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APPLICATION OF STRUVITE PROCESS FOR NUTRIENT RECOVERY FROM ANAEROBIC DIGESTERS OF LIVESTOCK WASTEWATER

Process of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) precipitation is a promising method for phosphorus recycling. The use of cheap magnesium ore for precipitation struvite as phosphate recovery has been examined. The optimal conditions for precipitation are pH 9.0 and $\text{Mg}^{2+} : \text{NH}_4^+ : \text{PO}_4^{3-}$ molar ratio 1.1:30.7:1. Linear correlation of experimental data is in qualitative agreement with modelling calculation. Surface characterization analysis demonstrates that struvite is the dominant component of precipitate. Fertility value tests show that struvite precipitate could be available as slow-release fertilizer.

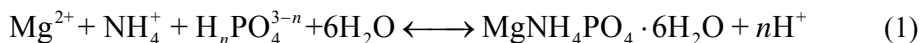
1. INTRODUCTION

In accordance with the sustainable development paradigm, current natural resources should be managed in a manner that allows future generations to have resources for their needs [1, 2]. However, rapid exhaustion of most resources is a threat that may cause depletion of existing natural resources within a period of one generation's life [3]. One of the critical problems is the scarcity of phosphorus compounds, which is a challenge for food security [4]. With the use of phosphorus rock as fertilizer, global reserves are predicted to last for approximately 125 years [5]. Therefore, new sources of phosphorus compounds must be found in order to sustain the global community.

Recovery of phosphorus from wastewater is a potential source of nutrient compounds [6]. Anaerobic digestion of livestock wastewater is a typical wastewater source that contains a large amount of phosphorus. Because of intensive livestock and poultry production in China, pollution by this wastewater is a significant problem. Several different biological and physicochemical methods such as biological uptake, ion exchange, adsorption, and crystallization have been employed to recover phosphorus from wastewater [7], struvite precipitation being the most preferable process [8, 9].

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Struvite is a white crystalline substance that consists of magnesium, ammonium nitrogen, and phosphate in equal molar concentrations. The basic chemical reaction for its formation is expressed by the reaction [10]



Practical application of struvite precipitation process is slowed by a high cost of the chemicals consumed. Use of several inexpensive chemicals and reuse of struvite as a fertilizer are two promising options to reduce the high treatment cost, the latter one minimizes expenses of precipitate disposal [11,12]. However, its usability and fertilizer value have not yet been investigated sufficiently [13]. Struvite characterization and its use as a resource of nutrient dynamic released for plant growth are key factors in the application of struvite precipitation.

The main objectives of our studies were evaluated as follows. Cheap magnesium ore was used and the phosphate recovery conditions were examined. The required reaction factors, pH level, and chemical doses were evaluated.

2. EXPERIMENTAL PROCEDURES

Materials. Wastewater sample used in the experiments was obtained from anaerobic digesters effluent of livestock wastewater from a plant located near Beijing. Specifically, it was obtained by settling and filtering the effluent, and prior to experiments being stored in an icebox. Table 1 shows the wastewater sample parameters.

Table 1

Characteristics of wastewater sample

Item		Value	Item		Value
pH		8.28	Cu	0.21	(mg/dm ³)
Turbidity	(NTU)	151.3	Zn	1.59	
Electrical conductivity	($\mu\text{S}/\text{cm}$)	9627	Mn	1.36	
COD	(mg/dm ³)	742	Pb	0.2376	
NH ₄ ⁺ -N		709	As	0.1086	
NO ₃ ⁻ -N		312	Hg	0.0043	
PO ₄ ³⁻ -P		51.1	Cd	0.0075	
K		350	Cr	0.0297	
Fe		1.13			

Magnesium ore used as a magnesium source was obtained from Haicheng (Liaoning Province, China). The composition of magnesium ore is given in Table 2.

Table 2

Composition of magnesium ore

Component	Contents [wt. %]
MgO	90.31
CaO	1.64
Fe ₂ O ₃	0.46
Al ₂ O ₃	0.48
SiO ₂	3.96
NaOH	3.15

