BIOMEDICAL AND ENVIRONMENTAL SCIENCES **22**, 201-209 (2009) www.besjournal.com

Struvite Recovery from Swine Waste Biogas Digester Effluent through a Stainless Steel Device under Constant pH Conditions[1]

P. W. ANTON PERERA, WEI-XIANG WU, YING-XU CHEN, AND ZHI-YING HAN[2]

College of Environmental and Resource Sciences, Zhejiang University,
Hangzhou 310029, Zhejiang, China

Objective To investigate the struvite precipitation under constant and non-constant pH conditions and to test a stainless steel device under different operating regimes to maximize the recovery of struvite. **Methods** The molar ratio of NH_4^+: Mg^{2+}: PO_4^{3-} was adjusted to 1: 1.2: 1.2 and pH was elevated to 9.0. The absorbance measurement was used to trace the process of struvite crystallization. Wastewater and precipitate analysis was done by standard analytical methods. **Results** The pH constant experiment reported a significantly higher struvite precipitation (24.6±0.86 g) than the non-constant pH experiment (19.8±1.86 g). The SAR ranged from 5.6 to 8.2 g $m^{-2}\,h^{-1}$ to 3.6-4.8 g $m^{-2}\,h^{-1}$ in pH constant and non-constant experiments, respectively. The highest struvite deposit on the device was found in regime 3 followed by in regimes 2 and 4. The highest PO_4^{3-} (97.2%) and NH_4^+ (71%) removal was reported in the R1 regime. None of the influent Cu^{2+} or Zn^{2+} was precipitated on the device. **Conclusion** A higher struvite yield is evident in pH constant experiments. Moreover, the stainless steel device facilitates the isolation of heavy metal free pure (around 96%) struvite from swine waste biogas digester effluent contaminated with cu^{2+} and Zn^{2+} and the highest yield is attainable with the device operating at 50 rpm with agitation by a magnetic stirrer.

Key words: Struvite recovery; Accumulation device; Swine waste; Constant pH; Struvite precipitation

INTRODUCTION

The generation of wastewater on a large scale is an inevitable consequence of modern societies. Wastewater is often harmful to humans and environment and it is important to treat it prior to its release. Obligatory anaerobic treatment of domestic and agro-industrial wastewater releases large amounts of phosphorus and nitrogen into wastewater, which is finally disposed into streams, lakes, seas, and land surfaces. These nutrients are directly responsible for the eutrophication, dissolved oxygen depletion and create imbalanced ecosystems in water bodies worldwide[1-3]. Further problems occur owing to the fact that certain forms of nitrogen, such as ammonia, nitrite and nitrate, are toxic to aquatic life or may lead to diseases in those who drink water contaminated with these compounds[4]. Consequently, more stringent standards for nutrient removal, particularly for the phosphorus removal, have been introduced globally[2]. In order to meet the set standards, a variety of wastewater treatment technologies have been developed. In all cases, phosphorus is removed by converting it into a solid fraction. This fraction can be an insoluble salt precipitate, a microbial biomass in activated sludge or a plant biomass in constructed wetlands. As a significant form of nitrogen, ammonia is treated mainly by the process of biological nitrification and denitrification[5-6]. However, none of the above treatments recycles phosphorus or nitrogen as a truly sustainable product.

As phosphorus and nitrogen are essential elements of all living organisms, the consumption of these elements is ever increasing[7-8]. The demand for phosphorus alone is projected to increase by 1.5% each year, suggesting that the available phosphorus resources can be exhausted within another 100-250 years[9]. The recovery of these elements, therefore, is an important priority, which is expected to contribute to sustainable development through saving essential raw materials. The recovery of phosphorus and nitrogen from the wastewater in the form of

---

[1] This research was supported by the National Key Basic Research Project of China (No. 2002CB410807) and the key Project of Science and Technology of Zhejiang Province (No. 021103723).

[2] Correspondence should be addressed to Zhi-Xiang HAN, Institute of Environmental Science and Technology, College of Environmental and Resource Sciences, Zhejiang University, 268 Kaixuan Road, Hangzhou 310029, Zhejiang, China. Tel: 86-571-86036462. Fax: 86-571-81604036. E-mail: hanzhiying@zju.edu.cn

Biographical note of the first author: P. W. Anton PERERA, born in 1964, Ph. D Scholar, Zhejiang University, majoring in environmental engineering. E-mail: pwaperera@yahoo.com

0895-3988/2009
CN 11-2816/Q

crystalline struvite ($MgNH_4PO_4 \cdot 6H_2O$) is found to be a sustainable option because the struvite is considered a possible fertilizer[10-11]. Under high pH conditions, dissolved NH_4^+, Mg^{2+}, and PO_4^{3-} ions combine and spontaneously precipitate to form scales that deposit on surfaces during anaerobic digestion and post digestion processes, which becomes a nuisance in the wastewater treatment industry[12-13]. The crystals attach to sludge particles in suspension and to surfaces of equipments, tanks and pipe walls in contact with the digested sludge, causing serious operational problems[14-15]. Several studies have been conducted to identify the fouling propensity of struvite on some materials that can be used in wastewater treatment facilities to minimize the scale deposition. Cast iron[16], metal parts[17], and stainless steel[18] have been found to be more susceptible to struvite scaling than other materials, such as PVC, plastic, Teflon, and acrylic. These findings can be effectively used to design technologies for better struvite recovery, when they are made to occur under controlled conditions. Since the studies on the use of fouling propensity of different materials to increase the struvite recovery are scarce, the authors have undertaken this study. Moreover, the stainless steel is found to be a more favorable material for scaling, and accordingly a device is designed with this material to maximize the recovery. In order to prevent the operational difficulties associated with heavy devices, the device has been designed with stainless steel wire mesh.

