Kaliumin saostaminen jätevesistä

Kestävämpää fosforitaloutta puhdistamolietteestä –webinaari
18. marraskuuta 2025

Dosentti Janne Pesonen

Kestävän kemian tutkimusyksikkö

Oulun yliopisto

SustainableNutrients

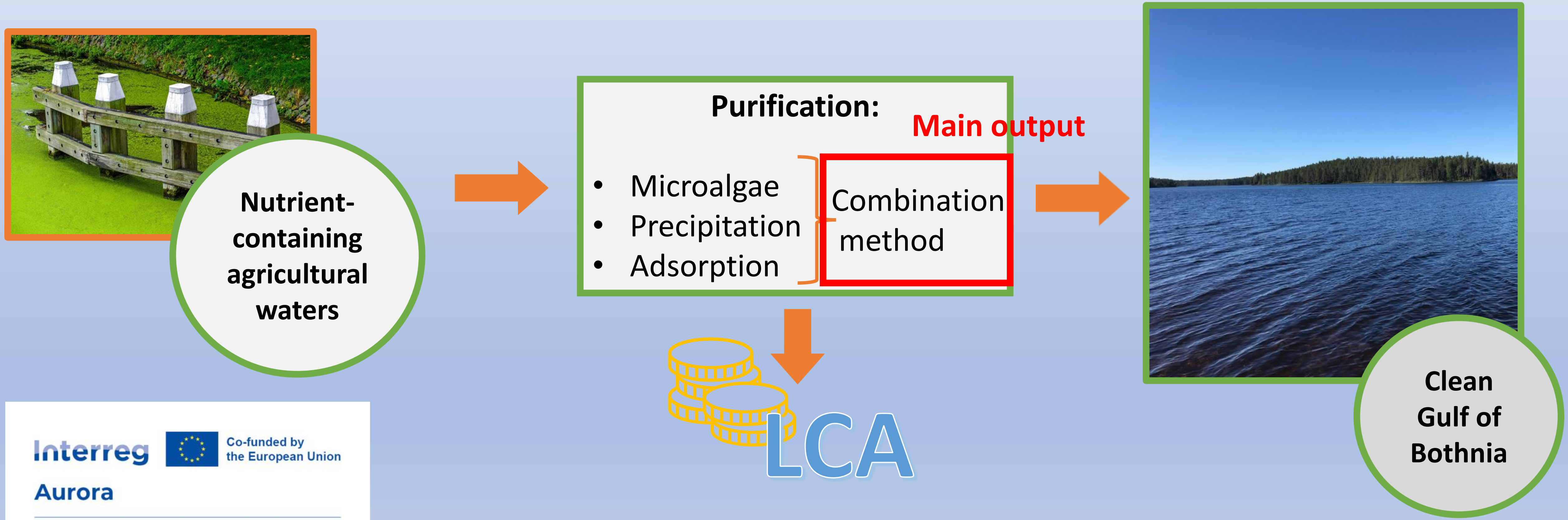
https://pixabay.com/en/canal-water-froth-alga-pier-2643420/

- **Interreg Aurora funded project**
- **Project duration 3 years: 01.01.2024 – 31.12.2026**
- **Partners University of Oulu (UOULU; lead partner), Kajaani University of Applied Sciences (KAMK), Swedish University of Agricultural Sciences (SLU)**
- **Budget 824 498 €**
  - 65 % of funding from Aurora program
  - 24.5 % co-financing from Lapin Liitto (Finland) and Region Norrbotten (Sweden)
  - 10.5 % own funding by project partners

Interreg Co-funded by the European Union
Aurora
SustainableNutrients

Sustainable nutrient management practices in the Gulf of Bothnia region (SustainableNutrients):

The overall objective of the project is to develop combination methods for nutrient removal (N, P, K) from agricultural waters, which could in long-term help to reduce the nutrients loads of Baltic Sea.



