

# Struvite precipitation from anaerobic co-digestion residues of poultry manure and maize silage

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## INTRODUCTION (1/3)

Anaerobic digestion (AD) of organic wastes including animal manure has been **applied successfully** to convert them into profitable **by-products as well as to reduce the pollution caused by these wastes.**

The effluent stream of AD is **rich in nutrients** and therefore can be used as a liquid fertilizer. However, the **unavailability of the land area** to which the liquid fertilizer can be applied, does not enable effective application of AD effluents and **cause several environmental problems** such as eutrophication in nearby water bodies.

Therefore, in order to avoid the adverse environmental impacts due to over application of AD effluents on limited land or leaching of liquor into the groundwater, **the nutrients must be completely or partially removed.**



## INTRODUCTION (2/3)

Moreover, there is an increasing awareness of **limited natural resources** and control over the sources of N&P shifted from **removal to recovery**.

This can be explained by the dependency of modern agriculture on P. There is **no substitute of P** in agriculture and it is a **non-renewable source**. With the present P utilization rates of 40 million tons of P as P<sub>2</sub>O<sub>5</sub> each year, the available resources of P are expected to be **exhausted in 100-250 years**. On the other hand, as a basic building block of plant protein; nitrogen is an essential element for agriculture and there is a **growing demand for the nitrogenous fertilizers** in the world.

Crystallization of N and P in the form of **magnesium ammonium phosphate** ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , struvite) is one of the possible techniques used to **remove and recover nutrients from wastewater**. This approach is based on resource recovery because struvite can be used in agriculture as a **fertilizer**.



## INTRODUCTION (3/3)

SP process has been applied to various wastes, such as calf manure, landfill leachate, etc. However, most of the studies in the literature focused on the removal/recovery of the **readily available nutrients** in the wastes.

Yet, in order to **recover the maximum amount of nutrients** particularly P from wastes the **dissolution/release of the bounded nutrients from the solid phase** to the aqueous phase is imperative. Therefore, recently a number of researchers focused on the extraction of the nutrients present in the solid phase residues of different wastes such as poultry litter, chicken manure incineration ash, and municipal wastewater treatment plant sludges.

There is a **very limited information in the literature on the recovery of N and P from the solid phase** of the anaerobically digested poultry manure.



## OBJECTIVE

The objective of this study was to investigate the **recovery** of N and P from the **both the liquid and the solid phase effluents** of a full-scale co-digestion plant utilizing poultry manure and maize silage.

To this purpose, the liquid and the solid phases of the AD sample were treated separately, and **acidic dissolution** was performed prior to SP from the solid phase of the sample.



# MATERIALS AND METHODS (1/5)

## *Waste characteristics*

The wastewater sample was taken from the primary anaerobic digester effluent of a **full-scale biogas plant, co-digesting poultry manure and maize silage** at a waste mixing ratio of 0.25:0.75 located in Freising Munich, Germany. The **solid-liquid separation** of the anaerobic digester effluent was achieved by **centrifugation and sieving**. The liquid phase was used **directly** for struvite precipitation experiments, where the solid phase was subjected to the **phosphorus dissolution** process before precipitation experiments. (Table 1).

## *Experimental set-up and procedures*

The experiments were performed at the laboratories of the Department of Wastewater Technology in the University of Stuttgart, Germany.

Table 1. Characterization of the phase-separated effluent.