A previous study of the authors reported that the pH decline occurred in the struvite reaction solution hinders further precipitation, although sufficient amounts of NH_4^+, Mg^{2+}, and PO_4^{3-} ions are available[19]. Therefore, a comparative study under constant and non-constant pH conditions was designed by keeping the other conditions identical.

The objective of the present study was to evaluate the effect of constant pH on the struvite yield and to assess the performance of the new stainless steel device under different operating regimes in isolating struvite from swine waste biogas digester effluent.

MATERIALS AND METHODS

Reactor Design

A laboratory scale reactor (15 cm diameter × 24 cm height) with the working volume of 3 L was used for the struvite precipitation and recovery experiments. The struvite-accumulating device (Fig. 1) comprised of 8 faces of steel mesh was fixed into the reactor. The mesh was woven with a 0.4 mm steel wire forming 1 mm holes. The total surface area of the accumulating faces was 576 cm^2 (8×6 cm×12 cm). This device was placed 4 cm above the bottom of the reactor.

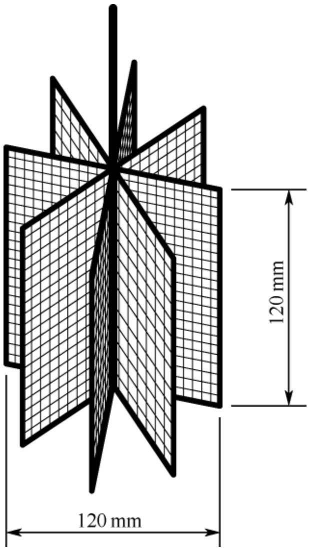

FIG. 1. Struvite accumulating device.

Quality of Wastewater and Operating Conditions

The swine waste biogas digester effluent (SWBDE) was obtained from the Xiasha Swine Farm in Hangzhou of Zhejiang province. The supernatant collected from the effluent discharge pond was stored at 4 ℃ for 24 h in a refrigerator to allow the solids to settle and was then separated and stored at 4 ℃ until further use. The water quality parameters of the effluent used for the experiment are summarized in Table 1. Two sets of experiments were undertaken to assess the potential of struvite accumulation on the newly designed device and the effect of maintaining a constant pH during the precipitation process. In one set of experiments, the initial pH was elevated to 9.0 and maintained at the same pH value throughout the 15 h experiment period. In the other set, the initial pH was similarly elevated to 9.0 and thereafter no effort was made to maintain a constant pH. The elevation and/or maintenance of pH were done with 1 mol/L NaOH solution.

In the other set, the struvite recovery with four different reactor-operating regimes was tested. In the first regime (R_1), 3 L of SWBDE was filled into the reactor, and the molar ratio and pH were quickly adjusted and agitated with a magnetic stirrer at 500 rpm (R_1= agitation + no device). It was operated without the struvite accumulating device (SAD) to assess whether the device influences the precipitation

TABLE 1

Selected Water Quality Parameters of the Wastewater Used in the Experiments

Parameter	Concentration/Value
pH	7.55
NH_4^+-N (mg L^{-1})	296
NO_3^--N	1.2
NO_2^--N (mg L^{-1})	0.28
PO_4^{3-}-P (mg L^{-1})	64.2
Mg^{2+} (mg L^{-1})	94
Ca^{2+} (mg L^{-1})	65
COD_{Cr} (mg L^{-1})	980
SS (g L^{-1})	1.4
Cu^{2+} (mg L^{-1})	0.2
Zn^{2+} (mg L^{-1})	0.4

of struvite. In the second regime (R_2), the device was permanently fixed in the reactor and the magnetic stirrer was also in operation (R_2 = agitation + fixed device). In the third regime (R_3), the device coupled with an overhead agitator, which rotates at 50 rpm, and the magnetic stirrer was also in operation in the same reactor (R_3 = agitation + rotating device). The final regime (R_4) comprised of a rotating device not agitated by the magnetic stirrer (R_4 = no agitation + rotating device). Except for these operating conditions, the same molar ratio and pH value were used in these experiments. The NH_4^+: Mg^{2+}: PO_4^{3-} molar ratio of 1:1.2:1.2 which was found in preliminary tests as the best ratio for optimum struvite recovery was used for all the experiments. Regent grade magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and potassium di-hydrogen phosphate (KH_2PO_4) were used to bring the NH_4^+: Mg^{2+}: PO_4^{3-} molar ratio to 1: 1.2: 1.2 in SWBDE at the beginning of each run.

