APPLICATION OF METAKAOLIN GEOPOLYMER FOR AMMONIUM REMOVAL IN SMALL-SCALE WASTEWATER TREATMENT SYSTEMS

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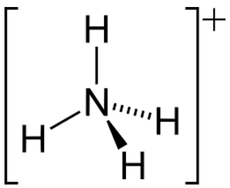
AMMONIUM, NH_4^+



- Nontoxic, necessary nutrient element for many kinds of living systems.
- Occurs in municipal wastewaters and industrial effluents.
- Major contributor to the eutrophication of water bodies.

→ The removal of nitrogen from wastewaters has become mandatory in several countries.

- The requirement for total nitrogen removal within small-scale wastewater systems generally 30% and in the areas defined sensitive for contamination 40% (Finland).
- NH_4^+ removal from municipal wastewaters is a challenge in small-scale wastewater treatment systems.

SMALL-SCALE TREATMENT SYSTEMS

- **Some treatment steps in small-scale wastewater systems remove N:**

- Septic tanks (3–20 % removal)
- Infiltration systems (10–40 %)
- Sand filters (10–80 %)

Nitrogen removal process:
- most likely a combination of microbial activity (nitrification-denitrification) and physico-chemical separation.

- Biological processes:

- Biofilms
- Membrane bioreactors
- Suspended growth active sludge process (large-scale wastewater treatment plants)

- **Biological nitrogen removal has a major limitation.**
- The temperature of **wastewater < +12˚C:**
  → The kinetics of nitrification and denitrification significantly hinder.
  → **Limits use only to a warm season in cool climate areas (e.g. in northern Scandinavia).**

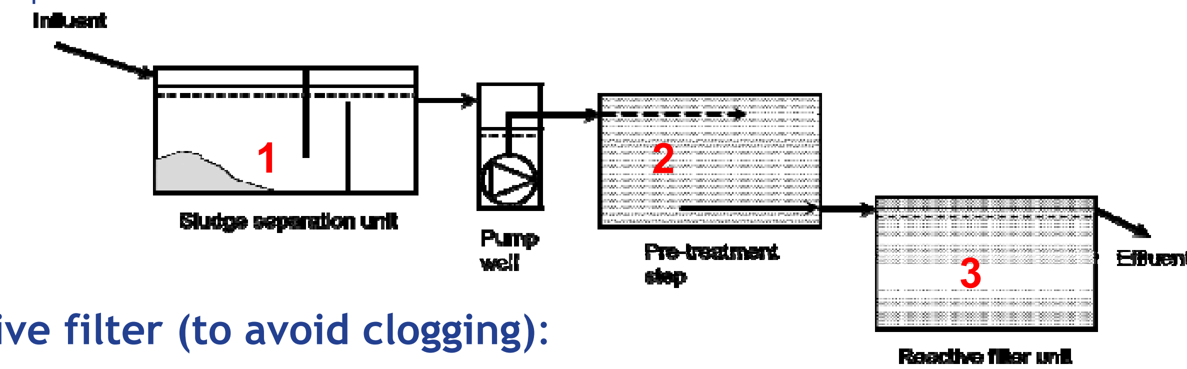
- Sorption-based approaches e.g. **reactive filter systems**

→ offer a simple and more robust alternative method for NH_4^+ removal.

SORPTION-BASED REACTIVE FILTERS SYSTEMS

Sorption-based approaches e.g. reactive filters systems:

- **A simple** and **more robust** alternative method for NH_4^+ removal.



- Main advantages:
  - low dependency on temperature
  - possibility to recover nutrients.

- **Pre-treatment is required before the actual reactive filter (to avoid clogging):**
  - the sludge separation unit (e.g. a septic tank): the largest particles are separated (1)
  - the pre-treatment step (e.g. gravel bed): removes organic material and suspended solids (2).

- **The reactive filter unit** (3):
  - **contains granular NH_4^+ sorbent material** such as **natural zeolites** (the most studied sorbents) e.g. clinoptilolite (the most used) or wollastonite.

