KOKKOLA MATERIAL WEEK 2020
Towards a sustainable future

KAMK • University of Applied Sciences

New options for nutrient recovery:

Ammonium adsorption and its sequential recovery by air-stripping or membrane technique

WaterPro

Kiertotalouden uudet prosessit veden ja jäteveden käsittelyssä

November 2020

tatiana.samarina@kamk.fi
esther.takaluoma@kamk.fi

<u>Tatiana Samarina,</u> Esther Takaluoma
Kajaani University of Applied Sciences, Finland

European Union
European Regional Development Fund
Leverage from the EU 2014–2020

Laboratory of Applied Geopolymer Technology
Kajaani University of Applied Sciences, Finland

KAMK • University of Applied Sciences

Sustainable construction and civil engineering solutions

Tailing pond construction and management

Tailing characterization

Potential of hazardous waste and tailings encapsulation

Recycling of gangue, bedrock, tailings in concrete production and road construction

https://www.kamk.fi/en/RD-and-Business-Services/Core-Ramp;D-Competences/Industrial-materials-applications

Laboratory of Applied Geopolymer Technology
Kajaani University of Applied Sciences, Finland

KAMK • University of Applied Sciences

Environmental and water management
in mine industry

Water and waste water treatment applications
(toxic metal(oid)s – removal and/or recovery)

Biogas purification techniques

Nurtient recovery approaches

Citizen science and participatory observation

https://www.kamk.fi/en/RD-and-Business-Services/Core-Ramp;D-Competences/Industrial-materials-applications

WaterPro

Kiertotalouden uudet prosessit veden ja jäteveden käsittelyssä

KAMK • University of Applied Sciences

European Union
European Regional Development Fund

Work package 1
Industrial by-products/side stream materials characterization

Work package 2
Electrochemical and chemical precipitation: nutrients, sulfates, metals

Work package 3
Removal and recovery of contaminants (lab-scale)

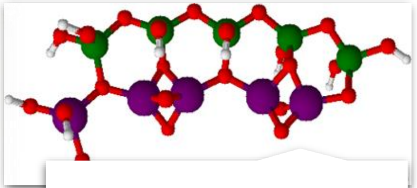
Work package 4
Regeneration or stabilization exhausted materials

Work package 5
Technical solutions for wastewater treatment and developed materials piloting

