Biological struvite crystal formation in sludge dewatering liquors
Phosphorus: a pollutant or a resource?

Guideline

UWTD (91/271/EEC)
2 mg/L (10k-100k p.e.)
1 mg/L (>100k p.e.)

New targets
0.01-0.1 mg/L P

Rock Phosphate Monthly Price - US Dollars per Metric Ton

http://www.indexmundi.com/commodities
Phosphorus (P) is an essential element to all life forms that is currently under source stress as economically relevant P ore reserves are limited. The worst case scenario predictions point that rock P will be exhausted within 75 years (1). As a consequence, countries such as USA have prohibit export of phosphorus ore in 1997 and China is also going to stop exporting (2). *

Currently the main technologies available for phosphate recovery/recycling are:

- recycling of sludge to land (when meeting existing agreements – about 49% of all the sludge produced at YW)**
- crystallisation processes - mainly through struvite precipitation from wastewater, sludge and liquors streams using chemical/physical processes is a reality in north America and more recently in the UK (Severn Trent is producing struvite from sludge liquors). Nevertheless this process requires complex reactors, expensive chemical addition and pH adjustments.†
- recovering P from adsorption media such as HIAK (still under development)
- a recent screening study in Cranfield, demonstrated the viability of selected bacteria to produce bio-struvite crystals in wastewater – activated sludge wastewater and sludge centrifuge liquors. Two strains (Bacillus pumilus and Brevibacterium antiquum) were capable of growing and producing high density phosphate crystals in wastewater. Microscope analysis showed presence of crystals as early as 3 days and visible crystals were seen in cultures after 10 days reaching up to 250 µm. The final concentration of phosphate in sludge centrifuge liquors reached 1.5 mg L⁻¹, indicating a 95% P removal.
- The application of this technology - Biological struvite production – could be very useful to reduce phosphate levels on the dewatering liquors that usually end up at the head of the treatment works contributing significantly for the total P load in a treatment plant. Further the P crystals can potentially be recovered and re-used as a product with a market value.
- Nevertheless, biological struvite production needs to be further developed and investigated in order to become a viable technology.


*P is essential, non-substitutable and the least abundant of the major plant nutrients, at the current rate of extraction today’s mines will be exhausted by the end of the century and estimates of future reserves are 200 to 400 years. WTO has ruled against restrictions on trade in P.

** About 80% of UK sludge is recycled to land

† There are more than 15 struvite plants in Europe from Paques, NuReSys and Airprex plus an Ostara plant at Slough UK. These have been built as the best cost option to meet legal requirements and/or to mitigate scaling further down the system.
World P resources

- Morocco and Western Sahara, 21 gigatonnes
- Rest of the World, 10.1 gigatonnes
- South Africa, 2.5 gigatonnes
- United States, 3.4 gigatonnes
- China, 10 gigatonnes

- Stopped exporting in 1997
- Planned bans on exportation

Recovery of phosphorus from wastewater enough?

42,000 tons P/Year (England alone)

Municipal wastewater treatment plant

Enough for up to 20% fertiliser requirements

Agriculture
Notes

**Slide 5** The water industry has the potential to fulfil part of the P demand because a high percentage of all the phosphorus used ends up in the wastewater treatment plants - just in England is estimated that 42,000 tons/year of P end up in the sewers*. The UK has no phosphorus resources therefore, recycle recovery and re-use of the phosphorus that occurs in the wastewater and sludge is a very important challenge that needs to be addressed.

assuming = 1 person discharges 0.7 kg P/year (1); England population is 51.8M and 95% of the population is connected to the sewer. A further 20% contribution is expected from laundry products. Contribution from trade effluents and diffuse sources was not accounted for.

**Slide 7** Tankers of the type shown in slide 7 have not been used in UK for 40 years.
Currently about 80% of UK sludge is used beneficially on land.
Options for P recovery

- Primary sedimentation or trickling filter
- Secondary sedimentation
- Tertiary treatment

- Sludge liquors have high P (20-200 mg/L)
- Biogas
- <50% sludge is recycled to land
- 20-30% sludge is incinerated

Wet and chemical processes for P recovery (Sephos, PASH, Electro-thermal etc.)
P recovery from sludge liquors

Struvite chemical precipitation

- Well known process installed at full-scale with a market

+- Recovery of 90% of phosphorus (10% left in the wastewater)

- Needs high phosphorus streams >100 mg/L

- Crystallisation through chemical process with chemical addition


Pratt C, Parsons SA, Soares A, Martin BD: Biologically and Chemically Mediated Adsorption and Precipitation of Phosphorus from Wastewater. Trends in Biotechnology
Sludge liquors have high P – other ways to recover P?

