Application of metakaolin geopolymer for ammonium removal in small-scale wastewater treatment systems

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Abstract

Ammonium (NH_4^+) removal from municipal wastewaters represents a challenge in small-scale wastewater treatment systems. One approach is to use reactive filters in which different kinds of natural zeolites are the most studied sorbents. In the present study, a novel NH_4^+ filter material is presented: metakaolin geopolymer. Screened and flocculated-sedimented municipal wastewaters were used in the experiments. Effects of dose and contact time were studied with powdered material: 0.5 g/L and 20–30 min proved to be sufficient to meet the Finnish guidelines: 30% removal of total nitrogen. Continuous experiments confirmed that metakaolin geopolymer can be used also as a filter medium. Finally, the material could be regenerated or used as a fertilizer after use.

Keywords

Ammonium removal; geopolymer; metakaolin; reactive filters; adsorption

INTRODUCTION

Ammonium (NH_4^+) is a major contributor to the eutrophication of water bodies since nitrogen is commonly the nutrient in shortest supply. Therefore, the removal of nitrogen from wastewaters has become mandatory in several countries, also in small-scale wastewater treatment systems. For example, in Finland, the requirement for total nitrogen removal within small-scale wastewater systems is generally 30% and in the areas defined sensitive for contamination 40% (Finnish Council of State 2011). Furthermore, the requirement for the reclamation of nutrients (N and P) is also becoming mandatory for instance in Sweden (Rastas Amofah & Hanæus 2006).

Many frequently used treatment steps in small-scale wastewater systems remove nitrogen to some extent: for example septic tanks (3–20%), infiltration systems (10–40%), or sand filters (10–80%) (Hedström 2006a). Nitrogen removal within these processes is most likely a combination of microbial activity (nitrification–denitrification) and physico–chemical separation. Furthermore, specifically designed biofilm (Rodgers *et al.* 2006; Fox *et al.* 2016), membrane bioreactor (Abegglen *et al.* 2008; Ren *et al.* 2010) or other biological processes can be used for nitrogen removal. Suspended growth active sludge process is used at large-scale wastewater treatment plants but might not be suitable for small-scale systems. Biological nitrogen removal has a major limitation: as the temperature of wastewater is below +12 °C, the kinetics of nitrification and denitrification are significantly hindered. This limits their use only to a warm season in cool climate areas, such as in northern Scandinavia.

Sorption-based approaches such as reactive filters systems (Figure 1) offer a simple and more robust alternative method for NH_4^+ removal. Their main advantages are low dependency on temperature and possibility to recover nutrients. However, pre-treatment is required before the actual reactive filter in order to avoid clogging. The sludge separation unit, where the largest particles are separated, can be a septic tank, for instance (Hedström 2006b). The pre-treatment step, for example gravel bed, removes organic material and suspended solids (Jenssen *et al.* 2005). The reactive filter unit contains granular NH_4^+ sorbent material such as natural zeolites (of which clinoptilolite is the most widely studied) or wollastonite (Hedström 2006b; Hedström 2006c).