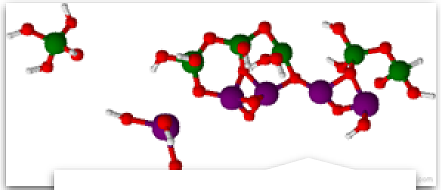
Leverage from the EU 2014–2020

Geopolymer preparation

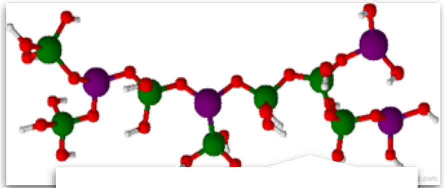
Crashed or powder form



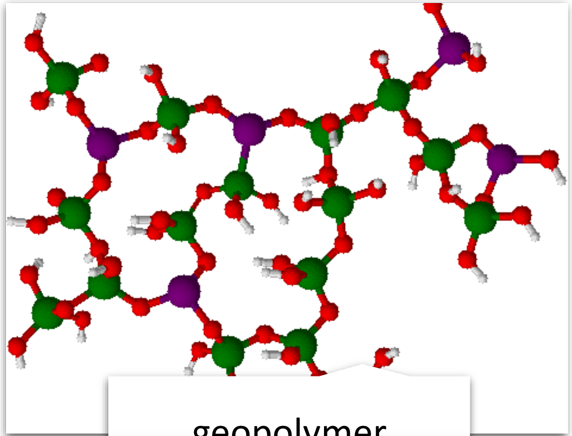
raw alumino silicate



activation

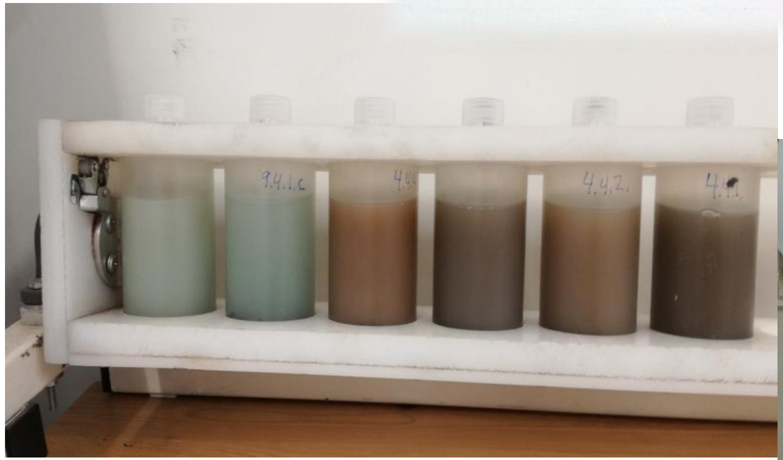


gelphase



geopolymer

Bulk geopolymer



Granulated form

Raw materials for geopolymerization approach

Waste-to-value concept

Circular Economy and green mining

Clays and minerals

Calcinaed materials

Metakaolin

Dolomite/magnesite

Industrial waste streams

Ashes

Pulp sludges

Mine tailings

Industrial by-products

Blast furnace slag (BFS/BOF)

Silica fume

Design of cost-effective adsorbents

Commercial adsorbents:

Activated carbons (PAC/GAC)
1200-3000 EUR/ton
GHG emission; energy demand;
loss of adsorbent on reg.stage;
utilization problems

Ion-exchange resins (polymers)
1700-3000 EUR/ton
energy demand; organic solvents;
utilization problems

Zeolites (natural minerals)
600-1500 EUR/ton
unsteady quality; limit abundances

Sands, gravels, etc.
50-350 EUR/ton
low capacity and nonspecific treatment

Geopolymers 150-300 EUR/ton

Cost-effective adsorbents for nutrient removal

Abundant and low cost source

- Natural zeolites and clays
- Industrial wastes and by-products
- Agricultural residues
- Bio-based materials

Manufacturing and remediation process

- Ease of handling
- Low energy consumption
- Low GHG emission
- High capacity and short removal time

Zero-waste

Waste produced

- Regeneration
- Recycling
- Reuse in other application

Diverse and eco-friendly manufacturing, valorisation of side streams, steady quality

KAMK • University

Drivers of nutrient removal and reuse technology

NEED

- Fertilizer production is energy-consuming process
- Discharge of nutrients to natural waters cause eutrophication problems
- Nitrogen load in sewage systems **25 000 ton/a** (Finland) and **60%** of it is removed and lost in current treatment processes
- Decrease of GHG emission
- **Recovery** could be valuable in near future
- Environmental limits for nutrients discharge

BENEFITS

- Technology for nutrient removal from low-laden or diluted streams: **variety of applications**
- Decreases expenses for **aeration** (conventional anaerobic treatment process) or final/polishing treatment
- Small dimensions and ease of integration
- Final product:

raw materials, advanced adsorbents, soil improvers or fertilizers

SOLUTION

- New geopolymer adsorbent from low-cost sources: unique properties and steady quality
- Combination of mature techniques:

Adsorption ⟶ **Air-stripping** ⟶ **Absorption**

Evaporation and concentration of final products

Capture in structure and stabilization

COMPETITION

- Biotreatment **AMMONOX** (Netherlands) – nitrogen removal only
- **RAVITA/NPHarvest** (Finland) – reject water and digestate, recovery of ammonium
- **ReNOx** (Austria) – natural zeolite adsorbents
- **RemNut** (Italy) – ion-exchange resins
- **Struvite precipitation** – nutrient ratio and Mg source

