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Carbon and struvite recovery from centrate at a Biological Nutrient Removal Plant

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ABSTRACT

Wastewater contains many valuable resources, however, recovering these resources is often a challenge. Nutrients such as phosphorus and nitrogen are

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very valuable resources which should not be wasted. Struvite is a compound containing magnesium, ammonium and phosphate that often forms naturally in wastewater treatment plants, sometimes accumulating in equipment and piping causing operational issues. However, struvite can also be recovered beneficially for sale and to result in improvements to other plant processes.

A pilot-scale demonstration study of volatile fatty acid and phosphorus recovery from the centrate of an Autothermal Thermophilic Aerobic Digestion (ATAD) system was carried out at the City of Salmon Arm Water Pollution Control Centre in British Columbia, Canada using a struvite crystallizer. Removal of phosphorus from the ATAD centrate, which was also has a high volatile fatty acid (VFA) concentration, allowed the centrate to be returned to the biological nutrient removal process without the use of metal salts, which are normally used to reduce the high concentration of phosphorus. Bench-scale batch tests were routinely carried out to model the impact of returning the VFA-rich centrate to the phosphorus removal process.

The ATAD process operates at high temperatures (40° to 70°C). This solubilises large amounts of phosphates and other nutrients, resulting in higher concentrations in the centrate than would be expected from other solids digestion processes at conventional secondary treatment plants. The proprietary struvite crystallizer, developed at the University of British Columbia and commercialized by Ostara Nutrient Recovery Technologies, was used to remove phosphate in crystal form from the dewatering centrate of the plant.

The study was successful in consistently producing good quality fertilizer struvite pellets (avg. 2mm in diameter) and removing approximately 80% of the orthophosphate and 35% of the ammonium-nitrogen from the centrate. This study also showed that the crystallizer effluent is a valuable product for improving the biological nutrient removal process and could potentially replace the need for acetate or other supplemental VFA sources.

In assessing the performance of the crystallizer, magnesium, ammonium, phosphate, pH, conductivity, temperature, solids, and VFA concentration were measured daily.

For the Salmon Arm pilot the combination of fermenter/ATAD and struvite crystallizer improved the performance of the nutrient removal process, eliminated the need for ferric or alum for phosphorus removal from the centrate, and provided consistent nutrient recovery in the form of a saleable end product.

1.1 INTRODUCTION

The City of Salmon Arm has a unique treatment process at their Water Pollution Control Centre (WPCC). The process includes a combination Fixed Growth Reactor (FGR) and suspended growth reactor (SGR) for biological nutrient removal (BNR) and an Autothermal Thermophilic Aerobic Digestion (ATAD) System for sludge digestion (Kelly et. al., 2005 and Kelly et. al., 2005). This combination provides a special opportunity for high amounts of nutrient recovery. The combination of these technologies is unique and uses an integrative approach with a valuable end product. The struvite crystallizer uses dissolved orthophosphate and ammonium in wastewater to produce a high quality, slow-release fertilizer product that is particularly valuable in locations where fertilization is critical (e.g. golf courses). Nutrient removal processes, such as the one in use in Salmon Arm, move the nutrients from the liquid effluent to the biosolids and therefore, there are high concentrations of phosphorus in the digestors. The ATAD System also has high levels of volatile fatty acids (VFAs) due to the nature of the digestion process. The ATAD functions as an acid digester in the initial stages as described by Chu (1996),, which is common to the first phase of a two phase acid-gas digestion process.

By using centrate from the dewatering of the digested biosolids leaving the ATAD process, high levels of phosphorus can be captured in the crystallizer, and the treated centrate, containing high levels of VFAs, can be returned to the BNR process. This would also eliminate the need to use alum to precipitate phosphorus salts from the centrate.

1.1.1 Description of Plant Process

The sludge digestion (ATAD) process involves treating both the solids from the primary sedimentation tanks and the waste biological sludge from the BNR process. In the digestion process, as the bacterial cells are broken down the accumulated phosphate is released into solution as dissolved ortho-phosphate.

