Enhancing struvite precipitation potential for ammonia nitrogen removal in municipal landfill leachate

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Abstract

This study was conducted to improve struvite precipitation for NH_4-N removal purpose in landfill leachate. For this purpose, we evaluated the effect of the feeding sequence of precipitating reagents (magnesium, orthophosphate, and buffering reagent) on NH_4-N removal by forming struvite deposits. Struvite precipitation effectively proceeded by an addition of excess magnesium and phosphate sources followed by an addition of the buffering reagent, in which condition the local formation of inappropriate deposits or the contamination of the desired struvite was minimized. We also tested the effect of struvite addition as the seeding materials on NH_4-N removal. Seed addition would increase the potential for the struvite crystal growth, which enhanced NH_4-N removal performance in landfill leachate treatment.
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1. Introduction

Landfill leachate treatment is an important issue of the waste management system in municipal areas because high contents of ammonia nitrogen (NH_4-N) and high COD/BOD ratio present difficulties in biological treatment of landfill leachate [1–3]. Specifically, NH_4-N has been identified as one of the major toxicants to microorganisms in the treatment system [4], suggesting that pre-treatment prior to the biological treatment system is required to reduce the concentration of NH_4-N [5,6].

As an alternative to eliminate high level of NH_4-N in leachate, the precipitation of NH_4-N by forming magnesium ammonium phosphate (Struvite, $MgNH_4PO_4 \cdot 6H_2O$) has been studied [5–7], demonstrating that struvite precipitation is an excellent pre-treatment process. Struvite crystallizes as a white orthorhombic crystalline structure, which is composed of magnesium, ammonium, and phosphate in equal molar concentrations [8]. Struvite precipitation is controlled by pH, supersaturation, temperature, and impurities such as calcium. The purity of struvite deposits may be determined by the final pH of the solution and the

feeding sequence of precipitating reagents [9]. Struvite solubility decreases with increasing pH, while above a pH of 9 its solubility begins to increase [9]. In general, crystal formation primarily proceeds by nucleation from crystal embryos followed by crystal growth [10]. Struvite precipitation will not occur without a nucleation in itself [10]. Wang et al. [11] found that struvite powder as the seeding material provided sustainable operational methods to enhance struvite precipitation in synthetic wastewater solutions, indicating that the seeding material can be considered to one of important factors contributing to struvite precipitation. In our best knowledge, the current studies [5–7] on the struvite precipitation process in leachate treatment focused on the comparison of treatment efficiencies between the struvite precipitation process and other processes such as ammonia stripping, fenton oxidation, and nitrification/denitrification. Further studies are still required to improve the performance of struvite precipitation in the landfill leachate treatment.

The objective of this study was to enhance struvite precipitation for NH_4-N removal in landfill leachate. For this purpose, this study focused on the following. First, since struvite precipitation is principally based on the thermodynamic equilibrium of constituent ions in the solution, this study was conducted in the assumption that a performance of struvite precipitation

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might vary according to feeding sequence of chemicals of magnesium, orthophosphate, and buffering reagent. NH_4-N removal by forming struvite deposits was thus, investigated as a function of the feeding sequence of reagents. Second, this study also attempted to examine the possibility that an addition of the pre-formed struvite as the seeding material could enhance the overall performance of NH_4-N removal in landfill leachate.

2. Experimental method and materials

2.1. Leachate characterization

Raw leachate obtained from the municipal landfill in CheongJu, Korea was analyzed and characterized in the laboratory. Samples were directly collected from the landfill leachate collection facility. The landfill opened for operation in 1994 and closed in 1998. The characteristics of raw leachate were summarized in Table 1. The techniques used for sampling and analyses were in accordance with the Standard Method for the Examination of Water and Wastewater [12].

