(Electro)chemical precipitation in the uptake of nutrients and metals

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Background

WaterPro WP 2: (Electro)chemical precipitation

The main aim in WP2 was to study chemical and electrochemical precipitation in the removal of nutrients, metals and sulfate from waters

- **Task 2-1: Electrochemical precipitation in the removal of nitrogen, phosphorus and metals**

❑ Aim 1: Nutrients electrochemical precipitation as struvite

❑ Aim 2: Metals and sulfate electrochemical precipation as ettringite

- **Task 2-2: Chemical precipitation in the removal of nutrients, sulfate and metals**

❑ Aim 1: Nutrients precipitation as struvite by chemical precipitation by using industrial sidestreams

❑ Aim 2: Hydroxylapatite precipitation from phosphorus-rich wastewaters

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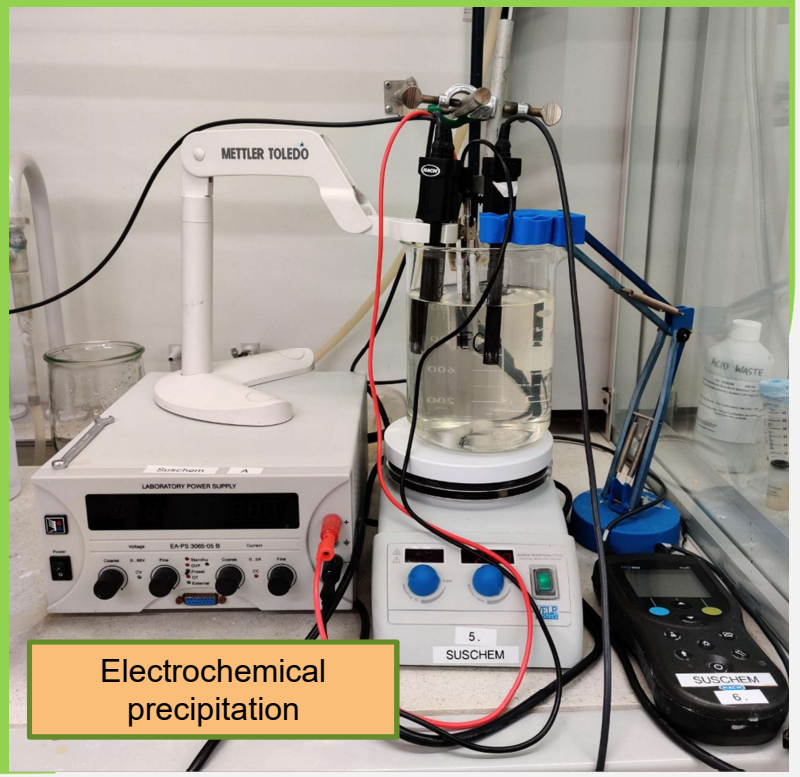
(Electro)chemical precipitation

Precipitation is the process in which dissolved impurities are transferred into an insoluble form by using precipitation agent

In chemical dosing commercial salts like $MgCl_2$, MgO and $Mg(OH)_2$ are used. Also industrial sidestreams are available.

In electrochemical dosing the precipitation agent is dissolved from anode by using electricity. Typical anode materials: aluminum, iron, magnesium

Chemical precipitation



Electrochemical precipitation

Struvite, hydroxylapatite and ettringite

- Ammonium and phosphate could be precipitated as a struvite ($NH_4MgPO_4 \cdot 6H_2O$) by using magnesium
- Phosphate can also be precipitated as hydroxylapatite ($Ca_5(PO_4)_3(OH)$) by using calcium
- Sulfate is typically removed via gypsum precipitation but ettringite ($(Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) precipitation gives better removal for sulfate and also metals can be removed

Struvite

Results

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
  - Struvite yield almost 100 %