Because phosphorus is released into solution during digestion, the plant operators are normally required to remove the phosphate from the centrate by adding alum to the digested sludge prior to centrifuging. If this is not done, phosphorus will be returned via the centrate to the liquid treatment process, thereby increasing the load on the biological phosphorus removal process. For this project, in order to keep the phosphate in solution, (in the centrate used for the study) alum was not added to the sludge before centrifuging. Instead, an increased amount of polymer was added, which clarifies the centrate without affecting the dissolved orthophosphate level.

1.1.3 Background

The key issues related to the need for the study include the following:

1. (1) Based on known global reserves, it is understood that the supply of phosphate will be exhausted by about 2050 and all means of phosphorus recovery and reuse will be of growing importance.
2. (2) It is well established in the literature that VFAs, such as acetic acid, are an important carbon source in the biological phosphorus removal process, as well as in denitrification, as they provide a readily accessible form of carbon (Metcalf & Eddy, 2003).

Although several pilot studies have been undertaken with this struvite crystallizer using various methods for thickening and separating solids after digestion, none of the studies to date have used ATAD for solids digestion. Because this plant includes biological nutrient removal (BNR) and ATAD, with its high temperatures, this results in much higher nutrient concentrations. This study is even more unique because of the focus on recovering VFAs for return to the BNR process.

1.1.4 Objectives

This nutrient recovery pilot test work was designed to fulfil the following main objectives:

(1) To capture VFA from the crystallizer effluent for reuse in the biological nutrient removal process.
(2) To remove excess phosphorus from the digester centrate so that the centrate can be returned to the biological nutrient removal process.
(3) To recover dissolved phosphorus in the form of a saleable fertilizer using the UBC Crystallizer and associated equipment.

1.1.5 Acknowledgements

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(4) Ostara Nutrient Recovery Technologies Inc.; and
(5) Dayton & Knight Ltd. Consulting Engineers.

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1.2 METHODS

To test the performance of this process, a pilot reactor was operated and several tests were carried out to assess its feasibility and efficiency. The struvite crystallizer was used to capture the phosphorus, while “batch tests” simulated the effect of returning the effluent to the treatment process.

During the study, the following parameters were monitored daily: dissolved ortho-phosphate, dissolved magnesium, dissolved ammonium, volatile fatty acid (VFA) content, pH, temperature, conductivity, and total suspended solids.

1.2.1 Crystallizer Operation

The crystalizer is a fluidized bed reactor, with sections of increasing diameter and a settling zone on top. The changes in diameter result in turbulent eddies at each transition and ensure sufficient mixing in the reactor. These different sized sections also help to classify the fluidized particles by size, so that only the largest ones will be harvested (Britton et al., 2005). This pilot reactor treated 1.7 L/min of centrate which is approximately 10% of the overall centrate generated at the WPCC (18 L/min).

The key ingredients for forming struvite crystals are magnesium, ammonium, and phosphate and, therefore, these were the key parameters that were monitored. These chemicals combine according to the following chemical equation:

$$Mg^{2+} + NH_4{}^{+} + HPO_4{}^{2-} + OH + 5H_2O \rightarrow MgNH_4PO_4.6H_2O$$

Because of the interconnectedness of many of the operating parameters, a computer model was developed by Ostara Nutrient Recovery Technologies Inc. to determine the optimal values of some parameters based on key inputs.

A diagram showing the pilot plant set-up and all included tanks and pumps is shown on Figure 1.1.