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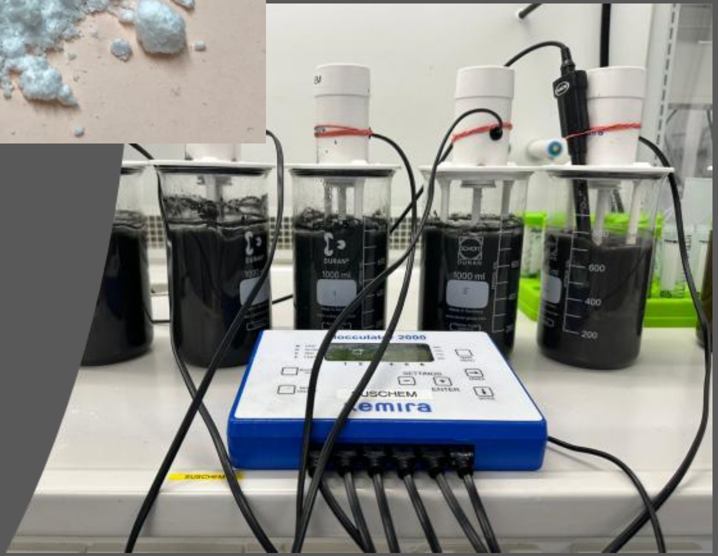
K-struviitti



- K-struviitti on struviitin K-vastine: $MgKPO_4 \times 6\ H_2O$
  - Ammoniumioni on korvautunut kaliumilla
- Muodostuu emäksisissä olosuhteissa
  - Optimi-pH alue 10 - 11

$$Mg^{2+} + K^{+} + PO_4^{3-} + 6H_2O \rightarrow MgKPO_4 \cdot 6H_2O$$

- Soveltuisi lannoitteeksi struviitin tapaan: sisältää kaliumia 14,7 m%; fosforia 11,6 m%

- Parhaillaan menossa yksi väitöstutkimus (Samuel Okyere Abayie)
  - Alkaliparistojen kierrätyksen pesuvedet
  - Synteettinen virtsa
  - Biokaasulaitoksen rejektivesi

Paristojen kierrätyksen pesuvedet

- Tracegrow valmistaa kierrätetyistä alkaliparistoista Zn-Mn lannoitetta
- Yhtenä prosessivaiheena musta massa pestään vedellä -> K-pitoinen jätevesi

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K-Struvite precipitation from source-separated battery wastewater

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ABSTRACT

Recovering nutrients from spent alkaline battery wastewater is important for environmental sustainability and resource management. Battery manufacturing and recycling processes often generate wastewater that contains a substantial amount of K^+. The current study aimed to evaluate the recovery efficiencies of K^+, PO_4^{3-}, and Mg^{2+}. This was achieved by precipitating Magnesium potassium phosphate hexahydrate (MPP) using three different models. In Model 1, the pH levels were adjusted to the desired levels (7, 10, 10.5, 11, 11.5, and 12) using NaOH. The highest recovery efficiencies for K^+ and PO_4^{3-} were 34.7 % and 52 % at a 1:1:1 molar ratio of Mg:K:P, while Mg^{2+} recovery ranged from 97 % to 100 %. In Model 2, the pH was maintained at pH 7. The K^+ removal efficiency ranged from 47.5 % to 54.8 %. In Model 3, the experiment compared two different MgO's at pH 7. By comparison, the results show that the maximum recovery of K^+ reached 65.1 % for MgO (95 %) and 59.5 % for MgO (71 %), respectively. The precipitates obtained were characterized through XRD, SEM-EDS, and ICP analysis. XRD confirmed a dominant pattern of K-struvite at a specific molar ratio of Mg:K:P of 0.5:1:0.5. Additionally, ICP analysis indicated that the permissible purity limits for heavy metals in fertilizers in Finland could be achieved at a pH of 7 for K-struvite. This study underlines the importance of considering optimal pH and Mg:P molar ratios for removing K^+ from spent alkaline battery wastewater to produce purified K-struvite and prevent impurity compounds.

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Table 2
Characteristics of spent alkaline battery water.