Analytical Procedure

The crystallization process was monitored by spectrometric absorbance measurements recorded at 385 nm. During the first 20 min of reaction, absorbance was recorded at every 2 min followed by records at every 10 min up to 1 hour and then once in every hour until the end of the 15 h experiment. In the experiment with non-constant pH, the variation of pH was recorded in every 5 min during the initial 30 min of the experiment and thereafter in every 10 min up to 180 min using a Sartorius PB-10 pH meter (Goettingen, Germany). The initial and final NH_4^+, Mg^{2+}, and PO_4^{3-} concentrations of the solution were measured with the standard analytical methods (APHA 1998)[20]. The precipitate deposited on the device was carefully removed with brushing after drying the device at 40 ℃ for 48 h. The precipitate settled at the bottom was first air-dried for 2 days and then oven dried at 40 ℃ for 48 h. The dried precipitate samples from the device and bottom sediments were dissolved in 0.1 mol/L HCl and analyzed for Mg^{2+}, NH_4^+, and PO_4^{3-} content as described elsewhere[21]. Magnesium, copper and zinc concentrations were determined with a thermo elemental solar M6 MK11 atomic absorption spectrophotometer (Thermo Electron Corporation, USA). Orthophosphate (PO_4^{3-}) was measured with the ascorbic acid colorimetric method and ammonia nitrogen was measured with a spectrometer (Unico UV-4802, China). All the analyses were performed in triplicate and the average figures were calculated. Statistical analysis of experimental data was performed using the analytical software SPSS 11.0 (SPSS Inc. USA).

RESULTS

Evolution of pH during Precipitation Process

Previous work revealed that the pH of struvite precipitation solution declines over time and struvite precipitation comes to an equilibrium state even though considerable amounts of Mg^{2+}, NH_4^+, and PO_4^{3-} ions are still available from the solution[19]. In the present study, therefore, struvite recovery was tested at both constant and non-constant pH conditions to evaluate any possible effect of a constant pH on the recovery of struvite. In the struvite recovery experiments with non-constant pH, the evolution of pH over time showed a unique pattern (Fig. 2). All the tested operating regimes showed that the initial pH was sharply declined in the first 15 min, moderately reduced in next 20-25 min and then maintained stable. Out of the four operating regimes tested, 3 regimes (R_1, R_2, and R_3) using the magnetic stirrer, reached almost a similar pH value after 90 minutes of operation. When the reactor was operated no agitated by the magnetic stirrer (R_4), the pH was slightly lower than that agitated by the magnetic stirrer.

Effect of pH on Struvite Yield

A different result was observed when the total precipitation in the pH constant and non-constant experiments was compared. The average amount of total precipitate found in the pH constant experiment

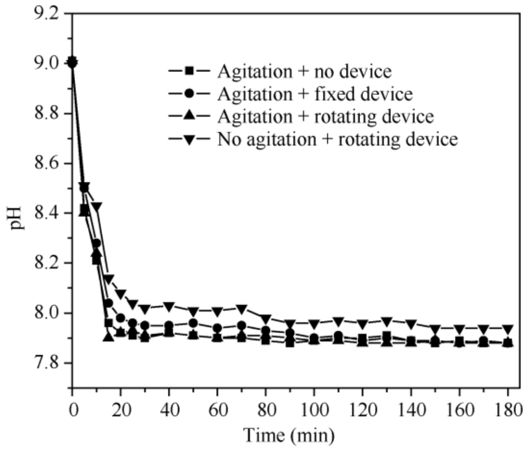

FIG. 2. Evolution of pH during struvite precipitation under different reactor operating regimes.

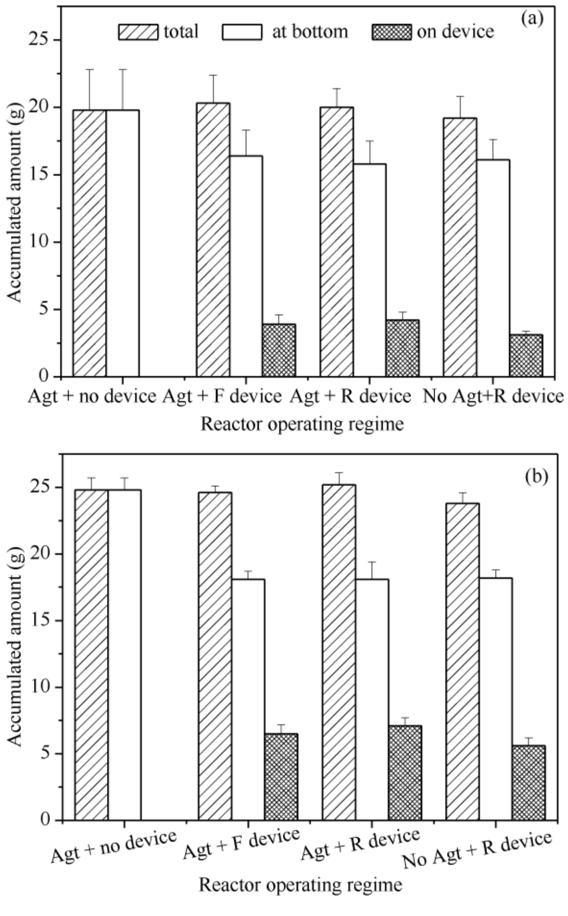

FIG. 3. Effect of non-constant (a) and constant (b) pH on the accumulation of struvite under different reactor configurations.

after 15 h of reaction was (24.6±0.86 g) significantly higher ($P<0.05$) than that observed in the non-constant pH experiment (19.8±1.86 g). In addition, the total amount precipitated with each operating regime in constant pH experiment was always higher than that precipitated with the operating regimes in the non-constant pH experiment (Figs. 3a and 3b). As indicated in Fig. 2, the final pH of the non-constant pH experiment in R1, R2, and R3 was 7.88 and 7.94 in R4 3 hours after experiment. The availability of the effective free ions became less under these low pH values[22] and consequently, a significantly lower struvite yield was found in the pH non-constant experiments (Fig. 3).