2.2. Materials

For struvite formation, magnesium chloride ($MgCl_2 \cdot 6H_2O$) solution of 70 g Mg^{2+}/L and potassium phosphate (KH_2PO_4) solution of 50 g PO_4^{3-}/L were used as alternate sources of magnesium ions and orthophosphate ions, respectively. In all experiments, magnesium and orthophosphate were fed to reach at the molar ratio of NH_4:Mg:PO_4 of 1:1.2:1.2 because the struvite precipitation occurs when the combined concentrations of the three components exceed the struvite solubility limit [13]. 7 N NaOH was used to control pH in the solutions. All chemicals used were analytical grade.

2.3. Experimental setup

Experiments were carried out at ambient laboratory temperature with a jar test apparatus. Jars were made of acrylic plastic with dimensions of 11.5 cm × 11.5 cm × 25 cm and held 1.0 L of liquid. The paddles at the end of each stirrer shaft had a diameter of 7.6 cm and height of 2.5 cm.

Table 1
The characteristics of raw leachate from the municipal landfill in CheongJu, Korea

Parameter	Concentration range
TSS (mg/L)	100–200
TCOD (mg/L)	1500–2500
SCOD (mg/L)	1300–1800
Orthophosphate (mg/L)	1–45
Ammonia-N (mg/L)	800–2200
pH	7.2–8.7
Total alkalinity, mg/L as $CaCO_3$	3300–7300
Turbidity (NTU)	25–97

Table 2
Experimental conditions for determining the feeding sequence of added reagents: pH was controlled using 7 N NaOH; $MgCl_2 \cdot 6H_2O$ and KH_2PO_4 solutions were used as alternate sources of magnesium ions and orthophosphate ions, respectively

Experiment	Feeding sequence
A1	$pH \rightarrow Mg^{2+} \rightarrow PO_4^{3-}$
A2	$pH \rightarrow PO_4^{3-} \rightarrow Mg^{2+}$
A3	$pH \rightarrow Mg^{2+}$ and PO_4^{3-}
A4	$Mg^{2+} \rightarrow pH \rightarrow PO_4^{3-}$
A5	$PO_4^{3-} \rightarrow pH \rightarrow Mg^{2+}$
A6	$Mg^{2+} \rightarrow PO_4^{3-} \rightarrow pH$
A7	$PO_4^{3-} \rightarrow Mg^{2+} \rightarrow pH$
A8	Mg^{2+} and $PO_4^{3-} \rightarrow pH$

2.3.1. Experimental setup: effect of feeding sequence of magnesium, orthophosphate, and buffering reagent

The effect of the feeding sequence of added reagents was first investigated. Feeding sequences of magnesium, orthophosphate, and buffering reagent tested were summarized in Table 2. Concentrations of NH_4-N and PO_4-P in landfill leachate tested were measured as 1380 mg/L and 10.9 mg/L, respectively. Experiments were carried out in independent eight jars. Since the chemical equilibrium of ions in the solution is reached in seconds, feeding interval between reagents was set up to 30 s. The pH in the solution was adjusted at the value of 9. The solution in jars was mixed at the mixing speed of 200 rpm and the mixing duration of 3 min. The mixed solution was allowed to be settled for the duration of 30 min. A syringe was used to withdraw 50 mL of the samples from each jar. The samples were filtered through membrane filters (pore size of 4.5 μm) prior to analysis.

2.3.2. Experimental setup: effect of the pre-formed struvite as the seeding material

The effect of struvite addition as the seeding material, in relation to magnesium and orthophosphate dosages, was evaluated. The seeding materials were prepared by drying and crashing the pre-formed struvite crystals. The seeding materials with a diameter ranging from 75 μm to 150 μm were sieved and collected. Concentrations of NH_4-N and PO_4-P in landfill leachate tested were measured as 1795 mg/L and 10.5 mg/L, respectively. According to the feeding sequence defined in the previous experiment, magnesium, orthophosphate, and buffering reagents were initially added into the solutions. The seeding materials were then applied in the ranges from 0 to 40 g/L in different jars. All experiments were conducted at pH ranging from 8 to 11. Subsequent experimental sequences were in accordance with those in the Section 2.3.1.