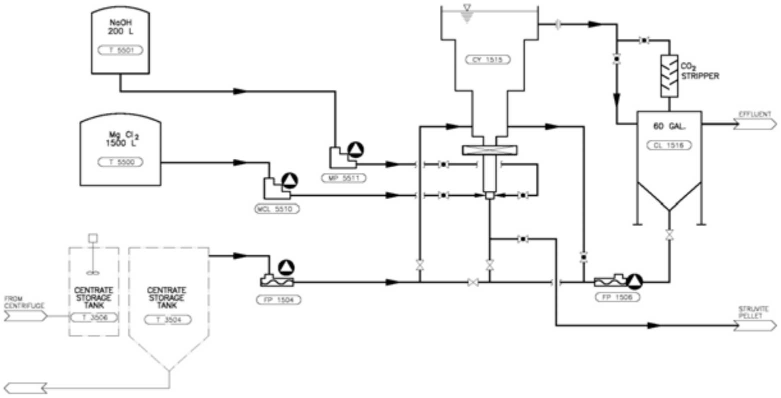


Figure 1.1 Process Flow Diagram

1.2.1.1 *Feed*

During the pilot test, after the ATAD liquid was centrifuged, it was stored in two equalization tanks. Each time the tanks were filled the centrate was allowed to settle overnight or longer in both tanks, before the supernatant was used in the crystallizer. The supernatant, (clarified centrate) was then pumped from the cone shaped tank up through the bottom of the crystallizer. The overflow from the crystallizer went into the crystallizer clarifier, and the overflow from the clarifier was recycled back into the crystallizer at multiples of the influent flow rate. This recycling is done to dilute the feed and achieve the desired super-saturation ratio (SSR). The recycle ratio used for this study was ten times the crystallizer influent flow rate.

1.2.1.2 *Magnesium*

Upon entering the crystallizer, the centrate was blended with magnesium chloride ($MgCl_2$) and caustic in a stainless steel injector block. The flow rates of these two chemicals were dictated by the computer spreadsheet model. The flow rate of $MgCl_2$ is determined based on the molar ratio of Mg:P that is desired, the concentration of magnesium in the centrate, and the concentration of magnesium in the magnesium chloride solution. For optimal struvite formation, a ratio of Mg:P of 1.2:1 or greater is needed (Fred Koch, pers. Comm.).

1.2.1.3 pH Control

The caustic flow rate was determined by the pH controller, which adjusted the flow rate automatically in order to reach the pH set point. The pH set point on the controller was one of the outputs of the computer model and is based on the desired super-saturation rates (SSR), the recycle ratio, temperature of the influent, and the influent concentration of magnesium, ammonium, and phosphate. The pH was affected by all these things and was set so that all nutrients stayed in solution and were available for struvite formation.

The key parameter for optimal operation of the crystallizer is the super saturation ratio (SSR) (Rahaman et. al., 2008). pH is the main parameter that can be manipulated in order to achieve the desired SSR.

1.2.2 Monitoring

Samples for VFA analysis were taken five days a week. The VFA samples were analyzed by a Gas Chromatograph using an HP-FFAP column. The Separation of Unsaturated Acids and Fatty Acid Methyl Esters was done using HP-FFAP and HP-INNOWax Columns.

Dissolved orthophosphate was measured as phosphorus, both in the influent and the effluent of the crystallizer, approximately five days a week. The samples were filtered through 0.45 µm filter paper and analyzed using a spectrophotometer according to *Standard Methods* Method 4500-P D.

In order to measure the magnesium concentration in the centrate on a daily basis, the Calculation Method was used from *Standard Methods*, Method 3500-Mg E except that polyaluminum chloride (PAC) was added to remove soluble phosphate, which is known to interfere with the test. According to Forrest et al. (2007), this is the most reliable method of measuring magnesium on-site.

Because of the importance of pH, an in-line pH probe was used to regulate the supply of caustic to the reactor, so that the desired pH was achieved. A second pH meter measured the pH in the clarifier, from which flow was recycled back into the crystallizer.

Dissolved ammonium concentration was determined using the Ammonia-Selective Electrode Method (Method 4500-NH_3 F from *Standard Methods*). This test was done five times per week and the results were entered into the model.

Temperature is important because of its effect on several other parameters, including conductivity and pH. The conductivity of a solution is dependent on the ions present within it. Therefore, as struvite crystals are formed in the crystallizer, the conductivity should increase. Temperature and conductivity were measured using the Oakton Instruments/ Eutech Instruments PC 300 probe.

