi Malaysia (UTM), 81310 Skudai, Johor, Malaysia*

²*Centre for Environmental Sustainability and Water Security (IPASA), Research Institute for Sustainable Environment (RISE), Universiti Teknologi Malaysia (UTM), 81310 Skudai, Johor, Malaysia*

*Corresponding author. Email: sjmohamad@utm.my

ABSTRACT

The crystallization of struvite ($MgNH_4PO_4 \cdot 6H_2O$) is known as an effective way for recovering nutrients from landfill leachate (LL). Recently, several studies have been done to examine nonconventional sources of phosphorus, in order to improve the applicability of struvite technology. This study aimed at investigating the applicability of recycled fish wastes as a new source of P to recover MAP from real LL. A solution rich with P (P-solution) was extracted from fish wastes ashes, and mixed with pure magnesium oxide (MgO) before applying the resulted mixture to leachate samples. The experimental results showed reductions of different parameters; total suspended solids (TSS), chemical oxygen demand (COD), turbidity and color were removed with approximate rates of around 32%, 31%, 37% and 51%, respectively. Besides, about 70% of ammonium-nitrogen (NH_4-N) was converted to struvite precipitate. X-ray diffractometry (XRD) test confirmed the presence of struvite crystals in the obtained precipitates. Moreover, the utilization of Mg-P mix was significantly competent in comparison with conventional reagents.

Keywords: *Phosphorus, ammonium, landfill leachate, fish waste, struvite*

1. INTRODUCTION

A global problem associated with environmental management is the landfill leachate (LL). The municipal landfill generates leachate with highly polluted waste stream that contain high levels of parameters and elements, such as ammonium-nitrogen (NH_4-N), heavy metals and organic material, which requires a series of treatment processes [1]. Anaerobic biological treatment is efficient in treating and reducing the chemical oxygen demand (COD) to acceptable levels. However, high concentrations of NH_4-N hinder the bacterial activity [2]. Therefore, it is necessary to apply a pre-treatment stage to reduce NH_4-N , to manage the LL effectively. A number of technologies was investigated for treating NH_4-N in LL, such as air stripping [3], membrane separation techniques [4] and chemical precipitation [5, 6].

Recently, recovering NH_4-N in the form of solid struvite mineral ($MgNH_4PO_4 \cdot 6H_2O$), or MAP, in LL has been thoroughly studied, because of the simple and rapid performance of this method [6]. Generally, two main elements are always required to form struvite: magnesium (Mg) and phosphorus (P) (Equation (1)). However, using the conventional sources of Mg and P is not suitable for large-scale application due to the high

cost [5]. Therefore, many studies have studied several alternatives of Mg including brine [7], seawater bittern [8] and pre-treated magnesite [9]. Besides, some phosphorus alternatives were investigated, such as bone meal waste [8] and waste phosphoric acid [5].



Extraction of phosphate from animal wastes by applying sulphuric acid (H_2SO_4) had been inspected by Cohen [10]. Additionally, Siciliano and De Rosa [8] were able to extract P from by-products of thermal treatment of meat wastes using H_2SO_4 . A similar technique was implemented in a previous study that explored P extraction from fish wastes bones ash, which was effectively applied in struvite crystallization [11]. The latest work showed that P content in fish waste bones ash was around 17% wt., which is notably high compared to other types of wastes. Interestingly, fish meals are very common in many countries, especially in South East Asia, which produce huge amounts of fish wastes annually, which hardly can be reused. Accordingly, the efficiency of utilizing phosphate recovered from waste bones ash (P-solution) for struvite crystallization in real leachate is lacking detailed

knowledge. As the complicated structure of LL can significantly affect the applicability of the acidic solution (rich with P), some oxidation side-reactions would occur if the P-solution was applied directly to the actual leachate. Practically, this issue could prevent supplying the required amount of P for MAP precipitation.

In the current work, in order to avoid potential oxidation reactions of organic matter with acidic P-extract, P-solution was completely mixed with MgO, which was followed by adjusting the pH value of the resulted mixture (Mg-P mix). This was done prior to application of the mixture in struvite precipitation [8]. To the best of our knowledge, the currently applied P-solution, as well as the new Mg-P mix, were not examined before as sources of P and Mg for struvite precipitation in actual LL. Moreover, by using Mg-P mix, the reactivity of MgO would be improved without adding excess Mg dosage or applying a pre-treatment stage of Mg source [9]. Therefore, the objective of this work is to evaluate the applicability of Mg-P mix for the recovery of struvite in actual LL.