Methods. Phosphate recovery tests. The phosphate recovery ratio (PRR) was calculated from the dependence:

$$PRR = \frac{[\text{PO}_4^{3-}\text{-P}]_{\text{untreated sample}} - [\text{PO}_4^{3-}\text{-P}]_{\text{treated sample}}}{[\text{PO}_4^{3-}\text{-P}]_{\text{untreated sample}}}$$

pH was 8.0–10.0. Magnesium ore was used as the Mg²⁺ source. Its added dose was 65.7–109.5 mg/dm³ to obtain Mg²⁺:NH₄⁺:PO₄³⁻ molar ratio (0.9–1.5):30.7:1. Batch experiments for phosphate recovery from the effluent of livestock wastewater anaerobic digesters were performed according to the following steps. First, magnesium ore and deionized water were mixed for 30 min at the volume ratio of 1:50 or 1:100. 30% HCl (6.3–31.5 cm³) was subsequently added to the solution of magnesium ore and deionized water at the volume ratio of 1:50 and mixed for 30 min to prepare MgO/HCl solution (1006.3–1031.5 cm³). 3.4–5.6 cm³ MgO/HCl solution (HCl:MgO molar ratio of 0.5:1) was then added to wastewater sample (1000 cm³) and mixed for 30 min. The formed precipitate was allowed to settle for 30 min. Finally, supernatant was filtered through a 0.45 μm membrane filter to measure PO₄³⁻-P and the precipitate was collected for the product characterization.

For calculation, the program PHREEQC was used. Saturation index (*SI*) was calculated to determine supersaturation of the precipitate phase in the solution.

$$SI = \log \frac{IAP}{K_{sp}}$$

where IAP is the free ionic activity product and *K_{sp}* is the thermodynamic solubility product constant. The solution is supersaturated if *SI* > 0. Compiled programs were calculated based on the PHREEQC.DAT database. The thermodynamic solubility product of struvite log *K_{sp}* equals 13.15 (at 298 K) [14].

Struvite characterization and fertility tests. Struvite precipitate was obtained at pH 9.0 and $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratio 1.1:30.7:1. The collected precipitate was washed three times with deionized water and dried in an oven at 313 K for 48 h. It was then analyzed via X-ray diffraction (XRD, Dmax/2400, Rigaku, Japan), Fourier transform infrared spectroscopy (FTIR, Nicolet 750, Nicolet, USA), and scanning electron microscopy (SEM, S-3400N, Hitachi, Japan).

Struvite precipitate collected from treated wastewater was used to characterize the nutrient dynamic release efficiency by continuous water extraction and interval water extraction as follows.

Continuous water extraction was performed through the subsequent steps. 10 g of struvite precipitate was added into 1000 cm³ of water at a given pH (6.0–8.0). The mixture of struvite and extraction water was then centrifuged at 2000 rad/min and the supernatant was filtered through a 0.45 μm membrane filter to measure NH_4^+ and PO_4^{3-} after it was centrifuged for 1, 2, 4, 8, and 24 h.

To perform interval water extraction, 10 g of struvite precipitate was added into 1000 cm³ of extraction water at pH 7.0. The mixture of struvite and extraction water was centrifuged at 2000 rad/min for 24 h to measure NH_4^+ and PO_4^{3-} . Then the extraction water was replaced by fresh water and the extraction process was repeated.

Analysis. The supernatant concentrations of NH_4^+ , Mg^{2+} , and PO_4^{3-} were measured by the standard methods [15]: ammonium-nitrogen (4500-NH₃ F. phenate method), orthophosphate (4500-P C. vanadomolybdophosphoric acid colorimetric method), magnesium (3120 inductively coupled plasma method).

3. RESULTS AND DISCUSSION

3.1. SOLUBILITY OF MAGNESIUM SOURCE

Use of cheap chemicals such as magnesium oxide leads to lower phosphate recovery than using $MgCl_2$ [13]. To enhance the phosphate recovery ratio, Di Iaconi et al. [12] doubled the added MgO dose and demonstrated that the excess amount of MgO decreased struvite purity. The dissolution of magnesium is the main problem because only the soluble form of Mg^{2+} can react with NH_4^+ and PO_4^{3-} to form struvite. To obtain the soluble form of Mg^{2+} source, the MgO/HCl solution was prepared. Mg^{2+} solubility ratio (Eq. (2)) was used to assess the optimum condition of MgO/HCl solution. $Mg^{2+}_{\text{solution measure}}$ was the measured Mg^{2+} concentration in the prepared solution, and $Mg^{2+}_{\text{magnesium ore}}$ was the theoretical Mg^{2+} mass content in magnesium ore:

$$Mg^{2+}_{\text{solubility ratio}} = \frac{Mg^{2+}_{\text{solution measure}}}{Mg^{2+}_{\text{magnesium ore}}} \quad (2)$$

The MgO/HCl solution was prepared as follows: Magnesium ore and deionized water were mixed at the mass to volume ratio of 1:50 or 1:100. Figure 1a shows the Mg^{2+} solubility ratio of magnesium ore at various mixing times. The experimental data are in agreement with a pseudo second-order kinetic equation, with $R^2 > 0.99$. The lower Mg^{2+} solubility ratio indicated that by using only deionized water it was not possible to obtain the complete dissolution of magnesium source. Then HCl was added and mixed for 30 min to further dissolve the residue magnesium ore. Figure 1b shows the Mg^{2+} solubility ratio of magnesium ore at various HCl:MgO molar ratios. Magnesium could completely dissolve at HCl:MgO molar ratio of 0.5:1. Thus, adding HCl is critical in obtaining the soluble form of Mg^{2+} .