TSS is an important parameter because of the influence solids can have on the operation of the crystallizer. Not only do solids provide extra nucleation sites for struvite to form but often high solids levels are anticipated to cause clogging in the tubing and the reactor which causes occasional shut-down for clean-up. The TSS test was done approximately five days per week according to Standard Methods Method 2540D.

The bench-scale experiments were typically carried out once a week and were designed to mimic the flow rates and hydraulic retention times (HRTs) in the three phases of biological phosphorus removal: anaerobic, anoxic, and aerobic; in order to determine the effect of returning the crystallizer effluent to the process. Two experiments were run simultaneously each time, one without crystallizer effluent, as a control, and one with crystallizer effluent.

For the test which included crystallizer effluent, the appropriate amount was included based on the amount of centrate that would be produced at full scale. Samples were withdrawn from the batch reactor every five to ten minutes and analyzed for ortho-phosphate concentration (PO_4-P).

1.3 RESULTS AND DISCUSSION

1.3.1 Reactor Operation

Although the reactor consistently produced struvite pellets, the size and quality of the pellets varied. Initially, pellets of up to 3.6mm in diameter with high strength were produced, but over the length of the study the average size was approximately 2mm in diameter. The quality and size of pellets can be improved by optimizing the reactor operation. Figure 1.2 shows struvite pellets formed during each of the first five weeks of the study.

Figure 1.2 Pellets formed during the study

1.3.2 Monitoring

1.3.2.1 Volatile Fatty Acids

The average volatile fatty acid (VFA) content of the crystallizer influent and effluent are shown in Table 1.3 (See also Figure 3-2). There was a decrease in VFAs through the crystallizer of 24%. The difference was significant and could be partially accounted for by measurement error. However, the decrease could also be due to entrained air from the recycle line which might lead to bacterial oxidation of VFA. Further research and analysis are required to confirm this hypothesis. However, the concentration of VFA in the effluent was still high enough to be beneficial to the biological nutrient removal process at the plant.

Table 1.1 Volatile Fatty Acid Content

	Influent (mg/L as acetic acid)	Effluent (mg/L as acetic acid)	% drop through crystallizer
Overall avg.	1259	946	24%
Overall St. dev.	620	518	20%