2. MATERIALS AND METHODS

2.1 Extraction of P from fish waste bones ash

Phosphorus solution was extracted from fish wastes bones ash by the acidic extraction approach, using sulphuric acid (H_2SO_4). The procedure of extracting P was basically established by Darwish, Aris [11], which mainly includes the dissolution of combusted bones (bones ash) in sulphuric acid (2M H_2SO_4) for 1.5-2 hours, and then filtering the solution and obtaining a clear solution highly concentrated with phosphate. Finally, the pH of the resulted solution (P-solution) was 2.5-3.0±0.10.

2.2 Leachate sampling

Samples of real LL were collected from a sanitary landfill site, located in Johor, Malaysia (1.6599° N, 103.7198° E). Before and during experimentation period, the sample was stored in 4°C and the experiment was completed in less than 14 days, to prevent any harmful changes in the sample composition.

2.3 Struvite recovery experiments

The mixture of MgO and P-solution was applied as the source of Mg and P, respectively. For each experimental run, a 1-L leachate batch was applied in a 1.5-L beaker,

and the Mg:P molar ratio of 1:1 was calibrated. Initially, the required amounts of P-solution, in addition to MgO, were well mixed in a small beaker to get the final Mg-P mix with pH of 5.0-5.5. The pH value of the obtained mixture was adjusted to around 6.5±0.2 using 2M NaOH solution. After that, the final mixture was added to the sample, and the resulted pH was consequently adjusted to 9.0±0.05. The sample was thoroughly stirred for a period of 30 min using the jar tester equipment (Chemix, CL4). Then, the sample was left to settle for another 30 min. The final supernatant of the sample was filtered using 0.45 µm Whatmann GF/C filter for the further analysis. The collected precipitates were dried at room temperature, after been washed with de-ionized water. For comparison purpose, two chemical combinations were tested as well: $MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O$ and $MgO + Na_2HPO_4 \cdot 12H_2O$, and their removal performance was recorded.

2.4 Analytical methods

All parameters were measured using standard methods. ammonium nitrogen in aqueous samples was tested using the method of Nessler with UV-spectrophotometer (DR6000, HACH Inc., USA), whereas PO_4 , COD and color were measured using standard HACH methods. The total organic carbon (TOC) was measured using TOC analyzer (Shimadzu Co., Japan, model 5050). In addition, turbidity of samples was tested using a portable turbidimeter (HACH, 2100Q, America). In order to analyze the concentrations of Ca, K, Mg and Fe, atomic adsorption spectroscopy (AAS, 3300, Perkin Elmer-USA) was applied. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS: OPTIMA 7300 DV, PerkinElmer, USA) was used to track the other heavy metals. The morphological structure of solid struvite was characterised using X-ray diffractometry (XRD) using a Siemens D501 diffractometer.

3. RESULTS AND DISCUSSION

Table 1 shows the major structure of the extracted P-solution. It can be noticed that the solution is highly concentrated with calcium (Ca) and potassium (K). Basically, it is well established that Ca and K could interfere with MAP precipitation and reduce the purity, as well as decrease the efficiency of NH_4 -N removal [12]. Even though the presence of Ca and K are significantly high in the P solution, their final diluted concentrations in the sample were considerably low, as only little amount of P solution was required for MAP precipitation. Therefore, Ca and K were not influential.

The characteristics of the actual leachate sample are shown in table 2. Taking the values pH (8.27) and COD / TOC ($1.22 < 3.0$) into account, the leachate can be classified as mature (old) [13]. The applied sample was dark-brown, alkaline, containing high amounts of $\text{NH}_4\text{-N}$, TSS and organic matter. The results of the current research were compared with the findings of synthetic solution experiment conducted by Darwish, Aris [11].