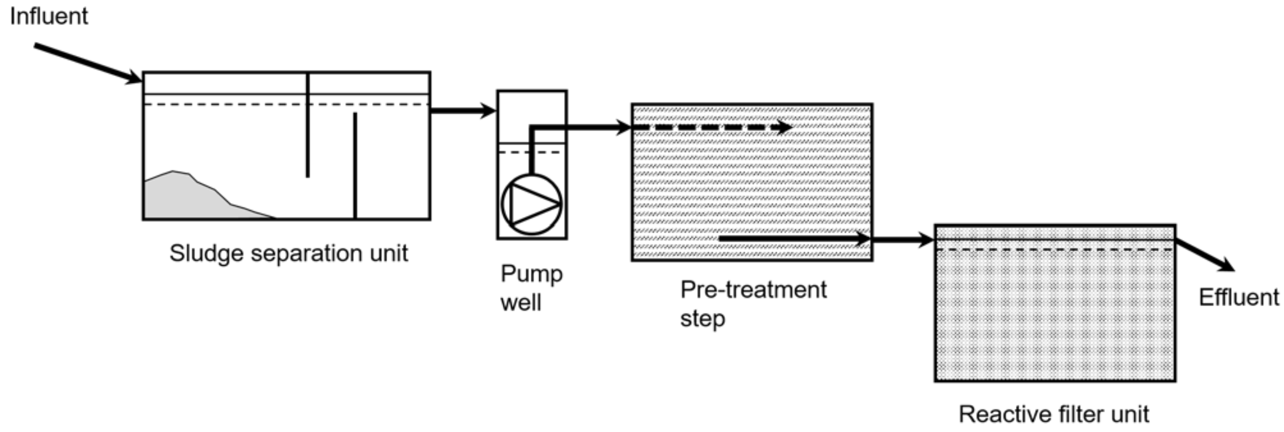

Figure 1. Small-scale wastewater treatment system involving sludge separation unit, pump well, pre-treatment step and reactive filter unit (Hedström 2006b).

Recently, a novel ammonium sorbent material was developed: metakaolin geopolymer (Luukkonen *et al.* 2016). The main advantages of this sorbent are simple and low-energy synthesis; low-cost and readily available raw materials; and higher ammonium removal capacity than with typical natural zeolites (Luukkonen *et al.* 2016). Geopolymers consist of an anionic framework of corner-sharing SiO_4 and AlO_4 where the exchangeable cations are located in the voids – similarly as with zeolites (Davidovits 2011). However, unlike zeolites, geopolymers are amorphous. The most common synthesis method involves a reaction between aluminosilicate raw material (such as metakaolin) and alkaline activator (commonly concentrated sodium hydroxide and silicate) at ambient or near-ambient temperature and pressure (Luukkonen 2016). The formation reactions of geopolymers include dissolution, gelation, reorganization, and hardening although the exact mechanism remains still unclear (Duxson *et al.* 2007).

Geopolymerization–granulation is a new method by which spherical geopolymer granules can be produced (Yliniemi *et al.* 2016). In short, the precursor particles are mixed inside a high shear granulator and as the alkali activator is added slowly on the particle flow, the particles begin to bind together by the surface tension of the liquid. In addition, the alkali activator starts to dissolve the precursor particles which enhance the binding. As the process continues larger and larger granules will form. The process is stopped once the desired granule size is achieved. Similarly to "normal" geopolymers, the granules are then left to harden to increase the strength of the granules.

In the present study, the geopolymerization–granulation process was applied for the first time in the production of NH_4^+ sorbent material. The resulting granules were studied for ammonium removal in a continuous filtration experiments with municipal wastewater. Different contact times and regeneration were studied. In addition, experiments with corresponding powdered sorbent were performed for comparison in synthetic and municipal wastewater. Based on the results, the suitability of metakaolin geopolymer granules for reactive filter systems is promising.

MATERIALS AND METHODS

Synthesis of geopolymers

Powdered geopolymer was synthesized by mixing metakaolin with alkaline activator in a liquid to solid weight ratio (L/S) of 1.0 for five minutes, allowed to consolidate at ambient temperature for three days, crushed to particle size of 63–125 µm, washed with deionized water, and stored in a desiccator before use. Alkaline activator contained 12 M sodium hydroxide (VWR Chemicals) and sodium silicate (Na_2O 8.2–9.2 % w/w, SiO_2 > 27.7 % w/w, VWR Chemicals) in a weight ratio of 1.2.

Granulated geopolymer was formed by mixing metakaolin powder in a high shear granulator (Eirich EL1) and dosing the alkaline activator drop-wise until an L/S ratio of 0.4 was reached. This L/S ratio was the maximum before agglomeration of granules started to occur. After granulation, the particle size of 1–4 mm was separated by sieving, granules were allowed to consolidate for three days, and material was washed with deionized water before use.

