

Phosphorus recovery from wastewater through struvite formation in fluidized bed reactors: a sustainable approach

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Abstract: Recovery of phosphate as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), before it forms and accumulates on wastewater treatment equipments, solves wastewater treatment problems and also provides environmentally sustainable, renewable nutrient source for the agriculture sector. A pilot-scale fluidized bed reactor was used to recover phosphate through crystallization of struvite, from anaerobic digester centrate at the Lulu Island Wastewater Treatment Plant, Richmond, British Columbia, Canada. The desired degree of phosphate removal was achieved by maintaining operating pH (8.0-8.2), and recycle ratio 5-9, to control the supersaturation conditions inside the reactor. The performance of the system was found to be optimal when in-reactor supersaturation ratio was 2-6. Among several other operating parameters, apparent upflow velocity and magnesium to phosphate molar ratio were also found important to maintain system performance, both in terms of efficiency of phosphate removal and recovery as struvite pellets. A narrow window of upflow velocity (400-410 cm/min) was found to be effective in removing 75-85% phosphate. TOC level inside the reactor was found to affect the performance to some extent. The precipitation potential of struvite could be successfully predicted using a thermodynamic solubility product value of 10-13.36 and its temperature dependence in $\text{pH} = \text{pH}^0 - \frac{\Delta H}{RT}$.

Keywords: crystallization; phosphate; struvite; supersaturation; sustainable

INTRODUCTION

The recovery of phosphates from biological wastewater treatment plants, through struvite or magnesium ammonium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) crystallization, offers an innovative and novel approach for the wastewater industry. It not only alleviates the chances of unwanted struvite deposits in anaerobic digestion and post digestion processes and return lines, but also ensures environmental sustainability.

The recognized phosphorus removal technologies include chemical precipitation, biological phosphorus (P) removal, crystallization, tertiary filtration, and ion exchange (Morse *et al.*, 1998). Most of these processes produce wastes which need to be landfilled or incinerated. The ethos of sustainability, however, makes these options unattractive (Durrant *et al.*, 1999). Crystallization processes stand out because they not only achieve high P removal, but also recover P from wastewater as useful products, including struvite and calcium phosphates. Struvite and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) can be used in agriculture as fertilizers; struvite, however, is preferred for numerous reasons (Wang *et al.*, 2005). First, nutrients are released at a slower rate compared to other fertilizers. Plants can take up the nutrients before being rapidly leached and less frequent application is therefore required. Second, the impurities caused by heavy metals in the recovered struvite are two or three orders of magnitude lower than the commercial phosphate fertilizers. Lastly, the essential nutrients P, nitrogen (N), and magnesium (Mg) are applied simultaneously, with no unnecessary components in the fertilizers.

To encourage the formation of struvite so as to minimize operational downtime, and offer the potential for cost effective recovery, the necessary conditions need to be established at a suitable location within wastewater treatment plants, in a reactor dedicated to the purpose. Research suggests that the ideal location for the recovery of struvite requires that the flow should have a high concentration of soluble $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$, a low concentration of suspended solids and a relatively high phosphorus load (Williams, 1999). Since anaerobic digestion results in the formation of elevated levels of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$, the most appropriate place for struvite

formation and recovery is from supernatant/centrate of an anaerobic sludge (Gaterell, 2000). The only limiting factors then maybe Mg and pH levels, which can be corrected relatively easily by dosing with chemicals.

Struvite usually precipitates as stable white orthorhombic crystals in a 1:1:1 molar ratio according to equation (1) (with n = 0, 1, and 2 as a function of pH) (Corre *et al.*, 2005):



Predicting the crystallization of struvite is complex, as it is controlled by combination of factors such as thermodynamics of liquid-solid equilibrium, phenomena of mass transfer between solid and liquid phases, kinetics of reactions, and several physiochemical parameters (Corre *et al.*, 2005). However, the precipitation of struvite occurs when the activities of magnesium, ammonium and phosphate exceeds the thermodynamic solubility product (K_{sp}) of struvite. As such, precipitation is probable when supersaturation ratio (W), as defined by equation (2), is greater than 1.

$$\Omega = \frac{\{\text{Mg}^{2+}\} \{\text{NH}_4^+\} \{\text{PO}_4^{3-}\}}{K_{sp}} \quad (2)$$

where, $\{\text{Mg}^{2+}\}$, $\{\text{NH}_4^+\}$, and $\{\text{PO}_4^{3-}\}$ are the activities of magnesium, ammonium and phosphate ions respectively. The determination of a thermodynamic solubility of struvite has been described elsewhere (Bhuiyan *et al.*, 2006).