Changes in Absorbance Measurements during the Precipitation Experiments

Absorbance measurements are used to monitor the nucleation and growth process in precipitation experiments[22]. The absorbance measurement corresponds to the quantity of energy absorbed or transmitted by the matter and, therefore, the evolution of absorbance of a solution at a specific wavelength indicates the advancement of the crystallization process and hence the particle growth. In the present experiments, absorbance measurements were used to investigate the variations in struvite nucleation and growth under constant and non-constant pH conditions with different reactor operating regimes. Just after the initial pH adjustment of both pH constant and non-constant conditions, the absorbance quickly reached the peak in the first 20 min and then gradually maintained a steady state (Figs. 4a and 4b). It was noticeable that the peak absorbance values observed in all the operating regimes in constant pH experiment were comparatively higher than those in the non-constant (variable) pH experiment (Table 2), suggesting that the constant pH condition created more struvite nuclei than the non-constant pH condition when all the other conditions were maintained constant. The highest peak absorbance of 0.43 was achieved by the 14th min and reached nearly stable absorbance of 0.37 after 6 h of reaction in the constant pH experiment with R_1 configuration (Fig. 4b, Table 2). Even though no significant difference was observed in the peak absorbance values, the time taken to reach the peak value in R_4 (18 min) was slightly longer than that of the operating regimes. Similarly, in the non-constant pH experiment, the highest (0.32) and lowest (0.26) peak absorbance values were observed with R_1 and R_4 regimes, respectively and it took 4 min more in R_4 to reach the peak absorbance than in the other regimes (Table 2). It was clear that the absorbance of steady state in R_1 and R_4 was higher than that in R_2 and R_3 in both constant and non-constant pH experiments, indicating the impact of operating regimes on the final absorbance (Figs. 4a and 4b).

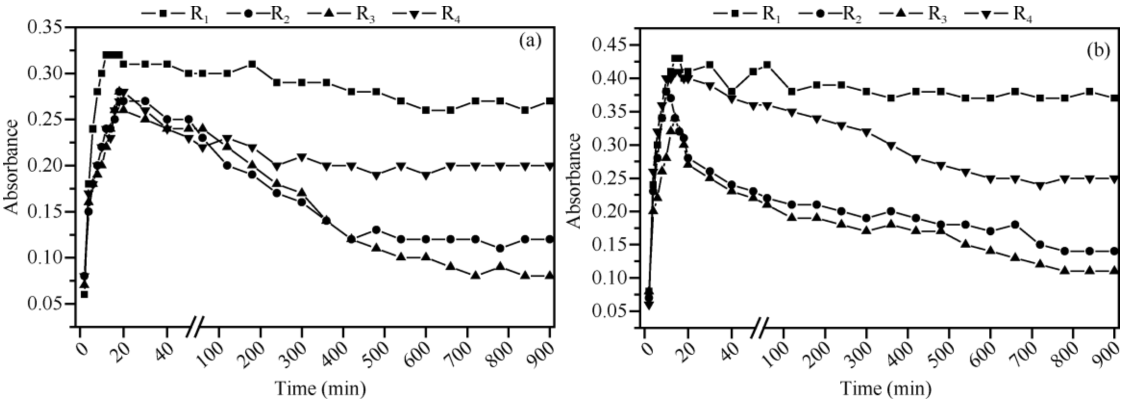

FIG. 4. Variation of absorbance at non-constant (a) and constant (b) pH at different reactor operating regimes. R_1 – agitation (with magnetic stirrer) with no device (■), R_2 – agitation with fixed device (●), R_3 – agitation with device rotating at 50 rpm (▲), R_4 – No agitation with device rotating at 50 rpm (▼).

TABLE 2

Absorbance and Related Data Observed with Different Operating Regimes under Constant and Non-constant pH Conditions

Parameter	Operating Condition							
	Constant pH				Non-constant pH			
	R_1	R_2	R_3	R_4	R_1	R_2	R_3	R_4
Peak Absorbance	0.43	0.40	0.39	0.38	0.32	0.28	0.28	0.26
Time at Peak Absorbance	14	14	14	18	16	16	16	20
Steady State Absorbance	0.37	0.14	0.11	0.25	0.27	0.12	0.08	0.20
Time to Reach Steady-state (h)	6	12	12	9	7	7	11	6

Note. R_1: Agitation by magnetic stirrer at 500 rpm without accumulating device; R_2: Agitation by magnetic stirrer at 500 rpm with accumulating device fixed to the reactor; R_3: Agitation by magnetic stirrer at 500 rpm with accumulating device rotating at 50 rpm; R_4: No agitation by magnetic stirrer with accumulating device rotating at 50 rpm.

Removal of Struvite Components in Constant pH Condition

Since a better performance of precipitate recovery was observed in the constant pH experiment, the removal of NH_4^+, Mg^{2+}, and PO_4^{3-} ions under each operating condition was evaluated. The highest PO_4^{3-} removal (97.2%) was observed in R_1 and R_2 operating regimes while the highest Mg^{2+} removal (97.3%) was achieved in R_1 and R_3 regimes. The highest NH_4^+ removal (71.0%) was observed in R_1 regime. The lowest removal of NH_4^+, Mg^{2+}, and PO_4^{3-} was reported in R_4 regime, accounting for 69.6%, 95.6%, and 94.7%, respectively (Fig. 5). However, the differences observed in the removal efficiency were not significant.

