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

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AMMONIUM, NH₄⁺

- 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).
- NH₄⁺ removal from municipal wastewaters is a challenge in small-scale wastewater 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 %)

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 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.
The most common geopolymer synthesis method:

- 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.

**Geopolymerization-granulation 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. Raw material: Metakaolin

2. Mixing (5 mins)

3. Vibrating (remove air bubbles)

4. Consolidating for 3 days

5. Crushing

6. Sieving
   63-125 µm (batch experiments)

7. Washing with distilled water

8. Drying +105 °C

12 M NaOH + SiO₂:Na₂O
1:2 (w/w)
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.
Sorption experiments

**Batch sorption experiments**  
(powdered metakaolin geopolymer):

→ 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 (NH₄⁺)  
- Adjusting initial pH (HCl, NaOH)

**2. Shaking**

**3. Separation**  
- Centrifuge  
- 5 min, 4000 rpm
Continuous experiments

Column properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height [cm]</td>
<td>9.9</td>
</tr>
<tr>
<td>Diameter (inner) [cm]</td>
<td>4.4</td>
</tr>
<tr>
<td>Surface area [cm²]</td>
<td>15.2</td>
</tr>
<tr>
<td>Volume [L]</td>
<td>150</td>
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</table>

Continuous experiments (granulated metakaolin geopolymer)

<table>
<thead>
<tr>
<th></th>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of sorbent [g]</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Particle size of sorbent [mm]</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Flow rate [L/h]</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Empty bed contact time (EBCT) [min]</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>

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 NH₄⁺ removal performance was tested after each regeneration cycle.
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 $\Rightarrow$ geopolymerization has taken place uniformly.
- Granules relatively high-strength (average 63.85 N)
- A large variation between individual granules (34-123 N, n = 11).
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.

**Materials and methods**

- 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
- 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:
- The trend of rate constants
  - synthetic wastewater > screened effluent > pre-sediment effluent.
- Calculated and experimental values in agreement.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Synthetic wastewater</th>
<th>Pre-sedimented effluent</th>
<th>Screened effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sips isotherm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m$, experimental [mg/g]</td>
<td>32.00</td>
<td>16.59</td>
<td>26.40</td>
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<tr>
<td>$q_m$, calculated [mg/g]</td>
<td>31.79</td>
<td>17.75</td>
<td>28.77</td>
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<tr>
<td>b [L/mg]</td>
<td>0.10</td>
<td>0.14</td>
<td>0.17</td>
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<tr>
<td>n</td>
<td>4.17</td>
<td>1.97</td>
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<tr>
<td>$R^2$</td>
<td>0.96</td>
<td>0.97</td>
<td>0.91</td>
</tr>
<tr>
<td>RMSE</td>
<td>2.53</td>
<td>1.08</td>
<td>2.86</td>
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<tr>
<td>$\chi^2$</td>
<td>2.29</td>
<td>2.45</td>
<td>16.18</td>
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<tr>
<td>Pseudo-second order rate equation</td>
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<tr>
<td>$q_{et}$, experimental [mg/g]</td>
<td>5.62</td>
<td>5.42</td>
<td>5.62</td>
</tr>
<tr>
<td>$q_{et}$, calculated [mg/g]</td>
<td>5.27</td>
<td>5.46</td>
<td>5.22</td>
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<tr>
<td>$k_{sp}$ [g/(mg min)]</td>
<td>0.24</td>
<td>0.04</td>
<td>0.12</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.97</td>
<td>0.99</td>
<td>0.98</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.28</td>
<td>0.16</td>
<td>0.26</td>
</tr>
</tbody>
</table>
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: $C_0$: $\approx$35.7 mg/L (the pre-sedimented effluent).
CONCLUSIONS

- **Granulated NH$_4^+$ sorbent from metakaolin**
  → Produced by using geopolymerization-granulation method.

- **Results:**

  **Continuous filtration experiments (granulated metakaolin geopolymer):**
  - 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.

  **Batch sorption studies (powdered metakaolin geopolymer):**
  - 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?