Sources of undesired nutrient emission

KAMK • University of Applied Sciences

Nutrient-contaminated streams

Low-laden – 10 – 100 mg N/L	N-P-K	High-laden – 100 – 5000 mg N/L

Agriculture, fishery, and forestry

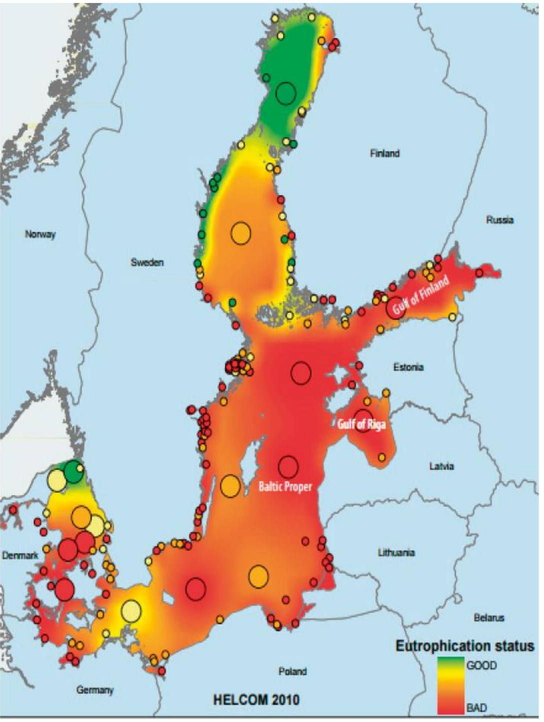
- Run-off and storm waters
- Facultative lagoons
- Air purification cattle farms
- Overfertilized fields
- Aquaculture operations
- Ditches and peat bogs

Nutrient close-loop concept and Environmental risk mitigation

Municipal and industrial waste- and processing waters

- Sludge digestates
- Dewatering streams of WWTP
- Reject waters of biogas stations
- Landfill leachates
- Textile industry processing waters
- Paper mills grey waters
- Food industry (meat and beverage)

”Urban mining” concept

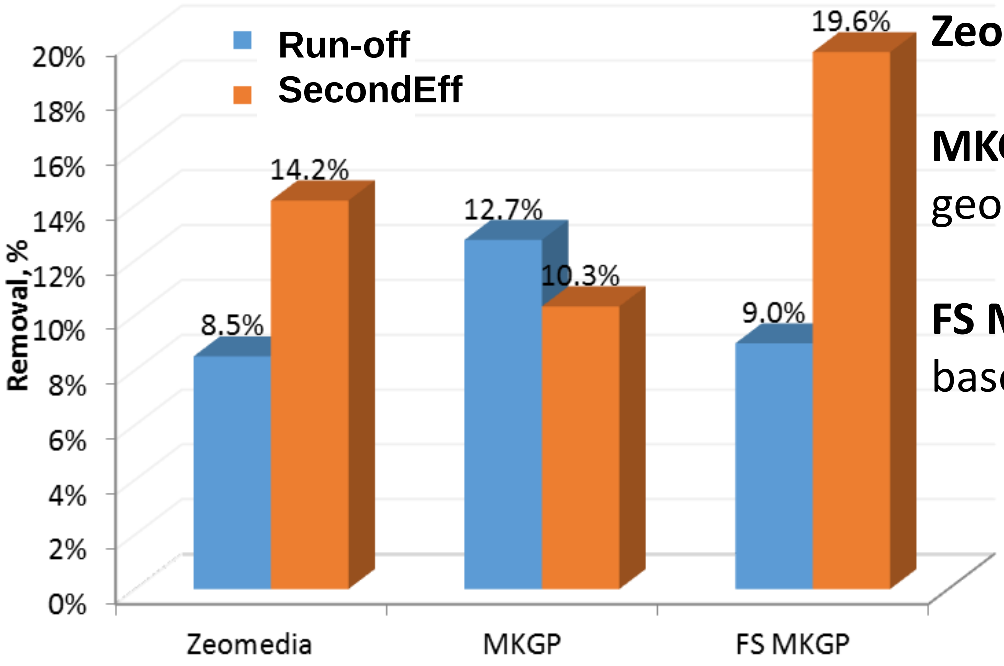


Helsinki Commission
Baltic Marine Environment
Protection Commission (2010)

POSSIBLE BUSINESS CASES

Real cases: wastewater treatment of municipal wastewater and mine drainage

Element	Industrial run-off water, mg/L	Secondary effluent, mg/L
Na	163	n/d
Ca	614	27
Mg	14.2	4.4
K	130	0.2
NH_4-N	36	31



Zeomedia - Clinoptilolite

MKGP - metakaolin-based geopolymer

FS MKGP - fiber sludge based geopolymer

Enrichment factor up to **20** were reached for industrial run-off waters, and up to **100** for WWTP effluents

Fixed bed column experiment: Adsorption and Regeneration

Adsorption:

Grain size
Flow rate
Temperature

Operation under arctic condition:
Same efficiency at 4°C and 20°C

EBCT was different for synthetic and real waters

Process easy to handle and maintain

Regeneration:

Regenerants:

Na-salts and K-salts

Cloride, sulfate, phosphate

Conditions:

Regenetant concentration

Alkalinity

Flow rate

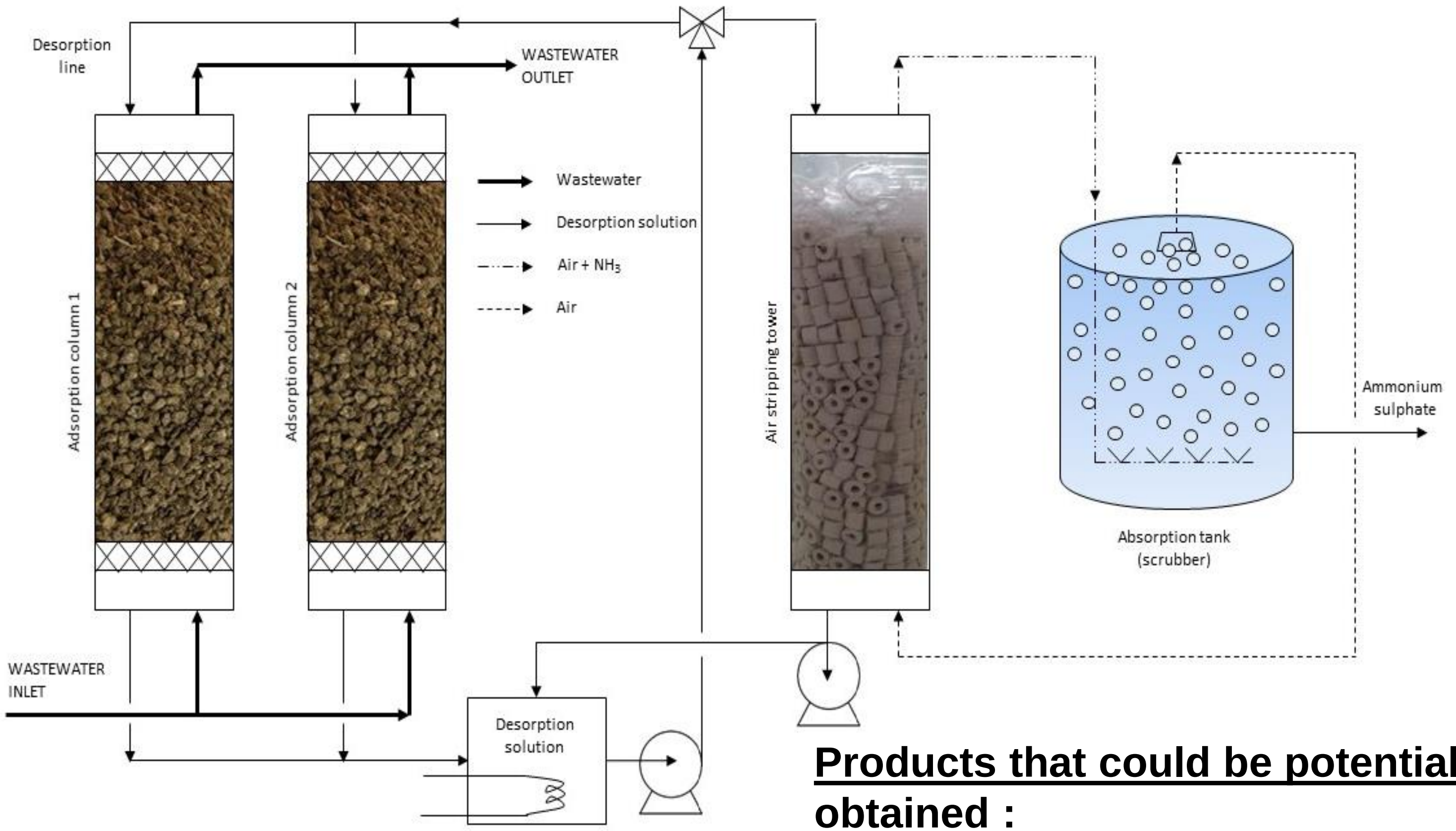
The higher concentration of salt used, the higher enrichment factor