Characterization of geopolymers

The composition of granule cross-sections were determined by FE-SEM-EDS (field emission scanning electron microscopy with energy dispersive X-ray spectrometer) using Zeiss Ultra plus instrument with Oxford Instruments INCA system EDS software. Prior the FE-SEM-EDS analysis, granules were cast in epoxy resin and polished to reveal the cross-section. Densities, amount of voids, and water absorption of granules were determined according to the standard methods (SFS-EN ISO 1097-3 1998; SFS-EN 1097-6 2014). Compressive strength of granules was determined with Zwick Roell Z010 instrument.

Sorption experiments

Two wastewater samples were collected from the Taskila wastewater treatment plant (Oulu, Finland): 1) after aerated sand removal and screening (referred to as “screened effluent”) and 2) after aerated sand removal, screening, coagulation with polyaluminium chloride, and sedimentation (referred to as “pre-sedimented effluent”). These two process phases were selected to simulate the sludge separation unit and pre-treatment shown in Figure 1. The effect of sorbent dose (0.5–25 g/L, 24 h contact time) and contact time (1–1440 min, dose 5 g/L) were studied. Similar experiments were performed also with model solution prepared of ammonium chloride (Merck). The effect of NH_3–NH_4^+ equilibrium on the removal was studied by adjusting the model solution pH in the range of 3–10 without sorbent, mixing for 24 h, and comparing to the results obtained with sorbent.

Continuous experiments were performed by weighing 50 g of granules (1–4 mm) into a plastic column (inner height 99 mm, width 44 mm, and volume 0.150 L), washing with deionized water, and pumping pre-sedimented effluent through the column using flow rates of 0.5 and 1.0 L/h corresponding to 3 and 6 min empty bed contact time, respectively. After filtration, the bed was flushed with 8 L of deionized water. Regeneration of sorbent was performed by pumping 2 L of 0.1 M NaOH and 0.2 M NaCl solution through the column using 2 L/h flow rate and rinsing with 8 L of deionized water. Regeneration was performed two times and the NH_4^+ removal performance was tested after each regeneration cycle.

RESULTS AND DISCUSSION

Characteristics of metakaolin geopolymer

Detailed characteristics of the metakaolin geopolymer powder are presented elsewhere (Luukkonen *et al.* 2016). In short, metakaolin geopolymer is X-ray amorphous and has higher specific surface area and is more porous than metakaolin. Infrared spectrum, ^{27}Si and ^{29}Al MAS-NMR (magic angle spinning nuclear magnetic resonance) spectra indicate change of chemical structure of metakaolin after geopolymerization. Zeta potential of metakaolin geopolymer is negative when pH > 4.5.

The cross-section of a granule (Figure 2) shows that the core (diameter of approx. 2 mm, highlighted with white) is denser than the porous surface layer (approx. 0.5 mm). However, there are no clear differences in the chemical composition (Table 1) across the granule indicating that geopolymerization has taken place uniformly.

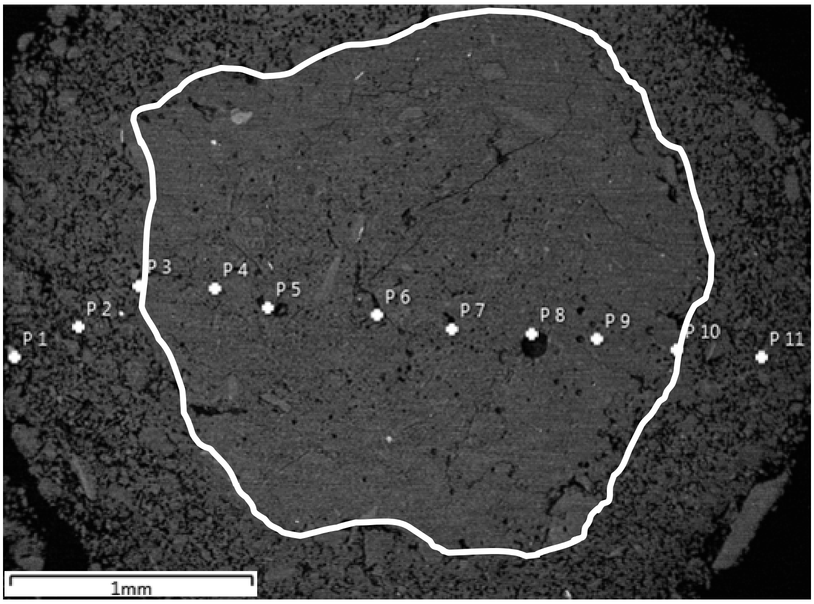

Figure 2. Cross section of metakaolin geopolymer granule. The results of point analysis are shown in Table 1. The inner denser core has been highlighted with white colour.

