Use of side-stream based $MgSO_4$ as chemical coagulant in the simultaneous removal of nitrogen and phosphorus from wastewaters

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Background

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https://pixabay.com/en/canal-water-froth-alga-pier-2643420/

- **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]

[1] Aho, M., Pursula, T., Saario, M., Miller, T., Kumpulainen, A., Päällysaho, M., Autio, M., Hillgren, A., Descombes, L.: Ravinteiden kierron taloudellinen arvo ja mahdollisuudet Suomelle. Sitra, Helsinki (2015)

[2] European Commission: Proposal for a regulation of the European Parliament and of the Council laying down rules on the making available on the market of CE marked fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 (2016)

Background

– **Ammonium and phosphate could be precipitated as a struvite ($NH_4MgPO_4 \cdot 6H_2O$)**
  - 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

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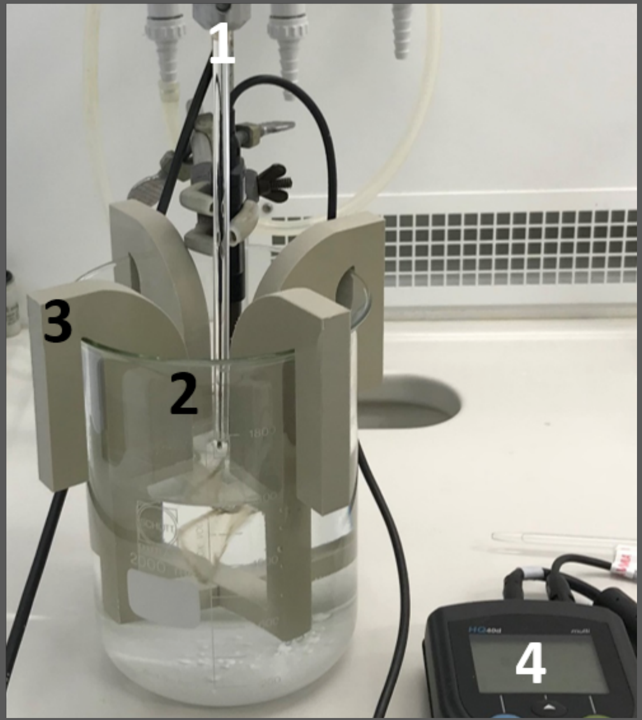
- **Solutions:**
- **$MgSO_4$ solution**: 50 g of dolomite or fly ash in 250 mL of 2M sulfuric acid (90 min; constant stirring 500 rpm). Precipitate settled (30 min) and filtered (2-5 µm filter paper). $MgSO_4$ solution collected and stored in glass bottles.
  - Ca and Mg oxides/carbonates react with H_2SO_4 to form insoluble $CaSO_4{\cdot}2H_2O$ and soluble $MgSO_4$
- **$(NH_4)_2HPO_4$ solution**: NH_4Cl and KH_2PO_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:

- Molar ratios Mg:P:N of 1.1-1.6:1-2:1-2
- pH 9.0
- Room temperature (20 °C)
- Time 6-24 h

- Coagulant solution added to $(NH_4)_2HPO_4$ 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 NH_4-selective electrode
- Precipitate: XRD and SEM
- Dolomite: SEM, XRF and TG-DSC
- Fly-ash: SEM, XRF

Results

Raw materials and $MgSO_4$ solution

- Main components CaO, MgO and SiO_2 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 $MgSO_4$ solutions