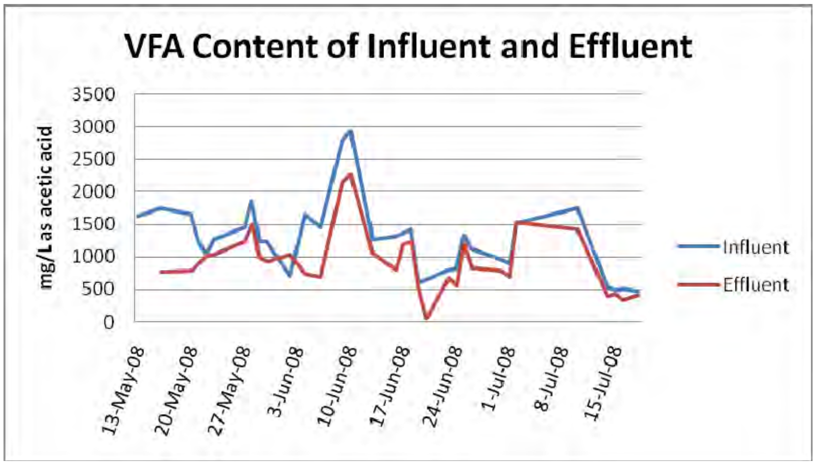


Figure 1.3 Variation in VFA in Crystallizer Influent and Effluent

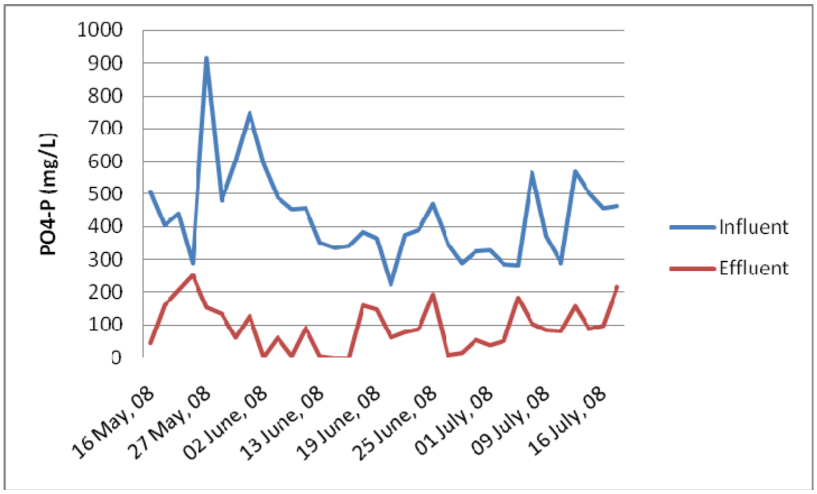
1.3.2.2 Phosphate

The average orthophosphate concentration of the crystallizer influent and effluent is shown in Table 1.2. The average phosphorus removal observed was 77% (see Figure 1.4). This is similar to what has been found in other pilot studies with similar influent phosphorus concentrations (Prasad et al., 2007). However, with lower influent phosphorus concentrations, higher removal percentages can sometimes be anticipated (pers. Comm. Ahren Britton). It is suspected that higher removals could also be achieved using this process given further optimization.

Table 1.2 Phosphate Concentrations and Removal

PO_4 -P (mg/L)	Influent	Effluent	% P removal
Overall average	433	92	77%
Overall Standard deviation	142	68	19%

Figure 1.4 Variation in Influent and Effluent Orthophosphate



The typical influent flow rate to the plant is 4600 m^3/d with an influent phosphorus concentration of 7.5 mg/L. This gives a daily phosphorus load of approximately 34.5 kg/d. The pilot crystallizer would remove 2.4% of this load if operated continuously and a full-scale reactor would remove approximately 26% of the total phosphorus load to the plant in the form of crystals. This phosphorus would be removed in the form of a saleable fertilizer and would decrease the amount of sludge produced through the current practice of adding alum to remove phosphorus.

1.3.2.3 Ammonium Nitrogen

On average 34% removal of ammonium nitrogen (NH_4^+-N) was achieved (see Table 1.4). This removal was higher than is normally achieved in struvite reactors and was partially due to the high influent concentration. Normally, the molar ratio of N:P removal is approximately 1.1:1 (Ahren Britton, pers. Comm.). However, in this study, a molar ratio of 1.7:1 N: P removal from the liquid was achieved. Several samples of struvite crystals were tested for composition by weight, of the three key elements (magnesium, nitrogen, and phosphorus). All samples had approximately a 1:1:1 molar ratio of P:N:Mg. The pellets were very close to pure struvite with about 1.1% by weight impurities. This shows that there was a loss of nitrogen that is unaccounted for. It is unclear why this extra removal was occurring.

Table 1.4 AMMONIUM NITROGEN CONCENTRATION AND REMOVAL

NH_4-N (mg/L)	INFLUENT	EFFLUENT	% REMOVAL
Overall avg.	871	566	34%
Overall st. dev.	199	157	13%

1.3.2.4 *Magnesium*

The on-site magnesium test was difficult to perfect and several different methods were tested in order to remove all of the PO_4 in the samples, so that there would be no interference with the hardness test. Previously, for other struvite pilot studies, magnesium had to be measured in a lab off-site, which meant a delay before getting the results back.

1.3.2.5 *pH*

Since the influent centrate was mixed with magnesium chloride and caustic to encourage formation of the struvite pellets, the pH of the effluent was always higher than that of the influent. The set point is the pH that was entered into the pH controller in order to regulate the flow of caustic.

Table 1.3 shows the overall average influent, effluent and set point pH and their standard deviations.

Table 1.3 pH Results

Date	Crystallizer Influent	Crystallizer Effluent	Set point
Overall Avg.	6.8	7.2	7.3
Overall St. Dev.	0.4	0.3	0.3

1.3.2.6 *Temperature*

The average temperature of the influent to the crystallizer was 23.9°C. Although the temperature in the ATAD was always higher the centrate cooled in the centrifuge and during storage. The difference between the maximum and minimum temperatures measured was 9°C.