Table 1. Semi-quantitative energy dispersive spectrum (EDS) analysis of points shown in Figure 2.

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	-	-	-	-	-

Physical properties of granules are shown in Table 2. Compressive strength gives an indication of granule quality: the obtained granules were relatively high-strength (average 63.85 N) but there was a large variation between individual granules (34–123 N, n = 11). Based on the performed filtration experiments, this strength appears to be sufficient.

Table 2. Physical properties of metakaolin geopolymer granules (1–4 mm).

Property	**Formula**	**Value**
Loose bulk density, ρ_b	$\rho_b = \frac{m_2 - m_1}{V}$	932.3 kg/m^3
Percentage of voids, v	$v = \frac{\rho_{rd} - \rho_b}{\rho_{rd}} \times 100$	57.9 %
Apparent particle density, ρ_a	$\rho_a = \rho_w \frac{M_4}{M_4 - (M_2 - M_3)}$	2510 kg/m^3
Oven dried particle density, ρ_{rd}	$\rho_{rd} = \rho_w \frac{M_4}{M_1 - (M_2 - M_3)}$	2220 kg/m^3
Saturated and surface-dried particle density, ρ_{ssd}	$\rho_{ssd} = \rho_w \frac{M_1}{M_1 - (M_2 - M_3)}$	2330 kg/m^3
Water absorption, WA_{24}	$WA_{24} = \frac{100 \times (M_1 - M_4)}{M_4}$	5.3 %
Compressive strength	-	63.85 N (average, n = 11)

m_2 = mass of the container and test specimen [kg], m_1 = empty container [kg], V = volume of the container [m^3], ρ_w = density of water [kg/m^3], M_1 = the mass of the saturated and surface-dried aggregate in the air [g], M_2 = the apparent mass in water of the basket containing the sample of saturated aggregate [g], M_3 = the apparent mass in water of the empty basket [g], M_4 = the mass of the oven-dried test portion in air [g].

Ammonium removal with powdered metakaolin geopolymer: batch experiments

The differences in the NH_4^+ removal from screened, pre-sedimented, and synthetic wastewater are small: in all cases up to 90% removal is reached (Figure 3). This indicates that the sorbent is selective towards NH_4^+ and wastewater physico–chemical characteristics (Table 3) have only a minor effect on the removal efficiency. The increase of sorbent dose (Figure 3A) up to approx. 4 g/L increases NH_4^+ removal results significantly but with larger doses the removal levels-off at 85–90%. The sorption equilibrium is reached after 30–90 min (Figure 3B).