Parameter	Concentration			
	Liquid phase	Unit	Solid phase	Unit
TS	39±1	g kg <sup>-1</sup>	175±10	g kg <sup>-1</sup>
VS	69±1	% of TS	79.6±0.6	% of TS
COD	44,208±658	mg L <sup>-1</sup>	nd	-
sCOD	27366±0	mg L <sup>-1</sup>	nd	-
TKN	6,173±136	mg L <sup>-1</sup>	30.1±2.8	mg g <sup>-1</sup> dry matter
NH4-N	3,907±105	mg L <sup>-1</sup>	nd	-
PO4-P	60.5±0.7	mg L <sup>-1</sup>	nd	-
TP	209±1	mg L <sup>-1</sup>	16.1±0.2	mg g <sup>-1</sup> dry matter
Al	6.7±0.1	mg L <sup>-1</sup>	878±101	mg kg <sup>-1</sup> dry matter
Ca	441±11	mg L <sup>-1</sup>	4,030±7	mg kg <sup>-1</sup> dry matter
Cd	<0.025	mg L <sup>-1</sup>	<2.3	mg kg <sup>-1</sup> dry matter
Co	0.2±0.0	mg L <sup>-1</sup>	3.12±0.07	mg kg <sup>-1</sup> dry matter
Cr	0.3±0.0	mg L <sup>-1</sup>	7.76±0.44	mg kg <sup>-1</sup> dry matter
Cu	3.4±0.0	mg L <sup>-1</sup>	113±1	mg kg <sup>-1</sup> dry matter
Fe	110±0	mg L <sup>-1</sup>	4715±2	mg kg <sup>-1</sup> dry matter
Hg	0.008	mg L <sup>-1</sup>	<0.078	mg kg <sup>-1</sup> dry matter
K	5,380±96	mg L <sup>-1</sup>	26,235±32	mg kg <sup>-1</sup> dry matter
Mg	10.5±1.8	mg L <sup>-1</sup>	8,018±108	mg kg <sup>-1</sup> dry matter
Ni	0.3±0.0	mg L <sup>-1</sup>	5.13±0.74	mg kg <sup>-1</sup> dry matter
Pb	0.3±0.0	mg L <sup>-1</sup>	<4.66	mg kg <sup>-1</sup> dry matter
Zn	15.5±0.1	mg L <sup>-1</sup>	649±2	mg kg <sup>-1</sup> dry matter
Conductivity	33	mS cm <sup>-1</sup>	-	-
pH	7.9	-	-	-



## MATERIALS AND METHODS (2/5)

### *Precipitation experiments*

Four consecutive steps are followed in the precipitation experiments conducted with the liquid phase and phosphorus-enriched phase of the biogas plant effluent; **(i) addition of chemicals, (ii) mixing, (iii) settling, (iv) filtration.** The experiments were conducted in continuously stirred batch reactors of 150 mL at room temperature (21-22°C). **The concentration of NH<sub>4</sub>-N was kept constant at its original level in all experimental runs. The amounts of Mg and PO<sub>4</sub>-P ions to be added** were calculated considering initial concentrations of these ions in wastewater and raised accordingly to adjust the desired total molar concentration ratio of Mg:N:P and/or Mg:P in the reactor. **After the pH of the solution became constant at the desired level with a variation of ± 0.01 pH units, 30 min of mixing was applied and at the end of the mixing period, the reactor content was allowed to settle down for 60 minutes.** Then the reactor content was **filtered** through a filter of pore size range of 4-12 µm and the filtrate was analyzed for its PO<sub>4</sub>-P, NH<sub>4</sub>-N and metal content. The precipitates were dried at 30±2 °C overnight. After drying, the precipitate was separated manually from the filter paper and kept at room temperature (21- 22°C) until analyzed for X-ray diffraction (XRD).



# MATERIALS AND METHODS (3/5)

## *Phosphorus dissolution process*

Phosphorus dissolution was achieved in four steps: **(i) dilution (ii) acidic dissolution (iii) mixing, and (iv) phase separation**. The solid phase was diluted by distilled water until the total solids (TS) concentration became **5 %**. Then, the pH of the diluted waste was **adjusted to 2.0** by the addition of 20 % HCl (v/v). The acidic mixture **was mixed at 250 rpm by using the jar test apparatus for two hours**. After the dissolution, separation of the phosphorus-enriched liquid phase from the remaining solid phase was achieved by **centrifugation and sieving**. The filtrate (phosphorus-enriched liquid phase) was characterized and kept refrigerated at 4°C until used (Table 2).

*Table 2. Characterization of the phosphorus-enriched liquid phase.*

Parameter	Concentration, mg L <sup>-1</sup>
NH <sub>4</sub> -N	1484±4
PO <sub>4</sub> -P	827±3
Mg	406±1
Al	2.11
Ca	1581
Cd	<0.025
Cu	0.284
Fe	122
K	1439
Ni	0.136
Zn	15.3





# MATERIALS AND METHODS (4/5)

## Liquid phase experiments

NH<sub>4</sub>-N is in excess in the biogas plant effluent and additions of Mg and PO<sub>4</sub>-P from external sources are necessary. This is because the molar ratio of struvite forming ions (Mg:N:P ratio) should be **at least unity** for intentional struvite precipitation whereas higher Mg can increase the removals of PO<sub>4</sub>-P and NH<sub>4</sub>-N from the wastewater. The effect of Mg:N:P molar ratio and the use of different P sources were tested. The experimental setup is depicted in Table 3.