To avoid the complexities associated with the calculation of solubility products of struvite, a simple concept of conditional solubility was used by several researchers (Adnan *et al.*, 2003; Britton *et al.*, 2005). The struvite conditional solubility product (P_s) is defined as the product of the analytical results for soluble magnesium, ammonia nitrogen, and ortho-phosphates:

$$P_s = C_{T, \text{Mg}} C_{T, \text{NH}_3} C_{T, \text{PO}_4} = \frac{K_{sp}}{\alpha_{\text{Mg}^{2+}} \alpha_{\text{NH}_4^+} \alpha_{\text{PO}_4^{3-}} \gamma_{\text{Mg}^{2+}} \gamma_{\text{NH}_4^+} \gamma_{\text{PO}_4^{3-}}} \quad (3)$$

where, g_i is the activity coefficient of ion i . The ionization fractions for Mg^{2+} , NH_4^+ , and PO_4^{3-} can be defined as $\alpha_{\text{Mg}^{2+}} = [\text{Mg}^{2+}] / C_{T, \text{Mg}}$, $\alpha_{\text{NH}_4^+} = [\text{NH}_4^+] / C_{T, \text{NH}_3}$ and $\alpha_{\text{PO}_4^{3-}} = [\text{PO}_4^{3-}] / C_{T, \text{PO}_4}$, where $C_{T, \text{Mg}}$, C_{T, NH_3} , and C_{T, PO_4} are the total analytical concentrations of magnesium, ammonia, and orthophosphates, respectively. Plotting P_{seq} calculated from the right side of equation (3) vs. pH establishes the struvite solubility limit curve for a particular ionic strength. The curve can be used to determine the struvite saturation condition of a process fluid by calculating P_s for that process fluid from analytical concentrations of the constituents (Ohlinger, 1998). A simple approach was taken by the previous researchers to draw such curves, using the experimentally determined equilibrium total concentrations of the constituents in a particular solution for a range of pH values (Adnan *et al.*, 2003; Britton *et al.*, 2005). The main disadvantage of using the conditional solubility values, thus determined, for describing a struvite crystallization system is that comparison between studies becomes more difficult, since any changes in wastewater composition would change its inherent P_{seq} value. Any variation in water chemistry will result in difference in ionic strength, thus changing the precipitation potential of the wastewater (Adnan *et al.*, 2003).

In this study, a pilot-scale reactor, developed at The University of British Columbia (UBC), was demonstrated at the Lulu Island Wastewater Treatment Plant (LIWWTP), in Richmond, BC, Canada. The specific research objective of this part of the study was to predict the precipitation potential of struvite by calculating saturation index ($SI = \log W$) with the help of phreeqc version 2.12 (Parkhurst and Appello, 1999), using the experimentally determined thermodynamic solubility product $K_{sp} = 10^{-13.36}$, and its temperature dependence (Bhuiyan *et al.*, 2006). The objectives also include the identification of the factors that effect struvite crystallization, with special attention to W inside the reactor, magnesium to phosphorus molar ratio, apparent upflow velocity and TOC.

MATERIALS AND METHODS

Reactor design and operation

Based on previous experience at a pilot scale reactor, designed and tested at the UBC Environmental Engineering Pilot Plant using a synthetic feed (Adnan *et al.* 2003), two scaled-up pilot-scale reactors were installed at the LIWWTP. The reactor for this study was operated for two months from mid-May to mid-July, 2006. Figure.1 shows the total crystallization system, including the reactor and the accessories. The reactor was designed as a fluidized bed with increasing diameter and a settling zone at the top. The diameter changes caused turbulent eddies above each transition, ensuring the sufficient mixing existed in the reactor, and also helped to classify the fluidized particles by size (Britton *et al.*, 2005). The larger crystals accumulated at the bottom and were harvested periodically. The centrate was fed from the holding tank (5600 litre) to the reactor using a pump equipped with a digital speed controller. The magnesium was added in the form of $MgCl_2 \cdot 6H_2O$ solution from a tank, using a peristaltic pump. Through out the operation, the target was to maintain a Mg:P molar ratio of about 1.3:1 within the reactor.

