

Ammonium uptake over analcime and its soil enhancer potential

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Abstract: Leaching of ammonium-nitrogen cause's eutrophication in water bodies and it evaporates easily as ammonia gas when applied as fertilizer. The use of industrial process based analcime to uptake ammonium (NH_4^+) from synthetic and authentic wastewaters for soil enhancer purposes was studied in this paper. Sorption occurred during the first 20 minutes of contact time. NH_4^+ removal improved with increasing analcime dose and removal decreased when initial NH_4^+ concentration increased above 150 mg/L. Temperature did not have a clear impact on the NH_4^+ removal up to temperatures of 90°C. However, at 120°C, the NH_4^+ uptake increased considerably and the NH_4^+ concentration in analcime was 2.85 m%. This was explained by the formation of ammonioleucite. With real agricultural slurry the removal percentages were small. Results show that analcime releases NH_4^+ slowly during a long time period. It could be mixed directly to soil together with NH_4^+ containing fertilizer to reduce ammonia losses.

Keywords: analcime; zeolite; ammonium; sorption; soil enhancer

1. Introduction

Zeolites are crystalline, hydrated aluminosilicate minerals with a three-dimensional framework, which consists of SiO_4 and AlO_4 tetrahedra linked with shared oxygen atoms. Zeolites possess large surface area and high cation exchange capacity and consequently they have been frequently applied as sorbents in water and wastewater treatment [1]. The most common types of zeolites are clinoptilolite, mordenite, dachiardite, analcime, phillipsite and heulandite. In addition to natural mineral sources, analcime [$\text{Na}_{16}(\text{Al}_{16}\text{Si}_{32}\text{O}_{96}) \cdot 16\text{H}_2\text{O}$] is formed as a by-product when lithium carbonate is produced from spodumene ($\text{LiAlSi}_2\text{O}_6$) using sodium pressure leaching process [2]. Zeolites have been reported to be effective in removing variable size cations from wastewaters, such as dyes [3,4], organics [5,6], NH_4^+ [7,8], and metal ions [9,10]. Also analcime has been reported to be a sorbent in the wastewater treatment [11–13].

Nitrogen rotation in ecosystems is one of the most critical factors globally for both the environment and the food supply. Nitrogen is one of the main nutrients in wastewaters promoting the growth of organic matter and algae, which cause eutrophication in water bodies. In fact, ammonium-nitrogen (NH_4^+) is more severe in term of eutrophication than the other common nitrogen species nitrate (NO_3^-) [14]. Discharges of nitrogen are known e.g. for agriculture and for biogasification reject waters. Nitrogen is often present in the form of NH_4^+ , the ion which is not easy to precipitate, and therefore it is removed in the biological process by nitrification and denitrification. One challenge is also pH as NH_4^+ -ammonia equilibrium is pH-dependent and NH_4^+ volatilizes easily as ammonia gas at alkaline conditions [15]. Also, nitrogen fertilizers are produced mainly by using the energy-intensive Haber–Bosch reaction, which causes large amounts of greenhouse gas emissions, as production consumes high amounts of natural gas [16]. The challenge of adequacy of nutrients and food production without increasing environmental load can be met by improving the circulation of nutrients in use. However, if agricultural sludges and manures are applied to fields as such, up to 30% of the NH_4^+ is volatilized as ammonia [17]. Ammonia losses could be reduced for example by binding NH_4^+ to zeolites. Zeolites release NH_4^+ into the soil slowly and gradually not only in the first year of the vegetation period but also in the following years. Clinoptilolite is already used commercially in agriculture as an ammonium carrier [18]. Also natural analcime has shown potential in NH_4^+ uptake [19].

