PROSPECTS FOR PHOSPHORUS RECOVERY FROM MAINSTREAM WASTEWATER: EXPERIMENTAL AND MODELLING STUDIES

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“Life can multiply until all the phosphorus is gone, and then there is an inexorable halt which nothing can prevent”
phosphorus recovery

- From wastewater treatment plants (WWTP) to water resource recovery facilities (WRRF): Energy (biogas, biomethane, hydrogen) and materials (N-P-based fertilisers, bioplastics, cellulose)

- Phosphorus (P) arises as a perfect candidate since:
  - P is essential for our society in the production of fertilizers
  - the main source of P is a non-renewable source which is envisaged to be depleted in the next 50-100 years.
  - 3 million tons of P are yearly removed via wastewater treatment in the planet (15-20 % of the global P demand could be covered)
wastewater treatment plants (WWTP)
**conventional P recovery**

- **Chemical precipitation** with Fe or Al in the tertiary step.

- **Struvite** \( \text{NH}_4\text{MgPO}_4\cdot6\text{H}_2\text{O} \) is a slow-release rate fertiliser is a good option for agricultural uses [vivianite, \( \text{Fe}_3(\text{PO}_4)\cdot8\text{H}_2\text{O} \)]

- **High concentrations of P, Mg}^{2+} and \text{NH}_4^+ \text{ or } \text{K}^+ \text{ and are needed so that struvite crystallisation becomes technologically viable (e.g. struvite precipitation in the tertiary step is not viable)**

- **BEST OPTION**: option seems to be the **digestate** (high ammonia and P concentrations). Drawbacks: complex operating conditions, unsatisfactory recovery efficacy, higher costs than obtaining fertilisers from mined P.

- Increase P content in sludge with **Enhanced Biological Phosphorus Removal (EBPR)**
Integrating EBPR

- A WWTP with EBPR is a double-edged sword: the sludge entering anaerobic digestion contains up to 20 times more P as Poly-P than a conventional sludge.
  - More P is released in the digestate and, thus, struvite recovery is facilitated.
  - undesired struvite precipitation that clogs pumps and pipes is a major issue when bio-P sludge is subjected to anaerobic digestion and P-recovery is not implemented.
- Lizarralde et al. (2019): struvite recovery has many benefits for the plant not only for its commercial value
  - reduction of pipe blockage,
  - sludge production
  - ferric chloride dosage
  - operation and maintenance costs of the plant.
mainstream P
wastewater treatment plants (WWTP)

INFLUENT → PRIMARY CLARIFIER (PRIM) → ACTIVATED SLUDGE (AS) → SECONDARY CLARIFIER (SEC2) → EFFLUENT

Anaerobic conditions

VFA → ATP → GLY → Acetil-CoA → Poly-P → PO₄³⁻

Poly-P: Polyphosphate
Gly: Glycogen

VFA: Volatile Fatty Acid
PHA: Polyhydroxyalkanoates

Guisasola et al. 2019 - P-recovery from mainstream
1) The effluent of the anaerobic phase contains high levels of dissolved phosphate and ammonium that could be recovered as struvite.

2) Undesired precipitation events in the anaerobic sludge digestion are minimized.

3) Higher loads of P could be treated within the same organic influent, i.e. the system would successfully treat influents with a lower COD/P ratio.

4) Anaerobic extraction opens the door to anaerobic purging:
   i) anaerobic sludge contains higher PHA levels (potential bioplastics)
   ii) sludge with PHA levels increase methane production (anaerobic digestion)
Increased BMP with PHA content

This work
BMP = 15.276·PHA + 240.04
\( r^2 = 0.8715 \)

Wang et al. (2016)
BMP = 13.646·PHA + 174.84
\( r^2 = 0.9840 \)

(Unpublished results)
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4) Anaerobic extraction opens the door to anaerobic purging:
   i) anaerobic sludge contains higher PHA levels (potential bioplastics)
   ii) sludge with PHA levels increase methane production (anaerobic digestion)
   iii) lower oxygen requirements: removal of biomass with high PHA and NH$_4^+$

5) Lower sludge production: part of the COD would be consumed by PAO rather than by heterotrophic aerobic processes and part of the ammonium would be recovered instead of being used for nitrifiers for growth.
mainstream P

experimental

Guisasola et al. 2019 – P-recovery from mainstream
There are several experimental studies aiming at recovering P from the anaerobic phase using the PAO ability of releasing P under anaerobic conditions.