- Sustainable (no chemicals)
  - High yield, good product quality
  - Usable for wastewater mixed matrix
  - High quality effluent

- Versatile (range of [P])
Bio-mineralisation and struvite production

Investigate the suitability of selected bacteria to produce struvite in wastewater and dewatering liquors

Silicate based minerals in diatom (algae)

Crystalline particles of magnetite (Fe3O4) in *Magnetospirillum magneticum* AMB-1
Bio-mineralization: Known mechanisms
Notes

Slide 10 Biomineralization

• Biomineralization is the process by which living organisms produce minerals, often to harden or stiffen existing tissues. Such tissues are called mineralized tissues. It is an extremely widespread phenomenon; all six taxonomic kingdoms contain members that are able to form minerals, and over 60 different minerals have been identified in organisms. Examples include silicates in algae and diatoms, carbonates in invertebrates, and calcium phosphates and carbonates in vertebrates. These minerals often form structural features such as sea shells and the bone in mammals and birds. Organisms have been producing mineralised skeletons for the past 550 million years. Other examples include copper, iron and gold deposits involving bacteria. Biologically-formed minerals often have special uses such as magnetic sensors in magnetotactic bacteria (Fe₃O₄), gravity sensing devices (CaCO₃, CaSO₄, BaSO₄) and iron storage and mobilization (Fe₂O₃•H₂O in the protein ferritin).

• In terms of taxonomic distribution, the most common biominerals are the phosphate and carbonate salts of calcium that are used in conjunction with organic polymers such as collagen and chitin to give structural support to bones and shells. The structures of these biocomposite materials are highly controlled from the nanometer to the macroscopic level, resulting in complex architectures that provide multifunctional properties. Because this range of control over mineral growth is desirable for materials engineering applications, there is significant interest in understanding and elucidating the mechanisms of biologically controlled biomineralization.

• http://www.tuat.ac.jp/~matunaga/biomineraleng.html

Slide 11 Specialized bacteria convert the ions in solution into crystal forms.

• Bacteria create micro-environments in which the crystals growth and development is promoted.
• Depending on the type of bacteria crystals form intra or extracellularly or both.
• The size and shape of crystal is specific to the chemical elements and bacterial species.

Slide 13 Several bacteria have been associated with the formation of struvite in synthetic culture media.
Microorganisms reported to form struvite

**Bacteria**
- *Bacillus pumilus*
- *Brevibacterium antiquum*
- *Staphylococcus aureus*
- *Streptomyces acidiscabies*
- *Chromohalobacter marismortui*
- *Myxococcus Coralloides*
- *Myxococcus xanthus*
- *Proteus mirabilis*
- *Idiomarina abyssalis*
- *Idiomarina baltica*
- *Idiomarina loihiensis*
- *Idiomarina sp*

**Archaea**
- *Halobacterium salinarum*
- *Halorubrum distributum*

**Eukarya**
- *Paramecium tetraurelia*
- *Trypanosoma cruzi*
Bio-mineralization bacteria selection: Cultivation in wastewater

Full-scale wastewater treatment plant (UK) PE 570,000.

- Screens
- Grit chamber
- Primary sed.
- Grit
- Secondary sed.
- Activated sludge
- Treated effluent
- Thick./dewatering
- Biogas
- Anaerobic digester
- Sludge
- Sludge liquors:
  - PO$_4$-P: 30 mg/L
  - NH$_4$-N: 629 mg/L
  - Mg: 39 mg/L
- ASP
  - PO$_4$-P: 2.3 mg/L
  - NH$_4$-N: 70 mg/L
  - Mg: 17.8 mg/L
### Bio-mineralization bacteria selection: Cultivation in wastewater

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>M. xanthus</th>
<th>B. pumilus</th>
<th>H. salinarium</th>
<th>B. antiquum</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Activated sludge wastewater</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Growth rate (1/h)</td>
<td>Negligible</td>
<td>0.001</td>
<td>Negligible</td>
<td>0.004</td>
</tr>
<tr>
<td>Crystal dry weight (mg/L)</td>
<td></td>
<td>137</td>
<td></td>
<td>113</td>
</tr>
<tr>
<td><strong>Sludge dewatering centrifuge liquors</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Growth rate (1/h)</td>
<td>Negligible</td>
<td>0.001</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Crystal dry weight (mg/L)</td>
<td>213</td>
<td></td>
<td>226</td>
<td></td>
</tr>
</tbody>
</table>

**Negative control:** Wastewater not inoculated – no crystal production

**Typical $\mu_{max}$:**
- Denitrifiers = 0.1 1/h
- Methanogens = 0.02 - 0.002 1/h
- Anammox = 0.001 - 0.004 1/h
Crystals formed by *B. antiquum* in sludge dewatering centrifuge liquors were approximately 250 µm
Bio-struvite characterisation

SEM images in sludge dewatering centrifuge liquors

Scanning electron microscope with energy dispersive x-ray spectroscopy (SEM-EDX)
## Effluent quality