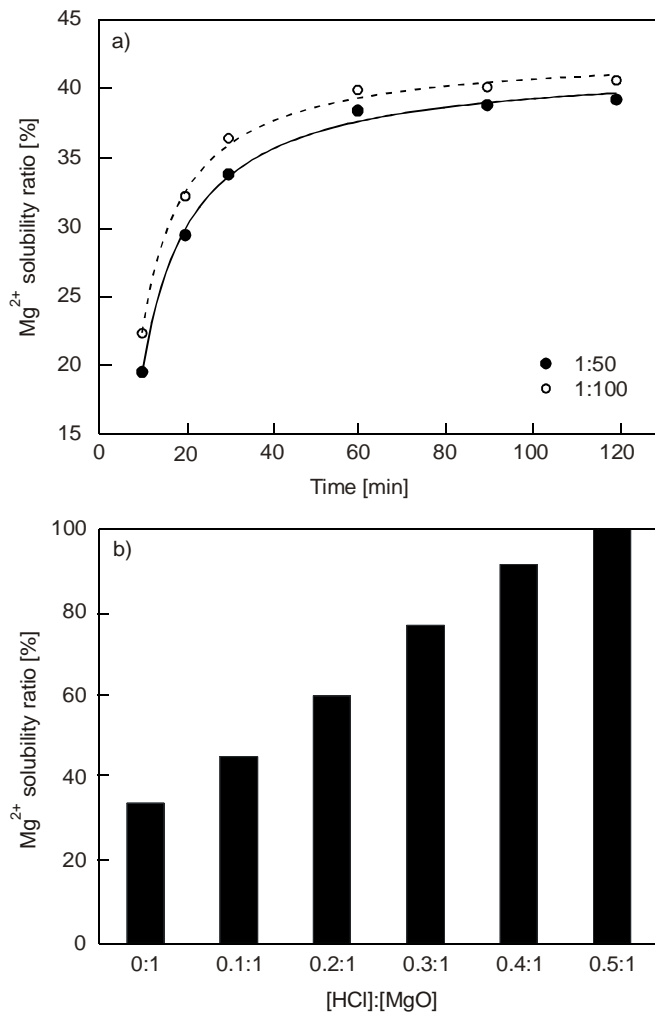


Fig. 1. Dependences of Mg^{2+} solubility ratio on: a) mixed time, b) HCl:MgO molar ratio

3.2. OPTIMAL REACTION CONDITIONS

pH of the solution is a key factor in the struvite process. Optimal pH for application of MgO/HCl solution for struvite crystallization was investigated. Because ammonium nitrogen in the livestock wastewater effluent of anaerobic digesters was high enough for struvite formation, only magnesium source was added. Batch experiments and thermodynamic modeling were conducted under the conditions of $Mg^{2+}:NH_4^+:PO_4^{3-}$ 0.9–1.5:30.7:1 and pH 8.0–10.0.

