New options for nutrient recovery: Adsorption and electrochemical precipitation (WaterPro project)

Kokkola Material Week

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Leverage from the EU 2014–2020

European Union
European Regional Development Fund

Background

WaterPro project: New processes of the circular economy in water and wastewater treatment

Project aims:

- **Development of water purification technologies and recovery of valuables**
  - By (electro)chemical precipitation
  - By adsorption in which industrial sidestreams are utilized
- **Pilot-scale experiments**

Project partners:

- **Kokkola University Consortium Chydenius / University of Jyväskylä**
- **University of Oulu (Research Unit of Sustainable Chemistry and Kerttu Saalasti institute)**
- **Kajaani University of Applied Sciences**

Implementation period: 1.5.2018-30.4.2021

UNIVERSITY OF JYVÄSKYLÄ
KOKKOLA UNIVERSITY CONSORTIUM CHYDENIUS
UNIVERSITY OF OULU
KAMK • University of Applied Sciences
KESKI-POHJANMAAN LIITTO
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Council of Oulu Region
Kainuun liitto

WaterPro project

Detailed aims of the project:

- Test laboratory and pilot scale to uptake nutrients and metals with different technologies
- Use local industrial sidestreams in water purification
- Develop further the characteristics of adsorbents (microstructure, properties, adsorption capacity)
- Regeneration of adsorbents
- Utilisation potential of precipitation sludge
- Develop material production technology and evaluation of commercialization potential

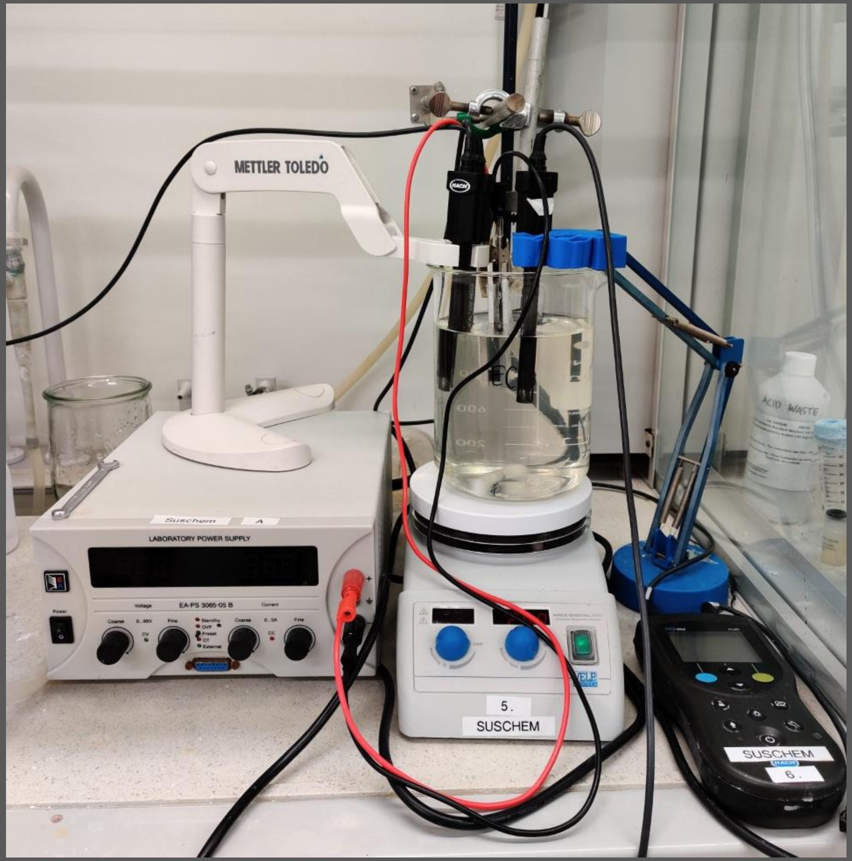
Adsorption or electrochemical precipitation in nutrients recovery

Background

- **Phosphorus (P) and nitrogen (N) are the main nutrients in wastewaters**
  - Runoffs to waterways causes eutrophication
  - Nitrogen typically as ammonium (NH_4^+) which evaporates easily as ammonia (NH_3) gas
- **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
- **Struvite can be precipitated chemically or electrochemically**
  - Magnesium dissolved chemically from magnesium salts or electochemically from magnesium plate
- **Ammonium can be adsorbed with adsorbents produced from variety of raw materials**