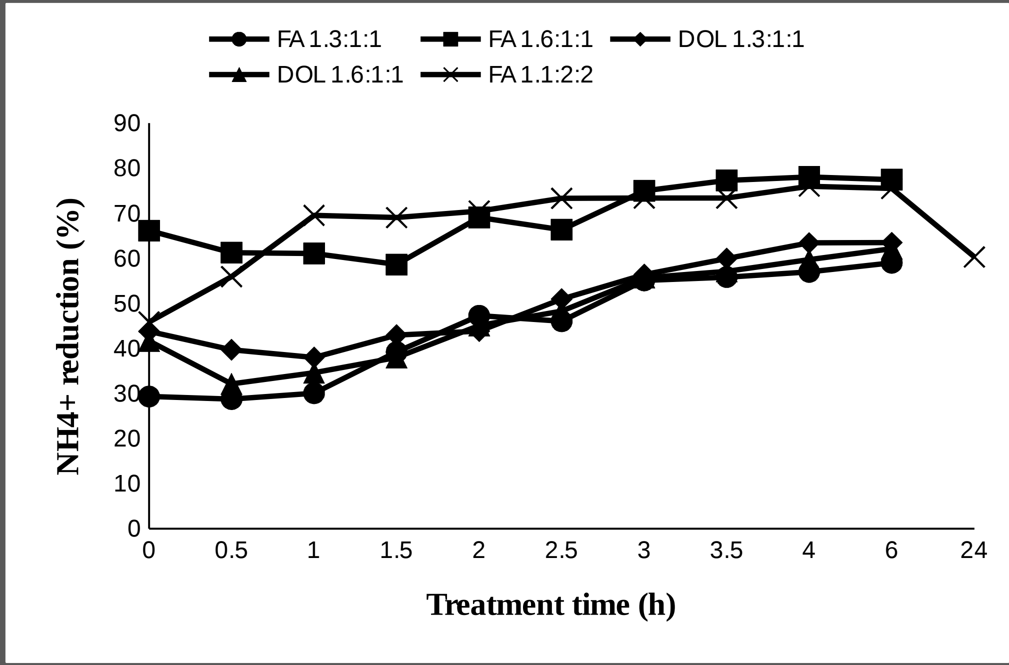
Main components (XRF) of the dolomite and fly ash

	CaO (%)	MgO (%)	SiO_2 (%)	Al_2O_3 (%)	FeO (%)	P_2O_5 (%)	K_2O (%)	Na_2O (%)	TiO_2 (%)	MnO (%)	Others (%)
Dolomite	37.9	16.5	10.4	3.1	3.5	0.1	1.1	0.2	0.3	0.1	26.8
Fly ash	36.9	14.2	17.7	8.1	8.9	1.6	0.5	0.5	0.3	0.3	11.0

Mg and Ca concentrations (ICP) of the $MgSO_4$ solutions

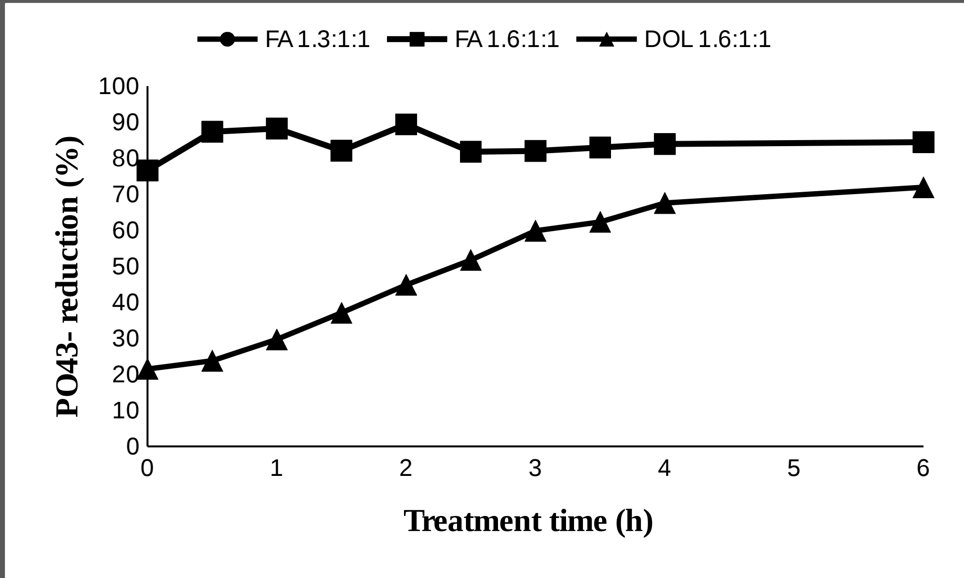
Sample	Mg (mg/L)	Ca (mg/L)
FA based $MgSO_4$	14500	483
DOL based $MgSO_4$	9430	494