Table 1 Characteristics of P-rich solution (pH=2.5-3.0)

<i>Parameter</i>	<i>Concentration (mg/L)</i>	<i>Parameter</i>	<i>Concentration (mg/L)</i>
PO ₄ -P	150,000 ± 500	Fe	28.12 ± 2.0
K	5,978 ± 100	Al	1.19 ± 0.5
Mg	2,699 ± 100	Zn	0.44 ± 0.2
Ca	1,191 ± 50	Cu	0.16 ± 0.03
As	106 ± 10	Cr	0.07 ± 0.01

Table 2 Composition of actual landfill leachate

<i>Parameter</i>	<i>Unit</i>	<i>Concentration</i>	<i>Parameter</i>	<i>Unit</i>	<i>Concentration</i>
pH	-	8.27	Na	mg/L	2,910
COD	mg/L	11,500±100	Ca	mg/L	212
TOC	mg/L	9,430±50	Mg	mg/L	174
NH ₄ -N	mg/L	2,530±60	Al	mg/L	4.56
PO ₄ -P	mg/L	55.32	Cr	mg/L	2.21
TSS	mg/L	1,154±70	Fe	mg/L	2.07
Colour	Pt Co	5,230	Zn	mg/L	0.08
Turbidity	NTU	538	Ni	mg/L	< 0.01
K	mg/L	3,423	Cd	mg/L	< 0.01

Struvite precipitation was performed using both unfiltered and filtered samples of leachate, in order to improve the understanding of the potential interference of Mg-P mix with organics and suspended solids. In general, the suspended solids in LL are composed of mineral sediments and organic compounds. Organics are mainly intensified in the fine fractions of the suspended solids. COD concentrations in the treated unfiltered leachate were expected to increase. This explains the effects of the removal of COD in unfiltered

leachate (20%), which was less (31.8%) than in filtered samples.

3.1 Recovery of NH₄-N

Since LL is typically characterised by a high concentration of NH₄-N (a major component of MAP), a special focus on the recovery of NH₄-N has been illustrated. A number of studies have shown the efficiency of struvite technology in recovering NH₄-N from wastewater [14]. Figure 1 shows that the efficiency

of the recovery of $\text{NH}_4\text{-N}$ using Mg-P mix in filtered and unfiltered leachate was around 70% and 63%, respectively. These percentages suggest that some of the added P (through the mixture of Mg-P) remained in the solution, which enhanced the leaching potential of P through the treated LL. For any further research projects, this topic is still a challenge. Principally, if the concentration of TSS reaches above 1,000 mg/L, this could interfere with the precipitation of MAP, as stated by Barnes, Li [15]. Looking at the initial TSS (1,580 mg/L), it is clear that TSS has interfered with $\text{NH}_4\text{-N}$ recovery, and hence resulted with some decrease. More than 90% of the $\text{NH}_4\text{-N}$ recovery in NH_4Cl solution was achieved in our previous research (Darwish et al. 2017), which was substantially higher compared to the current report. Apparently, unlike the synthetic solution of NH_4Cl , this may be due to interaction with organic compounds and suspended particles existed in the actual leachate. Moreover, the occurred reductions in COD, TOC, turbidity and colour (Figure 2), in addition to TSS, could be referred to organics' adsorption onto struvite crystals' surface.

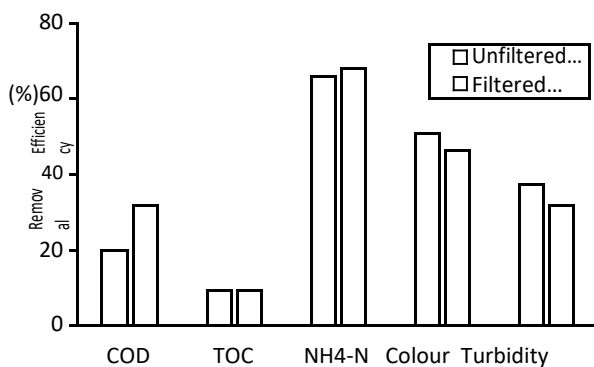


Figure 1 Removal efficiency of different parameters in actual landfill leachate (pH=9.0, Mg:N:P = 1:1:1)

3.2 Treatment of other parameters

Struvite recovery has led to a decrease in other parameters, including TSS, COD, colour and turbidity. With regards to TSS, a substantial decrease was observed, reaching nearly 32 percent in the unfiltered leachate. Color and turbidity were substantially reduced in unfiltered leachate by around 51.4% and 37.5% and in filtered leachate by 46.3% and 31.6%, respectively (Figure 2). Unlike the white coloured precipitates collected from the NH_4Cl solution (Darwish et al., 2017), the harvested precipitates from real leachate had a light brownish colour, as can be seen from Figure 3.