Materials and methods

Materials and methods: Struvite electrochemical precipitation



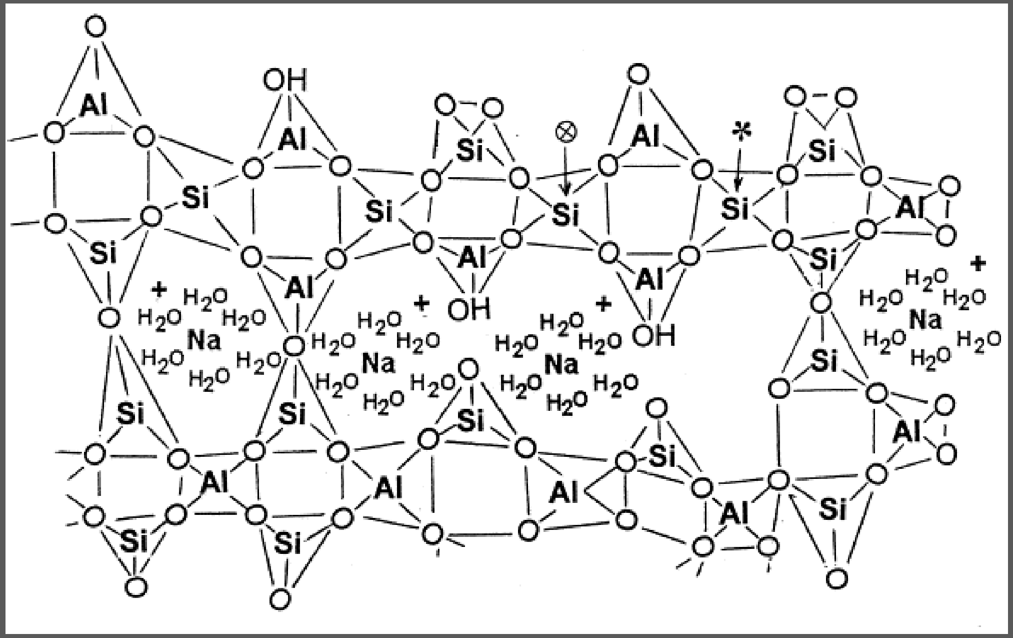
– Electrochemical precipitation:

- 2 L beaker with 1,6 L sample volume
- Stirring with magnetic stirrer
- Magnesium plate was used as an anode, steel plate as cathode
- Magnesium was dissolved by using electricity
- Water samples were taken in the beginning and after experiment
- pH adjusted by using NaOH or HCl
- Precipitation time max 4 h, sedimentation 24 h

- Analyzes:

- Water samples: residual magnesium with AAS, initial and final phosphate with IC and ammonium with NH_4-selective electrode
- Precipitate: XRD

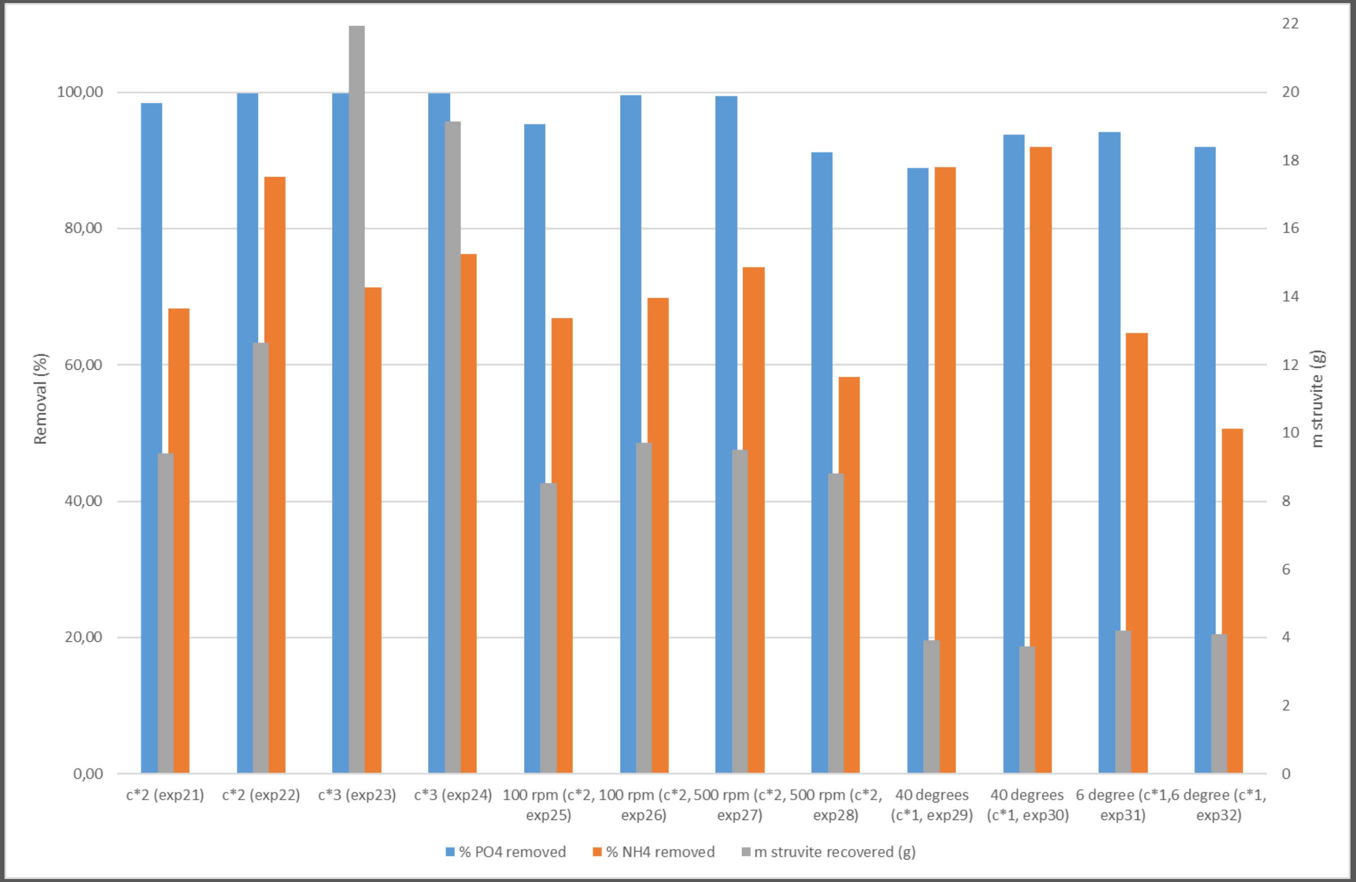
Materials and methods: Ammonium adsorption