2.4. Analytical method

Ammonium concentration was measured by using UV-Spectrophotometer (HACH DR-4000). Phosphate level was assessed by the ascorbic acid method. The pH of samples was measured with an Orion Model 720 pH meter. The dried
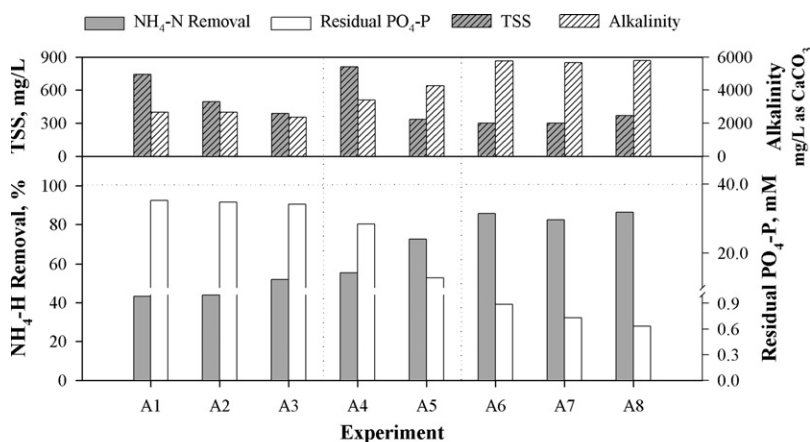
Fig. 1. Response of struvite precipitation to the experiment conditions in terms of NH_4-N removal, residual PO_4-P, TSS, and alkalinity: Initial NH_4-N concentration in solutions was 98.6 mM; initial PO_4-P, 0.35 mM; initial TSS, 115 mg/L; initial alkalinity, 6100 mg/L as $CaCO_3$. Magnesium and orthophosphate dosage for struvite precipitation was 1.0:1.2:1.2 in the molar ratio of NH_4-N:Mg:PO_4-P.

deposits produced in the experiments were characterized by X-ray diffraction (XRD, Model DMS 2000 system, SCINTAG).

3. Results and discussions

3.1. Effect of feeding sequence of magnesium, orthophosphate, and buffering reagent

The overall performance of the struvite precipitation in terms of NH_4-N removal, PO_4-P removal, TSS, and alkalinity is shown in Fig. 1. When buffering reagent was added for pH control prior to magnesium and orthophosphate (Experiments A1, A2, and A3), NH_4-N removal efficiencies were observed to be less than 50%. After the reaction, high level of PO_4-P was unexpectedly observed. Note that the residual PO_4-P will cause other nutrient problem in the aquatic system. In this study, pH was initially controlled to the value of 9, while after feeding magnesium, the final pH dropped as low as 6. Relatively low alkalinity corresponded. Stratful et al. [14] demonstrated that in terms of thermodynamic equilibrium, hydrogen is released into the solution when struvite is formed, resulting in a decrease in pH. It is therefore speculated that at low pH in the solution, further crystallization and precipitation of struvite was inhibited by the dissolution of struvite. This caused the increase in the residual concentration of PO_4-P.

In cases that magnesium was fed, followed by an addition of buffering reagent and orthophosphate (Experiment A4), NH_4-N removal efficiencies were still as low as 60%. High level of PO_4-P resided. It is speculated that magnesium ions predominately reacted with OH^- ions in the solutions readily to produce amorphous products such as $Mg(OH)_2$. These products correspondingly attributed to increased TSS in the solutions (see Fig. 1). When PO_4-P source was fed, followed by an addition of buffering reagent and magnesium (Experiment A5), NH_4-N removal efficiency was increased up to the 70% level and residual concentration of PO_4-P was relatively low as compared to the previous experiments. In case of Experiment A5, other ion, i.e., Ca^{2+} in leachate might preferentially react with PO_4-P to produce hydroxyapatite, dicalcium phosphate, and octacalcium

phosphate. Correspondingly, low level of residual PO_4-P was observed (see Fig. 1). In the raw sample solution, Ca^{2+} concentration was approximately 224 mg/L. Doyle and Parsons [15] discussed that struvite formation can be inhibited by the formation of calcium phosphates. Le Corre et al. [16] found an amorphous calcium phosphate in crystal formation of struvite when high concentration of Ca ions present in the solution.