Sampling and analysis

Samples of the centrate, effluent, and magnesium feed were collected on a daily basis. Conductivity and temperature were measured using an Oakton pH/CON 300 Deluxe Waterproof pH/Conductivity meter. Analyses for ortho-phosphate and ammonia were made using the flow injection method on a LaChat QuickChem 8000 instrument. Magnesium and calcium analyses were performed by flame atomic absorption spectrophotometry, using a Varian Inc. SpectrAA220 Fast Sequential Atomic Absorption Spectrophotometer. TC and TIC were analyzed by Shimadzu Total Carbon Analyzer TOC-500. TOC was calculated from their difference.

Product Identification

The pellets formed in the pilot-scale crystallizer were examined and identified by x-ray diffraction (XRD), using a Bruker D8 Advance X-ray diffractometer and $CuK\alpha$ radiation, with an average scanning rate of $2.0^{\circ} 2\theta \text{ min}^{-1}$. Identification was also made by the room-temperature infrared (IR) spectra in the wave number range of 400 to 4000 cm^{-1} , on a Perkin Elmer 1710 Infrared Fourier Transform Spectrometer. Analysis of the magnesium, ammonium and phosphate contents of weighed samples were done, after dissolution in 0.5% nitric acid solution.

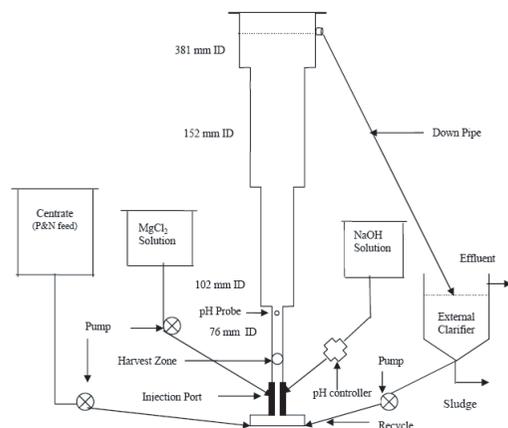


Figure 1 Pilot-scale struvite crystallization system.

RESULTS AND DISCUSSION

The crystallization system was found to successfully recover phosphate as struvite as in the previous studies (Adnan *et al.*, 2003; Britton *et al.*, 2005). The diameter of the pellets formed in this study ranged from 0.5 to 3.5 mm. The crystals were found to be nearly pure struvite ($98.0 \pm 1.0\%$), which agrees with findings of a previous study with the same centrate and reactor system (Fattah, 2004).

Centrate characteristics during the study

The characteristics of the centrate of LIWWTP, during the study, are reported in Table1. The value of Ω of the centrate was more than 1 in some instances because of the variable magnesium concentrations; however, this did not result any noticeable precipitation in the centrate tank.

Table 1 Centrate characteristics of the Lulu Island Wastewater Treatment Plant

Parameters (n=23)	Mean	Maximum	Minimum	SD
pH	7.79	8.27	7.28	0.29
Temperature	27.33	31.3	23.4	2.07
Conductivity(μ S/cm)	6467	6860	5970	310
PO ₄ -P (mg /L)	76.13	106.8	59.1	12.07
NH ₄ -N (mg /L)	757.41	842	647	47.76
Mg (mg /L)	12.31	21.36	2.04	4.35
Ca (mg /L)	19.13	28.2	10.3	5.89
Filtered TIC (mg/L as C)	707.57	1417.4	285.35	328.59
Filtered TOC (mg /L)	562.4	1340.61	37.4	325.3

Performance of the crystallization process

The performance of the system was analyzed both from its phosphate removal efficiency, and struvite recovery efficiency. The phosphate removal efficiency (%) was calculated from the difference of the PO₄-P concentrations in the influent and effluent of the fluidized bed reactor. Phosphate was made limiting adding magnesium in excess. Theoretically, 100% of the removed phosphate should have been recovered as phosphate according to equation (4)

$$\text{Struvite mass, Kg /day} = Q \cdot \Delta C_{PO_4} \cdot MW_s \quad (4)$$

where, Q = total flow in the reactor (L/day), ΔC_{PO_4} = decrease in phosphate concentrations (mol /L), and MW_s = Molecular weight of struvite (0.2454 Kg /mol). Based on the mass of seed added, mass of total struvite harvested, and the mass remaining in the reactor at the end, $83.0 \pm 2.0\%$ of the theoretical mass was recovered during operation. This difference may have occurred due to loss of some fines with the effluent, which was eventually deposited in the external clarifier, and some during drying.