Low-cost regenerant could be used: 5M NaCl at pH 12

K-salts reduced removal ability of FS MKGP by 55%

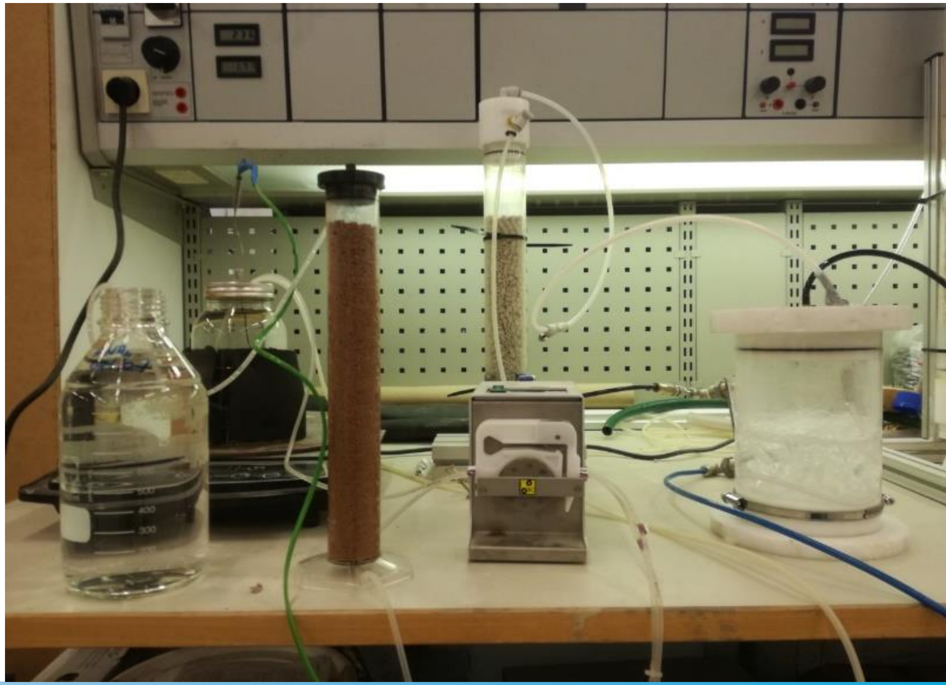
Up to 10 cycles of adsorption-regeneration with a decrease in efficiency of only 15%

Air-stripping experiments and ammonium recovery



Temperature 45±5ºC was enough to reached conversion rate 91 %.

After the regeneration solution was purified, it was used over 5 times for desorption procedure.



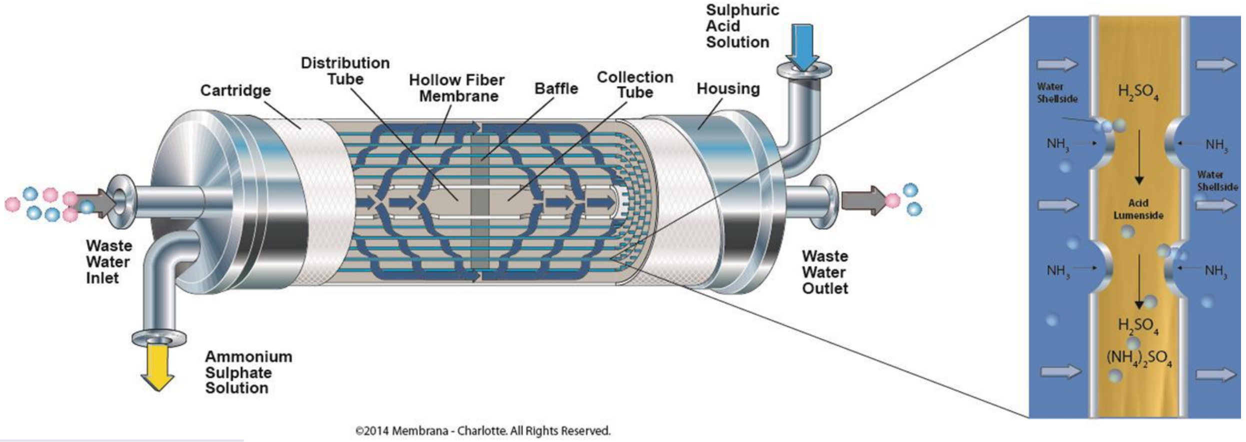
Products that could be potentially obtained :