The Rate of Struvite Accumulation on the Device

Struvite is well known for plugging pumps and fouling screens and other equipments[14] in wastewater treatment facilities and similarly, we did find that struvite

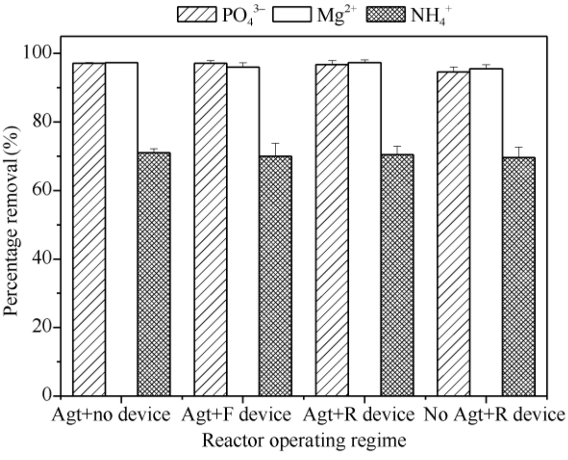

FIG. 5. Percentage removal of NH_4^+, Mg^{2+}, and PO_4^{3-} from the precipitation solution after 15 h of reaction with different operating regimes.

was deposited on the device. As rate of struvite deposition on a surface is a useful criterion for optimizing the recovery in the precipitation reactor, the rate of accumulation was compared in the operating regimes tested. The highest accumulation rate of 8.2 g m^{-2} h^{-1}, 7.5 g m^{-2} h^{-1}, and 6.5 g m^{-2} h^{-1} was achieved with R_3,, R_2, and $R_{4,}$ respectively, in the constant pH experiment (Fig. 6). A significantly different accumulation rate was found between R_3 and R_4 only. The same order of accumulation rates accounted for 4.8, 4.5 g h^{-1} m^{-2}, and 3.6 g h^{-1} m^{-2}, respectively, and a significant difference in the accumulation rate was observed in the non-constant pH experiment.

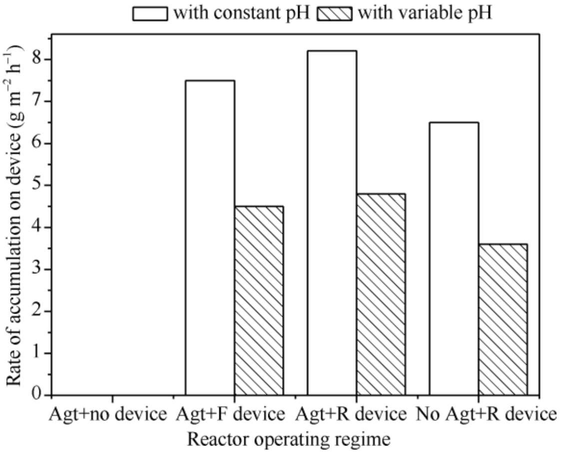

FIG. 6. Rate of struvite accumulation on the device under constant and non-constant pH with different operating regimes.

Effects of the Device and Operating Regimes on Struvite Precipitation

In order to find out any possible influence of the accumulating device on the overall recovery of struvite, reactor-operating regimes undertaken in this experiment (R_2, R_3, and R_4) were compared to those carried out under similar conditions except that the reactor was without device (R_1). The average amount of total precipitates (on the device + at the bottom) observed in the non-constant pH experiment with (SAD) was 19.8 ±1.57 g. An almost similar amount (19.8 ±3.04 g) was found in the absence of the device, but with the same conditions. Similarly, 24.6 ±0.89 g and 24.8 ±0.91 g of total struvite deposits were recorded with and without the device in the constant pH experiment. The statistical analysis suggested that the accumulating device had no significant effect on the total struvite precipitation in both constant and non-constant pH experiments.

In addition to the introduction of a device to accumulate struvite, different operating regimes were also studied, in order to identify the most suitable procedure to operate a struvite recovery reactor. It was evident that the presence of the device in the reactor provided a surface for the attachment of crystals formed in the solution as a white color material was deposited on the device. There was 6.4 ±0.84 g of deposits on the surface of the device in the constant pH experiment while 3.7 ±0.69 g was found on the device in the non-constant pH experiment. In the reactor with R_4 where the device rotated at 50 rpm but not agitated by a magnetic stirrer, the lowest amount of deposits on the device and the lowest total amount of precipitates were reported after 15 h of reaction in both experiments.

DISCUSSION

When the pH and concentration of struvite components are correctly adjusted, the pH decline in the reaction solution can be used to trace the struvite precipitation[8,19]. As the struvite nucleation is a rapid process under super saturation conditions, a greater amount of H^+ ions is released to the solution and hence a rapid decline of pH can be observed within a short period of time[23]. However, the availability of effective free ions for struvite precipitation becomes limited under these final low pH values (7.88 and 7.94)[24] and consequently a significantly lower struvite yield has been reported in pH non-constant experiments (Fig. 3). In contrast, the availability of struvite component ions is increased at pH 9.0 and above[25] and as a result, the struvite yields reporting a constant pH 9.0 with all the tested operating regimes are higher than those in non-constant pH experiments, suggesting that maintaining a constant pH 9.0 during the precipitation process can enhance the struvite yield.