- **Raw materials for ammonium adsorption:**
  - Metakaolin
  - Fly ash
  - Blast furnace slag
  - Ladle slag
  - LD converter slag
  - Analcime
  - Jarosite
- **Materials were geopolymerized → aluminum and silicates containing raw materials were activated with alkali (NaOH)**
- **Advantages of geopolymerization:**
  - Thermal and corrosive stability
  - (Micro)porous structure
  - High compressive strength (important for column adsorption)
  - Low solubility (inert material)
  - Environmentally friendly and economical
- **Adsorbent was mixed with ammonium solution, shaked 2 h (300 rpm), centrifuged**
- **Ammonium solution:**
  - Model solution OR
  - Real wastewater sample after struvite (electro)chemical precipitation
- **Analyzes:**
  - Water samples: initial and final ammonium with NH_4-selective electrode

Results

Struvite electrochemical precipitation: Model solution



- ❑ The effect of conditions for struvite electrochemical precipitation has been evaluated (pH, temperature, initial nutrient concentrations, stirring speed, sedimentation time of sludge)
- ❑ Optimum conditions:
  - ❑ pH 8,5-9 (depending e.g composition of the water)
  - ❑ Molar ratio 1:1:1 for Mg^{2+}:NH_4^+:PO_4^{3-} (model solution)
  - ❑ Stirring speed (100-500 rpm) has no huge effect to the nutrient removal
  - ❑Higher temperature decrease phosphate removal because ammonia has been evaporated
  - ❑ Sedimentation time 24 h

Struvite electrochemical precipitation: Real waters

- In ideal case for struvite formation, the concentration of phosphate is notable higher comparing to ammonium
- Case 1: Reject water from biogas plant include more ammonium than phosphate, include also solid matter → high residual ammonium concentration

