

**Phosphorus Removal from Synthetic
Anaerobic-Digested Manure Wastewater
Using an Upflow Fluidized Bed Reactor System**

ENE 806

Laboratory Feasibility Studies in Environmental Engineering

Spring 2006

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Report by

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PID: A36432706

April, 30th, 2006

Acknowledgment

First of all, I would like to thank Professor Syed A. Hashsham who instructed this course and gave me so many useful advices for my project. The Laboratory Feasibility Studies in Environmental Engineering course was wonderful because it provided me a lot of chances to think about goal-oriented experiment set-up instead of simply copying experiment techniques. Professor Hashsham has given me plenty of guidance, advices and patience, which was greatly helpful for the final successful running of the FBR system.

And, I am very thankful to Joseph Nguyen for his help and advices during this lab course. He showed me the measurement schemes involved in this project.

Last but not the least, I would like to thank all the classmates for their suggestions, encourage and interest in my project.

Ruifang Xu

May, 2006

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1. Introduction

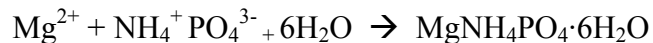
1.1. Phosphorus contents in anaerobic-digested manure wastewater

Total phosphorus is composed of organic phosphorus, hydrolysable phosphorus and dissolved orthophosphate (LaMotte auxiliary phosphorus test kit manual). In manure wastewater, more than 80% of phosphorus is in the hydrolysable forms. The dissolved orthophosphate is less than 5% of total phosphorus.

1.2. Accumulation of struvite

Accumulation of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) occurs usually in anaerobic digestion and post-digestion of phosphorus, ammonia and magnesium containing wastewater (Beal et al., 1999; Booker, 1999; Burns et al., 2001; Kalyuzhnyi et al., 2001; Ohlinger, et al., 2000; Nelson et al., 2000; Wrigley et al., 1992). As struvite can result in diminished pipe flow capacity, blinding and fouling of mechanical equipment and premature equipment failure, struvite accumulation is thought to be a costly problem in the wastewater treatment industry. However, this reaction can be employed for phosphorus removal and struvite formation (Ohlinger, et al., 2000) in the treatment of phosphorus-containing anaerobic-digested manure wastewater.

Studies have been made for struvite thermodynamics and kinetics (Ohlinger et al., 1998; Ohlinger et al., 1999). The reaction is shown as following:



It was indicated that the dissolved orthophosphate is more easily to be transferred to struvite. The content of dissolved orthophosphate in manure wastewater is a limiting factor in struvite formation (Zhao, 2004).

The struvite precipitation potential is highly pH dependent. The higher pH is, the larger the struvite precipitation potential is (Ohlinger, et al., 2000). pH level in the reactor is thus a key factor in struvite formation and precipitation. Basic environment encourages

struvite formation. However, an increase of dissolved orthophosphate content in the wastewater facilitates the struvite formation in a great extent. Because dissolved orthophosphate is more stable in acidic environment, the manure wastewater should be maintained at pH below 6.50 before being treated in the reactor. pH increase of the influent wastewater should occur in the reactor to encourage struvite formation on the carrier media (Zhao, 2004).

The struvite kinetics showed that struvite accumulation preferentially occurs in locations with high mixing energy (Ohlinger, et al., 2000). Because fluidized bed reactor (FBR) presents apparent advantage in mixing energy, it has been applied to struvite precipitation reaction (Ohlinger, et al., 2000; Hashsham and Zhao, 2004; Zhao, 2004). Besides, FBR is capable of achieving treatment in low hydraulic retention time (HRT) because distinct mechanical advantages and high contact area between media and the wastewater can be attained in the FBR. And, for comparable treatment efficiency, the required reactor volume is greatly reduced (Shieh et al., 1986; Sokol, 2003). A further advantage is the possible elimination of the secondary clarifier in the presence of sedimentation portion downstream the fluidization reaction portion (Sokol, 2003).

1.3. Objectives of the present study

The objectives of this study were to set up an upflow FBR system to remove the phosphorus and ammonia in the synthetic anaerobic-digested manure wastewater by virtue of struvite formation, and to study the influence of pH level inside the FBR on phosphorus/ammonium removal efficiency.

2. Materials, Equipments and Methods

2.1. Synthetic Anaerobic-digested Manure Wastewater

The wastewater was synthesized as per the contents of the major ingredients of real manure wastewater. Because this main purpose of this FBR experiment was to set up and study the performance of the FBR system, the recipe of the wastewater ingredients was simplified to access ideal phosphorus removal efficiency in the present project. Although dissolved orthophosphate constitutes a relatively small amount of total phosphorus in manure wastewater, it was used in the present study as the only phosphate source in the synthetic wastewater because it was shown to be more readily converted to struvite (Zhao, 2004).

The synthetic anaerobic-digested manure wastewater was made by three major constituents: phosphate, magnesium and ammonia (Table 1). Potassium orthophosphate (KH_2PO_4) and Dipotassium hydrogen orthophosphate (K_2HPO_4) were mixed by 1:1 as the dissolved orthophosphate source to maintain the influent pH level around neutral. Due to the high concentration and continuous mixing difficulty in the influent tank, some constituents were saturated. The influent contaminant concentration was determined by the same measurement to that of samples. The pH value of the influent was shown to be around 6.30.