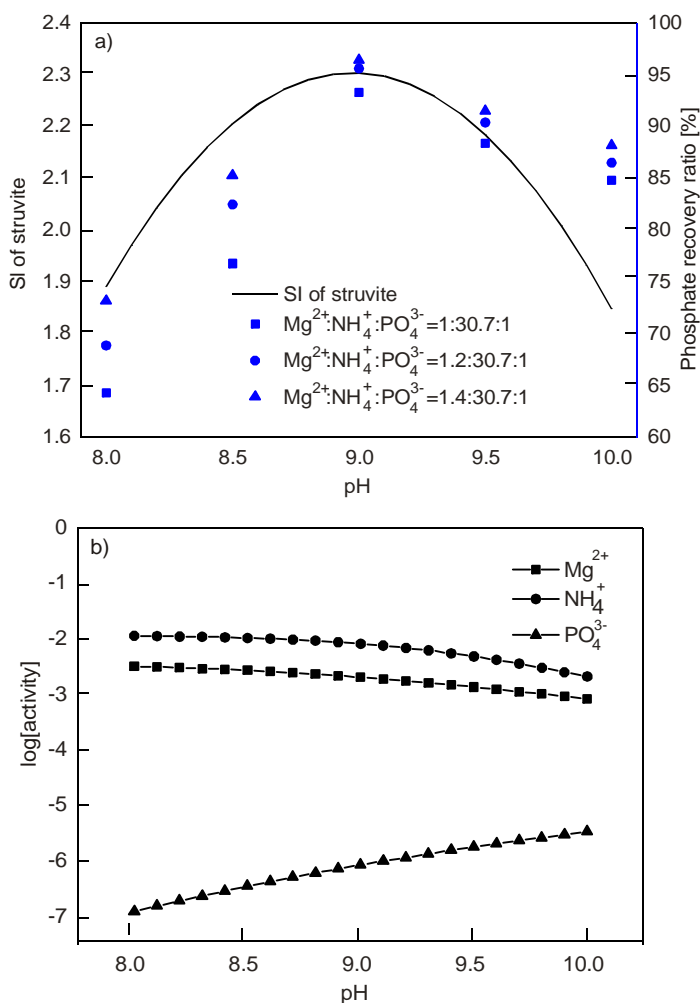


Fig. 2. The effect of pH on the efficiency of phosphate recovery:
 a) the efficiency of phosphate recovery at various pH values,
 b) thermodynamic modelling of ion activities at various pH values

Results of both batch experiments and thermodynamic modeling indicated that the optimal pH was equal to 9.0 (Fig. 2a). Linear correlation of batch experimental data was in qualitative agreement with modeling calculation. Minimal deviations in the trend between results of batch experiments and thermodynamic modeling could be assigned to chemical reaction of $\text{NH}_4^+ + \text{OH}^- = \text{NH}_3 \cdot \text{H}_2\text{O}$ [16]. When pH is higher than the optimal condition, $\text{Mg}(\text{OH})_2$ will be created instead of struvite formation [17]. When pH is lower than the optimal condition, hydrogen ions in the reaction solution inhibit struvite formation. A higher degree of supersaturation could increase struvite nucleation [8].

The effect of pH could be explained by its influence on ionic activity (Fig. 2b). Upon increasing pH in solution from 8.0 to 9.0, PO_4^{3-} ionic activity increased significantly, whereas those of Mg^{2+} and NH_4^+ decreased slightly, which resulted in an increase in *SI*. Further increase of pH from 9.0 to 10.0 resulted in slight increase of PO_4^{3-} ionic activity, whereas those of Mg^{2+} and NH_4^+ decreased significantly, which resulted in a decrease in *SI*. pH of the solution can influence the ionic activities of Mg^{2+} , NH_4^+ , and PO_4^{3-} , and can further change the *SI* of struvite.

More feasible data have been published on struvite solubility in wastewater treatment. pH 8.9–9.25 [18] and 9.5 [19] for struvite crystallization have been reported to be optimal. These findings are in agreement with the results of our study.

Because concentration of ammonium nitrogen in the livestock wastewater effluent of anaerobic digesters was high enough for struvite formation, magnesium ore was the only added chemical. Therefore, amount of magnesium added is a major factor in enhancing the efficiency of phosphate recovery.

Batch experimental results (Fig. 3) show that the optimal $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio for phosphate recovery was 1.1:30.7:1. With an increase in $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio from 0.9:30.7:1 to 1.1:30.7:1, the efficiency of phosphate recovery increased rapidly. With an increase in $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio from 1.1:30.7:1 to 1.5:30.7:1, the efficiency of phosphate recovery increase gradually.

The results of thermodynamic modeling (Fig. 3) indicate that *SI* of struvite significantly increased upon increasing Mg^{2+} concentration, followed by a logarithmic function of Mg^{2+} concentration. The effect of Mg^{2+} concentration on the *SI* of struvite can be explained with the use of equation [20].

$$SI = \log \frac{IAP}{K_{SP}} = \log \left[\left(C_{\text{Mg}^{2+}} f_1 \right) \left(C_{\text{NH}_4^+} f_2 \right) \left(C_{\text{PO}_4^{3-}} f_3 \right) \right] - \log K_{SP} \quad (3)$$

where $C_{\text{Mg}^{2+}}$, $C_{\text{NH}_4^+}$, and $C_{\text{PO}_4^{3-}}$ are concentrations of Mg^{2+} , NH_4^+ , and PO_4^{3-} in the modeling solution and f_1 , f_2 , and f_3 are the ionic activity coefficients. In Eq. (3), concentrations of Mg^{2+} , NH_4^+ , and PO_4^{3-} , as well as ionic activity coefficients have been

correlated with the *SI* of struvite. When two concentrations of the three constituents (Mg^{2+} , NH_4^+ , and PO_4^{3-}) were determined, the *SI* of struvite followed a logarithmic function of the remaining constituent ion (Mg^{2+} , NH_4^+ , and PO_4^{3-}) concentration.