K^+ (mg/ L)	NH_4^+ (mg/ L)	Mg^{2+} (mg/ L)	Na^+ (mg/ L)	PO_4^{3-} (mg/ L)
17250	559	0.037	721	14.6

Paristojen kierrätyksen pesuvedet

- Saostuskemikaalina kaupallinen MgO (97%) ja kaksi MgO-sivuvirtaa (metalliteollisuus)
- P-pitoisuutta säädettiin fosforihapolla
- T = 25 °C, t = 180 min., pH 7 – 11.5, Mg:K:P 0.5-1:1:0.5-1

Table 1
Composition of magnesium oxide.

Composition of MgO A	Na_2O	MgO	SiO_2	CaO	P_2O_5	Fe_2O_3	Al_2O_3	Cl	K_2O	MnO	SO_3	Cr_2O_3	NiO	CuO	ZnO	SrO	BaO	PbO
wt%	0.78	**85.64**	7.03	2.57	1.65	1.54	0.17	0.14	0.11	0.05	0.04	0.01	0.01	0.01	0.23	0.01	0.01	0.01
Composition of MgO B	**Na_2O**	**MgO**	**SiO_2**	**CaO**	**P_2O_5**	**Fe_2O_3**	**Al_2O_3**	**Cl**	**K_2O**	**MnO**	**SO_3**	**Cr_2O_3**	**NiO**	**CuO**	**ZnO**	**TiO_2**	**V_2O_5**	**C**
wt%	0.36	**70.01**	9.47	2.41	1.26	3.73	2.8	0.04	0.04	0.11	0.19	0.15	0.13	-	0.04	0.03	0.02	9.14

RESULTS

- ❑ **Model 1**

- **The pH levels studied were 7, 10, 10.5, 11, 11.5, and 12**
- **The highest recovery efficiencies for K^+ and PO_4^{3-} were 34.7% and 52% at a 1:1:1 molar ratio of Mg:K:P**
- **pH was adjusted with NaOH ->**
- **Na inhibits K-struvite formation especially at high pH**
- **$Mg(OH)_2$ starts to precipitate above pH 11**

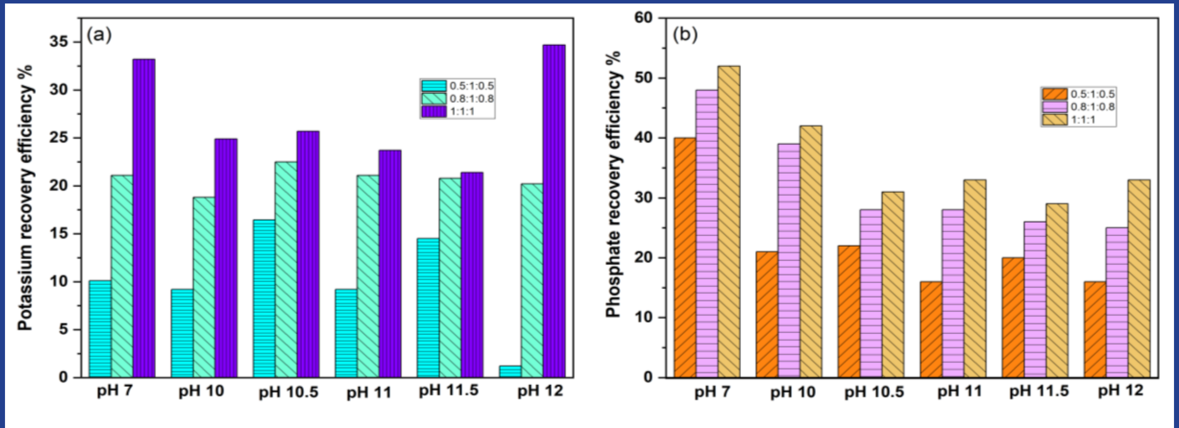

Figure 1. Recovery efficiencies at different pH levels and molar ratios. The effect of pH and molar ratios on (a) K^+ recovery, (b) PO_4^{3-} recovery