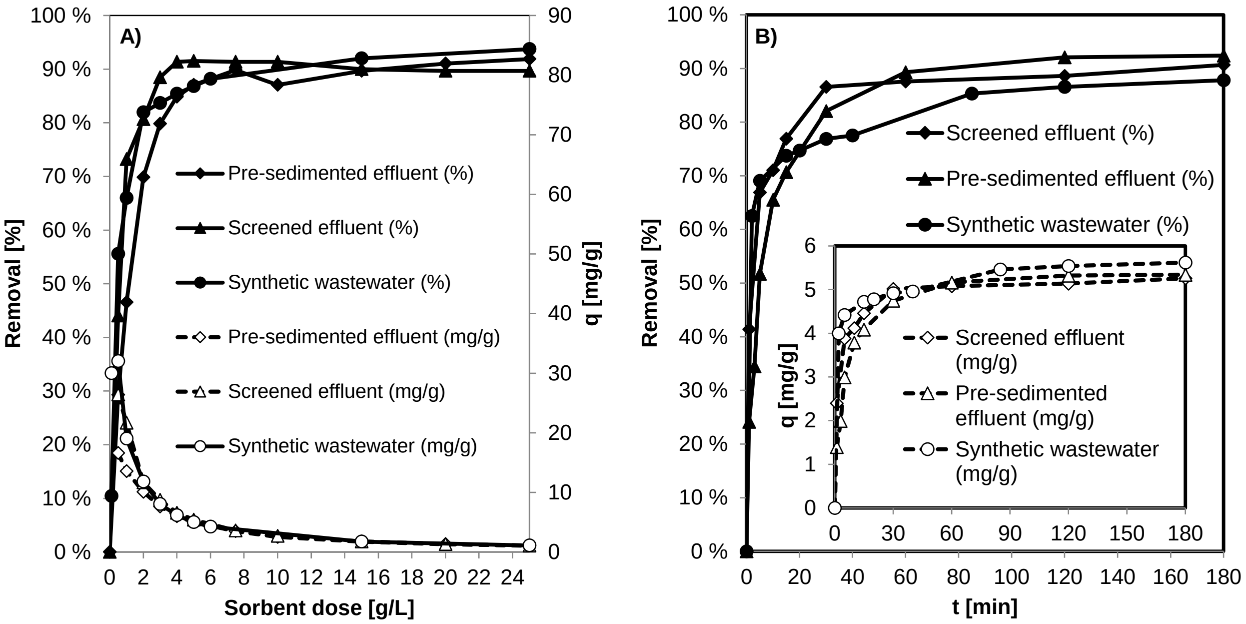

Figure 3. Ammonium removal results from screened, pre-sedimented, and synthetic wastewater: A) effect of sorbent dose and B) effect of contact time. Initial NH_4^+ was 32, 39, and 40 mg/L in synthetic, pre-sedimented and screened wastewater, respectively.

Table 3. Physico–chemical characteristics of synthetic, pre-sedimented and screened wastewaters.

Parameter	Synthetic wastewater	Pre-sedimented effluent	Screened effluent
pH	6.1	7.5	7.2
COD_{Cr} [mg/L]	-	570	642
TSS [mg/L]	-	419	550
NH_4^+ [mg/L]	32	37	40
Al [µg/L]	-	8	12
P [µg/L]	-	25	360
Ni [µg/L]	-	6.0	5.8
Cu [µg/L]	-	1.8	4.2
Zn [µg/L]	-	150	170
Ca [mg/L]	-	45	27
Mg [mg/L]	-	5.3	4.4
Mn [mg/L]	-	0.2	0.1

Based on the data presented in Figure 3A, isotherm fitting was performed. Several isotherms were applied and the best-fitting model was the Sips isotherm (Sips 1948) and thus only its data is shown. The Sips isotherm can be written as:

$$q_e = \frac{q_m (bC_e)^n}{1+(bC_e)^n} \tag{1}$$

where q_e (mg/g) is the equilibrium sorption amount; q_m (mg/g) corresponds to the maximum sorption capacity; b (L/mg) is a parameter related to the energy of sorption; C_e (mg/L) is the equilibrium concentration of NH_4^+; and the exponent n (dimensionless) describes the heterogeneity of the sorbent surface. The kinetics data (Figure 3B) was best described using the pseudo-second order rate equation (Equation 2) which can be integrated with the condition $q_t = 0$ when $t = 0$ (Equation 3).

$$\frac{dq_t}{dt} = k_{p2}(q_e - q_t)^2 \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_{p2}q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_t [mg/g] is the sorption amount at time t [min], k_{p2} [g/(mg min)] is the pseudo-second order rate constant.

