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Chemical Precipitation of Ammonia and Phosphate from Nam Son Landfill Leachate, Hanoi

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Abstract: Leachate from municipal landfills of the city is often contaminated heavily, especially for parameters such as organic components, heavy metals, microorganisms. However, leachate also contains amounts of valuable nutrients (e.g. N, P, K) which can be used for agriculture as fertilizers. Precipitated of N and P in the form of struvite ($MgNH_4PO_4.6H_2O$) might be applied as a technique for removal a huge amount of N as well as P in wastewater. This study investigated the recovery ability of N, P in leachate from Nam Son municipal landfill of Hanoi city. Different pH values, anaerobic time and stoichiometric Mg^{2+}: NH_4^+: PO_4^{3-} was tested to determine the optimal conditions for precipitating struvite. The effect of pH on the forming of struvite was between pH 9 to 11. The results showed that nutrients in landfill leachate could be recovered with the optimum pH around 9.5 and the optimum Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio as 1.15: 1: 1. With the anaerobic interval of 21 days, COD value in landfill leachate was decreased to 60%, the retrieval reached 80.6% for nitrogen and 82.7% for phosphorus. According to estimates, with the application of struvite precipitation technique, the average annual retrieval amount of NH_4^+ and PO_4^{3-} can reach 263 tons and 25 tons, respectively.

Key words: Landfill; Leachate; Nutrients; Retrieval; Struvite.

INTRODUCTION

Leachate is generated at any landfill by the contact of water with wastes and has a great potential to harm the environment. Leachate volume and pollutant concentration depends on a number of factors: the type of deposited wastes, hydrogeologic conditions, as well as the age of the landfill and the phase of waste decomposition [1]. Leachate is characterized by a high content of organic matters (expressed as COD, BOD_5 and TOC), a high concentration of nutrients (N, P) and microorganisms. Treatment of leachate is very complicated and generally requires various process applications due to high contents of ammonium and high COD/BOD ratio [2]. Anaerobic biological treatment systems are efficient to treat high concentrations of COD, but high concentrations of ammonium inhibit biological treatment systems. The ammonia in water is one of the major environmental pollutants, which may cause the increase of chlorine consumption and oxygen demand, toxicity to fish, eutrofication and diseases like ethaemoglobinaemia hypertension and stomach cancer, as well as other serious environmental [3]. Specifically, ammonium has been identified as one of major toxicants to microorganisms in the treatment system [4], suggesting that pretreatment of ammonium is very important in reducing the concentration of NH_4^+ [5–6].

In Vietnam, with the strong economic growth and seemly uncontrolled urbanization, the amount of solid waste generated has been increasing dramatically, especially in big cities such as Hanoi – the capital. Nam Son, the biggest landfill in Hanoi receives more than 3,500 tons of domestic waste per day. Landfill leachate is a serious problem there because there has not been an effective method for leachate treatment. Air stripping has been used in the pretreatment of ammonium from landfill leachate of Nam Son. However, the off-gas which contains high concentrations of NH_3 and other pollutants are released directly into the air without treatment. That is a cause of air pollution, the greenhouse effect and loss of nutrients such as NH_4^+.

Recently, control over the point sources of N ad P shifted from removal to recovery, with a particular emphasis on improving the sustainability of agricultural activities. This was mainly due to the increasing global demand for the nitrogenous fertilizer and the limited phosphorus rock reserves [7]. Therefore, the current attempts are not only to protect the water resources, but also to extract the maximum amount of N and P from the recoverable sources, such as landfill leachate.

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As an alternative to eliminate high level of NH_4^+ in leachate, the precipitation of NH_4^+ by forming magnesium ammonium (Struvite, $MgNH_4PO_4.6H_2O$) has been studied [6, 8]. Struvite is a white crystalline substance consisting of magnesium, ammonium and phosphorus in equal molar concentration. In addition, struvite is a valuable slow-release fertilizer, the production of which could offset much of the cost of chemical treatment [9]. The basic chemical reaction to form struvite has been expressed as equation $Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O$ with $pK_s = 12.6$ at 25°C [10-12]. The precipitation of struvite is affected by several factors, namely the pH, the chemical composition of the wastewater (degree of saturation with respect to magnesium, ammonium and phosphate; presence of other ions, such as, calcium, ionic strength of the solution), and the temperature of the solution [13,14].