Table 1. Recipe of the synthetic wastewater

Ingredients		MW (g/mol)	Influent Equivalent Ion Conc.		Influent Ingredient Conc.	
Dissolved Orthophosphate	KH_2PO_4	136.09	mg PO_4/L	310	mg/L	444.083
	K_2HPO_4	174.18	mg PO_4/L	310	mg/L	568.377
Dissolved Magnesium	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	203.3	mg Mg/L	445	mg/L	3,722.98
Ammonium	NH_4Cl	53.49	mg NH_3/L	1,200	mg/L	3,775.77

2.2. FBR System Set-up

2.2.1. FBR System Installation

Referred to Hashsham, et al. Scheme (Hashsham et al., 2004), a small pilot scale upflow FBR system was installed as shown in Figure 1. Fine sand was filled into the FBR column to facilitate the nucleation and separate struvite product from the liquid phase. A recirculation pump provided the buoyancy for fluidization of the sand particles. The FBR reactor was equipped with an automated pH control system and a base dosing line to maintain the pH level inside the FBR as desired.

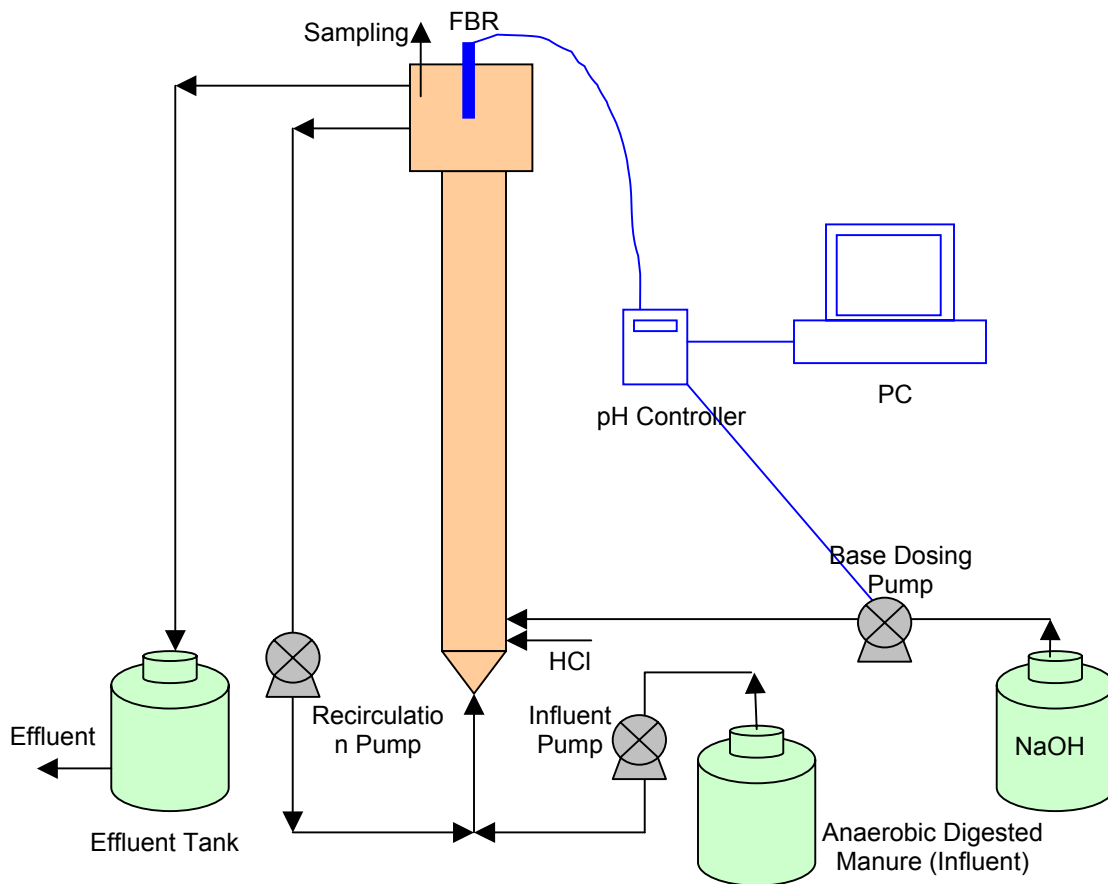


Figure 1. Pilot-scale upflow fluidised bed reactor system for phosphorus removal from synthetic anaerobic digested manure wastewater.

When empty the bed for next run, the mix liquid should be collected by an effluent tank. Sand discharge direct into the drain would cause serious clog.

2.2.2. FBR Specification

- Diameter:
- Fluidization volume (Low portion): 1.5 inch (3.8 cm)
- Sedimentation volume (Top portion): 3 inch (7.6 cm)
- Height:
- Fluidization volume (Low portion): 5 ft (152 cm)
- Sedimentation volume (Top portion): 9 inch (23 cm)
- Volume:
- Fluidization volume (Low portion): $3.14 \times (3.8/2)^2 \times 152 = 1722.98 \text{ mL}$
- Sedimentation volume (Top portion): $3.14 \times (7.6/2)^2 \times 23 = 1042.86 \text{ mL}$
- Carrier Media:
- Fine Sand (play ground sand) was used as the media for the struvite attachment. The sand media filled the FBR column up to 96 cm.
- By neglecting the void in the sand, the minimum effective working volume of the FBR: 1677.64 mL
- Fluidization volume (Low portion): $1722.98 \text{ mL} \times (152-96) \div 152 = 634.78 \text{ mL}$
- Sedimentation volume (Top portion): 1042.86 mL

2.2.3. FBR Operation Conditions

- Fluidization Rate: 1060.0 mL/min (tested in the empty bed when the pump was set at 120 RPM, the maximum flow rate).
 - Feeding Rate: 30.0 mL/min (tested when the reaction was in progress, the pump set at 3.0 rpm)
 - Up-flow speed
 - Low portion: $(1060.0 + 30.0) / [3.14 \times (3.8/2)^2] = 96.16 \text{ cm/min} = 1.60 \text{ cm/s}$
 - Top portion: $(1060.0 + 30.0) / [3.14 \times (7.6/2)^2] = 24.04 \text{ cm/min} = 0.40 \text{ cm/s}$
- When the fluidization rate and the feeding rate were set as above, the bed height was expanded from 96 cm to 148 cm, which provides a bed expansion as 54.17%. A 4 cm gap

between the expansion bed and the top sedimentation portion was used to better avoid the loss of sand media through the up-flow.