Table 3. The experimental set-up.

Exp. No	Tested molar ratio	Basis of chemical addition	Adjusted molar ratio	Chemicals added	pH
<i>Liquid phase experiments</i>					
L1 <sup>a</sup>	Mg:N:P	NH <sub>4</sub> -N	1:1:1	H <sub>3</sub> PO <sub>4</sub> , MgCl <sub>2</sub> .6H <sub>2</sub> O	8.5
L2 <sup>a</sup>	Mg:N:P	NH <sub>4</sub> -N	1.3:1:1	H <sub>3</sub> PO <sub>4</sub> , MgCl <sub>2</sub> .6H <sub>2</sub> O	8.5
L3 <sup>a</sup>	Mg:N:P	NH <sub>4</sub> -N	1.5:1:1	H <sub>3</sub> PO <sub>4</sub> , MgCl <sub>2</sub> .6H <sub>2</sub> O	8.5
L4	Mg:N:P	NH <sub>4</sub> -N	1:1:1	NaH <sub>2</sub> PO <sub>4</sub> .2H <sub>2</sub> O, MgCl <sub>2</sub> .6H <sub>2</sub> O	8.5
L5	Mg:N:P	NH <sub>4</sub> -N	1.3:1:1	NaH <sub>2</sub> PO <sub>4</sub> .2H <sub>2</sub> O, MgCl <sub>2</sub> .6H <sub>2</sub> O	8.5
L6	Mg:N:P	NH <sub>4</sub> -N	1.5:1:1	NaH <sub>2</sub> PO <sub>4</sub> .2H <sub>2</sub> O, MgCl <sub>2</sub> .6H <sub>2</sub> O	8.5
<i>Solid (phosphorus-enriched liquid) phase experiments</i>					
P1	Mg:N:P	NH <sub>4</sub> -N	1:1:1	H <sub>3</sub> PO <sub>4</sub> , MgCl <sub>2</sub> .6H <sub>2</sub> O	8.5
P2	Mg:N:P	NH <sub>4</sub> -N	1.3:1:1	H <sub>3</sub> PO <sub>4</sub> , MgCl <sub>2</sub> .6H <sub>2</sub> O	8.5
P3	Mg:N:P	NH <sub>4</sub> -N	1.5:1:1	H <sub>3</sub> PO <sub>4</sub> , MgCl <sub>2</sub> .6H <sub>2</sub> O	8.5
P4	Mg:P	PO <sub>4</sub> -P	1:1	MgCl <sub>2</sub> .6H <sub>2</sub> O	8.5
P5	Mg:P	PO <sub>4</sub> -P	1.3:1	MgCl <sub>2</sub> .6H <sub>2</sub> O	8.5
P6	Mg:P	PO <sub>4</sub> -P	1.5:1	MgCl <sub>2</sub> .6H <sub>2</sub> O	8.5
P7	- <sup>b</sup>	-	1:2 <sup>c</sup>	na <sup>d</sup>	8.5
P8	-	-	1:2	na	9.5

<sup>a</sup> Experiments conducted with 200 mL of sample.

<sup>b</sup> Not applicable

<sup>c</sup> Initial Mg:P ratio

<sup>d</sup> No addition



## MATERIALS AND METHODS (5/5)

### *Solid phase experiments*

In the experiments conducted with the phosphorus-enriched liquid phase, the effects of the molar ratio of Mg:N:P and the molar ratio of Mg:P were investigated separately. In order to observe the effect of the Mg:N:P molar ratio on the recoveries of NH<sub>4</sub>-N and PO<sub>4</sub>-P, **three different Mg:N:P ratios (1:1:1, 1.3:1:1 and 1.5:1:1) were used** (Table 3). In order to investigate the effect of the molar ratio of Mg:P on the recoveries of PO<sub>4</sub>-P and NH<sub>4</sub>-N, three different **Mg:P ratio, namely, 1:1, 1.3:1 and 1.5 :1 were used** in the experiments. To observe the effects of **external additions of Mg and P**, two experiments (Experiment P7 and P8) were conducted without addition of any chemical except the buffering reagent (20 % v/v NaOH) to adjust the pH of the solution.

