Valorisation of Phosphorus Extracted from Farm Yard Slurry and Municipal Solid Waste Digestates as a Fertilizer

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Phosphorus Issue

Phosphorus is essential and irreplaceable element for all forms of lives and does not occur by itself in nature.

Phosphate Rock

Source: https://geobancodedados.wordpress.com/2014/05/29/fosfato/

The reserves will reach their peak by 2030 and will be depleted in the next 50 - 100 years.
How can we Recover Phosphorus from Wastes and close the cycle for this nutrient?

Which wastes?
Recovery of phosphorus has been studied:

<table>
<thead>
<tr>
<th>Waste Stream</th>
<th>Method of P recovery</th>
<th>Recovered Product</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Municipal Sewage sludge ash</td>
<td>Acid Extraction followed by precipitation</td>
<td>Struvite</td>
<td>Xu et al (2012)</td>
</tr>
<tr>
<td>Poultry Manure</td>
<td>Quick Wash Method</td>
<td>P solid</td>
<td>Szogi et al (2009)</td>
</tr>
</tbody>
</table>

European Report indicate that municipal solid wastes and their incineration residues are an underestimated source of phosphorus.
In this work, the purpose was recovery of phosphorus from two different wastes:

- Farm Yard Slurries and;
- Digestates of municipal solid wastes.

The farm yard slurry was collected at a local farm.

The digestates of anaerobic process of municipal solid wastes were collected from a mechanical and biological treatment (MBT).
Methods

Wastes

1. HNO₃ extraction
2. HNO₃ extraction
3. Distilled Water
4. NaOH extraction

Precipitation of phosphorus
## Results

### 1. Wastes Characterization

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Farm yard slurry</th>
<th>MSW digestates</th>
<th>Portuguese Limiting Values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical and chemical characteristics</strong></td>
<td></td>
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</tr>
<tr>
<td>pH (H₂O)</td>
<td>6.6</td>
<td>7.8</td>
<td>-</td>
</tr>
<tr>
<td>Conductivity (mS cm⁻¹)</td>
<td>8.60 ± 0.18</td>
<td>5.22 ± 0.04</td>
<td>-</td>
</tr>
<tr>
<td>Water Content (%)</td>
<td>85.11 ± 0.08</td>
<td>63.40 ± 0.51</td>
<td></td>
</tr>
<tr>
<td>Ash Content (%)</td>
<td>4.49 ± 0.07</td>
<td>18.55 ± 0.88</td>
<td>-</td>
</tr>
<tr>
<td>Total P (mg g⁻¹)</td>
<td>4.04 ± 0.08</td>
<td>8.11 ± 0.25</td>
<td>-</td>
</tr>
<tr>
<td>Ca (mg g⁻¹)</td>
<td>142.82 ± 3.85</td>
<td>103.68 ± 3.64</td>
<td>-</td>
</tr>
<tr>
<td>Mg (mg g⁻¹)</td>
<td>4.04 ± 0.13</td>
<td>12.59 ± 0.39</td>
<td>-</td>
</tr>
<tr>
<td>K (mg g⁻¹)</td>
<td>13.70 ± 3.28</td>
<td>9.38 ± 0.19</td>
<td>-</td>
</tr>
<tr>
<td><strong>Macro Elements</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu (mg kg⁻¹)</td>
<td>42.41 ± 0.95</td>
<td>156.04 ± 3.77</td>
<td>1000</td>
</tr>
<tr>
<td>Zn (mg kg⁻¹)</td>
<td>177.71 ± 5.51</td>
<td>452.44 ± 15.59</td>
<td>2500</td>
</tr>
<tr>
<td>Pb (mg kg⁻¹)</td>
<td>16.69 ± 1.89</td>
<td>195.86 ± 8.55</td>
<td>750</td>
</tr>
<tr>
<td>Cd (mg kg⁻¹)</td>
<td>1.64 ± 0.07</td>
<td>2.17 ± 0.33</td>
<td>20</td>
</tr>
<tr>
<td><strong>Heavy Metals</strong></td>
<td></td>
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</tbody>
</table>
Key points for wastes characterization

- Both wastes had lower phosphorus content:
  - 0.8% for digestates of municipal solid wastes and;
  - 0.4% for farm yard slurries

- Calcium concentration in wastes was high;

- Both wastes do not exceed the heavy metals limiting values for sludge application in agricultural soils reported in the Portuguese legislation
Results

2. Extraction of phosphorus

- Highest extraction in farm yard slurry than digestates of MSW;
- Acid extractions was more effective than base;
- Phosphorus solubilisation was almost immediate (2.5 hours).
Results

3. Heavy Metals Extraction

- Cd extraction was highest compared with other heavy metals
- Around pH 7 to 8 the solubility of the heavy metals decreased considerably
## Results

### 4. Recovery of phosphorus

<table>
<thead>
<tr>
<th></th>
<th>Farm Yard Slurry</th>
<th>Digestates of MSW</th>
</tr>
</thead>
<tbody>
<tr>
<td>P removal efficiency</td>
<td>94.0 ± 0.3%</td>
<td>95.8 ± 0.8%</td>
</tr>
</tbody>
</table>

Harvested Precipitates in P precipitation experiments for Farm Yard Slurry (a) and digestates of MSW (b).
Results

X-ray diffractograms of precipitates from farm yard slurry (a), MSW digestates (b) and the standard struvite (c).

SEM-EDS pictures for Farm Yard Slurry (a) and digestates of MSW (b).

Amorphous Calcium Phosphate

Fertilizer or Raw Material for fertilizer industry
Conclusions

i) Extraction of phosphorus with acid (HNO$_3$) was more effective than base (NaOH)

ii) The phosphorus removal in precipitation experiments was very high

iii) The harvested precipitates was amorphous calcium phosphate that can used as a fertilizer or raw material for the fertilizer industry
Summary

- Phosphorus Issue
- Characterization of Farm Yard Slurries and Digestates of MSW
- Phosphorus Extraction from Farm Yard Slurries and Digestates of MSW at different pH values
- Heavy Metals Extraction from both wastes
- Recovery of phosphorus as a precipitate
Thank You!