Struvite chemical precipitation by calcined dolomite

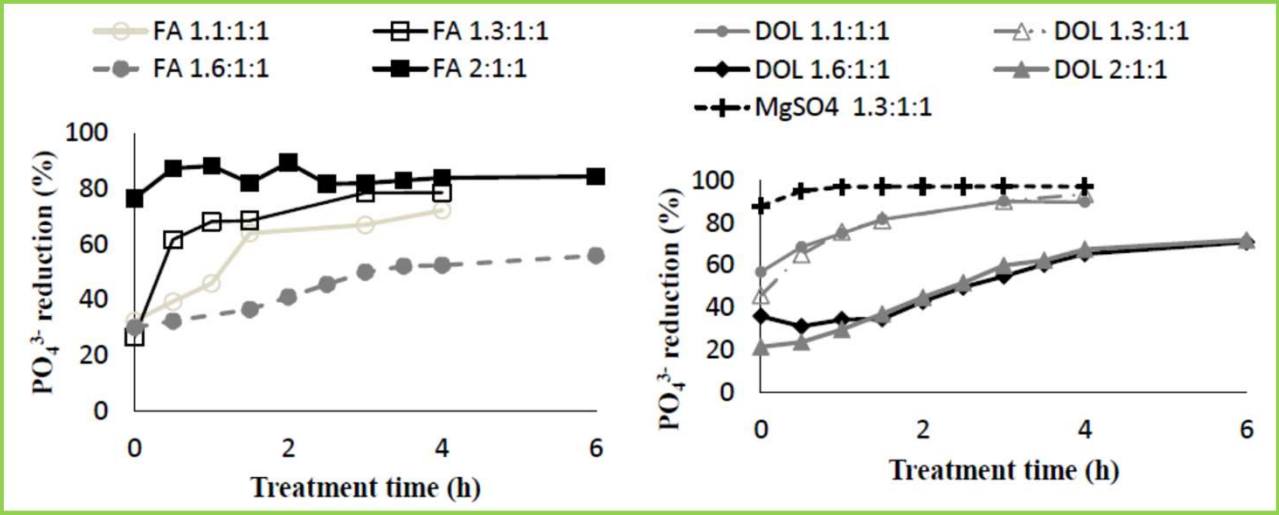
- Dolomite is carbonite mineral composed of calcium magnesium carbonate ($CaMg(CO_3)_2$, calcined at 750 °C or at 950 °C
- Commercial MgO as reference
- Model solution (200 mg/L NH_4^+ and 100-200 mg/L PO_4^{3-}) and agricultural sludge (137 mg/L NH_4^+ and 25 mg/L PO_4^{3-},(KH_2PO_4) added to obtain a molar ratio Mg:N:P 1.3:1:1
- Summary:
  - Calcined dolomite can be used for struvite precipitation after calcination at 750 °C
  - 24 hour precipitation time needed
  - Dolomite can also be used for agricultural sludge after phosphate concentration adjustment

Agricultural sludge

Pesonen J, Myllymäki P, Tuomikoski S, Vervecken G, Hu T, Prokkola H, Tynjälä P, Lassi U (2019) Use of calcined dolomite as chemical precipitant in the simultaneous removal of ammonium and phosphate from synthetic wastewater and from agricultural sludge, Chem Engineering mdpi, 3, 40 doi:10.3390/chemengineering3020040

Struvite chemical precipitation by dolomite and fly ash

- Ca-containing dolomite and fly ash were treated with H_2SO_4 to prepare $MgSO_4$ solution
- Commercial $MgSO_4$ as reference



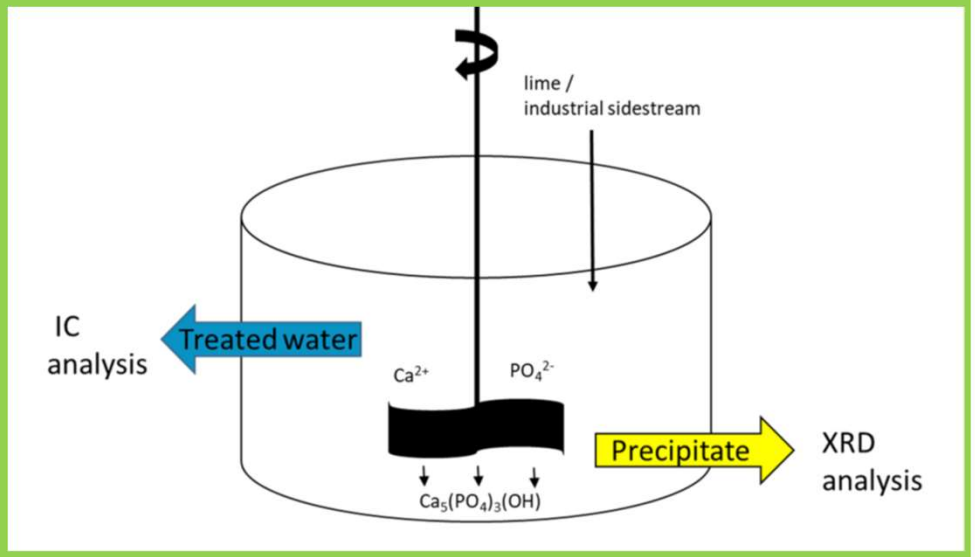
Ca precipitates phosphate as hydroxylapatite and less struvite is formed