### *Analytical methods*

The analyses were performed according to the Deutsches Institut für Normung e.V. (DIN) standards.



## RESULTS AND DISCUSSION (1/6)

The reductions in the concentrations of the ions are referred to as “**removal**” in liquid phase experiments. While the removal of the nutrients from the phosphorus-enriched liquid phase is referred to as “**recovery**” but not removal.

### *The liquid phase experiments*

The results of the liquid phase experiments indicated that the **variation of Mg:N:P from 1:1:1 to 1.3:1:1 led to an increase in the removal of PO<sub>4</sub>-P; from 90.3 % to 97.8 % and from 88.8 % to 97.8 %**, by the use of H<sub>3</sub>PO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O, respectively (Figure 1). However, the difference in the removal of PO<sub>4</sub>-P was **minimal by the variation of Mg:N:P from 1.3:1:1 to 1.5:1:1** (from 97.8 % to 98.4 % and from 97.0 % to 98.1 %, by the use of H<sub>3</sub>PO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O, respectively).

The **NH<sub>4</sub>-N removals** obtained in these experiments **ranged between 67.0-74.7 %** (Figure 1). There are **two major removal mechanisms of NH<sub>4</sub>-N** in systems with high concentrations of Mg and PO<sub>4</sub>-P, namely **SP and air stripping** (Uludag-Demirer and Othman, 2009). Even though SP leads to formation of other minerals containing Mg and/or PO<sub>4</sub>-P (e.g. hydroxylapatite, newberyite), examination of all the possible minerals indicated that the **only mineral containing NH<sub>4</sub><sup>+</sup> in its composition is struvite** (Uludag-Demirer and Othman, 2009).