■ Expected minimum HRT:

$$1677.64 \text{ mL} \div 30.0 \text{ mL/min} = 55.92 \text{ min.}$$

■ Experiment HRT:

Assuming the safety factor as 2, a HRT of 112 min was used in the experiments.

2.3. Experiment Methods

A series of beaker batch experiments was made to optimize the pH levels to be applied in the FBR system. Then, phosphorus in synthetic manure wastewater was removed by FBR system at two optimized pH levels to study the influence of pH level on FBR-based phosphorus removal.

2.3.1. Beaker Batch Experiment

Each 1000 mL beaker was filled with 350 mL of fine sand, then with the synthetic wastewater up to 700 mL. Six beaker batch reactors were set as pH levels of 7.5, 8.0, 8.5, 9.0, 9.5, 10.0 by base addition, respectively. 120 rpm mixing was applied in the reaction for 30 min. Then the six batch reactors were stayed for 30 min for sand and struvite precipitation. The supernatant was filtered by 0.45 μm filter for contaminant concentration measurement. The pH levels at which the contaminants are removed at greatest extent would be assumed as optimized and applied in FBR system.

2.3.2. pH Control

The pH level should be maintained as basic to access a good phosphorus removal (Ohlinger, et al., 2000; Zhao, 2004).). The manure wastewater should be maintained at pH below 6.50 before being treated in the reactor in order for more stable presence of

dissolved orthophosphate in the influent. The pH increase was fulfilled in the FBR reactor by a base dosing line. And, during struvite formation, the pH level in the reactor generally drops. Base dosing was controlled by an automatic pH control system to increase the pH back up. An additional acid dosing line was also prepared to offset high pH in the case of lagging pH response.

This pH control system was made up of a pH controller, a peristaltic pump, a base tank and a base dosing line. A Hanna Instruments pH probe was connected to a panel-mounted pH meter (pH500 mode). The system schematic was shown as following.

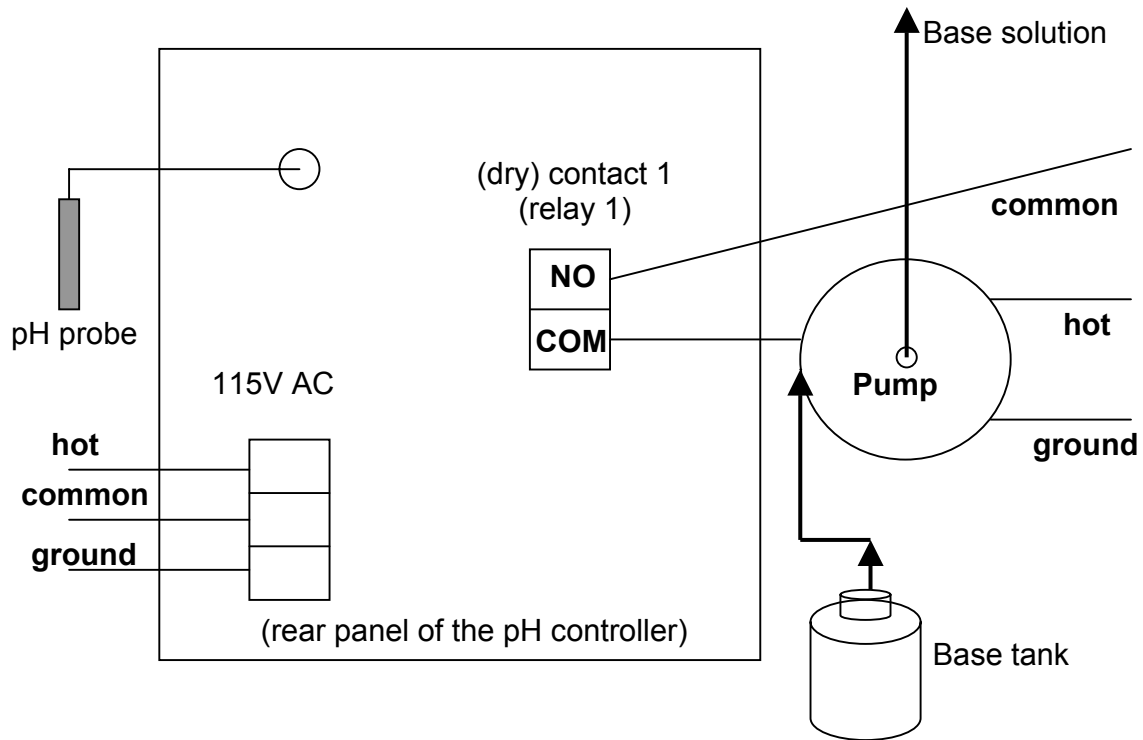


Figure 2. schematics of pH control system.

pH signals in the FBR reactor were measured by the pH probe and then transferred to the pH controller which can control the ON/OFF of the dry contact. This dry contact was connected to the base dosing pump and thus used to control the addition of the base solution. 2M NaOH was used to increase the pH levels in the FBR. A series D electronic metering peristaltic pump from Pulsatron Inc. was used to pump the base

solution. The power switch ON/OFF status can be changed under the control of the signal transferred from the pH control system.