The parameters obtained from isotherm and kinetics modelling are shown in Table 4. The maximum sorption capacity (q_m) is higher than typically reported for natural zeolites although some synthetic zeolites have still a higher capacity (Luukkonen *et al.* 2016). The maximum capacity is only slightly reduced when comparing synthetic wastewater and screened effluent. However, a significant decrease of q_m is observed with the pre-sedimented effluent. This could be due to the addition of flocculant and pH adjustment chemicals: for example calcium concentration (45 mg/L) is higher than with the screened effluent (27 mg/L) (see Table 2). This result indicates that NH_4^+ sorption with metakaolin geopolymer could be more efficient before possible chemical treatment steps (which are seldom used in systems shown in Figure 1). Also with the kinetics, the trend of rate constants is the same: synthetic wastewater > screened effluent > pre-sedimented effluent. Calculated and experimental capacity values from isotherm and kinetics modelling (q_m and q_e, respectively) are in agreement.

Table 4. The parameters for isotherm and kinetics models.

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

RMSE = residual mean square error, X^2 = chi square test.

Due to the alkaline synthesis conditions, metakaolin geopolymer increases pH even after careful rinsing (Figure 4A). The increase of pH is pronounced in synthetic wastewater due to the lack of pH buffering capacity. However, with well-buffered real wastewater effluents, pH begins to increase only when the dose of sorbent is larger than 5 g/L. A blank experiment without dosing sorbent but increasing pH was conducted to see the contribution of pH change and possible volatilization of NH_3 gas on the NH_4^+ removal. The results of the blank experiment (not shown) indicated that NH_3 volatilization started to contribute when pH was larger than 9 as suggested by the dissociation constant of ammonia: $pK_a = 9.25$ at 25 °C (Figure 4B) (Lide 2003). However, the contribution of volatilization was rather minor (max. 6 % removal) up to pH 11. Consequently, the volatilization of

NH_3 has some effect on the sorption of NH_4^+ from synthetic wastewater but only a minor effect in the case of municipal wastewater in the present experimental set-up.

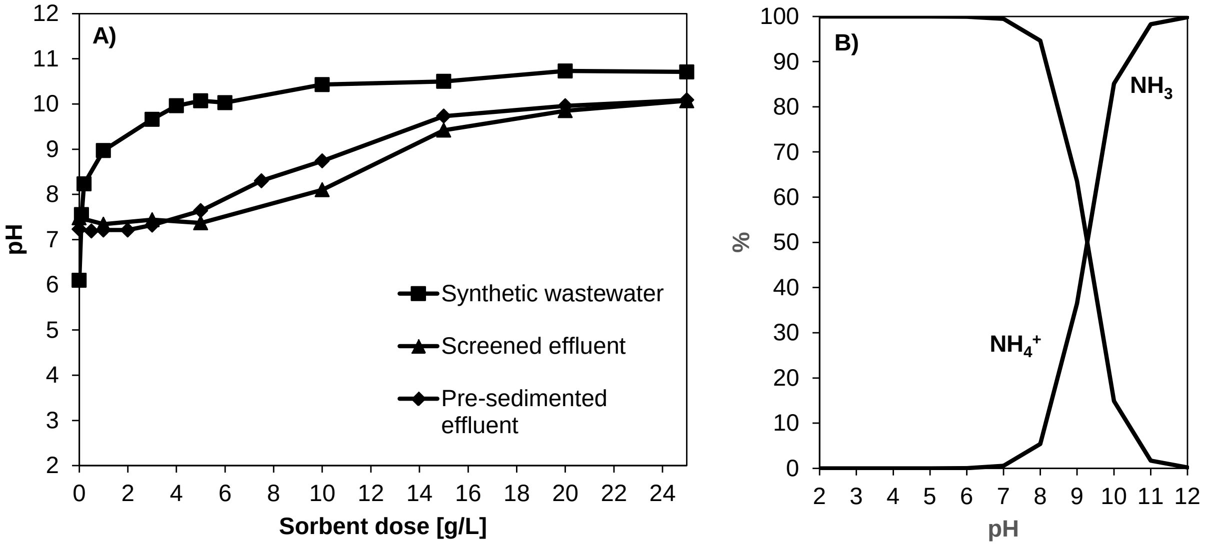

Figure 4. A) change of pH as a result of sorbent dose in synthetic wastewater, screened effluent and pre-sedimented effluent and B) speciation of NH_4^+ and NH_3 (calculated with MineQL+).