Supersaturation level

Saturation condition or supersaturation level is the key to struvite crystallization. It was measured, as defined in equation (2), and was calculated from S/I determined by phreeqC. The supersaturation level, that leads to struvite crystallization inside the fluidized bed reactor, was the Ω inside the reactor for a particular operational pH. The saturation level, determined with respect to the thermodynamic solubility product (Bhuiyan *et al.*, 2006), gives a precipitation potential of struvite which can be compared with another situation, regardless of pH's and ionic strengths. Because of the wide variation of the composition of the centrate being fed, the saturation level changed within the reactor even for a particular pH. However, a range of Ω (2-6) has been identified to achieve the desired phosphate removal (>80%), beyond which the change in phosphate removal efficiency was found to be insignificant (see Figure 2).

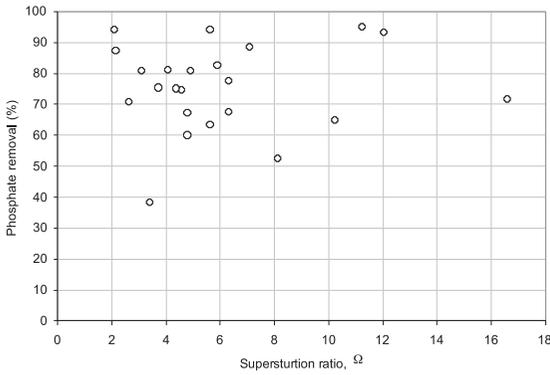


Figure 2 Supersaturation ratio vs. phosphate removal

The operational parameters such as recycle ratio, magnesium dosing, and temperature also contributed to the change in the supersaturation levels inside the reactor. A recycle ratio of 5-9 was maintained throughout the operation. Although, the value of Ω inside the reactor appeared to be the most reliable control parameter for operating the reactor in a previous study (Adnan *et al.*, 2003), the relationship between Ω and P-removal (%) was found to be affected by several other variables in this study. Figure 3a shows that with an increasing pH and Ω , the phosphate removal efficiency dropped at pH 8.1. However, Fig. 3b shows that the phosphate removal efficiency was lower at pH 8.1, perhaps due to higher level of TOC concentration, which implies the effect of organic ligands in phosphate removal. Inhibition of the crystal growth by blocking the active sites of the newly formed nuclei of hydroxylapatite by the organic ligands has been previously reported (Koutsopoulos & Dalas, 2000).

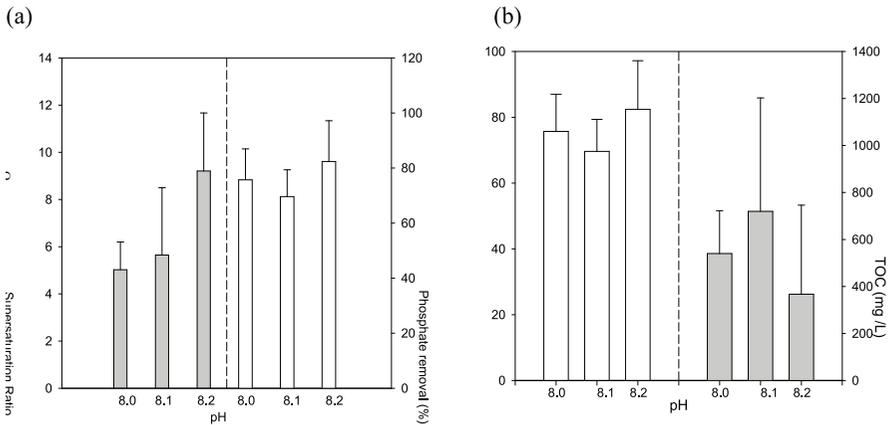


Figure 3 pH vs. (a) Supersaturation ratio and phosphate removal (b) TOC and phosphate removal

Upflow velocity and mixing

Although the in reactor saturation level was below the metastable limit of spontaneous homogenous primary nucleation of struvite (Bhuiyan, 2006), the nature of the process fluid and the high energy mixing at the inlet resulted in heterogeneous nucleation and lowered the metastable limit. The induction time in the reactor was, thus, lowered to a level where nucleation triggered immediately after the flow passed the injection port. This was observed by a pH drop due to the proton release as shown in equation (1). Once the pH dropped below the operational pH, the controller started to pump caustic.