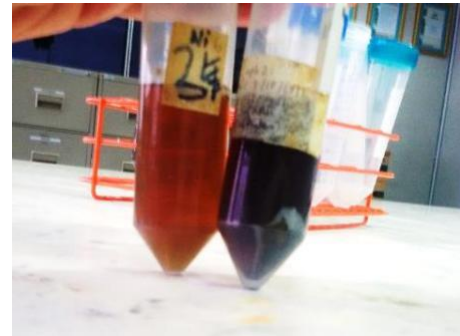


Figure 2 Colour reduction in filtered actual leachate (Right: before treatment, Left: after treatment)

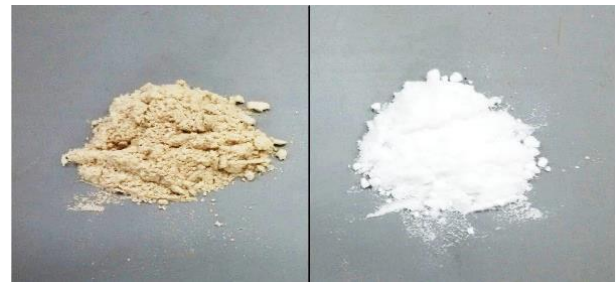


Figure 3 Harvested struvite from filtered actual leachate (left) and NH_4Cl solution (right)

Moreover, the organic matter was diminished to some degree, with considerably greater COD removal. In addition, it was observed that colour and turbidity reductions were higher in unfiltered leachate than in filtered one. The main explanation, possibly, is that suspended solids acted as seeds that increased the aggregation of struvite crystals and the flocculation of organic matter and particulates. Several studies have indicated that, along with the MAP recovery process, various parameters could be decreased. Akkaya, Demir [16] found that post-treatment of LL through chemical precipitation resulted in the elimination of COD, colour and turbidity of around 25.7%, 22.5% and 36.4%, respectively, while Gunay, Karadag [17] achieved a decrease of suspended solids and turbidity by more than 80% and 50%, respectively. The studies listed above showed that the prevailing mechanism of elimination of those parameters was adsorption of organics. Undoubtedly, the purity of MAP in the current work may have been compromised by such

adsorption. However, the findings of the XRD test presented in Figure 4 indicated that struvite was the dominant crystalline form in the precipitates, suggesting that in filtered and unfiltered leachate, MAP with high purity was obtained.

3.3 Treatment of leachate using conventional reagents

Two traditional chemical formulations were used to test the potency of the Mg-P mix: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and

$\text{MgO} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. The results are shown in Figure 5. Using the first chemical combination, significant struvite recovery efficiency was demonstrated [15], also at the stoichiometric molar ratio of Mg:P:N, while the latter was said to require certain modifications to boost reactivity [18]. Figure 5 presents the efficiency of removing $\text{NH}_4\text{-N}$ when applying conventional reagents. Basically, the results indicated that the maximum possible recovery of $\text{NH}_4\text{-N}$ ($\approx 95\%$) could be obtained by using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, whereas 70% of $\text{NH}_4\text{-N}$ was converted to struvite when Mg-P mix was used.

