Microbial fuel cell enables phosphate recovery from digested sewage sludge as fertilizer

Innovation Day
When Biotech becomes Cleantech
November 10, 2011
Presented by Fabian Fischer
HES-SO Valais Life Technologies Institute
Phosphor is an essential element

Corn with and without phosphor fertilizer in Brazil’s Cerrado region

K. Syers, et al., Phosphorous And Food Production, UNEP Year Book 2011.
Phosphate loss
The biggest problem you never heard of

K. Syers, et al., Phosphorous And Food Production, UNEP Year Book 2011.
Life-time of phosphor reserves

A reduced availability of phosphate will reduce the world's population

Phosphate has to be recycled!

What are the accessible renewable sources?

- Urban waste waters
- Sewage sludge and garbage incineration ash
- Bone and meat waste
- Biowaste from biorefineries
- Sea and river sediments
Sewage sludge is rich in phosphate

Because: \( \text{FeCl}_3 + \text{PO}_4^{3-} \rightarrow \text{FePO}_4 + 3\text{Cl}^- \)

ICP-OES Analysis indicates also As, Cd, Cr, Cu, Pb and others in trace elements.
Digested sewage sludge contains tons of phosphate

Toxic metals prevent direct use

8-9% Phosphate
What are the technical options?

- Acidic treatment of sewage sludge ash
  90% recovery but **contaminated**
- Basic treatment of sewage sludge ash
  30% recovery, **not contaminated**
- Plasma separation appears not economic but **pure**
  phosphate is recovered

Up to date no method is economically successful

Microbial fuel cells, a source of: power, protons and electrons

Power + H⁺ + e⁻

Biological systems stock hydrogen!
The fuel cell and the microbial version

Anode:

\[ x \text{ Bio-H}_n \rightarrow 2H^+ + 2e^- \]

Microbial fuel cell

Cathode:

\[ 2H^+ + 2e^- + O \rightarrow H_2O \]

Chemical fuel cell

Nafion membrane

**Diagram**

- Anode: \( x \text{ Bio-H}_n \rightarrow 2H^+ + 2e^- \)
- Cathode: \( 2H^+ + 2e^- + O \rightarrow H_2O \)
- Nafion membrane

**Equations**

- Anode: \( x \text{ Bio-H}_n \rightarrow 2H^+ + 2e^- \)
- Cathode: \( 2H^+ + 2e^- + O \rightarrow H_2O \)
Coulombic efficiency of a microbial fuel cell

When microbes starve and only glucose is provided a cumbic efficiency of 89% was achieved.

\[
\begin{align*}
C_6H_{12}O_6 &+ 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \\
6O_2 + 24H^+ + 24e^- &\rightarrow 12H_2O
\end{align*}
\]

\[
C_6H_{12}O_6 + 6O_2 + 24H^+ + 24e^- \rightarrow 6CO_2 + 6H_2O
\]

Electron harvest and products of microbial fuel cells

Anode harvests electrons: 
- bio-film
- collision
- pilli
- mediator

Cathode produces: 
- electricity
- hydrogen

Microbial fuel cell stacks for higher power
Power characteristics of microbial fuel cells

Microbial fuel cell enables phosphor bio-refining

F. Fischer et al., Bioresource Technology, 2011, 102, 5824–5830.
Cleantech through the integration of microbial fuel cell power and phosphate recycling

Remobilisation set-up

- Cathode
- Remobilisation
- Stirring motor
- Anode in bioreactor
Sewage sludge pretreatment

Non treated digested sewage sludge provides insufficient surface area for a productive phosphate extraction.
Sewage sludge needs to be grinded

- Grinded sewage sludge yields higher than untreated
- Milling with a 120 μm cut-off size
- Smaller particle formation is impractical due to overheating
Standing and working potential with an *E. coli* cultivation
Current flow into the sewage sludge cathode
Power current plot and polarization curve