In the present study, the final pH reached a more or less similar value in R_1, R_2, and R_3 regimes and was also slightly lower than that in R_4, suggesting that the difference in pH values between R_1, R_2, R_3, and R_4 is attributed to the variation among the operating conditions. The common operating condition found in R_1, R_2, and R_3 regimes is the agitation with a magnetic stirrer at 500 rpm that gives more opportunities for the struvite components to mix well and react with each other to form more struvites. Stratful *et al.*[26] reported that mixing is an important for homogeneity of the mixture that is essential for the effectiveness of struvite precipitation reaction. An overhead agitator working at 500 rpm[27] gives the best results and the mixing effect provided by the agitator is comparable to that by a magnetic stirrer running at 500 rpm in our experiment. The device rotated at 50 rpm in R_4 could not make sufficient mixing, thus affecting the nucleation and reflecting a relatively lower pH reduction in comparison with that in R_1, R_2, and R_3 regimes (Fig. 2). This phenomenon similarly affected the absorbance measurements (Figs. 4a and 4b), total amount of precipitates and the amount precipitated on the device (Figs. 3a and 3b), as well as the struvite accumulation rate (SAR) on the device (Fig. 6).

As suggested by Barett and Parsons[22], absorbance measurements can be used to define the results of our experiment. The lower peak absorbance observed with each tested operating regime in the non-constant pH experiment than in the constant pH experiment was due to the lower nucleation of struvite under uncontrolled pH conditions. The absorbance value of R_1 regime in both experiments remained high as the struvite crystals formed in the reactor were suspended in the solution in the absence of a device to attach to. The lowest absorbance reported with R_3 regime in both experiments (Figs. 4a and 4b) can be explained by the deposition of more struvite nuclei on the device aided by the dual type of mixing: agitation by the magnetic stirrer and rotating device, which was further supported by the fact that the highest amount of struvite in both experiments was deposited on the device in regime R_3 (Figs. 3a and 3b).

In the present study, the purity of struvite deposited on the device was nearly 96%, which is in agreement with the reported findings[21]. Although the amount of Cu^{2+} and Zn^{2+} was low in the wastewater used in the present study (Table 1), nearly 70% and 48% of these elements were settled with struvite at bottom of the reactor (Table 3). However, indiscriminate use of Cu^{2+} and Zn^{2+} as a growth promoter in swine and other livestock industries is a great concern today. Therefore, struvite recovered from livestock and other wastewaters with higher Cu^{2+} and Zn^{2+} levels, has the risk of contamination with these two elements. Since the precipitates found on SAD contain no Cu^{2+} and Zn^{2+} in detectable quantities (Table 3), it is a useful tool to recover uncontaminated phosphorus and nitrogen from the wastewater contaminated with these two heavy metals, and moreover, a cost effective alternative source of phosphate than rock phosphate minerals commonly contaminated with heavy metals such as cadmium and uranium with impurities like magnesium[28]. The reactor with a stainless steel wire mesh device has proved to be a feasible way of recovering fairly pure struvite from swine wastewater biogas digester effluents. Furthermore, it is worth to maintain constant pH as it permits to precipitate more struvite than the non-constant pH. The SAR observed on the device in the constant pH experiment ranged 6.5-8.2 g m^{-2} h^{-1}, which weas higher than 2.8-5.4 g m^{-2} h^{-1} observed with stainless steel coupons[18]. On the contrary, Suzuki *et al.*[21] reported that the accumulation speed was 16 g m^{-2} h^{-1} on stainless steel rods submerged in a struvite precipitation experiment in which the accumulation rate is 1.95-2.85 higher than that in the present study. However, this difference in accumulation rate could be attributed to the variation of surface roughness occurred in these two precipitation experiments. In our experimental set-up, the reaction time was only 15 h and struvite was accumulated on a stainless-steel wire-mesh surface whereas struvite continued to accumulate on a stainless-steel rod surface for few days as reported above[21]. Once the surface is covered with struvite, it provides a rough surface for further accumulation of struvite in an accelerated rate[18, 21] during the rest of the precipitation process. Therefore, the accumulation rate achieved in our experiment was comparable to the time of the struvite precipitation process. Although a higher struvite accumulation speed has been reported, the weight of the device made of stainless steel bars or coupons would create operational problems. Therefore, the stainless wire mesh device introduced in this study would be more feasible as it reduces the total weight which minimizes the handling and operational difficulties while allowing recovery of a sizable amount of struvite. The other single long-term study using swine wastewater with a struvite accumulation device[29] reported the accumulation rate ranges 1.87-4.5 g m^{-2} h^{-1} within the initial 7-month operating period. However, a comparatively higher rate of 12.9 g m^{-2} h^{-1} that could be attributed to the increased surface roughness due to continuous struvite accumulation has been observed beyond 7 months of operation. Therefore, the authors predict that a better SAR would be achieved with the long-term operation of the new device tested in this study.

Although different wastewaters such as centrate liquor[18], swine wastewater[21,29] and swine waste biogas digester effluent (present study) are used in struvite precipitation experiments, PO_4^{3-} and Mg^{2+} concentrations vary in a narrow range of 64.2-76 mg L^{-1} and 36-94 mg L^{-1}. It was reported the NH_4^+ concentration is 296 mg L^{-1} in SWBDE and 532 mg L^{-1} in swine wastewater[29]. However, the PO_4^{3-} removal efficiency was 96.7% in the current study and SAD, constant pH and molar ratio was much higher than the reported value (67.3%)[29].