The objective of this study is to evaluate the characteristic of Nam Son leachate and the recovery of nutrients based on the precipitation ability of struvite. Experimental study has changed the molar ratio to achieve the goal. In this study, the precipitation of struvite as a pretreatment of leachate from Nam Son landfill is investigated with the purpose to reduce harmful effects on the environment and retrieve nutrients.

MATERIALS AND METHODS

Nam Son landfill leachate: Nam Son landfill is located in Soc Son district and about 50km from the Hanoi city center. This landfill with area of 83.5 hectares has started mechanized operation in 1999 and designed to close in 2025. However, due to the overloading, it will be closed in 2013. Currently, Nam Son landfill receives about 3500 tons of waste per day. Municipal waste is mostly organic matters such as vegetable, fruit, grass, dead animals, etc. and a noticeable amount of packages such as nylon, plastic, paper is a component of the waste. The composition of inorganic material in typical wastes are glass, porcelain, pottery, cinder (coal), stone and building materials.

The leachate is collected by wells and tube network and discharged into the bio-lake. Each day, the lake receive approximately 2000 m^3 leachate, but the total capacity of the two wastewater treatment plants is only 1500 m^3/day. The raw wastewater used in the experiments was collected from bio-lake and stored in cold temperature prior to the experiments. Table 1 shows the characteristic of the wastewater sample.

Materials: For struvite formation, solutions of magnesium chloride ($MgCl_2.6H_2O$) and ($Na_2HPO_4.12H_2O$) were used as alternative sources of magnesium ions and orthophosphate ions, respectively. These solutions were prepared from the crystalline solid: $MgCl_2.6H_2O$ and $Na_2HPO_4.12H_2O$ dissolved in distilled water. 1N NaOH was used to control pH in the solutions. All chemicals used were analytical grade.

Leachate analysis: Ammonium concentration was measured by using UV-Spectrophotometer. Phosphate level was assessed by ascorbic acid method. The pH of sample was measured with a pH meter and the other parameters such as COD, Ca^{2+}, Mg^{2+} and TN were measured by the Standard Methods [15].

Bath experiment: All experiments were done at 25ºC. Three factors affecting nutrients recovery ability were evaluated, including pH, molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} and the anaerobic interval. Ammonium and phosphate removal ratios were the indicators for selecting optimum struvite sedimentation conditions.

Experiments for struvite precipitation were performed as follows. Firstly, add magnesium salt and phosphate to raw wastewater. Secondly, agitate the reaction solution by magnetic stirrers for 30 min, and then adjust pH, settle for 30min. Thirdly, filter the reaction solution first with the filter paper. Lastly, after filtration, the supernatant was collected to measure Mg^{2+} and NH_4^+ and collect the precipitates for surface characterization analysis. Time of anaerobic periods was 7 days, 14 days, and 21 days.

RESULTS AND DISCUSSION

The characteristics of Nam Son landfill leachate: The composition of leachate is very complicated. According to the previous studies, COD values vary from 500 mg/L to 10000 mg/L, even higher, NH_4^+ concentrations fluctuate between 200–1000 mg/L. The pH value of leachate was measured is 8.31 due to the anaerobic decomposition of microorganisms. Ammonium generated from the decomposition of organic compounds of nitrogen has increased the pH value. With the high concentrations of nutrients and the total capacity of leachate treatment system – 1500 m^3/day, leachate is the potential source to recover nutrients for agricultural purposes.