Ammonium removal with geopolymer granules: continuous column experiments

Metakaolin geopolymer granules were tested in column experiments using the pre-sedimented effluent. These tests were used to preliminarily determine the effect of empty bed contact time (EBCT) and compare the obtained results to the standard nitrogen removal requirement in Finland for small-scale wastewater treatment systems (i.e. 30%). The results (Figure 5A) indicate that already with relatively short contact times (3 and 6 min) it was possible to reach the requirement. The increase of EBCT from 3 to 6 min increases the NH_4^+ removal 10–20 percentage points. The regeneration with 0.1 M NaOH and 0.2 M NaCl solution was successful (Figure 5B) although the successive regeneration cycles decreased the NH_4^+ removal efficiency. However, at the beginning of the 2nd cycle (after the first regeneration) NH_4^+ removal was more efficient than with virgin metakaolin geopolymer for approx. 1 h.

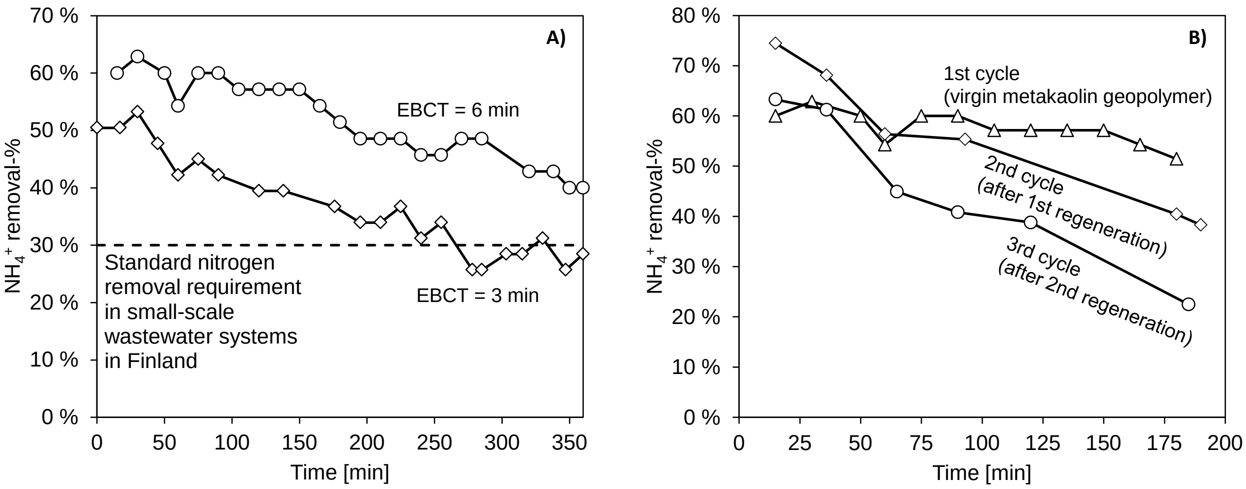

Figure 5. Continuous column experiments with pre-sedimented effluent: A) using empty bed contact times (EBCT) of 6 and 3 min; B) regeneration experiments. The initial NH_4^+ was 35.7 mg/L on average.

CONCLUSIONS

Geopolymerization–granulation proved to be a suitable process for producing granulated NH_4^+ sorbent from metakaolin. The sorbent can be utilized for instance in reactive filters used in small-scale municipal wastewater treatment systems. Continuous filtration experiment results indicated that the nitrogen removal requirement in Finland for small-scale wastewater treatment systems (30 or 40%) was possible to reach already with short contact times (3–6 min). Furthermore, it was possible to regenerate the granules successively with dilute NaOH/NaCl solution. Results from batch experiments with powdered metakaolin geopolymer indicated that the maximum NH_4^+ sorption capacity was 31.79 mg/g with synthetic wastewater and 28.77 mg/g with screened municipal wastewater according to the Sips isotherm. Therefore, the sorbent seems to be selective towards NH_4^+.

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