The reactor-operating regime seems to contribute to the struvite accumulation rate on the device. The differences in the amount of precipitates found in each operating regime could be attributed to the different mixing and nucleation conditions. Ohlinger

TABLE 3

Amounts of Struvite Constituents, Cu^{2+} and Zn^{2+} Removed from the Solution, Settled at the Bottom and Deposited on the Device (in mmol) with Different Operating Regimes after 15 h of Reaction

Fraction	Constituent and Ratio	Operating Regime			
		R_1	R_2	R_3	R_4
Removed from Solution	PO_4^{3-}	73.95	73.95	73.56	72.06
	Mg^{2+}	74.04	73.05	74.04	72.75
	NH_4^+	45.03	44.4	44.64	44.14
	Cu^{2+}	0.0061	0.0066	0.0066	0.0061
	Zn^{2+}	0.0087	0.0092	0.0092	0.0092
	NH_4^+: Mg^{2+}: PO_4^{3-}	1:1.64:1.64	1:1.64:1.65	1:1.65:1.64	1:1.65:1.63
Deposited on Device	PO_4^{3-}	-	26.5	28.94	22.46
	Mg^{2+}	-	26.0	28.94	23.65
	NH_4^+	-	25.4	29.52	21.75
	Cu^{2+}	-	-	-	-
	Zn^{2+}	-	-	-	-
	NH_4^+: Mg^{2+}: PO_4^{3-}	-	1:1.04:1.02	1:0.98:0.98	1:1.08:1.03
Settled at Bottom	PO_4^{3-}	73.95	47.50	44.62	49.60
	Mg^{2+}	74.04	47.05	45.10	49.10
	NH_4^+	45.03	19.0	15.12	22.38
	Cu^{2+}	0.0060	0.0063	0.0066	0.0061
	Zn^{2+}	0.0084	0.0090	0.0087	0.0089
	NH_4^+: Mg^{2+}: PO_4^{3-}	1:1.64:1.64	1:2.47:2.50	1:2.98:2.95	1:2.19:2.21

Note. R_1: Agitation by magnetic stirrer at 500 rpm without accumulating device; R_2: Agitation by magnetic stirrer at 500 rpm with accumulating device fixed to the reactor; R_3 :Agitation by magnetic stirrer at 500 rpm with accumulating device rotating at 50 rpm; R_4 :No agitation by magnetic stirrer with accumulating device rotating at 50 rpm.

et al.[30] suggested that the mixing energy disrupts the concentration gradients in boundary layers surrounding the growing crystals and increases crystal formation and growth. Therefore, the lowest yield in R_4 could be a result of the slower rotation of the device, which provides the only way for mixing the struvite components NH_4^+, Mg^{2+}, and PO_4^{3-} in the reaction solution and the mixing energy is insufficient to enhance the formation and growth of struvite crystals. As a result, the struvite nucleation and the total amount of precipitates were decreased. However, the total amount of precipitates in each regime was not proportional to the struvite accumulation rate on the device in the respective regime, suggesting that the conditions created in each operating regime have a different trapping effect on the suspended struvite crystals. This phenomenon is well supported by the observations made in the absorbance experiment. After the initial nucleation, there was no accumulating device in R_1 for the formed crystals to adhere to and consequently, the suspending struvite particles contributed to a higher steady state absorbance. In contrast, the device in R_2 and R_3 provided accumulating surfaces for struvite deposit and as a result the absorbance gradually declined. However, in R_3 regime, both magnetic stirrer and device rotated, depositing more struvite than in R_2, and the latter was only magnetically agitated. In regime R_4, the device rotated only at 50 rpm, which might not have a opportunity for the formed struvite particles to deposit on the device and consequently demonstrated a moderate absorbance.

Based on the above observations, it can be concluded that operating regime R_3 is more suitable to isolate the highest amount of almost pure struvite from the reactor. Although the amount of separable struvite was slightly lower in R_2 than in R_3, an overall economic analysis should be done to select the most appropriate operational regime in pilot or commercial scale operation. An increment of the rotation speed or a modification of the reactor in order to enhance mixing is an cost effective option to improve the struvite yield and the nutrient removal efficiency in operating regime 4 (R4). However, these aspects should be investigated before arriving at any conclusions.

Furthermore, it is hypothesized that struvite particles have a special affinity to the surface of the device, as the purity of deposits is over 96% despite the fact that there is an equal chance for organic matter and other impurities to deposit on the device.

CONCLUSION

- The maintenance of constant pH during the struvite precipitation process enhances the availability of struvite constituents and enables the recovery of a maximum amount of struvite under a given molar ratio.
- The operation regime, which governs the mixing properties of the reactor, affects the amount of struvite deposits on the device. The highest amount of precipitates on the device could be obtained in a reactor by rotating the device at 50 rpm together with magnetic stirrer working at 500 rpm.
- The use of an accumulating device has proved to be a promising way to recover Cu^{2+} and Zn^{2+} free pure struvite although the influent wastewater possesses these heavy metals.
- An increment of the rotation speed or a modification of the reactor is a cost effective option for further investigation to improve the struvite recovery.
- A pilot scale and long-term study accompanying economic analysis would be appropriate to determine the maximum SAR and an exact operating regime that ensures the optimum and cost effective recovery of struvite.

