Use of side-stream based MgSO$_4$ as chemical coagulant in the simultaneous removal of nitrogen and phosphorus from wastewaters

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Contents

1. Background
2. Materials and methods
3. Results
4. Summary
Background
Background

Phosphorus (P) and nitrogen (N) are the main nutrients in wastewaters and agricultural sludges

- Runoffs to waterways causes eutrophication
- Nitrogen typically as ammonium (NH$_4^+$) which evaporates easily as ammonia (NH$_3$) gas

Large commercial potential in the recycled fertilizer market

- Estimated market size in Finland alone 0.5 billion € annually [1]
- Recycled fertilizers will be included in the revised fertilizer legislation of the European Union [2]

Background

- Ammonium and phosphate could be precipitated as a struvite (NH$_4$MgPO$_4$·6H$_2$O)
  - Molar ratios Mg:P:N 1:1:1
  - Slow-release fertilizer
  - Typical precipitation reagents are commercial Mg-salts (MgCl$_2$, MgSO$_4$, MgO and Mg(OH)$_2$)
  - Cheaper precipitation reagents should be tested

- In this research, MgSO$_4$ solution was prepared from dolomite or fly ash (waste streams) for the struvite precipitation

- Dolomite is a carbonite mineral composed of calcium magnesium carbonate (CaMg(CO$_3$)$_2$)
  - Used e.g. as a soil improver

- Fly ash is fine-grained, inorganic residue that is left behind after combustion at a thermal power plant
  - Contains mostly Ca, Mg, Al, and Si oxides in varying proportions (depending on the fuel used)
  - Can be used as a fertilizer
Materials and methods
Materials and methods

- **Solutions:**
  - **MgSO\(_4\) solution:** 50 g of dolomite or fly ash in 250 mL of 2M sulfuric acid (90 min; constant stirring 500 rpm). Precipitate settled (30 min) and filtered (2-5 µm filter paper). MgSO\(_4\) solution collected and stored in glass bottles.
  - Ca and Mg oxides/carbonates react with H\(_2\)SO\(_4\) to form insoluble CaSO\(_4\)·2H\(_2\)O and soluble MgSO\(_4\).
  - **(NH\(_4\))\(_2\)HPO\(_4\) solution:** NH\(_4\)Cl and KH\(_2\)PO\(_4\) salts (100-200 mg/L NH\(_4^+\) and 1.05-2.1 g/L PO\(_4^{3-}\)) in de-ionized water
Materials and methods

Precipitation reactor consists of a curved blade (1) connected to a rotor; a 2 L decanter glass (2); stators (3); and a pH-meter (4)

- Precipitation:
  - pH 9.0
  - Room temperature (20 °C)
  - Time 6-24 h
  - Coagulant solution added to (NH₄)₂HPO₄ solution while stirring the solution at 450 rpm (1 minute)
  - Constant stirring during experiments (50 rpm)
  - Water samples taken every half an hour

- Analyzes:
  - Water samples: ICP, IC, and NH₄-selective electrode
  - Precipitate: XRD and SEM
  - Dolomite: SEM, XRF and TG-DSC
  - Fly-ash: SEM, XRF
Results
Raw materials and MgSO₄ solution

- Main components CaO, MgO and SiO₂ in both dolomite and fly ash
- Mg leached more easily from fly ash than from dolomite
- Only less than 500 mg/L of Ca left in MgSO₄ solutions

**Main components (XRF) of the dolomite and fly ash**

<table>
<thead>
<tr>
<th></th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>SiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>FeO (%)</th>
<th>P₂O₅ (%)</th>
<th>K₂O (%)</th>
<th>Na₂O (%)</th>
<th>TiO₂ (%)</th>
<th>MnO (%)</th>
<th>Others (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>37.9</td>
<td>16.5</td>
<td>10.4</td>
<td>3.1</td>
<td>3.5</td>
<td>0.1</td>
<td>1.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
<td>26.8</td>
</tr>
<tr>
<td>Fly ash</td>
<td>36.9</td>
<td>14.2</td>
<td>17.7</td>
<td>8.1</td>
<td>8.9</td>
<td>1.6</td>
<td>0.5</td>
<td>0.5</td>
<td>0.3</td>
<td>0.3</td>
<td>11.0</td>
</tr>
</tbody>
</table>

**Mg and Ca concentrations (ICP) of the MgSO₄ solutions**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg (mg/L)</th>
<th>Ca (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA based MgSO₄</td>
<td>14500</td>
<td>483</td>
</tr>
<tr>
<td>DOL based MgSO₄</td>
<td>9430</td>
<td>494</td>
</tr>
</tbody>
</table>
Ammonium removal

- Highest removal percentages (75.5%) were achieved for FA based MgSO₄ solution using molar ratios Mg:P:N 1.6:1:1 and 1.1:2:2.
  - Ammonium removal very fast in the first case
  - Excess ammonium present in the latter case
- Clear drop in the removal percentage after 24 h when molar ratio Mg:P:N was 1.1:2:2
  - Otherwise only a minor change in the removal percentages after 4 hours
Phosphate removal

- Best phosphate removal achieved with FA based MgSO₄ solution when the molar ratio Mg:P:N was 1.6:1:1 (84.5 %) or 1.1:2:2 (82.5 %)
- Also phosphate removal very fast in the first case
- Excess phosphate present in the latter case
Precipitate characterization, XRD and SEM

- All peaks associated with struvite
  - Intensities of some peaks seems to be reversed in the left picture
  - Could be due to the growth of crystal structure

XRD diffractograms of the precipitates after the 6-h (left) and 24-hour (right) experiments
Precipitate characterization, Yield

- Quite good yields in all experiments
  - Some phosphate or ammonium is adsorbed/co-precipitated on the struvite crystals in FA 1.1:2:2
  - Supported also by the ammonium and phosphate removal percentages

<table>
<thead>
<tr>
<th></th>
<th>FA 1.3:1:1</th>
<th>FA 1.6:1:1</th>
<th>FA 1.1:2:2</th>
<th>DOL 1.3:1:1</th>
<th>DOL 1.6:1:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (%)</td>
<td>67.2</td>
<td>79.7</td>
<td>125.4</td>
<td>78.4</td>
<td>65.8</td>
</tr>
</tbody>
</table>
Summary
Summary

- Highest removal percentages were achieved with FA based MgSO₄ solutions
- Reaction time of 4-6 hours was sufficient
- Good yields in all experiments, struvite being the only product
- Fly ash and dolomite based MgSO₄ solutions have great potential in the ammonium and phosphate precipitation
- Tests with authentic wastewaters, solubility tests and growth tests in greenhouses and fields should be conducted

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