THE AIM OF THIS STUDY

- Natural zeolites are the most studied sorbents and can be used in reactive filters.

- **The aim of this study: to produce new alternative sorbent materials from low-cost raw materials for NH_4^+ removal.**

→ **Metakaolin geopolymer.**

- **Geopolymerization-granulation process: the first time** in the production of **NH_4^+ sorbent material.**

GEOPOLYMERS

<u>The most common geopolymer synthesis method:</u>

- **Reaction between aluminosilicate raw material (e.g. metakaolin) and alkaline activator** (commonly concentrated sodium hydroxide and silicate) at ambient or near-ambient temperature and pressure.

- The formation reactions of geopolymers include:
  - **dissolution, gelation, reorganization, and hardening**
  - the exact mechanism still unclear.

<u>Geopolymerization-granulation</u> with high-shear granulator

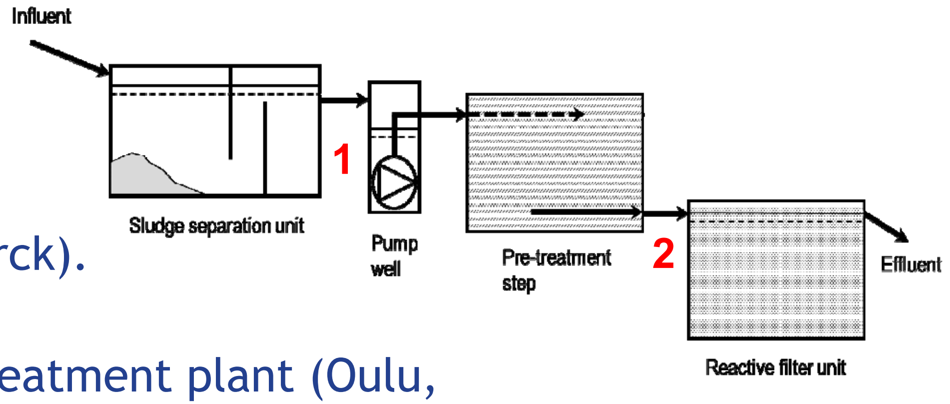
- The particles begin to bind together by the surface tension of the liquid
- The alkali activator starts to dissolve the precursor particles which enhance the binding
- Formation of alumina-silicate gel similar to “regular” geopolymers

ZEOLITES AND GEOPOLYMERS

- Geopolymers and zeolites consist of an anionic framework of corner-sharing SiO_4 and AlO_4 where the exchangeable cations are located in the voids