Model 1

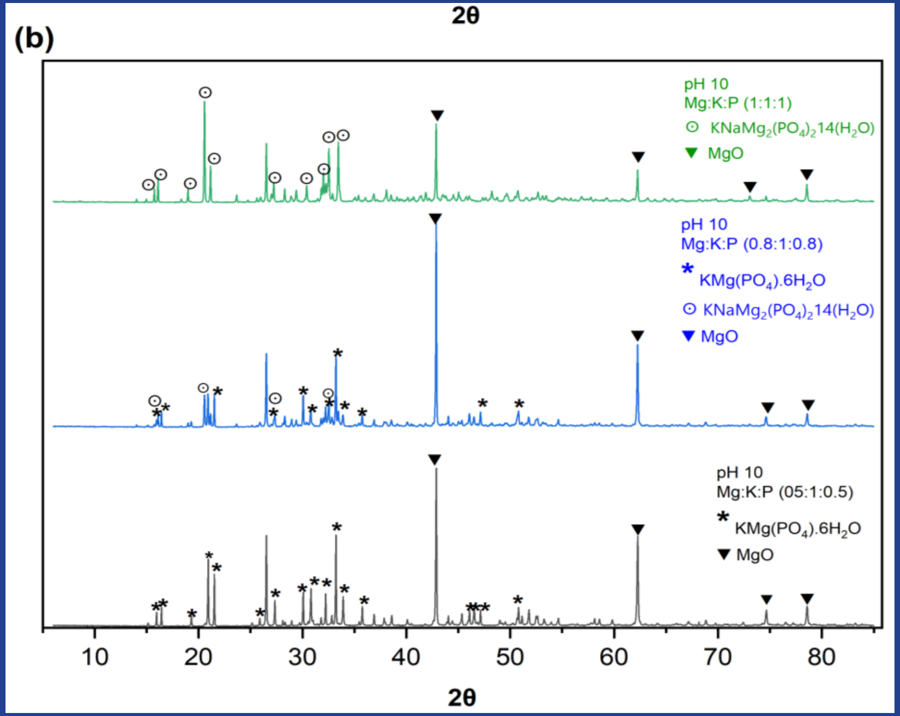

Figure 4. XRD diffractograms in the 2θ range of K-struvite (15°-40°), typical MgO (38°-78°), and hazenite (14°-35°) at (b) pH 10, at Mg:K:P molar ratios of 0.5:1:0.5, 0.8:1:0.8, and 1:1:1.

- In model 1, a clear pattern dominated K-struvite ($KMgPO_4 \times 6H_2O$) and MgO
- Also, Hazenite ($KNaMg_2(PO_4)_2 \times 14H_2O$) was present due to NaOH addition at high pH

RESULTS

- **Models 2 & 3**

– pH was maintained at pH 7 with HCl

– After MgO addition pH was allowed to raise to 7 while mixing

– Molar ratio Mg:K did not have a clear impact on K^+ removal

– Best results with Mg:K:P molar ratio 0.5:1:0.5 recovery of K^+ reached 65.1% for MgO (97%) and 59.5% for MgO (71%), respectively