REFERENCES

1. Lau P S, Tam N F Y, Wong Y S (1997). Wastewater nutrients (N and P) removal by carrageenan and alginate immobilized *Chlorella vulgaris Environ Technol* **18**, 945-951.
2. Ivanov V, Stabnikov V, Zhuang, *et al.* (2005). Phosphate removal from the retutned liquor of municipal wastewater treatment plant using iron-reducing bacteria. *J Appl Microbiol* **98**, 1152-1161.
3. Jaffer Y, Clark T A, Pearce P, *et al*. (2002). Potential phosphorus recovery by struvite formation. *Water Res* **36**, 1834-1842.
4. Lee S I, Weon S Y, Lee C W, *et al.* (2003). Removal of nitrogen and phosphate from wastewater by addition of bittern. *Chemosphere* **51**, 265-271.
5. Tunay O, Kabdasli I, Orhon D, *et al*. (1997). Ammonia removal by magnesium ammonium phosphate precipitation in industrial wastewaters. *Water Sci Technol* **36**(2-3), 225-228.
6. Turker M, Celen I (2007). Removal of ammonia as struvite from anaerobic digester effluents and recycling of magnesium and phosphate. *Bioresource Technol* **98**(8), 1529-1534.
7. Shu L, Schneider P, Jegatheesan *et al.* (2006). An economic evaluation of phosphorus recovery as struvite from digester supernatant. *Bioresource Technol* **97**(17), 2211-2216.
8. Kofina A N, Koutsoukos P G (2005). Spontaneous Precipitation of Struvite from Synthetic Wastewater Solutions. *Cryst Growth Des* **5**(2), 489-496.
9. Steen I (1998). Phosphorus availability in the 21st century: management of a non-renewable resource. *Phosphorus and Potassium* **217**, 25-31.
10. Johnston A E, Rechards I R (2003). Effectiveness of different precipitated phosphates as phosphorus sources for plants. *Soil Use Manage* **19**, 45-49.
11. Bashan L E D, Bashan Y (2004). Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). *Water Res* **38**, 4222-4246.
12. Corre K S L, Jones E V, Hobbs P, *et al*. (2005). Impact of calcium on struvite crystal size, shape and purity. *J Cryst Growth* **283**, 514-522.
13. Yoshino M, Yao M, Tsuno H, *et al*. (2003). Removal and recovery of phosphate and ammonium as struvite from supernatant in anaerobic digestion *Water Sci Technol* **48**(1), 171-178.
14. Ohlinger K N, Young T M, Schroeder E D (1998). Predicting struvite formation in digestion. *Wat Res* **32**(12), 3607-3614.
15. Suzuki K, Tanaka Y, Osada T, *et al*. (2002). Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration. *Water Res* **36**, 2991-2998
16. Borgerding J (1972). Phosphate deposits in digestion systems. *J Water Pollut Control Fed* **44**, 813-819.
17. Mohajith K, Bhattarai E, Taiganides P *et al*. (1989). Struvite deposits in pipes and aerators. *Biol wastes* **30**, 133-147.
18. Doyle J D, Oldring K, Churchley, *et al*. (2002). Struvite formation and the fouling propensity of different matrials. *Water Res* **36**, 3971-3978.
19. Anton Perera P W, Zhiying H, Yingxu C, *et al*. (2007). Recovery of nitrogen and phosphorus from swine waste biogas digester effluent. *Biomed Environ Sci* **20**(5), 343-350.
20. APHA (1998). Standard method for the examination of water and wastewater. 19th ed, American Public Health Association. Washington, DC.
21. Suzuki K, Tanaka Y, Kuroda K, *et al.* (2005). Recovery of phosphorous from swine wastewater through crystallization. *Bioresource Technol* **96**, 1544-1550.
22. Barret A R, Parsons S A (1998). The influence of magnetic fields on calcium carbonate precipitation. *Water Res* **32**(3), 609-612.
23. Bouropoulos N C, Koutsoukos P G (2000). Spontaneous precipitation of struvite from aqueous solutions. *J Cryst Growth* **213** (3-4), 381-388.
24. Ali M D I, Schinder P A, Neale Hudson (2005). Thermodynamic and solution chemistry of struvite. *J Indian Inst Sci* **85**, 141-149
25. Doyle J D, Parsons S A (2002). Struvite formation, control and recovery. *Water Res* **36**, 3925-3940.
26. Stratful I, Scrimshaw M D, Lester J N (2004). Removal of struvite to prevent problems associated with its accumulation in wastewater treatment works. *Water Environ Res* **76**(5), 437-443.
27. Ali M I, Schneider P A (2006). A fed-batch design approach of struvite system in controlled supersaturation. *Chem Eng Sci* **61**, 3951-3961.
28. Driver J (1998). Phosphate recovery for recycling from sewage and animal waste. First International conference on the recovery of phosphate for recycling from sewage and animal wastes. Warwick University, UK, 6-7 March 1998.
29. Suzuki K, Tanaka Y, Kuroda K, *et al*. (2007). Removal and recovery of phosphorous from swine wastewater by crystallization reactor and struvite accumulating device. *Bioresource Technol* **98**, 1573-1578.
30. Ohlinger K N, Young T M, Schroeder E D (2000). Post digestion struvite precipitation using a fluidized bed reactor. *J Environ Eng* **126**(4), 361-368.

(*Received February* 10, 2008 *Accepted December* 12, 2008)