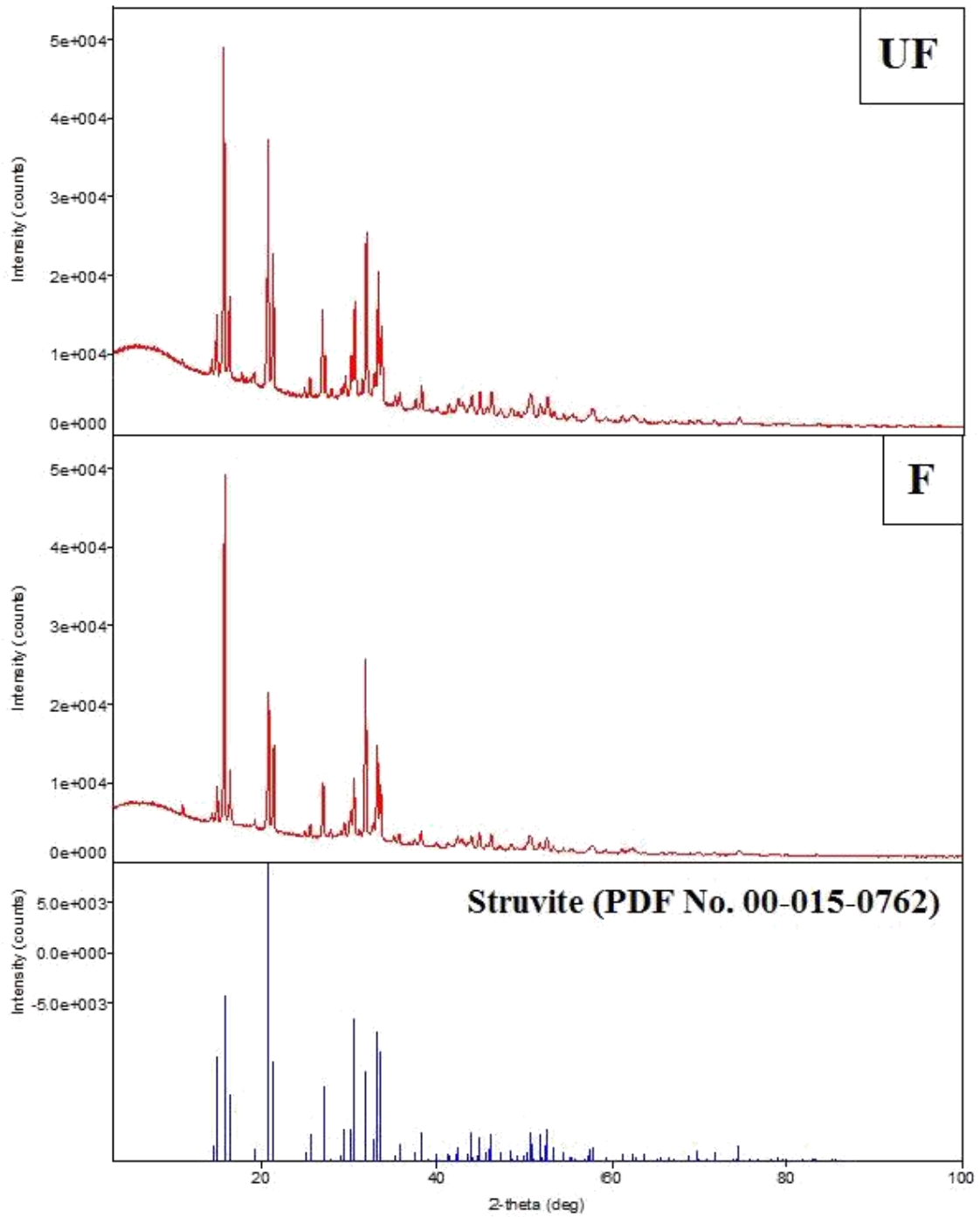


Figure 4
Filtered)

XRD analysis of struvite harvested in filtered and unfiltered actual landfill leachate. (UF: Unfiltered, F:

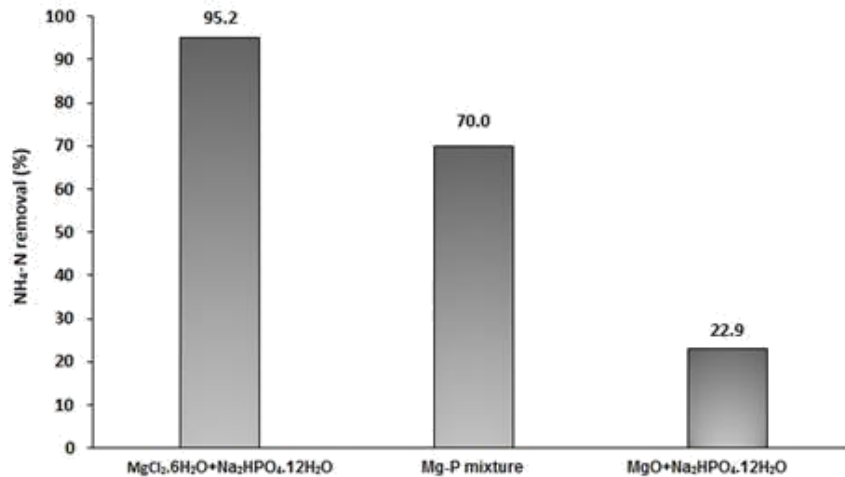


Figure 5 Efficiency of Mg-P mixture compared to conventional chemical combinations (pH=9.0, Mg:N:P = 1:1:1)

On the whole, the outcome of the recovery of NH₄-N using the mixture of Mg-P appears to be competitive, especially when compared to the low recovery (about 23%) achieved without any modification using MgO. This means that, in the future, the mixture of Mg-P could be successful, as it achieves more than one advantage; recycling of waste material (i.e. fish wastes bones), contribution to the protection of the natural supply of P and high recovery of NH₄-N in LL.