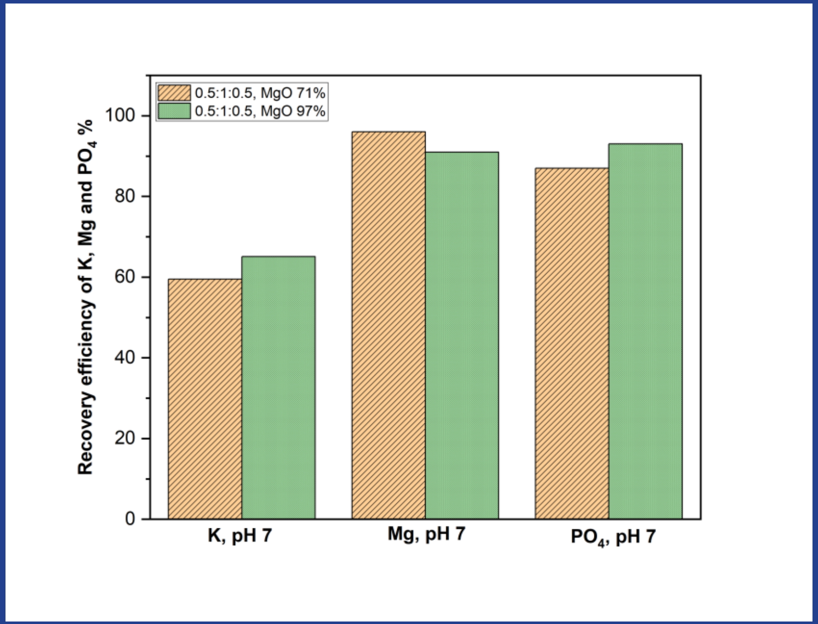

Figure 3. Recovery efficiency of K^+, PO_4^{3-} and Mg^{2+} using sidestream and commercial MgO

CHARACTERIZATION OF PRECIPITATE

- Cadmium content of the precipitate exceeds legislation limits in the case of sidestream MgO (85%)

Model 3

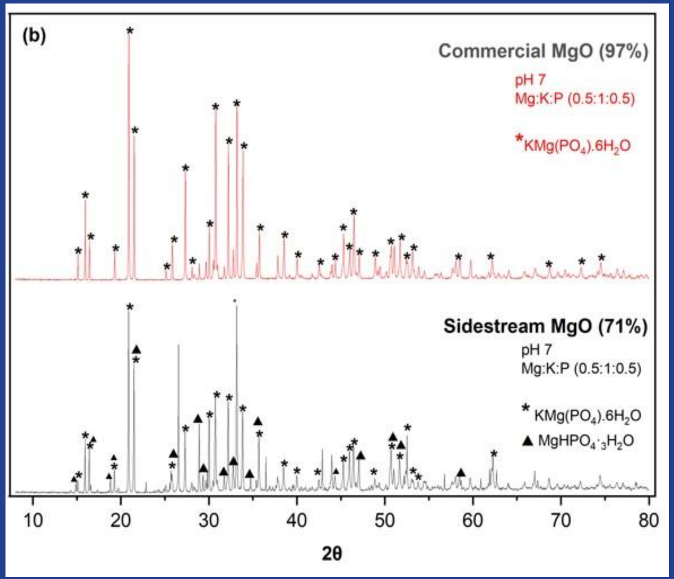

Figure 6. XRD precipitate patterns at pH 7 and molar ratios of 0.5:1:0.5 for only the first cycle

Table 3. Allowable purity limits for heavy metals in fertilizers in Finland, as specified in Fertilizer Product Decree 964 /2023, along with the results obtained from the produced K-struvite precipitate.

Heavy metals	Limit values c (mg/kg) (Inorganic macro-nutrient fertilizers)	Measured precipitate (mg/kg)	
		MgO 85% (sidestream)	MgO (commercial)
As	40	1	1.4
Cd	1.5	**2**	0.4
Cr	300	8	3.4
Cu	600	4.1	4
Hg	1	0.1	0.1
Ni	70	3	3
Pb	100	12.5	2.4
Zn	1500	608	439

- In model 3, the XRD results clearly confirmed the presence of K-struvite and newbereyite with sidestream MgO
- With commercial-grade MgO, only K-struvite was present

Saostuskokeet synteettisellä virtsalla

Table 2. Composition of synthetic urine (Udert et al. 2006)

Salt	Mass (g/l)	Molar quantity (mol)
NH_4Cl	1.80 (0.6)	0.0337
NaH_2PO_4	2.90 (2.29)	0.0242
KCl	4.20 (2.20)	0.0563
Na_2SO_4	2.30	0.0162
NaCl	0.183	0.0031
NaOH	0.230	0.0057
$MgCl_2$	0.370	0.0039
$CaCl_2$	0.510	0.0046