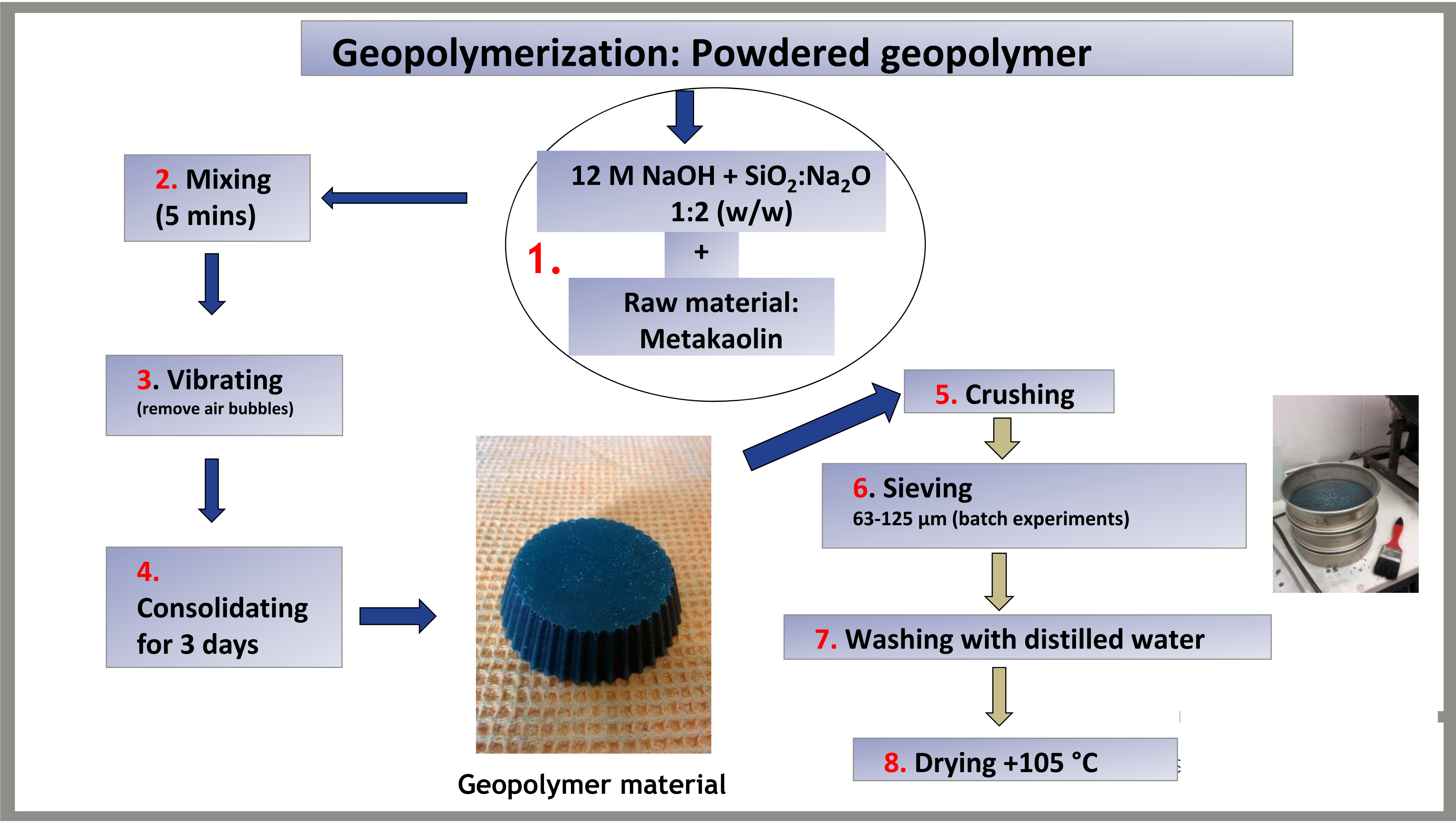
- **Main differences:**
  - Amorphous geopolymers vs. crystalline zeolites.
  - The synthesis of geopolymers is simpler and lower-energy compared to synthetic zeolites.
  - Geopolymer has higher ammonium removal capacity than typical natural zeolites.

MATERIALS AND METHODS



Samples

- **Model solution**: prepared of ammonium chloride (Merck).
- **Wastewater samples**: from the Taskila wastewater treatment plant (Oulu, Finland)
  → Collected samples:
  1) after aerated sand removal and screening (screened effluent).
  2) after aerated sand removal, screening, coagulation with polyaluminium chloride, and sedimentation (pre-sedimented effluent).


Geopolymerization: Powdered geopolymer
1.
12 M NaOH + SiO_2:Na_2O 1:2 (w/w)
+
Raw material: Metakaolin
2. Mixing (5 mins)
3. Vibrating (remove air bubbles)
4. Consolidating for 3 days
Geopolymer material
5. Crushing
6. Sieving 63-125 µm (batch experiments)
7. Washing with distilled water
8. Drying +105 °C

GEOPOLYMERIZATION: GRANULATED GEOPOLYMER

- Mixing metakaolin powder in a high shear granulator.
- Dosing the alkaline activator drop-wise until an L/S ratio of 0.4 (the maximum before agglomeration of granules started to occur) was reached.
- Sieving (1-4 mm).
- Consolidating for three days.
- Washed with deionized water before use.