<table>
<thead>
<tr>
<th>Wastewater samples</th>
<th>PO4-P (mg/L)</th>
<th>NH4-N (mg/L)</th>
<th>Mg (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge dewatering centrifuge liquors (inlet)</td>
<td>30.5</td>
<td>629</td>
<td>38.9</td>
</tr>
<tr>
<td>Sludge dewatering centrifuge liquors (outlet)</td>
<td>1.5</td>
<td>?</td>
<td>21.4</td>
</tr>
<tr>
<td>Removal rates</td>
<td>95%</td>
<td>?</td>
<td>45%</td>
</tr>
</tbody>
</table>
Bio-struvite formation in sludge dewatering liquors from a Bio-P site

- Struvite (mg) vs Time (days)
- Gas-closed and pH-corrected conditions

- Bacillus pumilus
- Halobacterium salinarum
- Brevibacterium antiquum
- Control (saline)
Bio-struvite formation in sludge dewatering liquors - influence of pH
Notes

Slide 21 The charts show bio-struvite formation in the inoculated tests. As opposed to the control non-inoculated tests.

- However, when changing the source of sludge liquors we faced a challenge with controlling the pH.
- It was observed that the degassing in sludge dewatering liquors with high dissolved CO$_2$ concentrations was inducing pH changes from 7.8 up to 9.7.
- pH change was limited by controlling the CO$_2$ degassing: in the first case by pH correction with acid (pH corrected); in the second case by gas-closing the reaction vessels to prevent the evolution of CO$_2$. – in both tests the pH was effectively controlled to values close to 8.2.
- Bio-struvite production reached 196, 198, and 135 mg/L for *B. pumilus*, *H. salinarum*, and *B. antiquum*, respectively.

Slide 22 After observing the potential impact of pH, we looked for more details of this impact on the formation of bio-struvite.

- What we observed was that the bacteria were having a positive impact on bio-struvite production at pH values not typically associated with struvite precipitation as 7.3, 7.8 and 9.1.

Slide 24 http://biomassmagazine.com/articles/1838/from-problem-to-profit
### Bio-struvite vs. chemical struvite

(10,000 m$^3$/day wastewater treatment plant producing 500 m$^3$/day of sludge liquors)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Biological P crystals</th>
<th>Chemical struvite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Production</strong> Kg/day</td>
<td>120</td>
<td>100</td>
</tr>
<tr>
<td>Capital costs</td>
<td>£</td>
<td></td>
</tr>
<tr>
<td>Fermentation reactor (10 days HRT)</td>
<td>630,000</td>
<td>Precipitation reactor</td>
</tr>
<tr>
<td>Blowers and diffusers</td>
<td>Not known</td>
<td>Blowers and diffusers</td>
</tr>
<tr>
<td>Filtration unit</td>
<td>100,000</td>
<td>Desludge pump</td>
</tr>
<tr>
<td><strong>Total capital costs</strong> £</td>
<td>total 730,000</td>
<td>total 1,325,000</td>
</tr>
<tr>
<td>Operating costs £/year</td>
<td>Electricity 10,000</td>
<td>Electricity 3,500</td>
</tr>
<tr>
<td>Chemical costs</td>
<td>13,000</td>
<td></td>
</tr>
<tr>
<td><strong>Total operating costs</strong> £/year</td>
<td>total 10,000</td>
<td></td>
</tr>
<tr>
<td>Income</td>
<td>£40,734</td>
<td>£33,945</td>
</tr>
<tr>
<td>Total Opex = £10,000</td>
<td>(23 years payback)</td>
<td>£16,500</td>
</tr>
<tr>
<td>(&gt;40 years payback)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Costs used in chemical precipitation are from 2001 (Jaffer et al.); struvite price $1500/ton*  
Conclusions

• Bacteria can produce struvite crystals in wastewater in simple way (no optimisation completed yet!)

• Presence of crystals as early as 2 days and visible crystals were seen in cultures after 10 days reaching up to 250 µm.

• Crystals can be separated by filtration/centrifugation

• The final concentration of phosphate in sludge centrifuge liquors can be as low as 1.5 mg/L, indicating a 95% P removal
Conclusions

- Bio-struvite production reached 196, 198, and 135 mg/L for *B. pumilus*, *H. salinarum*, and *B. antiquum*, respectively.

- High concentration of dissolved CO\(_2\) results in pH changes due to degassing, from 7.8 to 9.7.

- Bacteria can produce bio-struvite in sludge dewatering liquors with a pH up to 8.4 and low dissolved CO\(_2\) concentrations.

- For sludge dewatering liquors with high dissolved CO\(_2\) and pH >8.5 chemical struvite formation occurs naturally.

- The process can potentially be economically attractive.

- ..............But still a lot of work ahead!!
A new route to recover phosphorus from wastewater: Biological struvite production

Thank you for the attention spared!

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www.cranfield.ac.uk/SAS/water/