A low setpoint relay design as can be seen from the following graphs was used to control the base dosing pump. This low setpoint relay was energized when the pH value was below the setpoint and was de-energized when the pH value was above the sum of setpoint and the hysteresis. When the relay was energized, the dry contact was connected and the base dosing pump circuit was switched on; when the relay was de-energized, the dry contact was disconnected and the base dosing pump circuit was switched off.

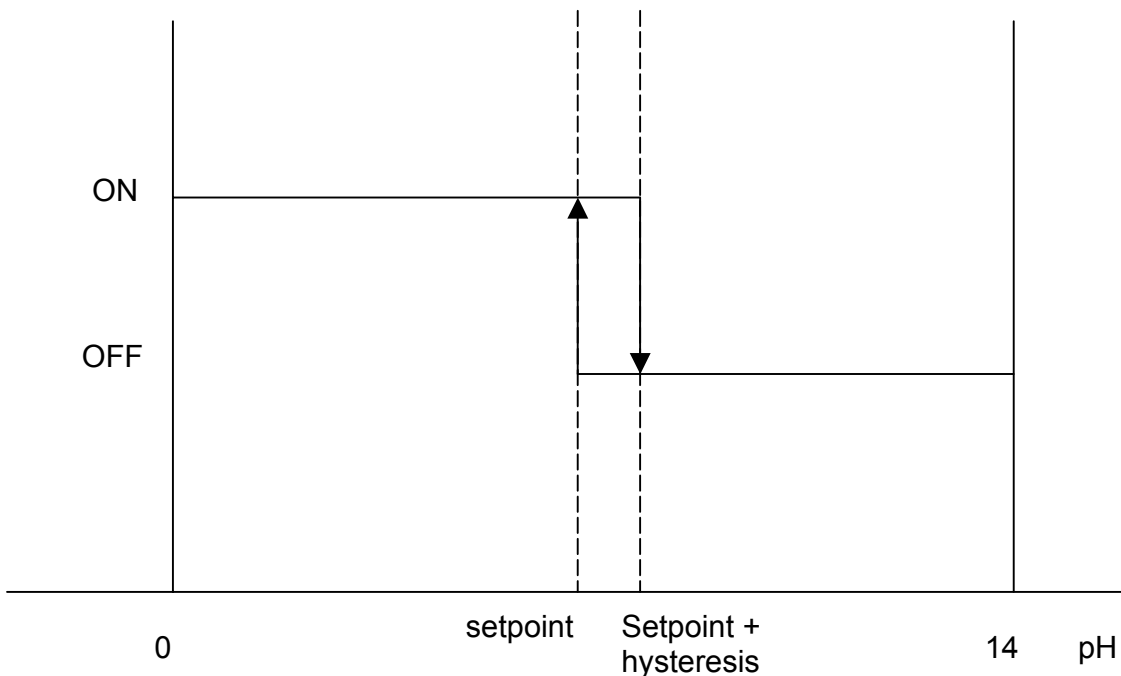


Figure 3. Low setpoint relay setting for base dosing pH control.

The performance of the pH control system is illustrated here by taking an example of low setpoint set at $\text{pH} = 9$: When the pH level of the reaction mix liquid in the reactor was above $\text{pH} = 9$, the base dosing pump circuit was disconnected and the pump was now working. When the pH level of the FBR drops down below $\text{pH} = 9 + 0.05$, the low setpoint relay was energized and the dry contact was connected. The pump starts to work to add the base into the FBR system and the pH level thus increases. When the pH level in the reactor increases to above $\text{pH} = 9$, the pump stops working.

Protocol of pH control system:

- Prepare 2M (80g/L) base solution NaOH.
- Assemble the suck tubing and effluent tubing to the base dosing peristaltic pump; dip the suck tubing into the 2M NaOH.
- Connect the pH probe to the pH controller; conduct the three-point calibration: pH = 7.01, 4.01, 10.01.
- Connect the signal input wire of the base dosing pump to the dry contact 1 of the pH controller.
- Prime the pump:

Air must be purged from the pump head before the pump will operate against pressure. Priming removes the air. It should be performed when the pump was first installed and whenever the fluid supply was changed. Pump priming was conducted by:

While pressing START/STOP button, apply the pump power until the congratulations information shows on the pump display.

The pump was then primed at the maximum fixed rate (100%) for 5 min. If the base solution was not transported to the connector converging into the influent tubing, restart the pump for another time of priming till the base dosing tubing was filled with the base solution.

- After pump priming, re-applying the pump power while holding the START/STOP button to enter the mode setting. Set the pump mode at fixed rate mode, and change the fixed rate to 15%. Now the pH control system was ready to control the base dosing for the FBR system.

Although theoretically only base dosing line was necessary for the struvite formation reaction, an acid dosing line was still needed in case that the pH level drops down below the setpoint too much. This might happen when the signaling was lagging behind of the real pH change inside the FBR reactor because a peristaltic pump se the pH signals were detected by the pH 500 probe set downstream (on the top of) the FBR. For

simplification, 2M HCl was injected into the joint of influent line and base dosing line by using a syringe, when needed.