In experiments when buffering reagent was fed subsequent to an addition of magnesium and orthophosphate (Experiments A6, A7, and A8), NH_4-N removal efficiencies reached at the 90% level. Residual PO_4-P and TSS concentrations were shown to be lower than those in other experiments. This indicated that a relatively pure precipitate of struvite could be driven by minimizing the potential for the unexpected reactions (i.e., reaction between magnesium ions and OH^-, reaction between PO_4^{3-} and Ca^{2+}). The results of this work demonstrated that high purity of struvite deposits could be achieved by an addition of magnesium and orthophosphate prior to the pH control.
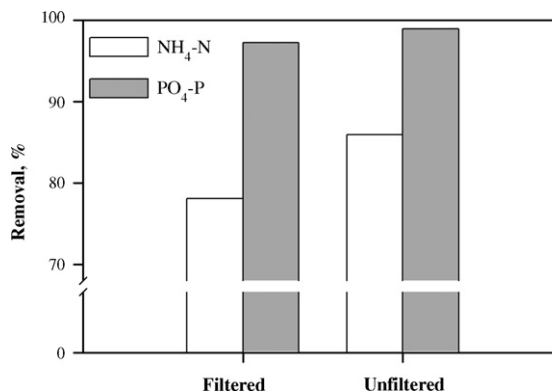

Fig. 2. NH_4-N and PO_4-P removal by forming struvite precipitation in landfill leachate. Sample solution filtered with 10 μm filter paper was compared to one unfiltered. Initial NH_4-N concentration in solutions was 134.6 mM; initial PO_4-P, 0.35 mM. Magnesium and orthophosphate dosage for struvite precipitation was 1.0:1.2:1.2 in the molar ratio of NH_4-N:Mg:PO_4-P.
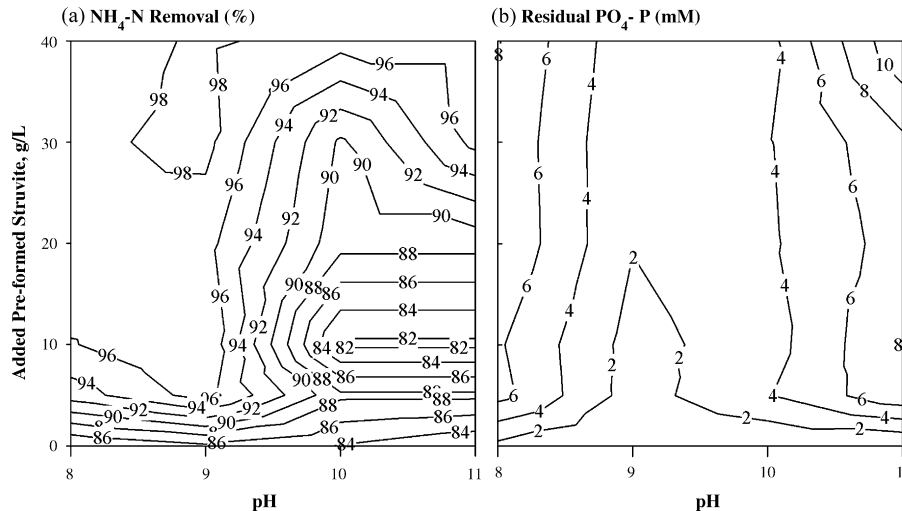
Fig. 3. Effect of pH and struvite addition on NH_4-N removal (a) and residual PO_4-P (b). Initial NH_4-N concentration in solutions was 128 mM; initial PO_4-P, 0.35 mM. Magnesium and orthophosphate dosage for struvite precipitation was 1.0:1.2:1.2 in the molar ratio of NH_4-N:Mg:PO_4-P.