BATCH SORPTION EXPERIMENTS

Sorption experiments

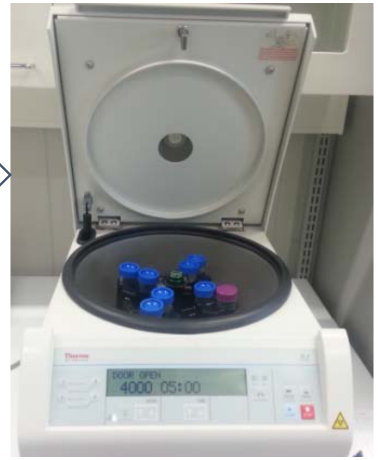
<u>Batch sorption experiments (powdered metakaolin geopolymer):</u>

→ effect of sorbent dose
(0.5–25 g/L, 24 h contact time)

→ effect of contact time
(1–1440 min, dose 5 g/L)

1. Mixing
- Adsorbent + Adsorbate (NH_4^+)
- Adjusting initial pH (HCl, NaOH)

2. Shaking



3.Separation
- Centrifuge
- 5 min, 4000 rpm

Continuous experiments

Column properties

Height [cm]	9.9
Diameter (inner) [cm]	4.4
Surface area [cm²]	15.2
Volume [L]	150

Continuous experiments (granulated metakaolin geopolymer)

	Test 1	Test 2
Mass of sorbent [g]	50	50
Particle size of sorbent [mm]	1–4	1–4
Flow rate [L/h]	0.5	1
Empty bed contact time (EBCT) [min]	3	6

1. Metakaolin geopolymer granules were washed (deionized water).
2. Pre-sedimented effluent was pumped through the column.
3. Effect of two contact times (EBCT): 3 and 6 min.
4. The bed was flushed (8 L of deionized water).

Regeneration

- Was performed two times

→ The NH_4^+ removal performance was tested after each regeneration cycle.

CHARACTERISTICS OF METAKAOLIN GEOPOLYMER

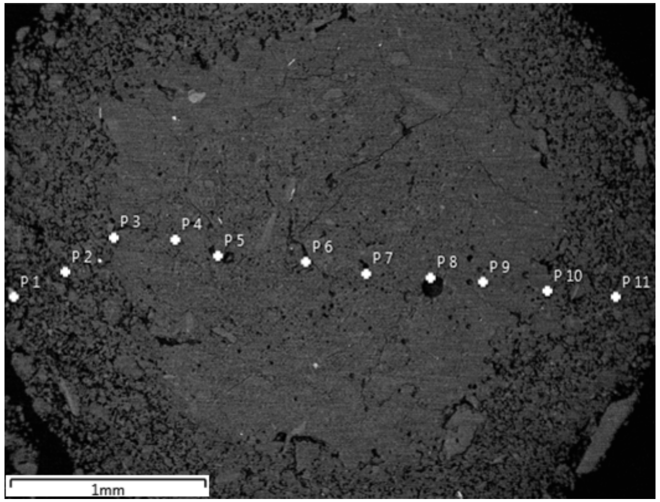
Characteristics of the metakaolin

- Amorphous material.
- Higher specific surface area and more porous than metakaolin.
- pH > 4.5, zeta potential negative.

- The core (diameter of approx. 2 mm, highlighted with white) denser than the porous surface layer (approx. 0.5 mm).

- No clear differences in the chemical composition across the granule → geopolymerization has taken place uniformly.

- Granules relatively high-strength (average 63.85 N)
- A large variation between individual granules (34–123 N, n = 11).