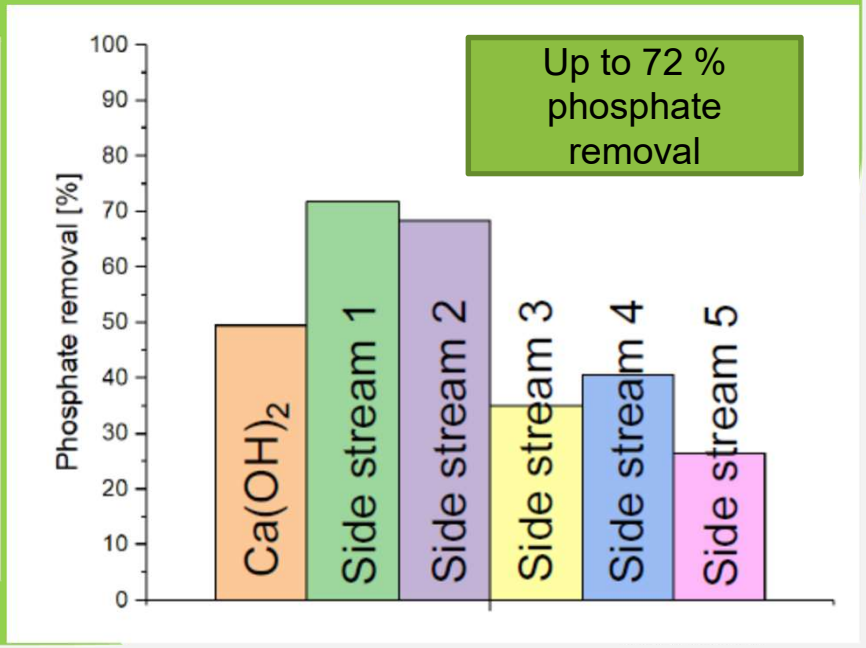
- Summary:
  - Best phosphate removal with commercial $MgSO_4$ (97 %)
  - 93.3 % phosphate removal with dolomite
  - 84.5 % phosphate removal with fly ash

Pesonen J, Sauvola E, Hu T, Tuomikoski S (2020) Use of side stream-based MgSO4 as a chemical precipitant in the simultaneous removal of nitrogen and phosphorus from wastewaters, Desalination and water treatment, 194: 389-395, doi: 10.5004/dwt.2020.26037

Hydroxylapatite ($Ca_5(PO_4)_3(OH)$) precipitation

- Alkaline calcium containing industrial sidestreams were used instead of commercial lime for phosphate removal
- Sidestreams: 1) partly burnt lime stored outdoors, 2) partly burnt lime stored in a silo, 3) kiln dust, 4) mixture of partly burnt lime and dolomite, 5) fly ash





Nurmesniemi, E.-T., Tuomikoski, S., Pesonen, J., Huhta, M. and Lassi, U. (2020) Phosphate removal and recovery from wastewater with industrial sidestreams, IWA Nutrient removal and recovery conference, Espoo September 2020.

Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) chemical and electrochemical precipitation

- Aluminum salts are typically used but also electrochemical dosage is possible
- Sulphate (1060 mg/L) removal from mine water

Treatment	Sulphate removal (%)	Purity of ettringite precipitate (%)	Cost (€/kg ettringite)	Cost (€/m³ of mine water)
Electrochemical dosage	99.0	92.5	0.42	2.43
Chemical dosage	98.6	92.6	0.40	2.33

- Advantages of electrochemical dosing:
  - Ease of handling
  - More dense precipitate formation
  - Quicker settling of precipitate
  - Only aluminum added, no counterions

Nurmesniemi E-T, Hu T, Rajaniemi K, Lassi U (2021) Sulphate removal from mine water by precipitation as ettringite by newly developed electrochemical aluminium dosing method, Desalination and water treatment, 217: 195-202, doi: 10.5004/dwt.2021.26920

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Conclusions

Conclusion

- Nutrient can be uptaken over chemical or electrochemical precipitation as struvite, also industrial sidestreams can be used
- Phosphate can be precipitated with industrial sidestreams as hydroxylapatite
- Both chemical and electrochemical dosing for ettringite precipitation are suitable
- Utilization applications of precipitates in the presentation of Janne Pesonen at 9:40

Thank you!

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