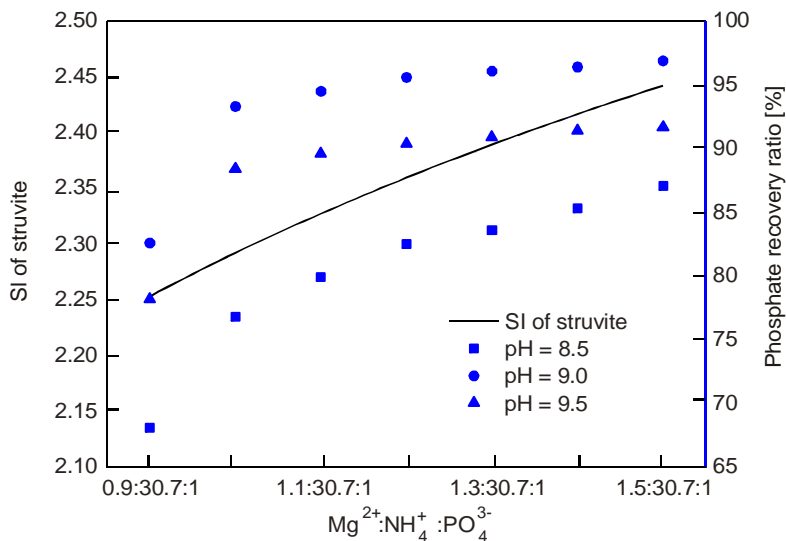


Fig. 3. The effect of molar ratio on the efficiency of phosphate recovery

Batch experiments data and thermodynamic modeling data showed that overdosing Mg^{2+} could induce high struvite crystallization potential and that Mg^{2+} concentration was a limiting constituent for phosphate recovery.

3.3. SURFACE CHARACTERIZATION OF THE STRUVITE PRODUCT

Surface characterization was employed to characterize the precipitate. XRD and FTIR analysis demonstrated that struvite was the dominant component of the precipitate. Figure 4a illustrates the results of XRD analysis which indicated that the prominent characteristic peaks of precipitate were close to those of struvite pattern standard (JCPDS 15-0762). Figure 4b shows the results of FTIR analysis which indicated that the infrared spectrum of precipitate conformed to that of struvite pattern as demonstrated in the previous research. The band $3700\text{--}2500\text{ cm}^{-1}$ exhibited the presence of crystalline hydrate. The 2360 cm^{-1} band was assigned to the water–phosphate hydrogen bonding. The 1670 cm^{-1} band indicated the water HOH bending modes. The 1440 cm^{-1} band was the ammonium nitrogen characteristic one. The 1000 cm^{-1} and 571 cm^{-1} bands represented PO_4^{3-} ions. The 756 cm^{-1} band corresponded to the water–water hydrogen bonding. Figure 4c displays the SEM analysis, which showed that the struvite precipitate crystal was unshaped and coarse, and its size was irregular ($30\text{--}100\text{ }\mu\text{m}$).