✓Scenario 1: Used the baseline concentration (original concentration) by adjusting only pH (8, 9, 9.5, 10, 11, and 11.5) -> no K^+ recovery

✓Scenario 2: Added only MgO at different Molar ratios and pH adjustment -> complete PO_4^{3-} removal, Low (18%) K^+ recovery

✓Scenario 3: Added H3PO4 and MgO at different Molar ratios and pH adjustment

RESULTS

- ***SCENARIO 3***

- The highest K+ recovery was 59% in a molar ratio of Mg:K:P (1.6:1:1.6) at a pH of 11.5
- PO_4^{3-} varied from 35% to 99.7%, while in Figure 2c, the recovery of Mg^{2+} ranged between 79.2% and 99.9%

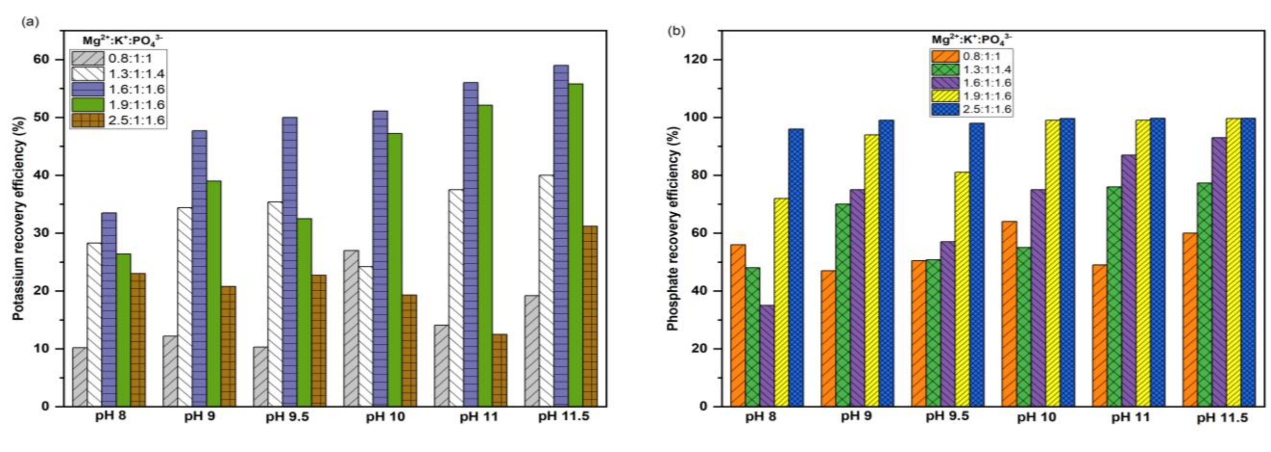

Figure 8. Recovery efficiencies at pH levels 8, 9, 9.5, 10, 11, and 11.5, as well as at different molar ratios when both MgO and H_3PO_4 were used.

CHARACTERIZATION OF PRECIPITATE

- ❑ Selected precipitates generated during scenario 3 were characterized using XRD.
- ✓ The XRD confirmed a clear pattern of mainly K-struvite ($KMgPO_4 \cdot 6H_2O$) and struvite ($NH_4MgPO_4 \cdot 6H_2O$) peaks