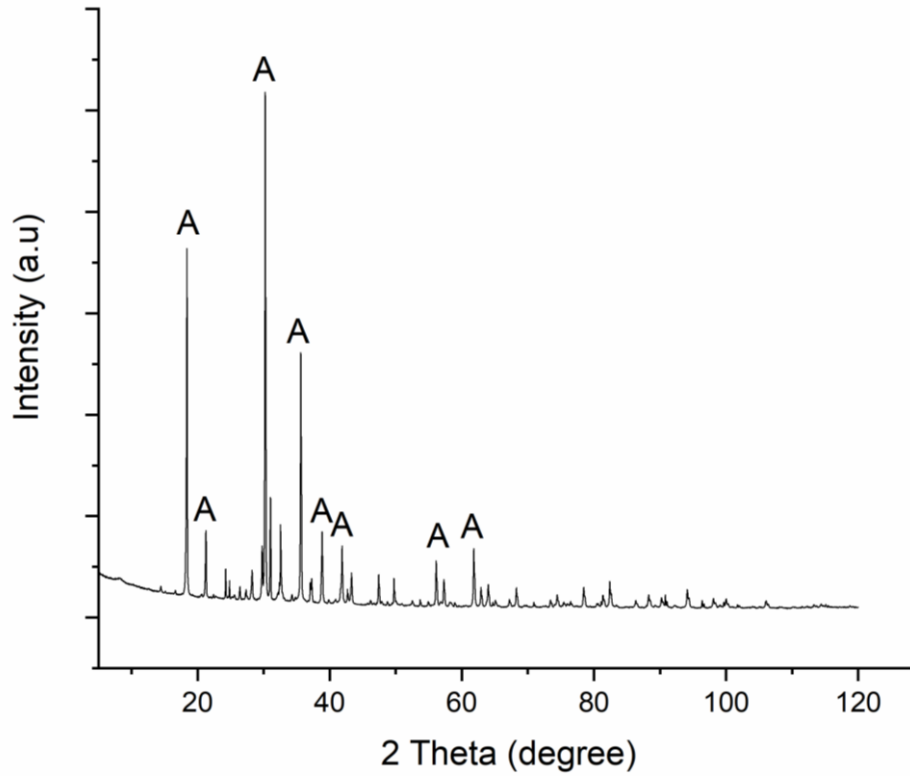
In the present study, the use of industrial process based analcime to uptake NH_4^+ -nitrogen via sorption for soil enhancer purposes was studied. The effect of analcime dosage, contact time, temperature, and initial NH_4^+ concentration on the NH_4^+ uptake potential of analcime was studied. Also, the leaching of NH_4^+ ions and the solubility of harmful elements from the analcime was studied to assess the potential of analcime to be applied as a soil improver.

2. Materials and methods

Analcime was received from a Finnish mining company. It was a side stream from lithium carbonate production. Analcime was dried in a hot air oven for 24–48 h at $105 \pm 2^\circ\text{C}$. Chemical composition of the analcime is presented in Table 1 and XRD diffractogram in Fig. 1. Main components were SiO_2 , Al_2O_3 and Na_2O . All the main spikes in the XRD diffractogram were associated with analcime.

Table 1 Chemical composition of analcime measured by XRF

	Na ₂ O (%)	MgO (%)	Al ₂ O ₃ (%)	SiO ₂ (%)	P ₂ O ₅ (%)	K ₂ O (%)	CaO (%)	TiO ₂ (%)	Cr ₂ O ₃ (%)	MnO (%)	FeO (%)
Analcime	9.4	0.5	19.2	53.2	0.2	0.6	1.2	0.1	0.02	0.4	3.5

**Fig. 1** XRD diffractogram of the analcime. A = analcime

NH₄⁺ uptake experiments were conducted in batch mode with synthetic NH₄⁺ solution and agricultural slurry from a Finnish farm. Synthetic NH₄⁺ solution was prepared from NH₄Cl salt. Agricultural slurry contained 176 mg/L NH₄⁺, 25 mg/L phosphate and the pH value was 8.95. Analcime dosage was 5–500 g/L, concentration of synthetic NH₄⁺ solution was 50–1000 mg/L, volume of NH₄⁺ solution was 50 mL (150 mL in autoclave), and initial pH 2 (adjusted with HCl). Used temperatures were 8 ± 1°C, 22 ± 1°C, 40 ± 1°C, 60 ± 1°C, 80 ± 1°C in water bath and 90 ± 1°C and 120 ± 1°C in autoclave. Samples were shaken or stirred during contact time. All NH₄⁺ uptake experiments were performed as duplicate. Solids were separated from NH₄⁺ solution by centrifuging before measuring NH₄⁺ concentration with a Hach Lange IntelliCal NH₄⁺ ISE- electrode.

The harmful element concentrations were characterized by aqua regia digestion according to standard ISO 11466 [20] and analyzed with ICP-OES technique (Perkin Elmer Optima 5300 DV). The 4-step sequential leaching procedure [21,22] used in this study is presented in Table 2. The eluates from each step were separated from the residue by centrifuging for 20 min (4500 rpm) and analyzed with ICP-OES.