Table1: Characteristics of raw leachate samples from Nam Son landfill

Parameters	Value
pH	8.31
COD	6400 mg/L
NH_4^+	161.3 mg/L
PO_4^-	17.4 mg/L
Ca^{2+}	25.6 mg/L
Mg^{2+}	65.7 mg/L
TN	354 mg/L
TP	22 mg/L

Influence of some factors to the recovery ability of N and P from leachate

Effect of pH: pH plays a vital role in determining the efficiency of struvite precipitation. The experiment was to identify the optimum pH for struvite formation in landfill leachate. This was tested by adding $MgCl_2.6H_2O$ and $Na_2HPO_4.12H_2O$ into the samples, and the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} was 1:1:1. The pH range was from initial pH to 11. Fig. 1 shows the maximum removal ratio of ammonium for raw wastewater was 9.5. When the pH was lower than the optimum point, hydrogen ion in reaction solution would inhibit struvite formation. As the result, the removal ratio of ammonium was lower. When the pH was higher than the optimum point, $Mg_3(PO_4)_2$ was formed instead of struvite along with pH raising, which lead to the decrease of ammonium removal ratio. The optimum pH for nutrients removal of the leachate was 9.5.

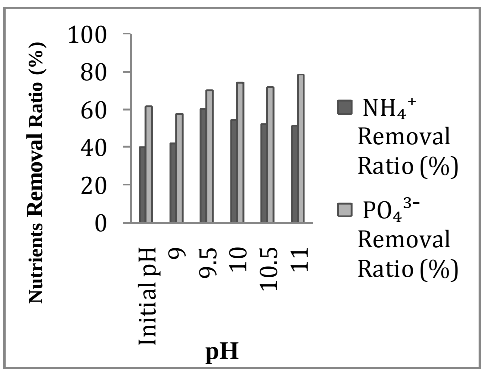

Fig. 1: Nutrients removal ratio at different pH

In the literature, there are some papers have reported that the optimum pH range for struvite formation is 8.5–9.5 [16, 17]. These results are similar range as our results. The optimum pH = 9.5 was fixed to investigate the next factors.

Effect of molar ratio: The molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} in precipitating struvite was varied to study the effect of Mg^{2+}: NH_4^+: PO_4^{3-} on the ability of nutrients removal. The experiments tested by adding $MgCl_2.6H_2O$ and $Na_2HPO_4.12H_2O$ into the samples and the pH was kept at 9.5 as determined in previous section as the best pH in struvite formation. Effect of the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-} on nutrients removal is shown in Figs. 2 and 3.

Fig. 2 shows the relationship between Mg^{2+} concentration and nutrients removal ratio. When Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio increased from 1:1:1 to 1.15:1:1, ammonium removal ratio increased from 58.1% to 69%. Any excess dose application for Mg^{2+} did not provide significant increase in ammonium removal ratio. However, phosphate removal ratio continued to increase from 59.2% to 75.9%. Because of the small concentration of phosphate in leachate,, in separate consideration of Mg^{2+} , the optimum Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio for nutrients removal was 1.15:1:1.

Fig. 3 elaborates the relationship between PO_4^{3-} concentration and nutrients removal. When Mg^{2+}: NH_4^+: PO_4^{3-} increased from 1:1:0.9 to 1:1:1.1., nutrients removal ratio increase from 41.5 to 63.7% with ammonium and from 43.1% to 59.7% with phosphate. Then any overdosing of PO_4^{3-} was not economical for additional nutrients removal. In separate consideration of PO_4^{3-}, the optimum Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio for nutrient retrieval was 1:1:1.1.