4. CONCLUSIONS

A vital research trend, especially in low-P waste streams, is the application of effective alternate P sources for MAP recovery. In the process of NH₄-N recovery from LL, phosphorus is a key driving element, as LL is low in P and highly polluted with NH₄-N. In this research, struvite recovery was implemented using P-solution derived from fish wastes bones ash, combined with MgO (forming Mg-P mix) in actual LL. The experimental findings revealed that it was possible to recover 70% of NH₄-N, in parallel with a considerable treatment of other parameters, where XRD analysis confirmed the existence of struvite crystals. The application of Mg-P mix to real LL is competitive in contrast to previous works, taking into account the side advantages obtained.

ACKNOWLEDGMENT

The authors would like to express sincere thanks to Ministry of Higher Education Malaysia, and Universiti

Teknologi Malaysia (UTM) for supporting this study via Fundamental Research Grant Scheme (FRGS 5F249).

REFERENCES

- [1] Jaafarzadeh, N., et al., Treatment of Mature Landfill Leachate by Chemical Precipitation and Fenton Advanced Oxidation Process. *Environmental Health Engineering and Management Journal*, 2016. 3(1): p. 35-40.
- [2] Chen, Y.-n., et al., Chemical precipitation and biosorption treating landfill leachate to remove ammonium-nitrogen. *Clean Technologies and Environmental Policy*, 2013. 15(2): p. 395-399.
- [3] Smaoui, Y., J. Bouzid, and S. Sayadi, Combination of air stripping and biological processes for landfill leachate treatment. *Environmental Engineering Research*, 2019. 0: p. 0-0.
- [4] Ilhan, F., et al., Evaluation of treatment and recovery of leachate by bipolar membrane electrodialysis process. *Chemical Engineering and Processing: Process Intensification*, 2014. 75: p. 67-74.
- [5] Huang, H., et al., Removal of ammonia from landfill leachate by struvite precipitation with the use of low-cost phosphate and magnesium sources. *Journal of Environmental Management*, 2014. 145: p. 191-198.
- [6] Siciliano, A., et al., Ammonium Removal from Landfill Leachate by Means of Multiple Recycling of

Struvite Residues Obtained through Acid Decomposition. *Applied Sciences*, 2016. 6(11): p. 375-392.

[7] Prabhu, M. and S. Mutnuri, Cow urine as a potential source for struvite production. *International Journal of Recycling of Organic Waste in Agriculture*, 2014. 3(1): p. 49.

[8] Siciliano, A. and S. De Rosa, Recovery of ammonia in digestates of calf manure through a struvite precipitation process using unconventional reagents. *Environmental Technology*, 2014. 35(7): p. 841-850.

[9] Krähenbühl, M., B. Etter, and K.M. Udert, Pretreated magnesite as a source of low-cost magnesium for producing struvite from urine in Nepal. *Science of The Total Environment*, 2016. 542, Part B: p. 1155-1161.

[10] Cohen, Y., Phosphorus dissolution from ash of incinerated sewage sludge and animal carcasses using sulphuric acid. *Environ Technol*, 2009. 30(11): p. 1215-1226.

[11] Darwish, M., et al., Waste bones ash as an alternative source of P for struvite precipitation. *Journal of Environmental Management*, 2017. 203: p. 861-866.

[12] Yan, H. and K. Shih, Effects of calcium and ferric ions on struvite precipitation: A new assessment based on quantitative X-ray diffraction analysis. *Water Research*, 2016. 95: p. 310-318.

[13] Lehmann, E.C., *Landfill Research Focus*. 2007: Nova Science Publishers.

[14] Kumar, R. and P. Pal, Assessing the feasibility of N and P recovery by struvite precipitation from nutrient-rich wastewater: a review. *Environmental Science and Pollution Research*, 2015. 22(22): p. 17453-17464.

[15] Barnes, D., X. Li, and J. Chen, Determination of suitable pretreatment method for old-intermediate landfill leachate. *Environ Technol*, 2007. 28(2): p. 195-203.

[16] Akkaya, E., et al., Post-treatment of anaerobically treated medium-age landfill leachate. *Environmental Progress & Sustainable Energy*, 2010. 29(1): p. 78-84.

[17] Gunay, A., et al., Use of magnesit as a magnesium source for ammonium removal from leachate. *Journal of Hazardous Materials*, 2008. 156(1-3): p. 619-623.

[18] Capdevielle, A., et al., Optimization of struvite precipitation in synthetic biologically treated swine wastewater—Determination of the optimal process parameters. *Journal of Hazardous Materials*, 2013. 244-245(0): p. 357-369.