Table 2 4-step sequential leaching procedure [21,22]

Step	Fraction	Extractant	Experimental conditions
F1	Water-soluble	40 cm ³ H ₂ O at pH 4 (with HNO ₃)	16 h at 22 ± 1°C, constant shaking
F2	Exchangeable and acid soluble	40 cm ³ HOAc 0.11 mol/L	16 h at 22 ± 1°C, constant shaking
F3	Reducible	40 cm ³ NH ₂ OH·HCl 0.5 mol/L at pH 1.5 (with HNO ₃)	16 h at 22 ± 1°C, constant shaking
F4	Oxidizable	10 cm ³ H ₂ O ₂ 300 g/L	1 h at 22 ± 1°C, occasional manual shaking, then 1 h 85 ± 2 °C. Reduce the volume to less than 3 cm ³
		10 cm ³ H ₂ O ₂ 300 g/L	1 h at 85 ± 2°C. Reduce the volume to 1 cm ³
		50 cm ³ NH ₄ OAc 1 mol/L at pH 2 (with HNO ₃)	16 h at 22 ± 1°C

Neutralizing values were determined according to European standard EN 12945 [23]. The composition of the analcime was characterized using a sequential XRF (S4 Pioneer, Bruker AXS) and XRD (Rigaku SmartLab 9 kW with PDXL2 software). Nitrogen contents in the analcime after NH₄⁺ uptake were measured by using a Perkin Elmer 2400 series II CHNS/O analyser.

Release of NH₄⁺ ions from the analcime was tested after NH₄⁺ uptake experiments (1000 mg/L NH₄⁺ solution, 4 h contact time, temperature 22 ± 1°C, and analcime dose 5 g/L) by shaking the analcime after ammonium uptake for 24 h at room temperature 22 ± 1°C, either in distilled water (stages 1–2) or in 0.1 M NaCl solution (stages 3–10). Liquid was separated from the solid matter by centrifuging (20 min., 4500 rpm) and NH₄⁺ concentration was measured with a Hach Lange IntelliCal NH₄⁺ ISE- electrode. Procedure was repeated ten times (10 stages in total).

3. Results and discussion

3.1 NH₄⁺ uptake experiments

Effect of analcime dose

Effect of analcime dose (5-500 g/L) on the removal percentage of NH₄⁺ is presented in Fig. 2. NH₄⁺ model solution concentrations were 50 mg/L or 1000 mg/L with treatment time 4 h at room temperature (22 ± 1°C). The NH₄⁺ removal percentage increased as the analcime dose increased. The NH₄⁺ removal was 37.4% as analcime dose was 200 g/L and 70.8% as analcime dose was 500 g/L. However, when analcime dose was 500 g/L, the pH increased to 9.5, which could partly explain the quite high removal percentage. With the 50 mg/L NH₄⁺ solution, the NH₄⁺ removal increased up to 53.1% (analcime dose 200 g/L). The sorption capacity (q) decreased with increasing analcime dose. The highest sorption capacity (3.55 mg/g) was achieved with analcime dose 20 g/L when initial NH₄⁺ concentration was 1000 mg/L. Final pH of the solution was below 7.5 up to analcime dose of 200 g/L, indicating that no losses of ammonia occurred during experiments.