## RESULTS AND DISCUSSION (2/6)

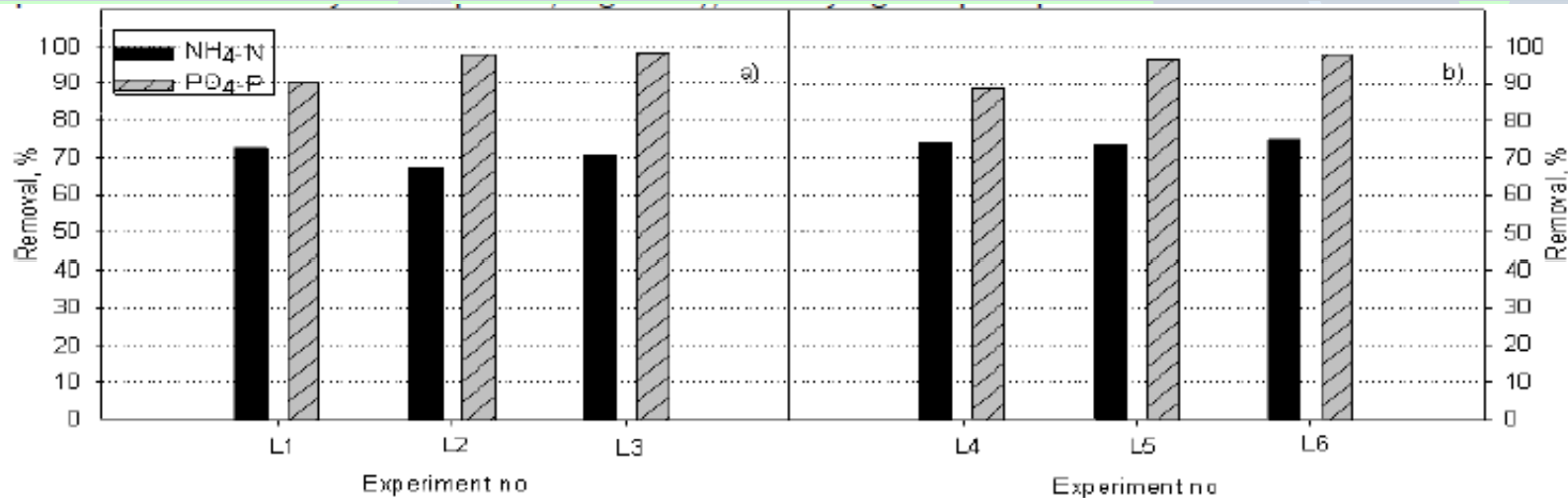


Figure 1: Removal efficiencies of the liquid phase experiments by the use of a)  $H_3PO_4$  b)  $NaH_2PO_4 \cdot 2H_2O$ .

The rate of air stripping on the removal of  $NH_4-N$  was not determined in this study. However, the average  **$NH_4-N$  removals via air stripping at pH level of 8.5 at room temperature (21-22°C) was recorded as 2 %** in another study which used the effluent of a bench scale poultry manure digester (Yilmazel et al., 2011). This suggests that **at pH level of 8.5 there is negligible loss of ammonia to atmosphere**. Therefore, high removal efficiencies of  $NH_4-N$  in the experiments (L1-L6) can be considered as an indication of formation of struvite in the reactors. The **XRD** pattern generated from the sample collected from Experiment L6 matched with the database standard for struvite **identifying the precipitate to be struvite**.



## RESULTS AND DISCUSSION (3/6)

### *Solid phase experiments*

The recovery of N and P can only be achieved by using the dissolved fraction, but most of the nutrients are bounded in the solid phase. For this purpose, the **solid phase was subjected to the phosphorus dissolution process** which led to the transformation of available phosphates into the orthophosphate. This can be attributable to the disintegration of the cell walls and mineralization of the microbial cells. This process also releases P from insoluble inorganic phosphate complexes.

In Experiment P1, **considerably high recovery efficiencies of N and P** (89.1 % and 81.8 % for  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$ , respectively) were achieved (Figure 3).

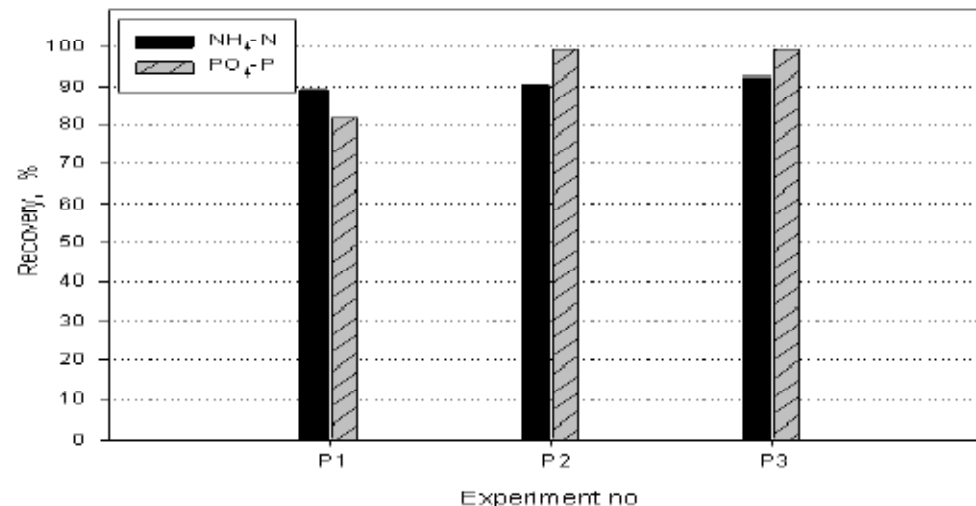


Figure 3: Recovery efficiencies of the solid phase Mg:N:P molar ratio experiments.