The cross-section of a granule

Chemical composition

Spectrum Label	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11
O	50.3	48.5	45.4	48.1	45.8	52.0	48.9	46.9	46.0	42.2	48.2
Na	2.0	6.7	6.3	6.7	7.5	3.8	3.1	5.4	7.1	6.0	7.0
Mg	0.2	-	0.33	0.7	0.3	1.6	0.2	0.6	0.4	0.25	0.4
Al	7.6	18.8	17.4	17.5	18.1	10.0	22.1	11.6	18.1	14.45	18.4
Si	8.4	23.4	25.4	22.3	24.0	18.6	24.2	14.5	23.7	28.64	23.9
S	-	-	-	0.2	-	1.2	-	-	-	-	-
K	0.5	0.8	1.6	1.9	1.7	1.7	0.7	1.1	2.5	6.39	1.0
Ca	29.7	-	0.3	0.3	0.2	5.3	-	-	-	-	-
Fe	1.2	1.7	3.2	2.2	2.4	4.6	0.7	20.0	2.2	2.1	1.2
Cu	-	-	-	-	-	1.4	-	-	-	-	-

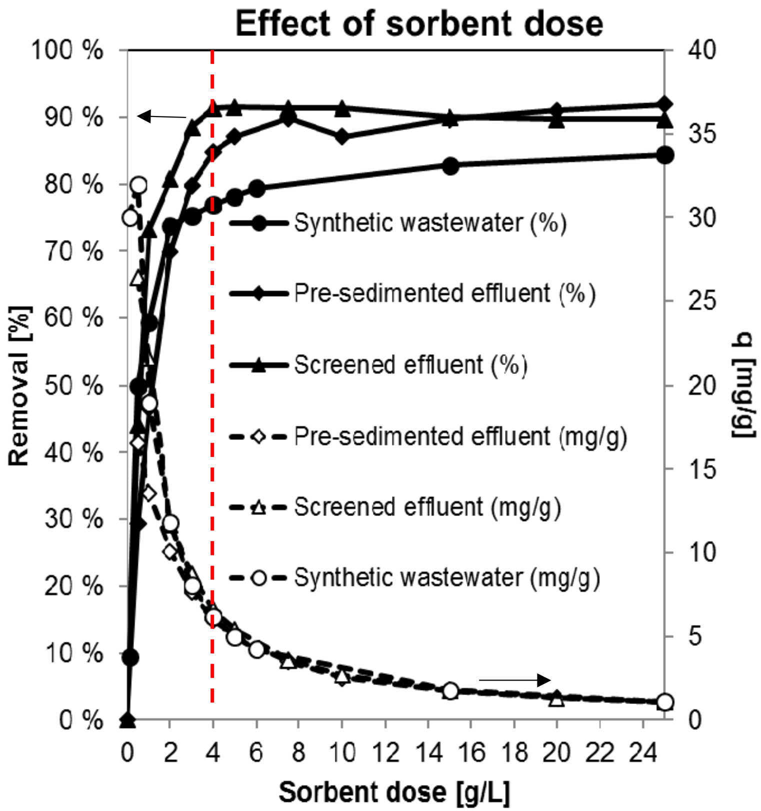
RESULTS: BATCH SORPTION STUDIES

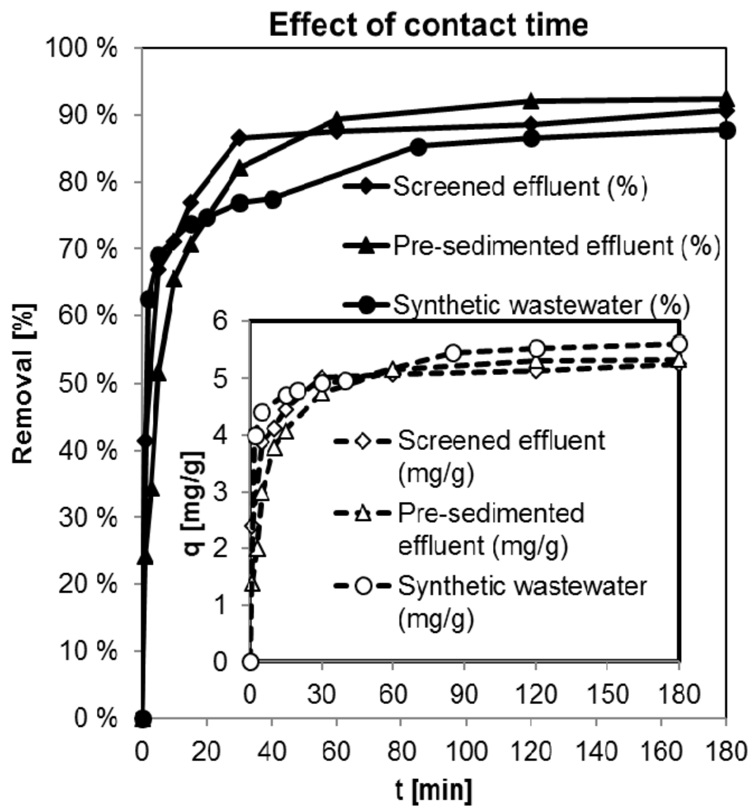
Effect of sorbent dose

- **Up to 80% removal reached.**
- **Selective towards NH_4^+.**
- **Wastewater physico-chemical characteristics** only **a minor effect on the NH_4^+ removal efficiency.**
- The increase of sorbent dose up to approx.4 g/L
  → increases NH_4^+ removal results significantly.
- **With larger doses**
  → the removal levels-off at **85–90%.**

Effect of contact time

