PHOSPHATE REMOVAL FROM AN ANAEROBIC DIGESTOR SUPERNATANT BY CHEMICAL PRECIPITATION

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State of the art:

- Problems with struvite formation date back to the 1960s when it was noticed at the Hyperion treatment plant, Los Angeles (Borgerding, 1972), in that case the pipeline size was reduced from twelve inches (30.5 cm) in diameter to six;

- Dewatering of the anaerobic digested sludge by centrifugation was found to be a critical stage for precipitation in many wastewater treatment plants in Germany (Heinzmann et al., 2005), downstream of the centrifugation of the sludge, precipitation was so significant that the outgoing pipes were fully blocked;

- The Murcia Este wastewater treatment plant is largest wastewater treatment plant in Murcia (Spain), the plant operators have continuously found pipe blockage and accumulation of solids on equipment surfaces during the anaerobic digestion and post-digestion processes (Barat et al., 2009);

- Benisch et al. identified annual costs related to struvite scales typically range between $2,000 and $10,000 per MGD of secondary dry weather capacity for the majority of treatment plants with anaerobic digesters (Benisch et al., 2000).
State of the art:

- The relationship between pH and $K_{sp}$ shows that struvite solubility decreases with pH increasing;

- The temperature influences the struvite solubility product, although this parameter has a lower impact on struvite precipitation than other parameters such as pH and supersaturation (Durrant et al., 1999);

- The excess of supersaturation can involve a relatively quickly struvite formation;

- The struvite deposit represents a good resource in order to obtain phosphorous, for examples, struvite recovered from wastewaters by Unitika Ltd., Japan, is already being sold to American fertilizer companies (Driver et al., 1999).
Thesis purposes:

- To optimize values for the parameters that condition the precipitation in order to improve this process efficiency;

- Preventative method identification is essential for sites where struvite precipitation may become or already is a serious problem;

- Production of a high amount of struvite then a large amount of fertilizers resource.
Nitrogen, phosphorous and potassium characteristics:

- Nitrogen, phosphorous and potassium are three of the substances more commonly used as nutrients in the world (their percentage inside packages of fertilizer is respectively: 19%, 12% and 5%);

- The nitrogen is the most diffused gas in the atmosphere (with a percentage of 79%), it’s also present in a lot of mineral deposits as nitrate;

- Potassium is an alkali metal; it is possible find the potassium inside potassium salt deposits;

- It is possible find phosphorus in the organic world as phosphate and also is commonly used to make fertilizers; when basic ph occurs, phosphorus precipitates as insoluble matter inside earthly and aquatic sediments.
Nitrogen, phosphorous and potassium characteristics:

- There is enough amount of nitrogen and potassium;
- Phosphorus reserves are concentrated in U.S., South Africa, China and Morocco;
- U.S. mines doesn’t supply enough phosphorus to satisfy the country’s production of fertilizer;
- China has high-quality reserves but it doesn’t export.
Information about phosphorous:

- Phosphorous occurs in natural water and in wastewaters almost solely as phosphates;
- Phosphates are classified as orthophosphates, condensed phosphates (pyrophosphate, metaphosphate and other polyphosphate) and organically bound phosphates;
- Organic phosphates are formed primarily by biological processes;
- They can be found inside sewage because the body wastes and food residues;
- Phosphates also occur in bottom sediments and in biological sludges, both as precipitated inorganic forms and incorporated into organic compounds (A.P.H.A. et al., seventeenth edition).
Phosphorous problems:

- As a nutrient, phosphorous can involve eutrophication problems;

- A strong amount of nutrients input inside the aquatic environments causes the algal blooms;

- The oxygen absence causes the anaerobic microorganisms growth that produces toxic and smelly substances.

- During anaerobic conditions, the PAOs release orthophosphates and produce;
Struvite characteristics:

- With certain conditions and the presence of dissolved calcium and magnesium, the orthophosphate inside the supernatant can precipitate as a mineral named struvite;

- Struvite (ammonium magnesium phosphate) is a phosphate mineral with formula: MgNH$_4$PO$_4$(H$_2$O)$_6$. It forms according to the reaction shown below;

$$\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} \rightarrow \text{MgNH}_4\text{PO}_4(\text{H}_2\text{O})_6$$

- Struvite crystallizes in the orthorhombic system and it is slowly soluble in neutral and alkaline conditions, but readily soluble in acid.
Struvite characteristics:

• Its precipitation occurs when the combined concentrations of Mg$^{2+}$, NH$_4^+$ and PO$_4^{3-}$ exceed the struvite solubility product ($K_{sp}$);

$$K_{sp} = [Mg^{2+}] * [NH_4^+] * [PO_4^{3-}]$$

• Struvite precipitation is not simply a problem of BNR treatment works (Parsons et al., 2004), but also for the EBPR processes.
Batch experiments (initial P concentration: 110 and 24 ppm):