## RESULTS AND DISCUSSION (4/6)

The analysis of the resulting solution from Experiment P1 revealed that **Mg at a concentration higher than the stoichiometric ratio was required** to achieve higher recovery and **thus the limiting component is Mg**. This may imply the **precipitation of other Mg containing minerals in the reactor**. To test this XRD analysis of the precipitate collected from Experiment P1 performed (Figure 4). The results **confirmed the presence of newberyite [MgHPO<sub>4</sub>.3H<sub>2</sub>O] together with struvite.**

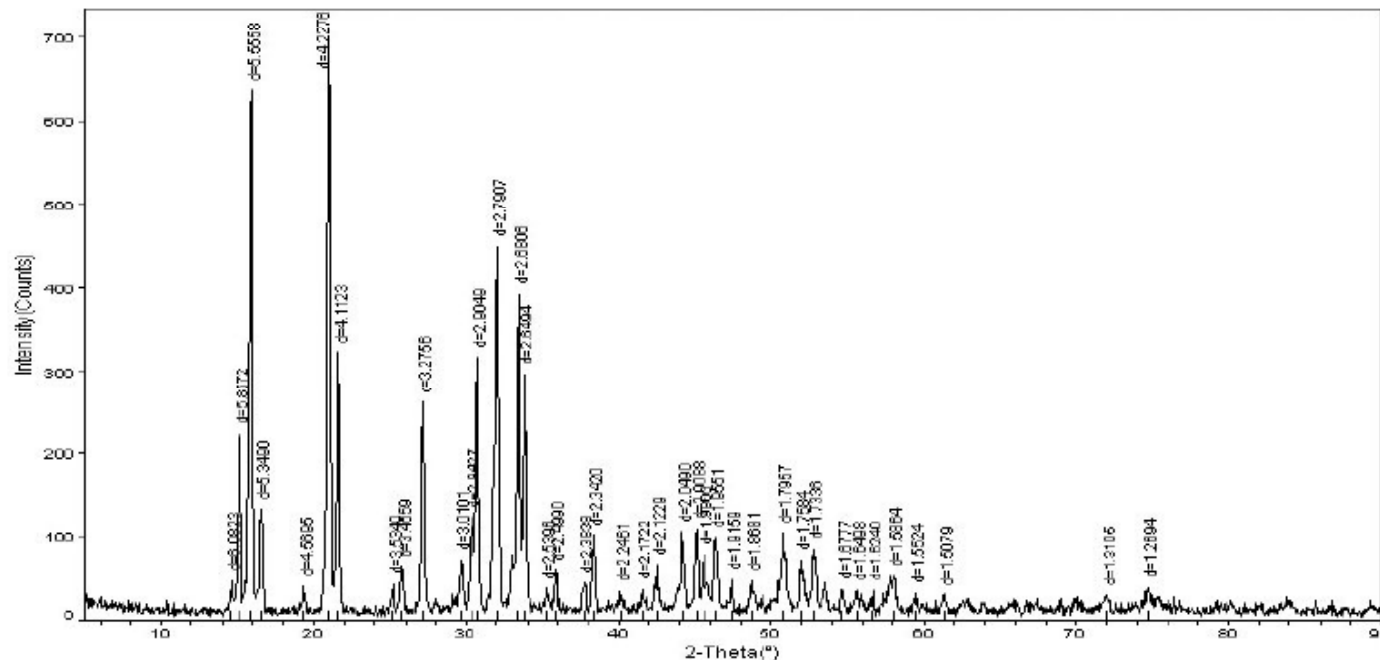


Figure 4: XRD patterns of the precipitate collected from the Experiment P1.

[The d-spacing of the strong lines of struvite are 4.25, 5.60, 5.90, 2.92, 2.69, 2.66, 4.14, and 2.80. Retrieved from powder diffraction (PDF) card 71-2089. The d-spacing of the strong lines of newberyite are 5.94, 4.71, 3.46, 3.04, 5.34, 3.09, 4.50, and 4.14. Retrieved from powder diffraction (PDF) card 72-0023.]



## RESULTS AND DISCUSSION (5/6)

The comparison of the Experiment P2 and P3 indicated that there is **no need for further increase of Mg concentration** because the variation of Mg:N:P ratio from 1.3:1:1 to 1.5:1:1 **no longer affect PO<sub>4</sub>-P recovery efficiency**. The efficiency leveled out at about 99.2 %, which is considerably high (Figure 3). The XRD analysis of the precipitate collected from Experiments P3 **confirmed the presence of struvite** (data not shown).