- The sorption equilibrium reached after 30–90 min.





- **Sorbent:** Metakaolin geopolymer granules.
- **Initial NH_4^+ concentration** C_0:
  - ~ 32 mg/L (synthetic solution)
  - ~ 39 mg/L (pre-sedimented wastewater)
  - ~ 40 mg/L (screened wastewater)

RESULTS: ISOTHERMS AND KINETICS

Isotherms:

- The best-fitting model: Sips $q_e = \dfrac{q_m (K_s C_e)^{\beta_S}}{1 + (K_s C_e)^{\beta_S}}$
- Calculated and experimental values in agreement.
- The trend of q_m values:
  - synthetic wastewater > screened effluent > pre-sediment effluent.
- The pre-sediment effluent

→ A significant decrease of q_m
  - Addition of flocculant
  - pH adjustment chemicals (e.g. Ca concentration, pre-sediment effluent: 45 mg/L, screened effluent: 27 mg/L).

Kinetics:

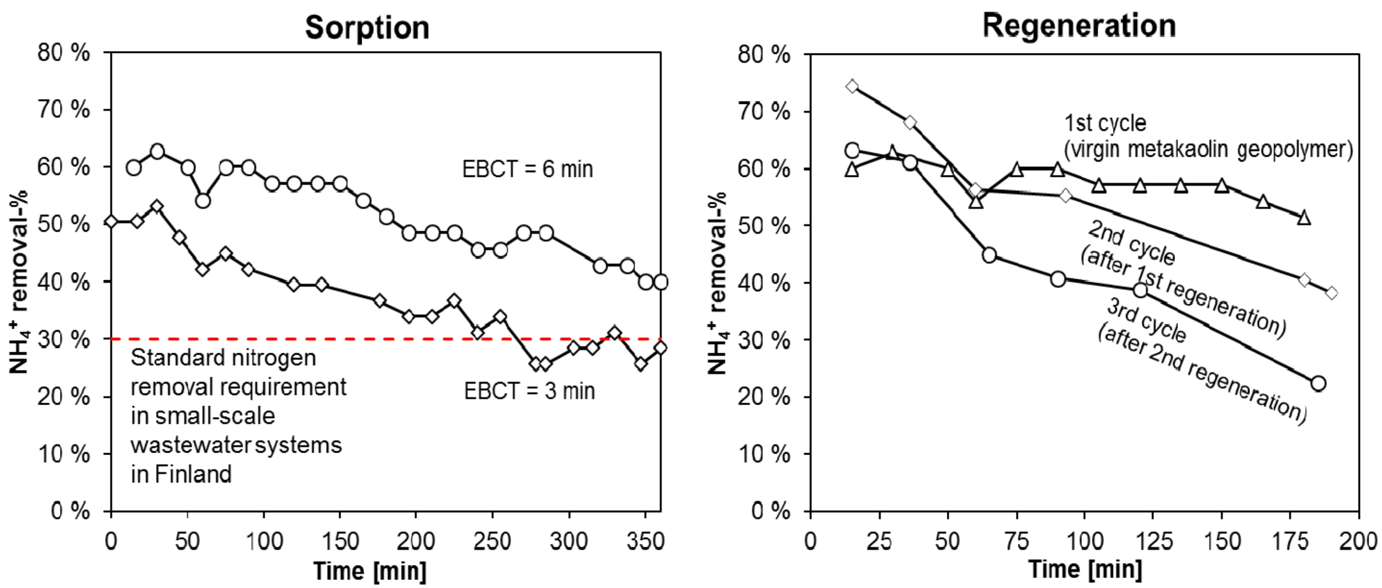
- The best fit model: Pseudo-second order model: $\dfrac{t}{q_t} = \dfrac{1}{k_s q_e^2} + \dfrac{1}{q_e} t$
- The trend of rate constants
  - synthetic wastewater > screened effluent > pre-sediment effluent.
- Calculated and experimental values in agreement.