\( R_{\text{int}} = 2.6 \ \text{k}\Omega \)
### Remobilisation results

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sludge (FePO$_4$) [g (mg)]</th>
<th>Time [d]</th>
<th>Particles [μm]</th>
<th>Yield H$_3$PO$_4$ [g/L]</th>
<th>Yield H$_3$PO$_4$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.7 (240)</td>
<td>7</td>
<td>~10$^6$</td>
<td>0.003</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>1.7 (240)</td>
<td>7</td>
<td>50</td>
<td>0.104</td>
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<tr>
<td>3</td>
<td>3.3 (470)</td>
<td>7</td>
<td>50</td>
<td>0.308</td>
<td>4.4</td>
</tr>
<tr>
<td>4</td>
<td>1.7 (240)</td>
<td>6</td>
<td>50</td>
<td>0.337</td>
<td>9.2</td>
</tr>
<tr>
<td>5</td>
<td>1.9 (270)</td>
<td>19</td>
<td>50</td>
<td><strong>0.594</strong></td>
<td>14.6</td>
</tr>
<tr>
<td>6</td>
<td>0.4 (60)</td>
<td>9</td>
<td>50</td>
<td>0.213</td>
<td>22.5</td>
</tr>
<tr>
<td>7</td>
<td>0.2 (30)</td>
<td>14</td>
<td>50</td>
<td>0.201</td>
<td>43.4</td>
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<tr>
<td>8</td>
<td>0.3 (40)</td>
<td>21</td>
<td>50</td>
<td>0.404</td>
<td>68.2</td>
</tr>
<tr>
<td>9</td>
<td>0.2 (30)</td>
<td>21</td>
<td>50</td>
<td>0.372</td>
<td><strong>82.3</strong></td>
</tr>
</tbody>
</table>
How does the reduction work?

$$3 \text{Fe}^{(\text{III})} \text{PO}_4 + 3\text{e}^-/3\text{H}^+ \rightarrow \text{Fe}_3^{(\text{II})}(\text{PO}_4)_2 + \text{H}_3\text{PO}_4$$

A hypothetically formed intermediate is Vivianite.

$$\text{Fe}_3^{(\text{II})}(\text{PO}_4)_2 + n\text{e}^- + n\text{H}^+ \rightarrow \text{H}_2\text{PO}_4^- + \text{Fe}^{n+}$$

The reduction reaction is not proven because FePO$_4$ is integrated in amorphous sewage sludge.
**How does the reduction work?**

Model system with pure FePO$_4$ shows that iron accumulates in remaining sludge particles.

<table>
<thead>
<tr>
<th>Fe/P ratio</th>
<th>Reference</th>
<th>Grain</th>
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<tbody>
<tr>
<td></td>
<td>FePO$_4$</td>
<td></td>
</tr>
<tr>
<td>% weight</td>
<td>2.03</td>
<td>2.48</td>
</tr>
<tr>
<td>% atom</td>
<td>1.13</td>
<td>1.37</td>
</tr>
</tbody>
</table>
Basic recovery principle with a microbial fuel cell

\[
\text{Fe}^{(III)}\text{PO}_4 + 3\text{e}^-/\sim3\text{H}^+ \rightarrow \text{H}_2\text{PO}_4^- 
\]

Sludge

Microbial fuel cell

Pure ortho-phosphate is recovered from sewage sludge as shown by phosphorous $^{31}$P-NMR.
Tox free fertilizer, struvite

H₂PO₄⁻ + Mg²⁺ + NH₄⁺ → NH₄MgPO₄

Elemental analysis of struvite (RDX)

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample</th>
<th>Reference</th>
<th>Match [%] % weight</th>
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<tbody>
<tr>
<td>N</td>
<td>6.05</td>
<td>6.16</td>
<td>98</td>
</tr>
<tr>
<td>O</td>
<td>60.28</td>
<td>63.09</td>
<td>96</td>
</tr>
<tr>
<td>Mg</td>
<td>12.10</td>
<td>14.07</td>
<td>86</td>
</tr>
<tr>
<td>P</td>
<td>14.82</td>
<td>16.068</td>
<td>92</td>
</tr>
<tr>
<td>Na</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>1.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Struvite

Non toxic impurities
Green recovery fits in

Microbial fuel cell

Mining

Raw phosphate

- Superphosphate 18-20% $\text{P}_2\text{O}_5$
- Triple superphosphate 40-48% $\text{P}_2\text{O}_5$
- Ammonium phosphate 46-48 $\text{P}_2\text{O}_5$
- Obtained struvite ~ 33% $\text{P}_2\text{O}_5$
Conclusions

- A cleantech concept:
  The integration of power generation by microbial fuel cell technology and phosphate recovery is possible
- Produced phosphate fertilizer is non toxic
- Phosphate demands and prices will rise
- Decentralized sustainable phosphate production
Thank you for your attention

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