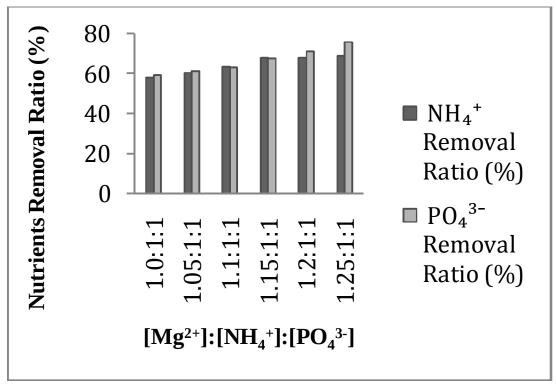

Fig: 2: Nutrients removal ratio at different molar ratio of Mg^{2+}

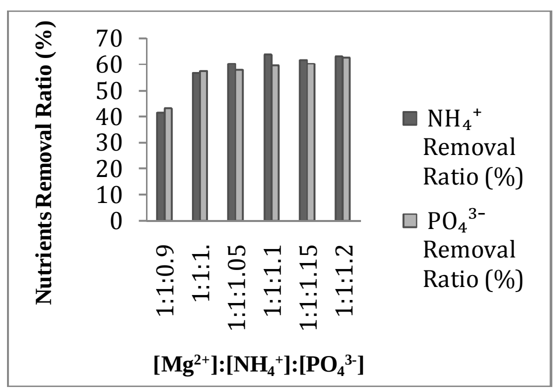

Fig. 3: Nutrients removal ratio at different molar ratio of PO_4^{3-}

Overdosing either Mg^{2+} or PO_4^{3-} can further lower the remaining ammonium concentration. However, from the environmental point of view, overdosing PO_4^{3-} will generate higher concentration of PO_4^{3-} in the effluent [2]. As a result, the removal efficiency Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio in case control at 1.15:1:1 in order to remove nutrients effectively from landfill leachate as well as to avoid higher concentration of phosphate in the effluent.

Effect of anaerobic period: Because nitrogen in leachate exists mainly in two forms: ammonium and organic nitrogen so in the anaerobic period, microorganisms decompose organic nitrogen and increase ammonium concentration in the sample which is significant in the recovery of nitrogen and phosphorus. Samples were divided into clean and to anaerobic during the period of 7 days, 14 days and 21 days at room temperature. After this period, the samples were analyzed some parameters: pH, NH_4^+, PO_4^{3-}, COD and investigated the recovery ability at the optimum pH and molar ratio. The result has shown the possibility to recover nutrients after the anaerobic process. Table 2 shows the characteristic of leachate after different anaerobic periods.

Table 2: Characteristics of leachate after different anaerobic periods

Parameters	Initial sample	After 7 days	After 14 days	After 21 days
pH	8.31	8.40	8.57	8.68
COD (mg/L)	6400	4350	2760	2470
NH_4^+ (mg/L)	161.3	197.5	250.2	305.7
PO_4^{3-} (mg/L)	17.4	17.9	18.3	18.5

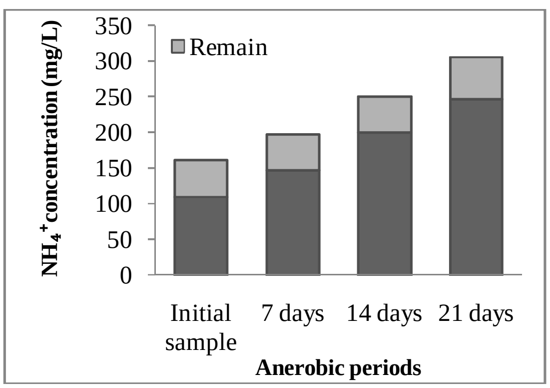

Fig. 4: a) Effect of anaerobic period on NH_4^+ removal

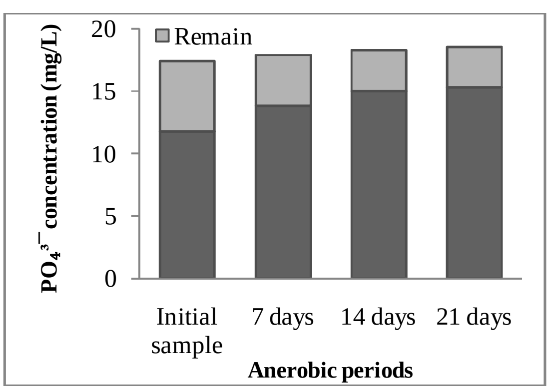

Fig. 4: (b) Effect of anaerobic period on PO_4^{3-} removal

The result shows that when the anaerobic period was increased, the value of pH, concentration of ammonium and phosphate both increase, moreover COD value of leachate had decreased by more than 60% after 21 days anaerobic period.