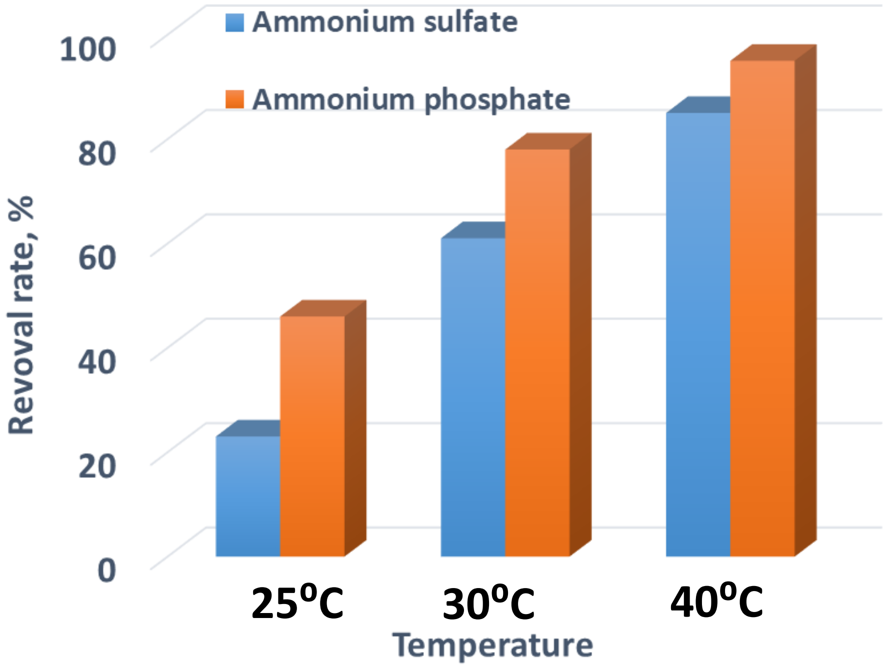
Ammonia water (5% NH_4OH)
Anhydrous ammonia (25% NH_4OH)
Liquid ammonium sulfate

Recovery of ammoniacal nitrogen Transmembrane Chemical Absorption

KAMK • University of Applied Sciences

- **3M Liqui-Cel® membrane contactor**
- Technology still under development





The concentration of ammonium-content salt in a resulting received phase were 17% and 22% for phosphate and sulfate salt, respectively.

Conclusions:

Leverage from the EU 2014–2020
A74635 EAKR, Keski-Pohjanmaan Liitto/Kainuun Liitto/Pohjois-Pohjanmaan liitto.
European Union
European Regional Development Fund

NEXT STEPS

- **Decrease substantially CAPEX**
- **Economical evaluation and LCA**
- **Construction of piloting mobile treatment unit**

Conclusions:

Conventional system is biotreatment in aerobic basins

- Aeration – up to 60% of WWTP energy
- Odor and sludge
- Low temperature is a problem
- We **not recover N**, we have lost it!
- Source of carbon needed (methanol/acetic acid) in polishing step

Innovation approach
is RECOVERY of the valuable resource

- **Smaller footprint**
- **Less GHG emissions**
- **Better water quality**
- **Possibility to reduce energy consumption and chemicals**
- **Getting valuable products to cover expenses**

AMMONNOX - 3€/ N kg
Conventional air stripping - > 6€/ N kg
NutriCON (KAMK) - 4.5 €/ N kg **AIM - 1.5-2 €/ N kg**

KAMK • University of Applied Sciences

Conclusions:

- Adsorption has great potential as remediation technique under arctic condition.

- The capacity tests for adsorbent should be repeated with the water being treated. The capacity of the adsorbent granules used in the calculations may be lower than actually used.

- It has now been found in laboratory and pilot experiments that regeneration is possible at least 20 times without significant decrease of capacity even for complex matrices.

- Nitrogen could be recovered as valuable industrial and agricultural products.
- Phosphorous could be removed effectively and potentially recovered locally as soil improver.

KAMK • University of Applied Sciences

www.kamk.fi