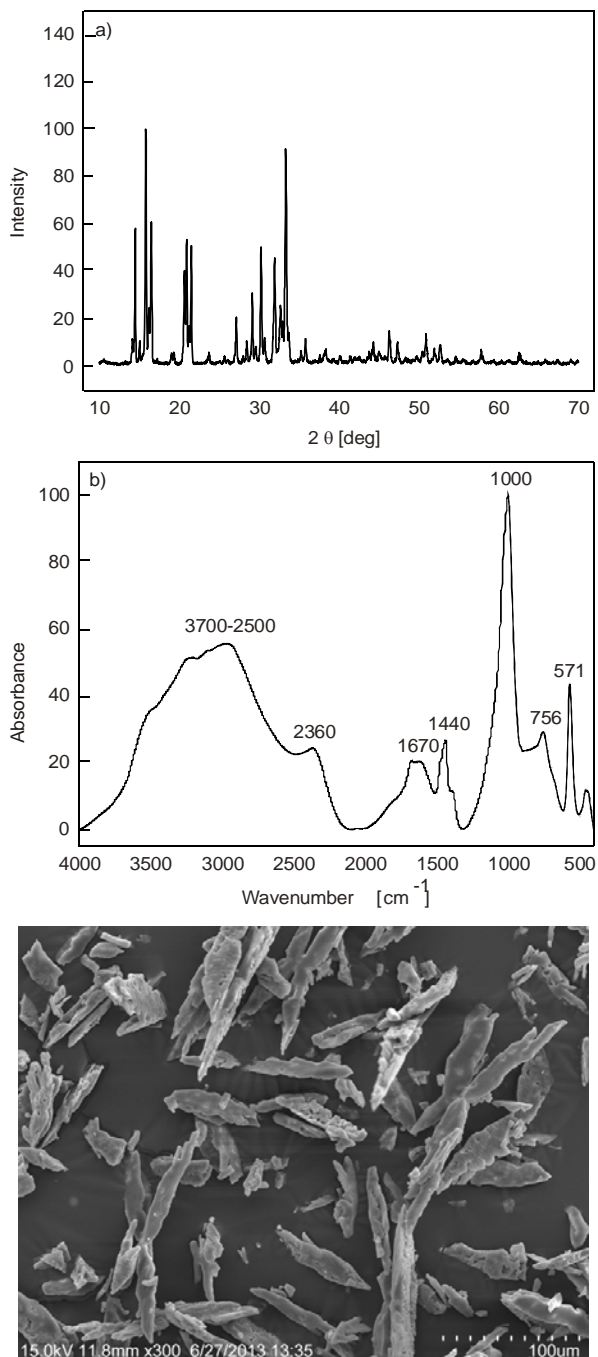


Fig. 4. Surface characterization of struvite precipitate: a) X-ray diffraction analysis, b) Fourier transform infrared spectroscopy analysis, c) scanning electron microscopy analysis

3.4. STRUVITE FERTILITY VALUE

Efficiency of the nutrient dynamic release was investigated to characterize the availability of struvite precipitate as an agricultural fertilizer. To specifically investigate this efficiency, water extraction tests were performed.

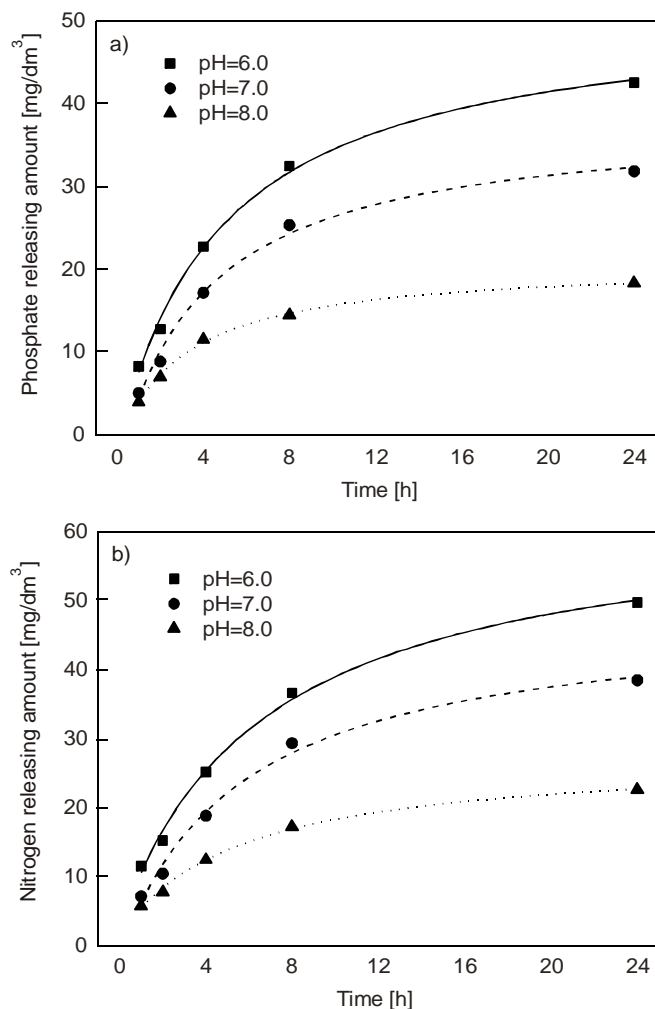


Fig. 5. Continuous water extraction of struvite precipitate:
a) phosphate releasing amount at different extraction times,
b) nitrogen releasing amount at different extraction times

