Control of the phosphorus recirculation by CO$_2$ stripping of anaerobic digested sludge in a WWTP running only Bio-P.

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ABSTRACT

In order to avoid eutrophication of water bodies, stringent regulations limit the phosphorus (P) concentration in the outlet of Waste Water Treatment Plants (WWTP). While chemical precipitation of phosphate tends to be replaced by the Bio-P process (biological phosphorus removal, or EBPR), the use of anaerobic digestion for sludge stabilization implies a strong phosphorus recirculation back to the head of the plant, which might affect the stability of the process. Öresundsverket WWTP, located in southern Sweden, gradually stopped iron precipitation to finally run Bio-P without chemical addition. The recent implementation of Bio-P in the whole WWTP increased the recirculation from 40% up to more than 65% of incoming phosphorus which was found to overload the process.

The study of the mechanisms responsible for P-fixation shows that apatite and struvite crystallizations are responsible for the fixation of 40% of total phosphorus in the digested sludge while the organic part represents about 13%.

CO$_2$ stripping experiments imply that further struvite and apatite crystallization can be obtained in the digested sludge permitting fixation up to 100 mgP/l without chemical addition. This could solve the recirculation problem depending on full scale results.

Key words: Bio-P, EBPR, struvite, CO$_2$ stripping, phosphorus removal, anaerobic digestion.

INTRODUCTION

Öresundsverket, treating 150000 pe (person equivalent), was one of the first WWTP in Sweden to implement the Bio-P process for phosphorus removal. Considering the satisfactory cleaning results (92% TP) obtained with half the WWTP running in Bio-P, it was decided to try to run the whole plant with Bio-P without chemical addition. After two months, the recirculation increased in such extent that it overloaded the process and iron were added for 2 weeks to stabilize the process.

The problem of phosphorus recirculation in WWTP running Bio-P in combination with anaerobic digestion is well known and it was shown that the understanding of the P-fixation mechanisms in the anaerobic digester was essential for predicting internal phosphorus flows.

Several methods, permitting to reduce the phosphorus concentration in sludge treatment sidestreams, have been suggested by different authors. Among them, crystallization of struvite (MAP, MgNH$_4$PO$_4$•6H$_2$O) seems to offer an interesting solution because of the high concentration of its constituents in the digested sludge and its potential as long term fertilizer.

Review on struvite crystallization:

- All poly-P are released and hydrolyzed in the digester [1] implying a release of magnesium in a theoretical ratio of 1:3 (Mg/P) [2]. (all the ratios are given in mol/mol)
- Struvite crystallization occurs with Mg:P ratio in the range 1.05 - 1.3 [2].
- Struvite crystallization is very depending on pH and the pH of minimum solubility is found around 9.0 [3].

The objective of this study is to determine a method to avoid the overload caused by the strong phosphorus recirculation.
MATERIAL AND METHODS
Quartz and Struvite were identified in the digested sludge sample by mean of X-ray diffraction (XRD).
A phosphorus fractionation experiment has been conducted based on J.J. González Medeiros et al. [4]. This permits to fractionate the total phosphorus (TP) into the organic (OP) and inorganic (IP) parts as well as the apatite (AP) and non-apatite inorganic (NAIP) parts. It should be noticed that no statements about dissolved phosphorus (Sol-P) or struvite are made in the protocol. Real digested sludge was used on triplicate samples.
A CO\textsubscript{2} stripping experiment was realized on real digested sludge and on centrifuge reject in a 3 liter jar (2 l sludge). A continuous air flow [5] was blown in the sludge and samples were withdrawn and analyzed about every 0.25 pH increase. pH and phosphate were directly analyzed after filtration; magnesium concentration was measured at the beginning and at the end of the experiment. The chemical analyses were done with Dr Lange kit. (LCK 348 for PO\textsubscript{4}-P and LCK 326 for Mg)

RESULTS AND DISCUSSION

Degree of recirculation:
The overload of the process after 2 months shows that Bio-P is not stable without further control. It was caused by an increase of TP concentration in the centrifuge reject from 200 mg/l to 350 mg/l, increasing the recirculation to the head of the plant from 46%TP,in to more than 65%TP,in.
The maximal phosphorus recirculation that can be tolerated by the process has not been assessed in the present study but the objective was set at 200 mgTP/l in the digester centrate. It can be noticed that the concentration of 200 mgTP/l is quite high compared to published values but the Bio-P process gives very good cleaning results with this recirculation rate (average 2005).
A phosphorus mass balance in the process was drawn (Figure 1) considering 1 year average and based on 200 mgP/l in the centrifuge reject. This permits to assess the relative influence of each flow. It can be noticed that the recirculation of primary sludge is quite high but this should not influence the Bio-P process. This also allows predicting the flow of magnesium entering the digester and thus the theoretical potential for struvite formation. Considering 260 kgP/d of bio-sludge entering the digester and 13%TP contained as OP, about 230 kgP/d are released by PAOs. Assuming Poly-P
release as the only source of Mg with a ratio of 1:3, 70 kgMg/d is expected to enter the digester, which represents a potential of 26%TP fixation by struvite.