Parameter	Synthetic wastewater	Pre-sedimented effluent	Screened effluent
Sips isotherm			
q_m, experimental [mg/g]	**32.00**	**16.59**	**26.40**
q_m, calculated [mg/g]	**31.79**	**17.75**	**28.77**
b [L/mg]	0.10	0.14	0.17
n	4.17	1.97	2.64
R^2	**0.96**	**0.97**	**0.91**
RMSE	2.53	1.08	2.86
X^2	2.29	2.45	16.18
Pseudo-second order rate equation			
q_e, experimental [mg/g]	**5.62**	**5.42**	**5.62**
q_e, calculated [mg/g]	**5.27**	**5.46**	**5.22**
k_{p2} [g/(mg min)]	0.24	0.04	0.12
R^2	**0.97**	**0.99**	**0.98**
RMSE	0.28	0.16	0.26

RESULTS: CONTINUOUS COLUMN EXPERIMENTS

Target:

- **To test the effect of empty bed contact time** (EBCT).
- **To compare the results to the standard nitrogen removal requirement in Finland** for small-scale wastewater treatment systems (i.e. 30%).



Results:

- **Possible to reach the requirement** with relatively short contact times (EBCT) - 6 and 3 minutes.

→ **The regeneration** (0.1 M NaOH and 0.2 M NaCl) **was succesful.**

- **Sorbent:** Metakaolin geopolymer granules.
- **Initial NH_4^+ concentration:** C_0: ~35.7 mg/L (the pre-sedimented effluent).

CONCLUSIONS

- **Granulated NH_4^+ sorbent from metakaolin**
  → Produced by using geopolymerization-granulation method.

- **Results:**

<u>Continuous filtration experiments (granulated metakaolin geopolymer):</u>

– The nitrogen removal requirement **(30– 40%)** for small-scale wastewater treatment systems (In Finland) possible to reach.
  → **Short contact time** (3–6 min).
  → **Possible to regenerate the granules** with dilute NaOH/NaCl solution.

<u>Batch sorption studies (powdered metakaolin geopolymer):</u>

– The maximum NH_4^+ sorption capacities:
  → **31.79 mg/g** with synthetic wastewater.
  → **28.77 mg/g** with screened municipal wastewater.

- **Summary:**

– Produced sorbent (metakaolin geopolymer):
  → **selective towards NH_4+.**
  → **the suitability for reactive filters** used in small-scale municipal wastewater systems **is promising.**
  → **could be regenerated or used as a fertilizer after use.**


THANK YOU FOR
YOUR ATTENTION
Questions?