2.3.3. FBR Operation

- Assemble the FBR system according to the schematics (Figure 1).
- Load the FBR with fine sand up to the half of the bed height, 96 cm; make a maker.
- Set the pH probe near the overflow port of the FBR column (on the top of the FBR).
- Turn on the influent pump at a flow rate of 30 mL/min (pump set as 3.0 RPM). The flow rate was double checked during the experiment.
- When the liquid level in the FBR reaches the overflow port for the recirculation circuit, turn on the recirculation pump to the maximum rate, 120 rpm, to initiate the fluidization in the FBR; the recirculation flow rate was supposed to be around 1060.0 mL/min; make sure the expansion height was around 148 cm.
- After the pH level in the FBR reached and maintained around the target values under the control of the pH control system, the experiment was assumed as initiated. An experiment run time was set as 60 min, referred to the empty bed HRT of 54.41 min.
- After one run of experiment at a specific pH level, do sampling:
The effluent was sampled from the top of (downstream) the FBR; the influent sample was directly obtained from the influent tank. Then, the samples was filtered by using 0.45 μm liquid filters to remove the solids so that the samples can be measured by Ion Chromatography and Flame Atomic Absorption in the subsequent steps. The samples were diluted to the test range of standard curves before measurement.

2.3.4. Measurement Methods

2.3.4.1. pH measurement

The pH 500 probe was set at the overflow port on the top of (downstream) the FBR column. The pH values were read by the pH controller.

2.3.4.2. PO_4^{3-} measurement

The concentration of the anion PO_4^{3-} was measured by Ion Chromatography (IC).

Protocol of Ion Chromatography:

- make Eluent Solution, sodium bicarbonate-sodium carbonate, 0.0017M $NaHCO_3$ -0.0018M Na_2CO_3 : Dissolve 0.5712 g $NaHCO_3$ and 0.7632 g Na_2CO_3 in water and dilute to 4 L.
- make Regenerant Solution, H_2SO_4 , 0.025N: Dilute 2.8 mL conc H_2SO_4 to 4L.
- add the eluent solution into the eluent solution carboy and the regenerant solution into the regenerant solution carboy; close the caps.
- Make sure the waste outlets go to the waste carboy.
- Turn on the power for IC.
- Turn on the air; make sure the air pressure is between 70 to 80 psi.
- Set the inlet pressure to the IC at 10 psi.
- Switch on <Cell>.
- Wait for 10~30 min till the conductivity goes down to 10 μs .
- During the waiting, program the software Turbochrom:
go to TC4>TCNav navigator.
go to Methods and then the menu Instruments>Data channels, set the run time as 7 min (Notes: the effluent time of PO_4^{3-} is about 4~6 min).
go to Setup and then the menu File>open, open the file with default setting C:\TC\ene806\spr2006\ic.mth, set the name of starting file for saving the IC result information.
- Turn on Auto Offset.
- Turn off <Inject> on the control box.

- Rinse the sample syringe by DI water and then take 500~1,000 μL of sample by a syringe and inject the sample into the IC equipment.
- Turn on < Inject >.
- Go to the data collection box and push <start> on the panel to start IC reading.
- After the run is done, open Graphic and then return, open the “New Data File”, open the new file, open Peak Report, write down the peak area value ($\text{uV}\cdot\text{sec}$) at the target peak position (referred to standard curve peak position).
- Repeat from the inject step for next sample.

PO₄³⁻ Concentration Standard Curve:

A standard curve was made before the measurement of samples. The standard solution series was prepared as per the following recipe (Table 2).

Table 2. Concentration series recipe for PO₄³⁺ standard curve.

Dilution #	#0	#1	#2	#3	Blank
Total Equivalent PO ₄ ³⁻ (mg/L)	100.0	75.0	50.0	25.0	0
Equivalent PO ₄ ³⁻ (mg/L)	50.0	37.5	25.0	12.5	0
KH ₂ PO ₄ (mg/L)	71.626	53.720	35.813	17.907	0
Equivalent PO ₄ ³⁻ (mg/L)	50.0	37.5	25.0	12.5	0
K ₂ HPO ₄ (mg/L)	91.674	68.756	45.837	22.919	0

The PO₄³⁻ standard curve (Figure 4) was obtained from the IC peak area values of the PO₄³⁻ standard solutions (Table 3). The effluent peak was at about 2.5 min after injection.

Table 3. Results for PO₄³⁺ standard curve.

PO ₄ ³⁺ Dilution	Blank	#1	#2	#3	#4
Total Equivalent PO ₄ ³⁻ (mg/L)	0	25	50	75	100
IC Peak Area ($\text{uV}\cdot\text{sec}$)	0	929,974.83	1,688,730.02	2,523,192.16	3,618,088.96

The PO_4^{3-} concentration standard curve turned out to be a good linear fitting:

$$\text{IC} = 35318 \cdot [\text{PO}_4^{3-}] - 13882$$

where: IC — IC read: effluent peak area (uV·sec);

$[\text{PO}_4^{3-}]$ — PO_4^{3-} concentration (mg/L) of the sample;

R^2 is equal to 0.9961, as shown in the following figure.