3.2. Effect of the pre-formed struvite as the seeding material

In this study, the experimental feeding sequence of added reagents was based on the obtained results in Section 3.1. The experiment was initially conducted without any seeding materials. Fig. 2 shows the obtained results from samples filtered with 10 μm filter paper as compared to one unfiltered. High percent removals of NH_4-N and PO_4-P were observed in the unfiltered sample, speculating that suspended solids above particle size of 10 μm might play a role in the embryo for the crystal nucleation. This resulted in enhancing NH_4-N and PO_4-P removals by forming struvite precipitation. Wang et al. [11] discussed that larger crystals were preferred in struvite precipitation due to its fast settling time.

In order to improve further the performance of struvite precipitation by increasing the potential for the crystal growth, pre-formed struvite was fed in the sample solution as the seeding material. Fig. 3a was developed from the observed results of NH_4-N removal as a function of pH and the amount of added struvite. pH varied from 8 to 11 and the seeding material was added from 0 to 40 g/L. As shown in Fig. 3a, NH_4-N removal varied as a function of pH as well as the amounts of pre-formed struvite. At all pH, the overall performance of NH_4-N removal was enhanced by adding pre-formed struvite as the seeding material. It is believed that at low level of the seeding material, struvite precipitation proceeds by two mechanisms, namely the crystal nucleation and the crystal growth, while at high level of the seeding material the crystal growth is preferred to the crystal nucleation. For observing the dissolution of PO_4-P deposits, residual PO_4-P concentrations were plotted in Fig. 3b as a function of pH and the seeding material. It is speculated that dissolution of the non-equilibrium precipitates of struvite increased residual level of PO_4-P. It is important to note that residual orthophosphate brings other nutrient problem in the aquatic environment. At pH 9, residual PO_4-P concentration was lower than at other pH values, indicating that determination
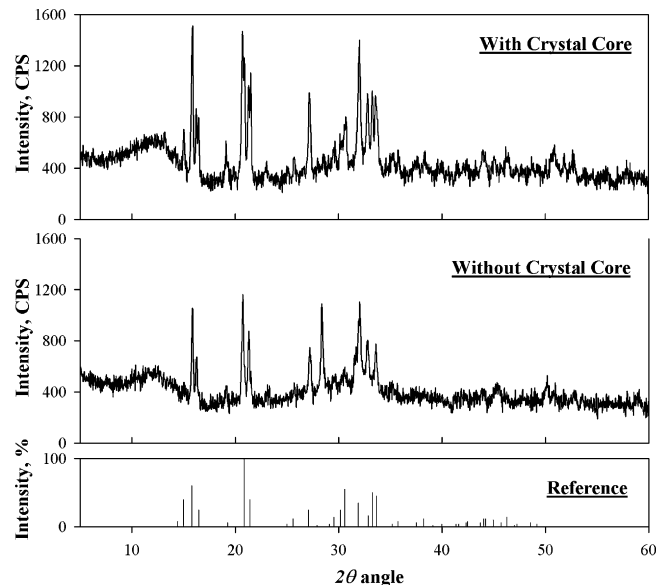

Fig. 4. XRD diffractogram of precipitate collected after crystal core addition compared to precipitate without crystal core addition.

of addition of the seeding material requires consideration of pH effects on thermodynamic equilibrium in the solution. Fig. 4 shows X-ray diffractograms of the precipitated matters, demonstrating that the peaks at both cases exhibited several peaks indicative of the presence of struvite.

4. Conclusion

For NH_4-N removal purpose in landfill leachate, the precipitation of struvite was performed with an excess of precipitating reagents, magnesium and orthophosphate. Particularly, struvite precipitation from landfill leachate rich in NH_4-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 stru-

vite precipitation. Adding the reagents in reverse sequence caused local formation of inappropriate deposits, which contaminated the desired struvite. Precipitation of struvite was further enhanced by seed addition. When struvite is used as the seeding material, the dissolution of precipitating reagents should be considered. Finally, struvite precipitation for NH_4-N removal in landfill leachate was improved by the careful consideration of the feeding sequence of added reagents and seed addition.

Acknowledgement

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