Figs. 4(a) and 4(b) show the relationship between anaerobic period and nutrients removal. When anaerobic period reached 2 weeks, nutrients removal ratio increased from 67.9% to 80% with ammonium and 67.8% to 82.9% with phosphate. However, any excess time application for anaerobic period did not prove significant increase in nutrients removal ratio.

Nutrients Retrieval Possibility: Leachate of Nam Son landfill contains 200 mg/L to 1000 mg/L NH_4^+ and 5 mg/L to 100 mg/L orthophosphate so average value for treatment was selected: 600 mg/L NH_4^+ and 55 mg/L PO_4^{3-}. The current capacity of the wastewater treatment plant in Nam Son is 1500 m^3/day and when we apply anaerobic process combined with struvite precipitation with nutrients retrieval yield of 80%, we can calculate the amount of ammonium and orthophosphate recovered in a year as follow:

Amount of recovered NH_4^+:
= (600 mg/L x 1500 m^3) × 365 days × 80% = 262800000 g = 262.8 tons.

Similarly, we calculate the amount of recovered PO_4^{3-}.

Amount of recovered PO_4^{3-}:
= (55 mg/L x 1500 m^3) × 365 days × 80% = 24090000 g = 24.09 tons.

The nutrient recovery from leachate is of great significance in agriculture. In additional, struvite is a valuable slow-release fertilizer the production of which could offset much of the cost of chemical [9].

Reducing greenhouse gas emission: recovering NH_4^+ is not only to recover the nutrients for agriculture purposes by forming the fertilizer as struvite but also to reduce the emission of greenhouse gases into the atmosphere significantly. Ammonia emission from landfill leached eventually contributes to atmospheric N input into natural or near natural ecosystems, not only promoting eutrophication but also causing N_2O emissions, thus being an indirect greenhouse. Currently, Nam Son landfill using the technology of air stripping to remove NH_4^+ from the wastewater. This technogoly is based on the principle of following chemical reactions:

$NH_4^+ + OH^- \rightarrow NH_4OH$

$NH_4OH \rightarrow NH_3\uparrow + H_2O$

Alkaline wastewater is led through the air stripping system in which a large amount of NH_3 is separated from wastewater and then enter the atmosphere. Thus, there can be up to 248 tons of NH_3 per year which are released directly into the air daily. Amonia is not considered a direct greenhouse gas because of its short lifetime in the atmosphere. It is postulated, that 1% of emitted NH_3-N is converted to N_2O-N, therefore it is possible to intergrate NH_3 losses into Global warming potential [18, 19]. Hence, the retrival of NH_4^+ in this study by forming the chemical precipitation can recove a significant amount NH_4^+ and limit the amount of greenhouse gases equivalent of 740 tons CO_2 into the atmosphere significantly.

CONCLUSION

Leachate of Nam Son landfill has high concentration of organic matters and nutrients (COD = 6400 mg/L, NH_4^+ = 161.1 mg/L, TN = 354 mg/L). Ammonium treatment method applied in Nam Son is air stripping, NH_3 and off-gases have discharged into the atmosphere which causing air pollution and greenhouse effect. In this study, struvite precipitation is used to recover nutrients at the optimum conditions. At pH 9.5, nutrient recover ratios are 60.3% and 70% for ammonium and phosphate, respectively. When the Mg^{2+}: NH_4^+: PO_4^{3-} molar ratio is 1.15:1:1, retrieval efficient for ammonium is 67.9% and for phosphate is 67.8%. And after the anaerobic period of 14 days, COD value fell up to about 60% and nutrient recovery ratio increased significantly, just over 80%. The leachate of Nam Son landfill is a potential source for N and P recovery. Application of struvite precipitation method will save the nutrients in leachate and reduce environmental pollution.

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