Figure 5 shows the continuous water extraction of struvite precipitate. The time of dynamic release of struvite precipitate was 1–24 h, and the pH was 6.0–8.0. Results

demonstrated that both phosphate and nitrogen release rates were low (approximately 24 h was required to reach an equilibrium) and the release efficiency in acidic extraction water was higher than that in alkaline extraction water. These findings indicate that struvite is more suitable for acidic soil. A pseudo second order kinetic equation was used to describe the phosphate and nitrogen release in the extraction water:

$$\frac{t}{C_t} = \frac{1}{k_{ds}C_e^2} + \frac{t}{C_e} \quad (4)$$

where C_t (mg/dm^3) represents phosphate or nitrogen concentration at t , C_e (mg/dm^3) represents phosphate or nitrogen concentration at release equilibrium, and k_{ds} ($\text{dm}^3/(\text{mg}\cdot\text{h})$) represents the kinetic constant of the second order equation.

Although there are intense action forces between magnesium, phosphate, and nitrogen, only small amounts of phosphate and nitrogen were released when the solution reached equilibrium. However, interval water extraction experiments (Fig. 6) demonstrated that nutrients could be released continuously in interval extraction water. The release rate of phosphate was over 2.2% of the total available phosphate amount, and the release rate of nitrogen was over 6.2% of the total available nitrogen amount, which indicated that struvite could be used as slow release fertilizer. These results are in accordance with the findings of other authors [21, 22].

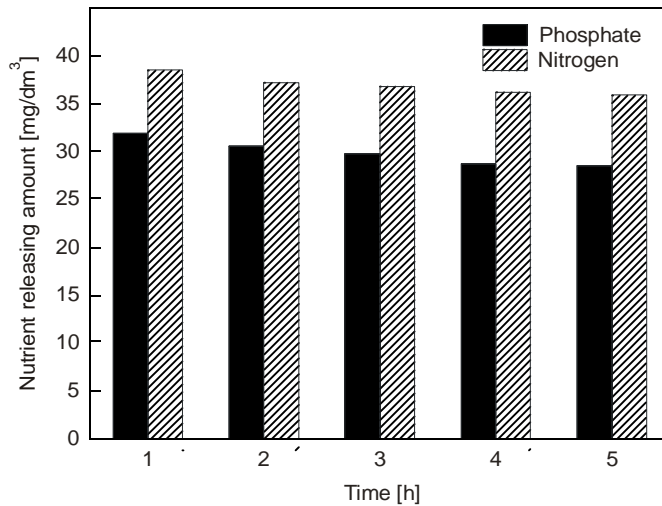


Fig. 6. Interval water extraction of struvite precipitate

Economic evaluation analysis was conducted in consideration of the cost of chemicals (i.e., magnesium ore, HCl, and NaOH). Manpower costs and energy consumption were not considered. The livestock wastewater anaerobic digester was treated via stru-

vite crystallization under the conditions of $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratio 1.1:30.7:1 and pH 9.0. Market prices and consumed amount of chemicals were calculated, as shown in Table 3. The total cost of chemicals to obtain 1 kg of struvite was approximately 0.5319 \$. Struvite is a slow-release fertilizer that can be sold at an affordable price considering its purity. Specifically, when its purity level is over 90%, the price is approximately 1 \$/kg. Therefore, if the value of the struvite product is considered as fertilizer income, then the struvite crystallization process can be more competitive for phosphate recovery from wastewater.

Table 3

Economic evaluation analysis

	Price (\$/kg)	Amount (kg/kg struvite)	Cost (\$/kg struvite)
Magnesium ore	0.087	0.20	0.0174
HCl (30%)	0.048	0.27	0.0129
NaOH	0.38	1.32	0.5016
Total Cost			0.5319

4. CONCLUSIONS

Recycling of phosphorus compounds is a practical solution to sustainable development principles. One potential resource is recovery of phosphorus compounds from wastewater by the process of struvite precipitation. We have undertaken research on the recovery of struvite from wastewater and our research leads to the following conclusions:

- To prepare MgO/HCl solution, the molar ratio of HCl:MgO should be equal to 0.5:1 to completely dissolve MgO in magnesium ore.
- The optimal conditions for phosphate recovery from effluent of livestock wastewater anaerobic digesters were pH 9.0 and $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratio 1.1:30.7:1 by using MgO/HCl solution as magnesium source. Linear correlation of experimental data was in qualitative agreement with the thermodynamic modeling calculation.
- Surface characterization analysis demonstrated that struvite was the dominant component of precipitate.
- Fertility value tests indicated that struvite precipitate could be available as slow-release fertilizer. Economic evaluation analysis showed that the struvite crystallization process could be more competitive for phosphate recovery if struvite value would be considered as fertilizer income.