Ammonium removal



- **Highest removal percentages (75.5 %) were achieved for FA based $MgSO_4$ 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

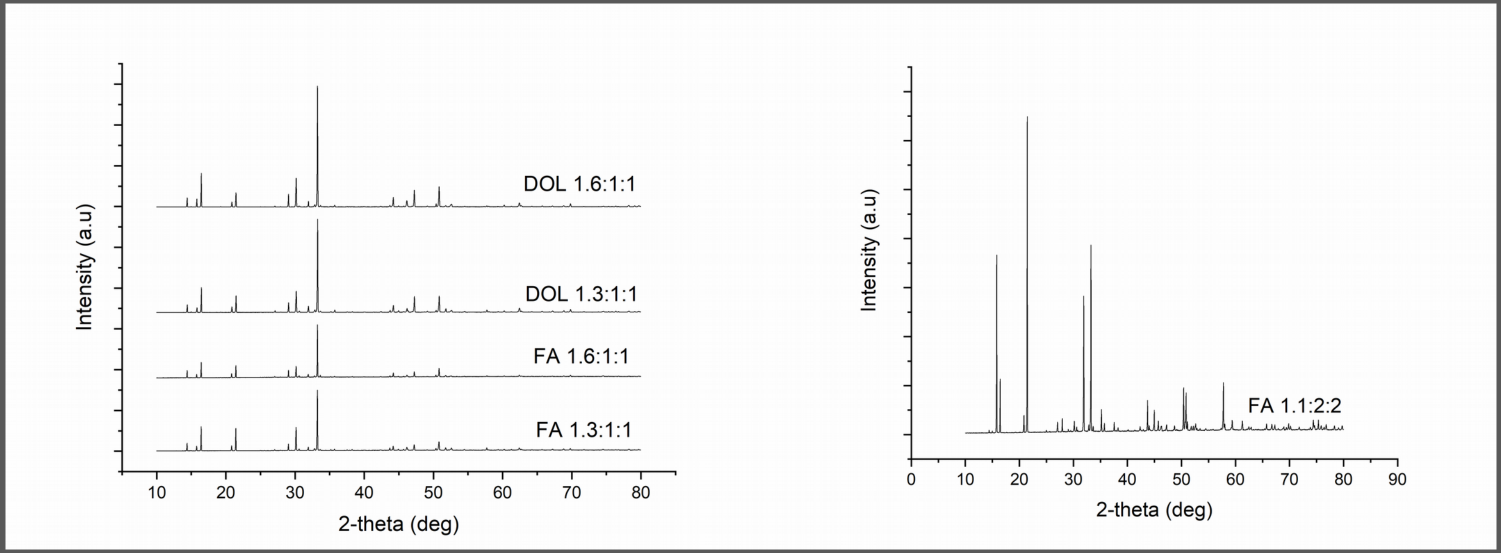


– **Best phosphate removal achieved with FA based $MgSO_4$ solution when the molar ratio Mg:P:N was 1.6:1:1 (84.5 %) or 1.1:2:2 (82.5 %)**

- 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

	FA 1.3:1:1	FA 1.6:1:1	FA 1.1:2:2	DOL 1.3:1:1	DOL 1.6:1:1
Yield (%)	67.2	79.7	125.4	78.4	65.8

Summary

Summary

- Highest removal percentages were achieved with FA based $MgSO_4$ solutions
- Reaction time of 4-6 hours was sufficient
- Good yields in all experiments, struvite being the only product
- Fly ash and dolomite based $MgSO_4$ 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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