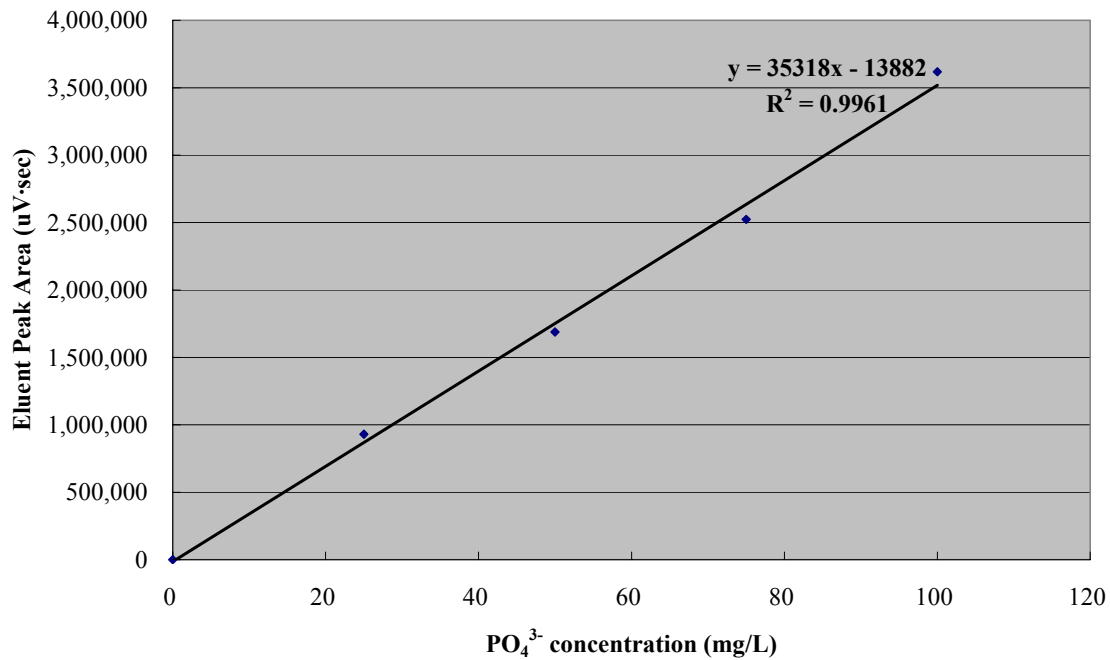


Figure 4. . PO_4^{3-} concentration standard curve.

2.3.4.3. Mg^{2+} measurement

Flame Atomic Absorption (AA), with a ppm detection limit, was used to measure the magnesium ions in the samples.

Protocol of Flame Atomic Absorption:

- Turn on the exhaust fan;
- Turn on the power.
- Install the Mg^{2+} lamp; plug in the pin to fix the lamp to the 10 o'clock position.

- Open acetylene cylinder and turn on the set the pressure at 14~15 psi.
- Turn on the AA power.

Check the manual book Analytical Methods for Atomic Absorption Spectroscopy for the parameter setting for Mg^{2+} ; set the standard conditions accordingly:

- λ : 285.2 nm;
- SBW (Windows): 0.7;
- program the Flame AA:

Press <Param. Entry>:

lamp current: 6~15 mA; choose a medium value: 10 mA.

INT Time: 0.10.

Replicates: 3.

Calibration: NONLIN (non-linear)

Press <En> (Energy): to make energy at the maximum level.

Adjust the coarse knob and the fine knob to adjust <CTS> to around 109.

Press <GAIN> to relate <CTS> to <EN> (Energy): 67 (key energy setting).

Press <Cont> and <A/Z> to check the deviation of the signal baseline.

- Measure the standard solutions or the samples:
- Turn on the Air-Acetylene in <Oxidant>; hold <ignite> for about 5 seconds to ignite the flame.
- Dip the sample tubing into the DI water to check the baseline signal; press <A/Z> to set the blank value.

(Notes: the blank sample, i.e., DI water, should not change the blue flame color too much.

Too yellow flame indicates the contamination of the DI water).

- Dip the sample tubing into the sample; press <Data> and then <Read> to get the mean value of the three sample replicates, write down the number.
- Go to next sample.
- Turn off air in <Oxidant>.
- Turn off acetylene cylinder (general switch).
- Turn on air in <Oxidant> again to burn out the residual gas.

- Turn off air in <Oxidant” till air meter comes down to 0.
- Turn off power for the AA.
- Turn off the exhaust fan.

Mg²⁺ Concentration Standard Curve:

A standard curve was made before the measurement of samples. The standard solution series was prepared as per the following recipe (Table 4).

Table 4. Concentration series recipe for Mg²⁺ standard curve.

Mg ²⁺ Dilution	Blank	#1	#2	#3	#4	#5	#6	#7	#8
Equivalent Mg ²⁺ (mg/L)	0	5	10	15	20	25	50	75	100
MgCl ₂ •6H ₂ O (mg/L)	0	41.83	83.66	125.49	167.33	209.16	418.32	627.47	836.63

The Mg²⁺ standard curve (Figure 5) was made from the Flame AA reads of the Mg²⁺ standard solutions (Table 5).

Table 5. Results for Mg²⁺ standard curve.

Mg ²⁺ Dilution	Blank	#1	#2	#3	#4	#5	#6	#7	#8
Equivalent Mg ²⁺ (mg/L)	0	5	10	15	20	25	50	75	100
Flame AA Reads	0	0.378	0.618	0.786	0.863	0.929	1.140	1.238	1.290

The standard curve is in a non-linear fitting with the Mg²⁺ concentration, but it appeared to be a good exponential fitting with the Mg²⁺ concentration over the test range:

$$AA = 0.3053 \cdot \ln[Mg^{2+}] - 0.0744$$

where: AA — Flame AA read;

[Mg²⁺] — Mg²⁺ concentration (mg/L) of the sample;

with R² equal to 0.9915, as shown in the following figure.