1. The BCFS® process (Biological-chemical phosphorus and nitrogen removal) (Van Loosdrecht et al. 1998) is a modification of the UCT design where part of the anaerobic supernatant is sent to the sludge thickener where iron chloride is dosed. Thus, EBPR is combined with chemical precipitation of P.

2. Hao and Van Loosdrecht (2006) developed a model to simulate the effect of anaerobic stripping and showed that there was an optimal stripping flow rate. Their simulations indicated that influent COD/P ratio could be lowered from 20 to 10 with 36% of P-recovery.

3. Barat and Van Loosdrecht (2006) simulated different control strategies in the plant and stated that the maximum potential recovery under this operation could be increased up to 60% of the influent P.
4. Kodera et al. (2013) proposed a trickling filter enriched in PAO, which was exposed to alternating anaerobic-aerobic conditions. A stream with high VFA concentration (up to 2000 mgCOD/L) to enhance P-release during the anaerobic batch stripping phase. A high enriched P stream (125 mg P·L$^{-1}$) was obtained that could be used for P recovery (a value of almost 60% was also obtained).

5. Zou and Wang (2016) proposed another configuration combining EBPR and an induced P crystallization for recovery. A P-recovery of up to 59% was achieved with a lateral flow ratio of 0.3.

6. Shi et al (2015) proposed two different alternatives for the conventional A$^2$O process, where crystallization was induced from a side stream obtained at the end of the anaerobic stage. The percentage of chemical P removal to total P removal was around 15-17 % during all the process.
7. Valverde-Pérez et al. (2015) proposed a novel configuration for nutrient recovery called enhanced biological P removal and recovery (EBP2R). P was obtained as an enriched orthophosphate stream from the anaerobic effluent. They obtained by simulation a maximum P-recovery up to 70% of the influent P by diverting 30% of the influent flow as a P-stream at an SRT of 5 days.

8. Lv et al. (2014) operated a 10 L sequencing batch reactor (SBR) under anaerobic/aerobic conditions, which performed successful EBPR to study the competition between PAO and GAO when part of the P was precipitated from the anaerobic phase. They subjected the SBR to side-stream stripping treatment once every 3 cycles. At the end of the anaerobic stage, after a settling period, 5 L enriched P supernatant was separated for chemical precipitation. They observed that, in the long-term, the concentration of intracellular poly-P decreased and the EBPR activity was deteriorated and a transition between PAO and GAO.
(Guisasola et al. 2019)

<table>
<thead>
<tr>
<th>Period</th>
<th>Extracted Volume (L/cycle)</th>
<th>COD (mg/L)</th>
<th>P (mg P/L)</th>
<th>COD/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>300</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>II</td>
<td>1</td>
<td>300</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>III</td>
<td>1.5</td>
<td>300</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>IV</td>
<td>1</td>
<td>300</td>
<td>40</td>
<td>7.5</td>
</tr>
</tbody>
</table>

10 L reactors
Cycle 360 min
90 anaerobic
91 settling
5 anaerobic extraction
210 aerobic
25 settling
5 efluent
**Guisasola et al. 2019 – P-recovery from mainstream experimental studies**

(Guisasola et al. 2019)

![Graph showing P influent (dashed line), P content in the anaerobic liquid (▲), and P effluent (●)]