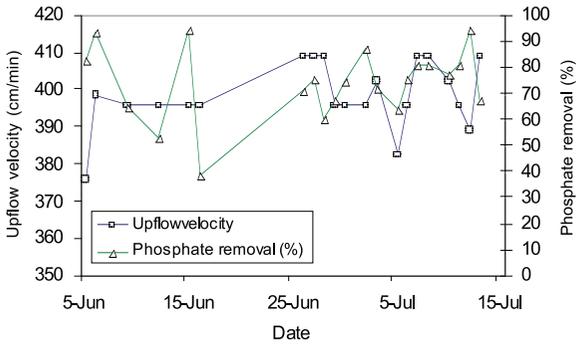


Figure 4 Upflow velocity and phosphate removal with time.

The transition of the sections in the reactor also gave aid to adequate mixing, while the seeds resulted in surface secondary nucleation. The nucleation and/or growth inside the reactor took place within the HRT of the system (4.44 ± 0.26 min.). This was also supported by the presence of a very little amount of fines accumulated in the external clarifier. Upflow velocity in the bottom section was found to be another parameter of importance. From Figure 4, it can be seen that for a very narrow window of the apparent upflow velocity (400–410 cm/min), 75–85% phosphate removal was achieved.

Mg:P molar ratio

Previous research suggested that a stoichiometric excess of ammonium would help drive the reaction to form relatively pure struvite (Stratful et al. 2001), while excess magnesium decreases purity (Demeestere et al., 2001). Figure 5 (a) shows that phosphate removal efficiency maintains a good correlation ($r = 0.65$, $p=0.000$) with Mg:P ratio inside the reactor, and the efficiency was not found to change significantly after a Mg:P ratio around 2.

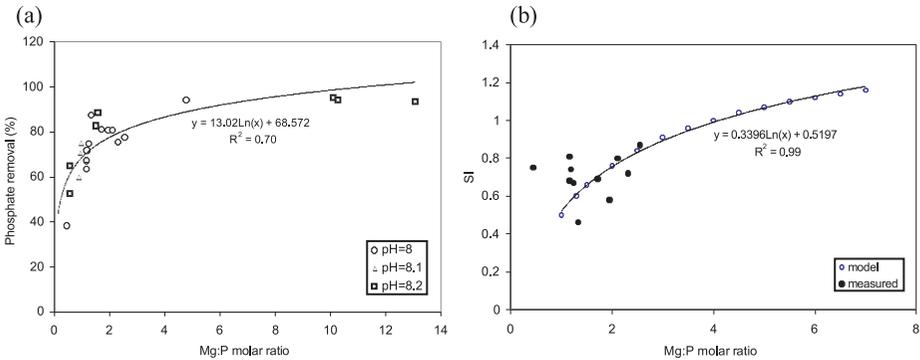


Figure 5 Mg:P molar ratio vs. (a) phosphate removal and (b) model calculated SI.

For concentrations of the available parameters near the mean of the in-reactor concentrations during operation ($PO_4\text{-P} = 25$ mg/L, $NH_4\text{-N} = 690$ mg/L, $Ca = 15$ mg/L, $TIC = 5000$ mg/L as $CaCO_3$) and $pH=8.0$, phreeqC model was used to determine the variation of SI with Mg:P ratio. Figure 5 (b) shows that the measured values lie closely around the curve of model calculated values, while the dispersion in measured values maybe due to the effects of other variables and partly due to measurement errors.

CONCLUSIONS

Based on the results obtained from this study of struvite recovery from an anaerobic digester centrate, using the results of a thermodynamic study, the pilot-scale struvite recovery reactor developed at UBC was found to be effective in recovering phosphate in the form of nearly pure struvite product. The desired degree of phosphate removal was achieved by maintaining operating pH 8.0-8.2, and recycle ratio 5-9, to control the supersaturation conditions inside the reactor. The performance of the system was found to be optimal when in-reactor supersaturation ratio was 2-6. Among several other operating parameters, apparent upflow velocity and magnesium to phosphate molar ratio were also found important to maintain system performance. Upflow velocity of 400-410 cm/min in the bottom section of the reactor was found to be effective in removing 75-85% phosphate. TOC level inside the reactor was found to affect the performance to some extent, perhaps by inhibiting the crystal growth.

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