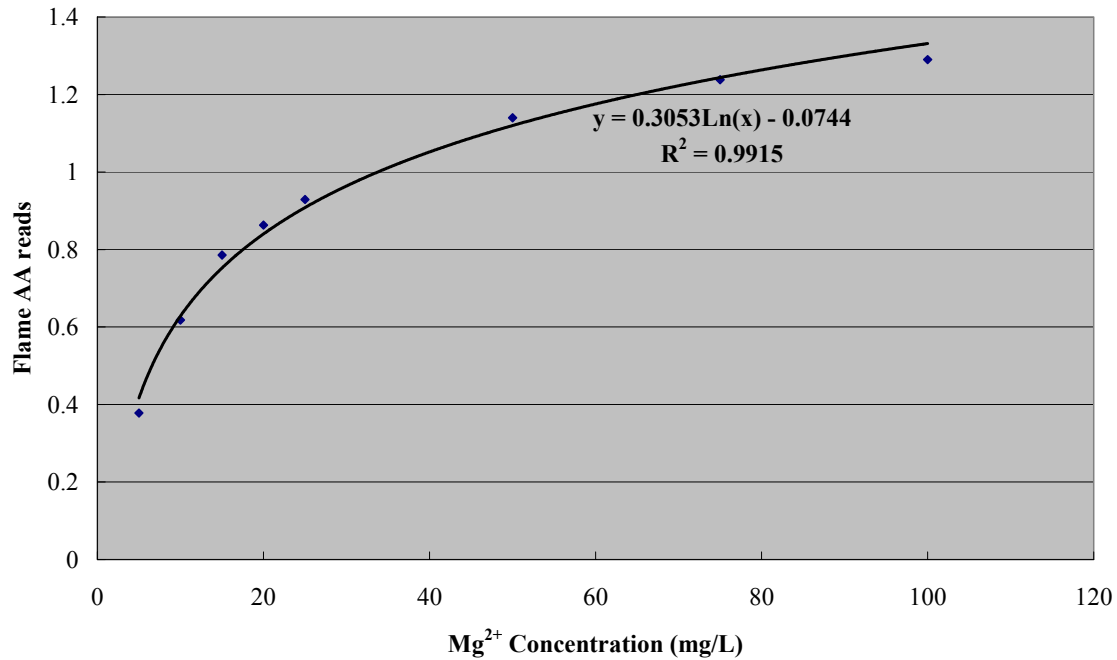


Figure 5. Mg²⁺ concentration standard curve.

2.3.4.4. Ammonia and Ammonium ions measurement

A gas-sensing ammonia electrode of model 95-12 (Orion Research Incorporated Laboratory Products Group) connected to an Orion pH meter allowed fast and accurate measurements of dissolved ammonia in aqueous solutions. The ammonium ions present in the samples was converted to ammonia in more basic environment created by Ionic Strength Adjustor (ISA) immediately before the measurement.

Protocol of ammonia meter:

(Notes: The detection volume of each calibration solution or sample should be at least 100 mL. In this case, the detection volume was set as 100 mL).

- Electrode preparation:
- Fill the probe with the filling solution.
- Change the probe membrane if it is over two or three months old.
- Prepare 100 mL of 0.45 μm filtered sample.

- A two-point calibration was conducted before the use of ammonia meter:
- Prepare 100 mL fresh standard calibration solution right before measuring the samples (Notes: the ammonium samples are not stable in aqueous solutions. It would be better if the calibration can be made immediately before the sample measurement).

Table 6. Recipe for ammonium calibration solutions.

	Calibration solution 1	Calibration solution 2
Equivalent NH_4^+ (mg/L)	100	1,000
NH_4Cl (mg/L)	314.647	3,146.47

- Turn on the power switch of the ammonia meter;
- Turn on the magnetic stirrer;
- Put a magnetic stirrer stick into the 100 mL Calibration solution 1.
- Add 2 mL of pH-adjusting ISA solution into the sample.
- When the reads on the display of the ammonia meter becomes steady, press <Cal> and <Enter>, press the up and down arrows to select the concentration of the calibration solution under measurement, then press <Enter>, the LED of the Calibration 1 would be lighted up. When this first calibration is done the LED would be automatically turned off and the LED for Calibration 2 would be lighted up, which indicates that the Calibration 2 is ready to be conducted.
- Take the ammonia probe out of the Calibration solution 1 and rinse it by DI water; put it into the 100 mL Calibration solution 2.
- Repeat the above steps for Calibration 2, and the LED of Calibration 2 would be turned off automatically when the Calibration 2 is done. At the same time, the LED of Sample would be on, which indicates that the sample measurement is ready.
- Check if the electrode operation slope is normal as shown in the Table 4 in Orion Model 95-12 ammonia electrode instruction manual (Orion research incorporated laboratory products group).
- Sample measurement:
- Take the ammonia probe out of the Calibration solution 2 and rinse it by DI water; put it into the 100 mL sample.

■ Add 2 mL ISA solution and wait for about 30~60 seconds until the read on display becomes steady and the LED “ready” is on. Write down the read as the ammonium concentration of the sample.

(Notes: If the sample concentration is way above 1,000 mg NH₄⁺/L, the sample has to be diluted to fit the range of 0 ~ 1,000 NH₄⁺/L before measurement).

3. Results and Discussion

The batch reaction in the beakers showed that the higher pH level, the better the effluent quality (Figure 6).

Table 7. Results for beaker batch experiment

	Influent	Effluent					
		7.5	8.0	8.5	9.0	9.5	10.0
pH	6.3						
AA read	1.043	1.04	1.028	1.03	1.001	0.949	0.935
Sample [Mg ²⁺] (mg/L)	310.89	307.85	295.99	297.93	270.93	228.50	218.26
PO ₄ ³⁻ Removal %	N/A	0.98%	4.79%	4.17%	12.85%	26.50%	29.79%
NH ₃ (mg/L)	495	467	460	447	427	383	339
NH ₃ Removal %	N/A	5.66%	7.07%	9.70%	13.74%	22.63%	31.52%