<table>
<thead>
<tr>
<th>Period</th>
<th>Extracted volume (L)</th>
<th>Influent P (mg P/cycle)</th>
<th>RemE (%)</th>
<th>RecE (%)</th>
<th>BioE (%)</th>
<th>Effluent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>100</td>
<td>98% ± 1</td>
<td>53 ± 8</td>
<td>45 ± 10</td>
<td>2 ± 1</td>
</tr>
<tr>
<td>II</td>
<td>1</td>
<td>150</td>
<td>67% ± 10</td>
<td>66 ± 14</td>
<td>0 ± 23</td>
<td>33 ± 10</td>
</tr>
<tr>
<td>III</td>
<td>1.5</td>
<td>150</td>
<td>82% ± 14</td>
<td>69 ± 16</td>
<td>13 ± 25</td>
<td>18 ± 14</td>
</tr>
<tr>
<td>IV</td>
<td>1</td>
<td>200</td>
<td>77% ± 6</td>
<td>33 ± 4</td>
<td>44 ± 9</td>
<td>23 ± 6</td>
</tr>
</tbody>
</table>

RemE: removal efficiency
RecE: recovery efficiency
BioE: biological removal efficiency
(references in the full paper)

<table>
<thead>
<tr>
<th></th>
<th>Influent COD/P (gCOD gP⁻¹)</th>
<th>Influent P (gP m⁻³)</th>
<th>P recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guisasola et al. (2019)</td>
<td>15</td>
<td>20</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>30</td>
<td>66</td>
</tr>
<tr>
<td>Acevedo et al. (2015)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xia et al. (2010)</td>
<td>44</td>
<td>36</td>
<td>79.0</td>
</tr>
<tr>
<td>Zou et al. (2014)</td>
<td>25</td>
<td>10</td>
<td>70.2</td>
</tr>
<tr>
<td>Barat et al. (2016)</td>
<td>54</td>
<td>3.7</td>
<td>~60</td>
</tr>
<tr>
<td>Kodera et al. (2013)</td>
<td>40</td>
<td>5</td>
<td>~60</td>
</tr>
</tbody>
</table>

Is there a maximum amount of P that we can recover?
mainstream P
experimental
modelling

Guisasola et al. 2019 - P-recovery from mainstream
1. A single SBR reactor operated with anaerobic extraction of the supernatant (COD, N and P removal).

2. A two-sludge system aiming at simultaneous COD, N and P removal where autotrophic and heterotrophic populations are physically separated. The system requires a third vessel acting as an interchange vessel to allow liquid exchange between the two SBRs.
   - Heterotrophic SBR (anaerobic/settling/extraction/anoxic/aerobic/settling)
   - Autotrophic SBR (aerobic/settling) with (partial) nitrification

Experimental results with a similar configuration in Marcelino et al. [38] and, currently, this system has been scaled-up in the frame of the SMART-plant H2020 project (www.smart-plant.eu).
modelling studies

Guisasola et al. 2019 – P-recovery from mainstream
modelling studies: effect of the extracted Volume

Anaerobic P (mg/L) and P-recovery (%)

% Volume extracted for P-recovery

Anaer P
P recovery
XPAO
X_N_SBR1
X_H_SBR2

SINGLE-SBR
TWO-SBR

XPAO and XH (mg/L)

% Volume extracted for P-recovery

0 5 10 15 20
0 2000 4000 6000 8000 10000

0 500 1000 1500 2000 2500

Guisasola et al. 2019 – P-recovery from mainstream
Phosphorus recovery from mainstream is an alternative to face potential P shortages and to move one step beyond when converting WWTP in WRRF. Almost 60% of the influent P could be recovered if part of the supernatant was extracted.

An extraction volume of 5-10% of the total SBR volume seems an adequate option to balance P-recovery and PAO activity.
"We may be able to substitute nuclear power for coal, and plastics for wood, and yeast for meat, and friendliness for isolation—but for **phosphorus** there is neither substitute nor replacement"
The Alchymist, in search of the philosopher’s stone discovers Phosphorus...

Joseph Wright (1771) about the life of Hening Brandt
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Recovering nutrients from wastewater is not a revolutionary idea. The Romans already taxed urine since it could be used as bleaching/tannery agent or fertiliser.