- Samples were mixed with slow rotation and taken at 1, 2 and 3 hours;
- After each sampling, pH was been measured by pH meter;
- 0 g/l, 0.1 g/l, 0.3 g/l, 0.5 g/l, 0.8 g/l were used;
- The one without lime were done adjusting the pH with NaOH 3N, while other tests were done using both dolomite lime and pH adjusting after 3 hours with NaOH 3N and Na₂CO₃ 1M.
Continuous experiments (initial P concentration: 120 ppm):

- Continuous experiments were carried out by column with a flow from bottom to the top;

- The total flow rate inside column was 7 ml/min, in order to have a retention time of 120 min;

- A first series of experiments were carried out for 6 hours with an amount of 0.1 g/l, 0.35 g/l, 0.5 g/l of lime;

- A final column experiment was done for 36 hours in 10 days with an amount of 0.5 g/l of lime.
Phosphate analysis

- Phosphate concentration analysis were done with an absorption spectrophotometer;

- Samples volume of 1.5 was centrifuged by an IEC MicroMax centrifuge;

- The ascorbic acid method was followed for the analysis.
The analysis for Ca$^{2+}$ and Mg$^{2+}$ were conducted with the inductively coupled plasma (ICP);

From each sample to be analyzed were taken 1.5 ml of wastewater in order to centrifuge;

1 ppm yttrium internal standard solution was used.
Acid digestion:

- Phosphorous also may occur in combination with organic matter, this fraction is the “organic phosphorous” or “organically bound phosphorous”,

- The digestion method can be useful to determine total phosphorous, with a colorimetric method, because it allows to oxidize organic matter effectively to release phosphorous as orthophosphate;

- The method followed in this thesis work was the perchloric acid method;

- The solution was heated on a hot plate at a 150 °C temperature about.
Acid digestion analysis results:

For both plant influent and effluent the flow was 28 mgal/d, the anaerobic digester effluent flow was 165600 gal/d and the sludge flow was 64800 gal/d;

The solid content of sludge was 7% about and the specific weight evaluate was 1.032 kg/l;

The initial soluble phosphate concentration far the plant influent was 3 ppm about, while for the plant effluent was 1.5 ppm about, the initial concentration in the anaerobic digester effluent before acid digestion was 120 ppm about;

Plant effluent flow and sludge flow were subtracted to the plant influent flow for the mass balance; the value is not null but it is very close to zero (10-12 ppm).

<table>
<thead>
<tr>
<th>P</th>
<th>Plant Influent</th>
<th>An. Digester</th>
<th>Plant Effluent</th>
<th>Cake (1,032 kg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total P (ppm)</td>
<td>6,9</td>
<td>250,6</td>
<td>3,8</td>
<td>260,1</td>
</tr>
<tr>
<td>Total P (kg/day)</td>
<td>625,3</td>
<td>157,1</td>
<td>392,1</td>
<td>63,8</td>
</tr>
</tbody>
</table>
Phosphate analysis results (110 ppm):

- For the first two hours, phosphate concentration decreasing rate it’s higher than the last hour where the process seems that is reaching its steady state;

- With 0.8 g/l after the second hours the phosphate concentrations is approximately the same for both the cases;

- Higher the initial dolomite concentration is, higher and faster pH increases.
Phosphate analysis results (110 ppm):

**P concentration**
- P concentration with 0.1 g/l of lime, pH adjusted with NaOH 3N to 8.52, after 3 hr
- P concentration without lime, pH adjusted with NaOH 3N to 8.59
- P concentration with 0.3 g/l of lime, pH adjusted with NaOH 3N to 8.64 after 3 hr
- P concentration with 0.5 g/l of lime, pH adjusted with NaOH 3N to 9.21 after 3 hr

**pH**
- pH (0.5 g/l of lime, pH adjusted with NaOH 3N to 9.21 after 3 hr)
- pH (0.1 g/l of lime, pH adjusted with NaOH 3N to 8.52 after 3 hr)
- pH (0.3 g/l of lime, pH adjusted with NaOH 3N to 8.94 after 3 hr)
- pH (without lime, pH adjusted with NaOH 2N to 8.59)
Phosphate analysis results (24 ppm):
Phosphate analysis results (120 ppm):
Calcium and magnesium analysis results (110 ppm):
Calcium and magnesium analysis results (24 ppm):
Calcium and magnesium analysis results (120 ppm):
Conclusions:

- For both batch and continuous experiments it was possible to notice that the best removal was with a 0.5 g/l of dolomite lime;

- From the experiment with pH adjusting a little improvement about removal process can be noted (pH optimal range was between 8.5-9.0);

- The final result is similar to the final concentration obtained from the batch experiment with 0.5 g/l and an higher initial phosphate concentration;

- To improve the precipitation the increase of retention time could be used;

- From Ca$^{2+}$ and Mg$^{2+}$ analysis different results have been obtained: these showed that not for every experiment the phosphate precipitates as struvite.
References:


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