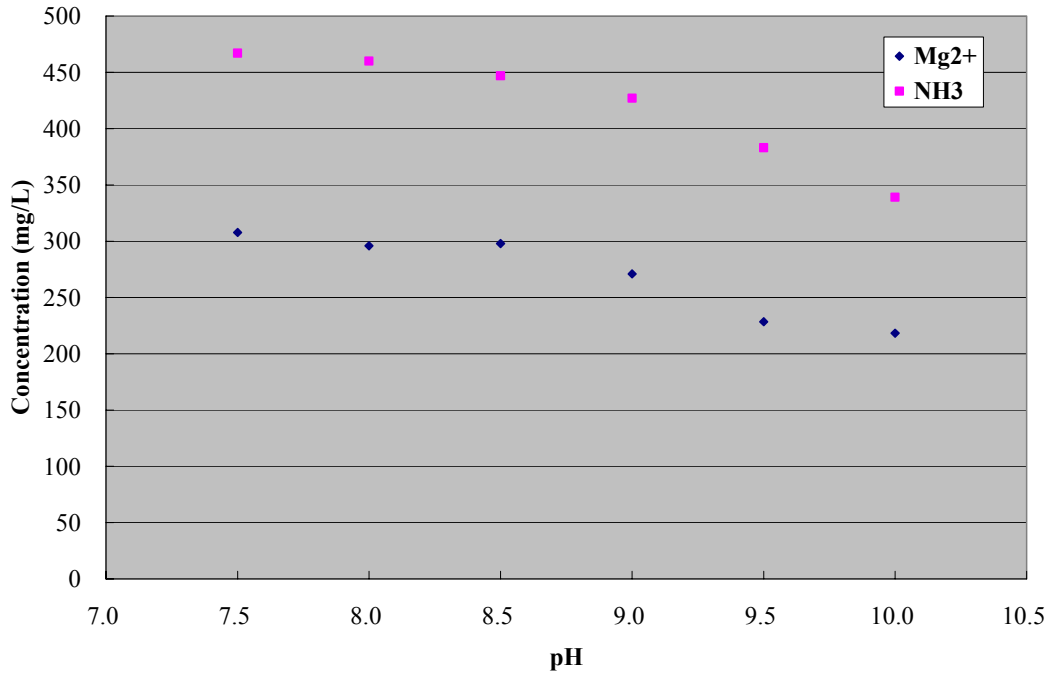


Figure 6. Beaker batch experiment for pH optimization.

Considering cost efficiency of pH adjustment, experiments at two different pH levels: (1) pH = 9; (2) pH = 10 were tried respectively. The measures were made and the results used to evaluate the performance of the FBR system on synthetic anaerobic-digested manure wastewater treatment (Table 8).

Table 8. Results of FBR experiments.

Ingredients	Equivalent Ion Conc.	Reaction @ pH ≈ 9				Reaction @ pH ≈ 10			
		Influent (mg/L)	Effluent (mg/L)	Removal Efficiency (%)	Removal (mmol/L)	Influent (mg/L)	Effluent (mg/L)	Removal Efficiency (%)	Removal (mmol/L)
KH ₂ PO ₄	mg PO ₄ ³⁻ /L	424.86	17.25	95.94%	4.29	503.96	15.82	96.86%	5.14
K ₂ HPO ₄									
MgCl ₂ •6H ₂ O	mg Mg/L	312.94	288.33	7.86%	1.01	290.23	216.13	25.53%	3.05
NH ₄ Cl	mg NH ₃ /L	1400	1260	10.00%	7.78				

(Notes: the data for NH₄⁺ concentration in the pH 10 experiment was not obtained due to broken ammonia probe.)

Both of the experiments in basic environments (pH = 9, 10) showed very good FBR performance in phosphorus removal. More than 95% of dissolved phosphate was removed. The pH 10 reaction presented a better phosphorus treatment performance than the pH 9 level reaction, but the difference was not significant.

The removed amounts of the contaminants were compared to study the mechanism of this treatment process. If the phosphorus in the wastewater had been effectively transferred to struvite, the removed amounts of the three major constituents of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), PO_4^{3-} , Mg^{2+} and NH_3 , should constitute a molar ratio of 1:1:1. However, it was not fully proved by the results. Compared to phosphate removal, the removed amount of magnesium was below the expected level, whereas the removed amount of ammonia was higher than expected (Table 8). Further analysis needs to be made to explain the product chemistry. The recommendation method is to take out the final aggregate product attached on the surface of sand media and the aggregate in the reactor mix liquid for air drying. The dry product is re-dissolved by water or acid for the measurement of the concentration of the three ions. This further study would need to be conducted at different pH levels. In the meanwhile, the struvite precipitate on the surface of sand media would need to be studied for pH optimization. Optimal pH environment is assumed to facilitate greater struvite precipitation instead of small struvite suspended particles in the mix liquid. All these would help to explain the mechanism causing the difference in removal efficiency in different pH environments.

Further work would be attempted to treat real anaerobic-digested manure wastewater with phosphorus mainly from hydrolysable phosphorus by using this FBR system. First, increase in the content of dissolved orthophosphate in anaerobic digestion process would be a great help for the post-digestion FBR treatment for phosphorus removal. Second, parameter setting of FBR system would have to be adjusted to treat different make-up manure wastewater.

And, the abundance of ammonium in the wastewater after phosphorus removing is a problem. Ammonia removal has to be done for the manure wastewater before the final discharge.

The major operation problem in this struvite formation study was pH adjustment. Because the pH probe was sitting on the top of the FBR reactor, downstream the whole system, a large delay of pH detection was determined due to the small overall flow rate. Even with low concentration and slow dosing rate of the base and the acid, it was difficult to automatically control the pH level at the target ones using the pH control system. In this study, a 10~15% fixed rate of 2M NaOH dose pumping appeared to optimally balance the pH drop along the reaction progress, but the tubing connection and the influent concentration would highly influence the optimal base pumping rates.

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