**Phosphorus fractionation:**
This experiment gave accurate results concerning the fractionation into OP and IP considering the standard error of 2% on 3 samples. The fractionation into AP and NAIP gave less exploitable results because of the high Sol-P concentration and maybe because of a partial recovery of struvite.

However, the results of this experiment show that 13%TP is organic and that about 20%TP is fixed as apatite. The fraction of struvite was calculated to about 20%TP which was validated by the stripping experiment. It has been assumed that around 12%TP (“other” in Figure 2) is either adsorbed in the sludge matrix or bound to aluminum or iron [1].

![Figure 2: P-fractions in the digested sludge.](image)

Finally a concentration of about 350 mgP/l can be expected in the digested sludge with Bio-P without chemical additions under steady state conditions (200 mgP/l in the reject). Thus 150 mgP/l should be removed in order to reach the objective and stabilize the process.

**CO₂ stripping batch experiment:**

By stripping CO₂ in the digested sludge the pH increased from 7.2 to 8.4 in 70 minutes implying the fixation of 26%Sol-P. The results are presented in Figure 3 and Table 1.

It can be first noticed that phosphorus fixation occurs mainly in the metastable zone of struvite and apatite which means that crystals grow on existing embryos ([6], results not shown).

![Figure 3: phosphate removal by CO₂ stripping.](image)

**Table 1: CO₂ stripping results.**

<table>
<thead>
<tr>
<th></th>
<th>Digested sludge</th>
<th>Reject from centrifuge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial PO₄-P (mg/l)</td>
<td>224</td>
<td>209</td>
</tr>
<tr>
<td>Final PO₄-P (mg/l)</td>
<td>165</td>
<td>195</td>
</tr>
<tr>
<td>Initial Mg (mg/l)</td>
<td>37</td>
<td>21.1</td>
</tr>
<tr>
<td>Final Mg (mg/l)</td>
<td>17.3</td>
<td>4</td>
</tr>
<tr>
<td>ΔPO₄-P (mg/l)</td>
<td>59 (26%)</td>
<td>19 (9%)</td>
</tr>
<tr>
<td>ΔMg (mg/l)</td>
<td>19.7 (47%)</td>
<td>17.1 (81%)</td>
</tr>
<tr>
<td>ΔMg / ΔPO₄-P (mol/mol)</td>
<td>0.43</td>
<td>1.15</td>
</tr>
</tbody>
</table>

As indicated by the ΔMg/ΔP ratio in Table 1, struvite formation is not the only mechanism responsible for phosphate fixation in the digested sludge (ratio 1:1 in struvite). As apatite has also been found in the fractionation experiment, it is likely to fix the rest of phosphorus. However, calcium was not assumed to have a major importance and thus its concentration had not been measured.

The final magnesium concentration shows that further struvite crystallization might occur at higher pH. Assuming a constant Mg:P ratio of 1:0.43, a total fixation of 50%Sol-P could be obtained, which would fulfill the objective. However further analysis is required for more precise conclusions.

The initial concentration of dissolved magnesium in the digested sludge represents only 23% of the incoming magnesium. This indicates that struvite crystallization is already responsible for the fixation of about 23%TP while apatite would count for about 28%TP (assuming a ratio of 1:0.57). This is in the same range as the
fractionation results and thus it confirms the presence of about 20%TP apatite. Full scale CO$_2$ stripping in the digested sludge could be easily done by simple aeration in the sludge tank (retention time of more than 2 days) but the high pH might induce bad smell because of the formation of ammonia. Thus, full scale tests have to be performed in order to validate the feasibility of this method.

The results obtained with the centrifuge reject show that struvite crystallizes with an Mg:P ratio of 1:1.15. Considering the low final Mg concentration, further crystallization might occur with magnesium addition. The phosphorus removal rate depends greatly on the concentration in the reject but considering 350 mgP/l, 70 kgMg/d would be needed for 90%Sol-P fixation, producing 100 kgP/d of struvite. This method has not been more deeply studied because the high costs induced by a crystallization reactor cannot yet compete with phosphate rock on the fertilizer market.

**CONCLUSIONS**

Bio-P without chemical addition at Öresundsverket does not seem stable without further control of the recirculation stream. An objective of 200 mgP/l in the centrifuge reject seems reasonable for Bio-P in steady state conditions.

The phosphorus mass balance and fractionation show that further fixation of about 150 mgP/l (15%TP, 43%Sol-P) is needed to reach the objectives.

Batch experiments show that phosphorus removal can be obtained by stripping CO$_2$ in the digested sludge. Full scale tests have to be conducted to validate this method but this could represent an interesting alternative to chemical precipitation.

**REFERENCES**