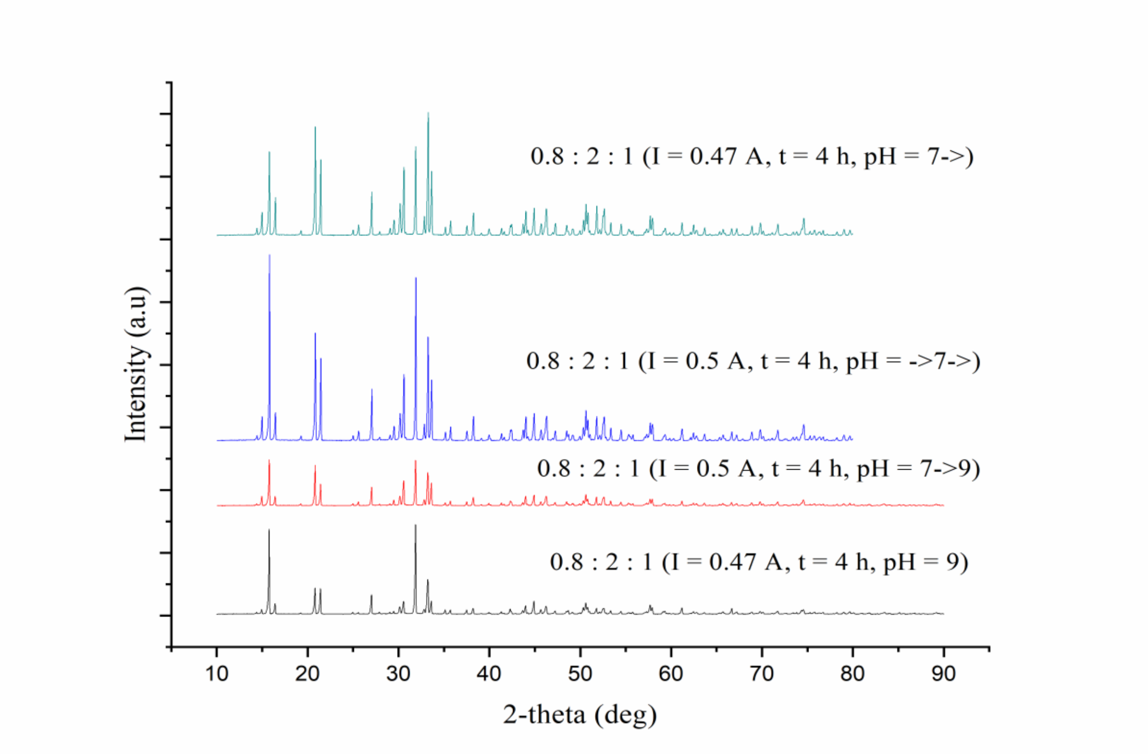
- Case 2: Two kind of nutrient containing process waters from Finnish industry was mixed to obtain optimal nutrient concentrations for struvite precipitation
  - Different molar ratios for Mg^{2+}:NH_4^+:PO_4^{3-}, in optimum case 2:1 for NH_4^+:PO_4^{3-}
  - High phosphate removal (even 99 %), ammonium removal slightly lower
  - pH adjusting, used current and initial nutrient concentrations affect to the magnesium plate destroying
  - Struvite yield almost 100 %

After non-optimised precipitation

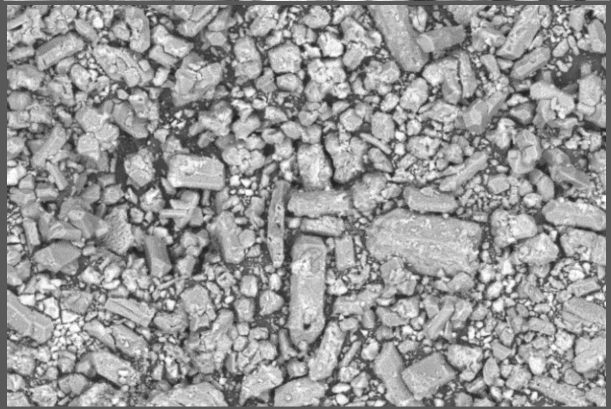
After optimised precipitation

Precipitate characterization, XRD and SEM

- Four experiments with different conditions
- All peaks positions are similar and match with struvite
- Trace amounts of some other compounds (like potassium magnesium phosphate hydrate, hazenite, silicon oxide, calcium phosphate hydroxide etc.) could be detected in some precipitates
- SEM shows typical struvite structure



XRD diffractograms of the precipitates in case 2 with different conditions



Adsorption: Ammonium removal in hybrid tests

- Residual ammonium after electrochemical struvite precipitation was removed by adsorption
- Adsorbent dosage 5 g/L, adsorption time 2 h
- After precipitation, residual ammonium concentration 40 mg/L
- Geopolymer prepared from blast furnace slag and ladle slag removed 43 % (q = 2.6 mg/g), pH 7
- Geopolymer from blast furnace slag, ladle slag and LD converter slag removed 72 % (q = 4.3 mg/g), pH 9
- Geopolymer prepared from analcime removed 51 % (q = 4.0 mg/g), pH 4

Adsorption: Ammonium removal in hybrid tests

- Residual ammonium after chemical struvite precipitation (different molar ratios) was removed by adsorption
- Ammonium concentration after precipitation was 278 mg/L
- Adsorbent dosage 5 g/L, adsorption time 2 h
- Geopolymer prepared from jarosite removed 59 % (q = 11.6 mg/g), pH 8.8
- Geopolymer from blast furnace slag removed 62 % (q = 12.2 mg/g), pH 9

Summary

Summary

- **In real waters concentrations of ammonium and phosphates are not optimal → mixing two types of process waters**
  - High phosphate removal (even 99 %)
  - Struvite yield almost 100 %
- **Steel industry slags, jarosite or analcime have potential to adsorb residual ammonium after (electro)chemical precipitation**
- **Nutrient can be uptaken over electrochemical struvite precipitation or adsorption (part of WaterPro project)**

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Thank you for your attention!