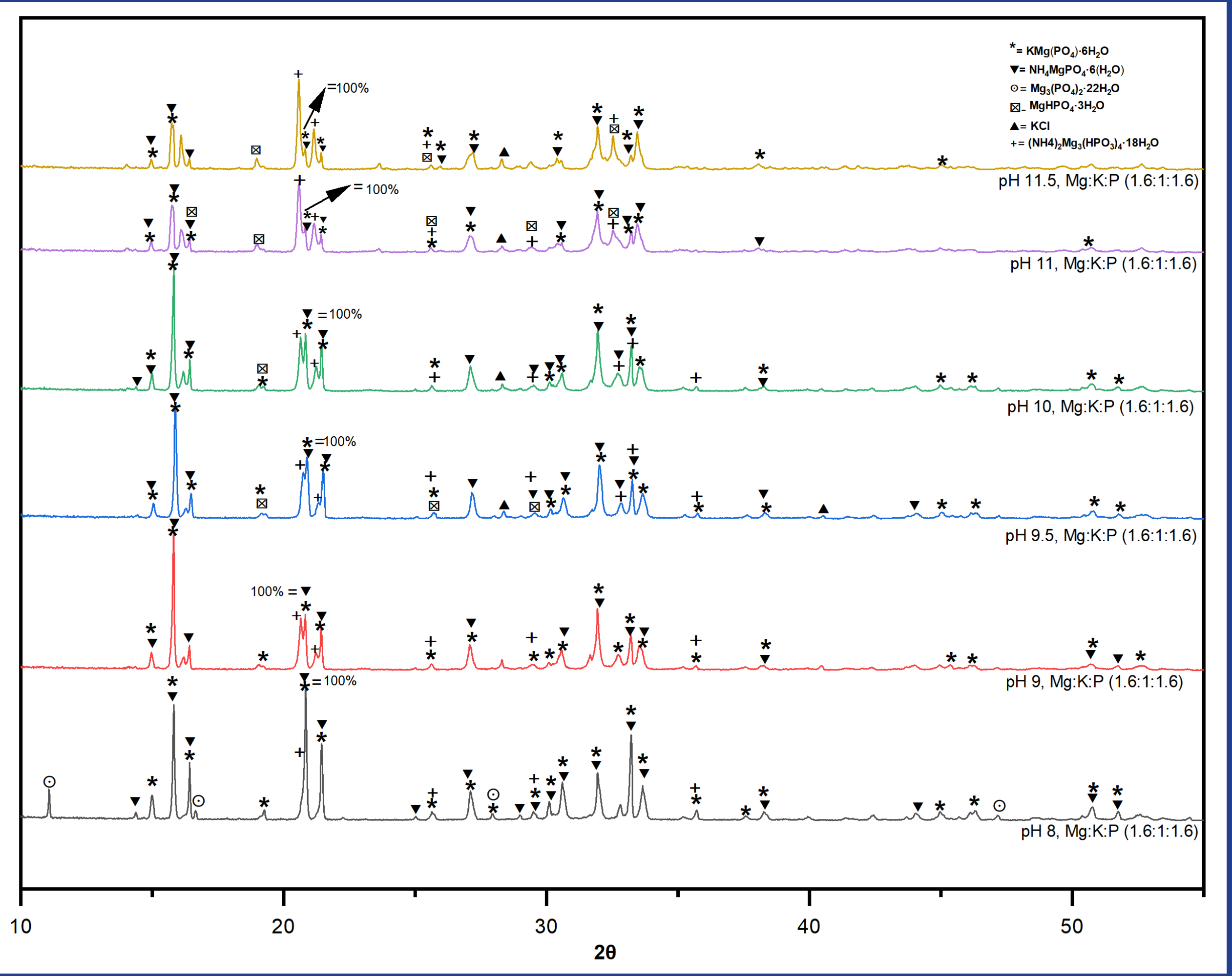

Figure 9. XRD diffractograms in the 2θ range of K-struvite (15°-55°), typical struvite (14°-45°)

Yhteenveto

- **K-struviitti voisi olla lupaava lannoite**
- **Saostuksen optimiolosuhteet riippuu voimakkaasti jäteveden koostumuksesta (mm. NH_4^+ , Na^+, Cl^-)**
- **Paristojen kierrätyksen jätevesillä ja synteettisellä virtsalla tehdyissä kokeissa päästiin n. 60 – 65 % K-poistoihin**
- Isot natriumpitoisuudet haittaavat saostusta erityisesti korkeassa pH:ssa
- Kloridi muodostaa liukoista kaliumkloridia
  - KCl/K-struviitti tasapaino

Kiitos!

Kommentteja & kysymyksiä?

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