ACKNOWLEDGEMENTS

The work was supported by a grant from the Beijing Natural Science Foundation (6144026), Specialized Research Fund for the Doctoral Program of Higher Education of China (20120008120013), the China Scholarship Council (201206355006), and Chinese Universities Scientific Fund of China Agricultural University (2011JS169).

The authors thank to the Analytical Instrumentation Center of Peking University.

REFERENCES

- [1] IKERD J., *Sustainable Capitalism: a Matter of Common Sense*, Kumarian Press, Inc., Bloomfield 2005.
- [2] FIUT I.S., *Sustainable development: the upcoming revolution of civilization*, Probl. Ekorozw., 2012, 7 (2), 43.
- [3] KOSTECKA J., *Self-evaluation on the way to retardation of pace life and resources transformation*, Probl. Ekorozw., 2013, 8(2), 93.
- [4] ELSER J., BENNETT E., *Phosphorus cycle. A broken biogeochemical cycle*, Nature, 2011, 478, 29.
- [5] GILBERT N., *Environment. The disappearing nutrient*, Nature, 2009, 461, 716.
- [6] LIU Y., KUMAR S., KWAG J., RA C., *Magnesium ammonium phosphate formation, recovery and its application as valuable resources. A review*, J. Chem. Technol. Biotechnol., 2013, 88, 181.
- [7] RITTMANN B.E., MAYER B., WESTERHOFF P., EDWARDS M., *Capturing the lost phosphorus*, Chemosphere, 2011, 84, 846.
- [8] DOYLE J.D., PARSONS S.A., *Struvite formation, control and recovery*, Water Res., 2002, 36, 3925.
- [9] ZHANG T., LI Q., DING L., REN H., XU K., WU Y., SHENG D., *Modeling assessment for ammonium nitrogen recovery from wastewater by chemical precipitation*, J. Environ. Sci., 2011, 23 (6), 881.
- [10] LE CORRE K.S., VALSAMI-JONES E., HOBBS P., PARSONS S.A., *Phosphorus recovery from wastewater by struvite crystallization. A review*, Crit. Rev. Environ. Sci. Technol., 2009, 39, 433.
- [11] ZENG L., LI X.M., *Nutrient removal from anaerobically digested cattle manure by struvite precipitation*, J. Environ. Eng. Sci., 2006, 5, 285.
- [12] DI IACONI C., PAGANO M., RAMADORI R., LOPEZ A., *Nitrogen recovery from a stabilized municipal landfill leachate*, Bioresource Technol., 2010, 101, 1732.
- [13] RYU H.D., LIM C.S., KANG M.K., LEE S., *Evaluation of struvite obtained from semiconductor wastewater as a fertilizer in cultivating Chinese cabbage*, J. Hazard. Mater., 2012, 221–222, 248.
- [14] CELEN I., BUCHANAN J.R., BURNS R.T., ROBINSON R.B., RAMAN D.R., *Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure*, Water Res., 2007, 41, 1689.
- [15] *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington DC, USA, 2012.
- [16] HAO X.D., WANG C.C., LAN L., VAN LOOSDRECHT M.C.M., *Struvite formation, analytical methods and effects of pH and Ca^{2+}* , Water Sci. Technol., 2008, 58 (8), 1687.
- [17] CELEN I., TURKER M., *Recovery of ammonia as struvite from anaerobic digester effluents*, Environ. Technol., 2001, 22, 1263.
- [18] WARMADEWANTHI, LIU J.C., *Recovery of phosphate and ammonium nitrogen as struvite from semiconductor wastewater*, Sep. Purif. Technol., 2009, 64, 368.
- [19] ZHANG T., DING L.L., REN H.Q., *Pretreatment of ammonium removal from landfill leachate by chemical precipitation*, J. Hazard. Mater., 2009, 166, 911.

- [20] WANG J.S., SONG Y.H., YUAN P., PENG J., FAN M.H., *Modeling the crystallization of magnesium ammonium nitrogen phosphate for phosphorus recovery*, Chemosphere, 2006, 65, 1182.
- [21] KAAAN Y., ZEHRA S.Z., *Recovery of ammonium nitrogen from the effluent of UASB treating poultry manure wastewater by MAP precipitation as a slow release fertilizer*, J. Hazard. Mater., 2009, 166, 260.
- [22] EL DIWANI G., EL RAFIE S., EL I BIARI N.N., EL-AILA H.I., *Recovery of ammonia nitrogen from industrial wastewater treatment as struvite slow releasing fertilizer*, Desalination, 2007, 214, 200.