1.3.2.7 *Total Suspended Solids*

Table 1.5 shows the average total suspended solids (TSS) concentration of the crystallizer influent and effluent. The solids level in the effluent was higher than the influent because of fines formed in the reactor. Solids were anticipated to be a major operational difficulty, as struvite reactors have not previously been run with such high levels of solids. However, because a higher polymer dosage was used, and sufficient time was allowed for settling, none of these problems were encountered. High solids however, were likely the source of many of the fines in the reactor as they can act as nucleation sites. This can hinder the formation of larger struvite pellets, since there are more nucleation sites available.

Table 1.5 TOTAL SUSPENDED SOLIDS

TSS (mg/L)	Influent	Effluent
Overall avg.	351	716
Overall standard deviation	235	489

1.3.3 Batch Test Results

Batch tests were typically done weekly, to determine the effect of returning the VFA-rich crystallizer effluent to the beginning of the nutrient removal process. Several different configurations were used in order to better understand the effect the effluent would have.

Since the centrifuge was installed in 1998, the centrate from the ATADs has been returned to the primary tank at the head of the plant through the use of alum. This has provided, in combination with the VFA in the influent sewage, sufficient fatty acids to achieve biological phosphorus (bio-P) removal. The average total P concentration in the plant effluent between Jan 2005 and June 2008 was 0.44 mg/L. Therefore, using the centrate return flow has consistently allowed the plant to meet its permit requirements regarding phosphorus removal.

The goal of adding extra VFA to the process is to encourage greater uptake of phosphorus by the phosphate accumulating organisms (PAO) and to stabilize the process. During the anaerobic stage of the nutrient removal process, the PAOs release phosphate and uptake VFAs such as acetate. The more acetate they assimilate in this stage (and the more phosphorus released), the greater the amount of phosphate they will be able to uptake in subsequent phases. Therefore, the amount of PO_4-P released during the anaerobic stage is a measure of the performance of the process. For all the batch tests, the phosphorus that was released in the anaerobic phase was assimilated by the PAOs during the subsequent aerated phase or more was assimilated with the centrate than without.

Overall, for all configurations, the average phosphorus release was higher in the experiment than in the control and had a lower standard deviation, indicating that addition of the crystallizer effluent led to more consistent phosphorus release in the anaerobic phase. This indicates that the VFAs from the crystallizer effluent would improve the performance of the phosphorus removal process and provide more consistent operation. Some results are shown in Table 1.6.

Table 1.6 PHOSPHATE RELEASE DURING ANAEROBIC PHASE

Date	Control	Experiment
12-May	1.4	11.6
21-May	0	14
27-May	22.1	16.2
12-Jun	16.8	13
20-Jun	18	0
27-Jun	-1	16
11-Jul	0	9
15-Jul	12	8
17-Jul	0	7
Average	**7.7**	**10.5**
St. Dev.	**8.9**	**4.9**

1.4 CONLUSIONS

Overall, this study demonstrated that a struvite crystallizer can be effectively used to capture phosphates and ammonium from ATAD centrate, and that the treated crystallizer effluent can improve and stabilize the biological phosphorus removal process. The following further conclusions are based on the results of this study.

(1) Biological phosphorus removal sludge can be combined with primary sludge, digested, and used for recovery of VFA and phosphate.

(2) Using the struvite crystallizer removed sufficient phosphorus from the centrate to allow the effluent to be beneficially used in the biological phosphorus removal process.

(3) Returning the VFA-rich stream to the BNR anaerobic phase increases the amount of phosphorus release and uptake, and provides consistent operation.

(4) An average of 77% phosphorus removal from the centrate was achieved consistently over the course of the short study.

(5) An average of 34% ammonium-nitrogen removal from the centrate was achieved throughout the course of the study.

(6) The average total suspended solids concentration in the influent to the crystallizer was 354 mg/L. The reactor operated well, even at this high concentration and no problems with clogging were encountered.

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