The impact of the variation of the molar ratio of Mg:P from 1:1 to 1.5:1 on the **recovery of NH<sub>4</sub>-N was negligible** (15.8 % - 17.2 %) and the **recovery efficiency of PO<sub>4</sub>-P (Table 4) leveled out at about 99.9 %**.

The results from **XRD** analysis of the precipitate collected from Experiment P6 clearly depicted the **presence of struvite** (data not shown).

*Table 4. Results of the solid phase Mg:P molar ratio experiments.*

Exp	Molar Ratio of Mg:P	% Recovery	
		NH <sub>4</sub> -N	PO <sub>4</sub> -P
P4	1:1	17.2	99.8
P5	1.3:1	16.4	99.8
P6	1.5:1	15.8	99.9
P7	1:2	15.7	99.2
P8	1:2	13.4	99.9

# RESULTS AND DISCUSSION (6/6)

Based on the results it can be interpreted that Mg concentration controls both the removal of N and P, and it was obvious that PO<sub>4</sub>-P concentration controls the removal of NH<sub>4</sub>-N, significantly. This is because the major removal mechanism of NH<sub>4</sub>-N was by SP, while PO<sub>4</sub>-P removal may be by the precipitation of several minerals including struvite (Uludag-Demirer, 2008). The evaluation of the solid phase experiments with highest recovery efficiencies are summarized in Table 5.

Table 2. Characterization of the phosphorus-enriched liquid phase.

Parameter	Concentration, mg L <sup>-1</sup>
NH <sub>4</sub> -N	1484±4
PO <sub>4</sub> -P	827±3
Mg	406±1
Al	2.11
Ca	1581
Cd	<0.025
Cu	0.284
Fc	122
K	1439
Ni	0.136
Zn	15.3



Table 5. Evaluation of the solid phase experiments with highest recovery efficiencies.

AD effluent composition	Exp. No.	Molar ratio of Mg:N:P	Final Concentration, mg L <sup>-1</sup>		Advantages	Disadvantages	Proposed Application
			NH <sub>4</sub> -N	PO <sub>4</sub> -P			
Original with addition of extra Mg	P6	1.5:3:1	1250±10	1.20±0.00	No addition of PO <sub>4</sub> -P, high recovery of PO <sub>4</sub> -P, struvite purity is higher in comparison to P8	Addition of Mg, poor recovery of NH <sub>4</sub> -N, high concentration of NH <sub>4</sub> -N in effluent	Only for the recovery of PO <sub>4</sub> -P
Original with pH increase to 9.5	P8	1.6:2 <sup>a</sup>	1286±5	0.90±0.00	No addition of Mg and PO <sub>4</sub> -P, high recovery of PO <sub>4</sub> -P,	Purity of struvite is poor, high concentration of NH <sub>4</sub> -N in effluent, poor recovery of NH <sub>4</sub> -N	Only for the recovery of PO <sub>4</sub> -P
Simulating struvite stoichiometry with excess Mg	P3	1.5:1:1	114±0	6.43±0.08	High recoveries of PO <sub>4</sub> -P and NH <sub>4</sub> -N, purity of struvite is high, nearly four times higher amount of precipitate was obtained	Addition of PO <sub>4</sub> -P and excess Mg	For the recoveries of both NH <sub>4</sub> -N and PO <sub>4</sub> -P

<sup>a</sup>Initial molar ratio of the phosphorus-enriched liquid phase

Over 92% NH<sub>4</sub>-N and over 99% PO<sub>4</sub>-P Removal/Recovery





# CONCLUSIONS

- ⇒ The effect of P source on the removals of  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$  is not considerable.
- ⇒ The influence of excess Mg in the removal/recovery of  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$  was significant.
- ⇒ The use of the acidic phosphorus dissolution process was applicable to the solid phase of the AD effluent and can be used as a preliminary step of SP experiments to obtain a nutrient rich solution.
- ⇒ By only adding Mg to the phosphorus-enriched solution, all available  $\text{PO}_4\text{-P}$  was recovered, with only partial recovery of  $\text{NH}_4\text{-N}$ .
- ⇒ External addition of Mg and P led to more than 90.0 % recoveries of both  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$  from the phosphorus-enriched solution.



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# THANK YOU FOR YOUR ATTENTION...

If you have questions or ideas to discuss, please do not  
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