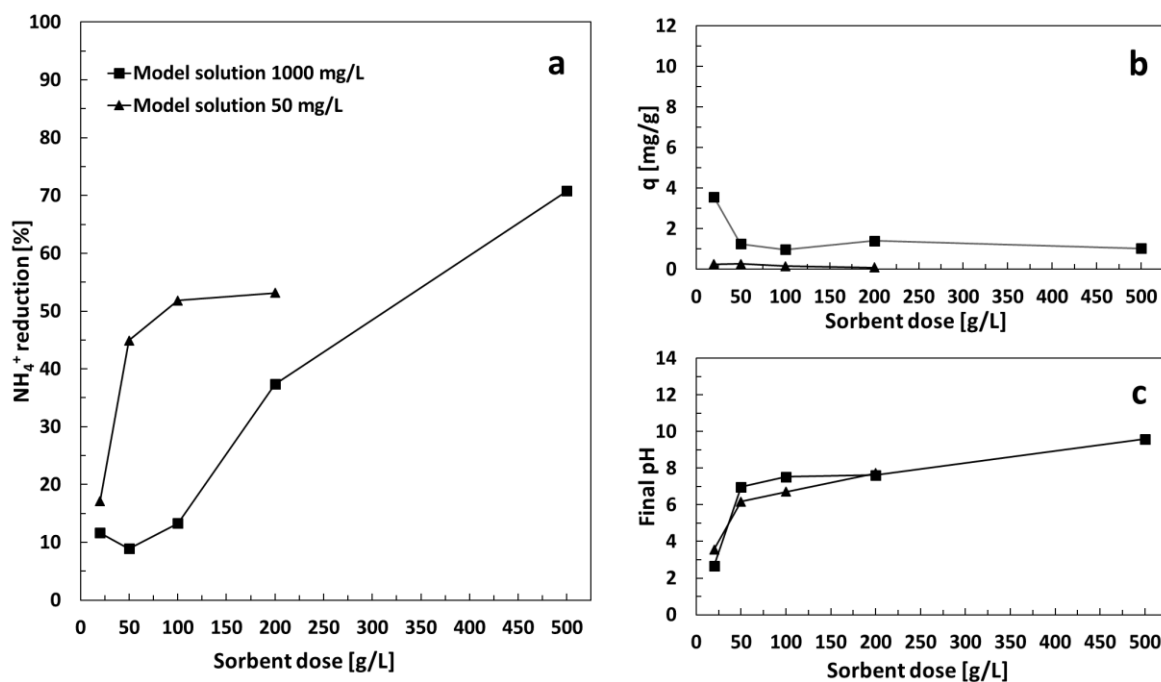


Fig. 2 Effect of analcime dose on the removal percentage (a) and sorption capacity (b) of NH_4^+ , and the effect of analcime dose on the final pH value (c). NH_4^+ model solution concentrations were 50 mg/L or 1000 mg/L, treatment time 4 h at room temperature ($22 \pm 1^\circ\text{C}$)

Effect of initial NH_4^+ concentration

Effect of initial NH_4^+ concentration (25–1000 mg/L) on the removal percentage of NH_4^+ is presented in Fig. 3. Analcime dose was 200 g/L with 4 h treatment time at room temperature ($22 \pm 1^\circ\text{C}$). The highest removal percentage (62.4%) was achieved as the initial NH_4^+ concentration was 150 mg/L and the lowest removal efficiencies (33.1–37.4%) were achieved when the initial NH_4^+ concentration was 800–1000 mg/L. However, the sorption capacity (q) increased with increasing NH_4^+ concentration (from q : 0.04 mg/g (25 mg/L) to 1.4 mg/g (1000 mg/L)). The increase of sorption capacity as a function of increasing initial NH_4^+ concentration indicate that suitable specific sorption sites are occupied at first [24]. The final pH of the solution decreased from 9.1 to 7.6 as initial NH_4^+ concentration increased from 25 mg/L to 1000 mg/L apparently because the increasing ionic strength caused by NH_4Cl causes some buffering.

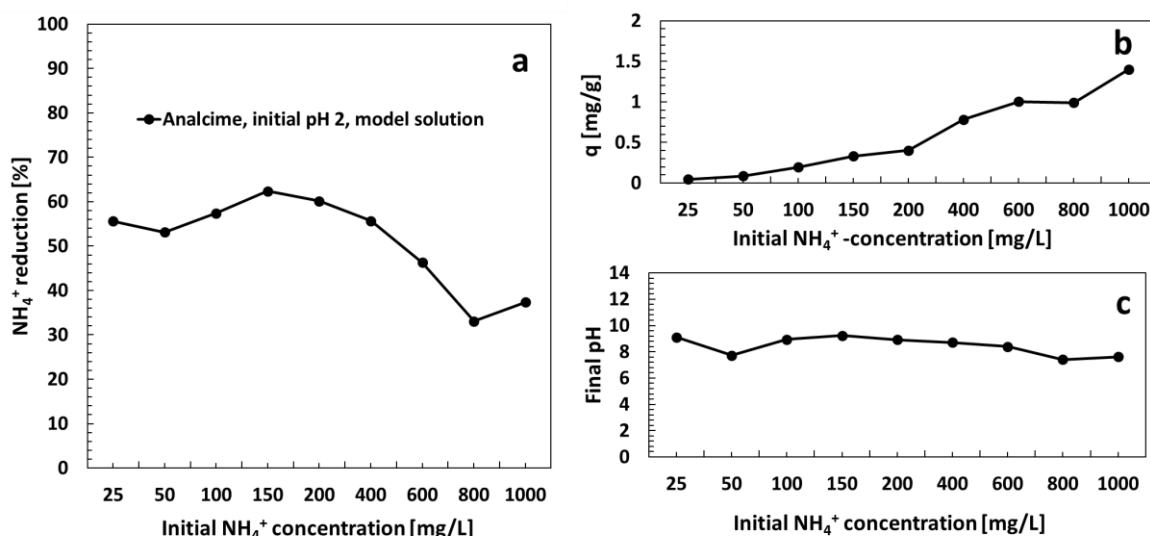


Fig. 3 Effect of initial NH_4^+ concentration on the removal percentage (a) and sorption capacity (b) of NH_4^+ , and on the final pH value (c). Sorbent dose was 200 g/L, treatment time 4 h at room temperature ($22 \pm 1^\circ\text{C}$)

Effect of contact time

Effect of contact time (0-360 min.) on the removal percentage of NH_4^+ is presented in Fig. 4. Removal percentage rose to around 40% during the first 20 minutes and settled there until 180 minutes. At the end of the experiment, the removal percentage was 56%. However, results showed that total sorption equilibrium was not reached within 360 minutes and therefore it is possible that some NH_4^+ evaporated as ammonia gas, which would explain why removal percentage keeps rising after 180 minutes.

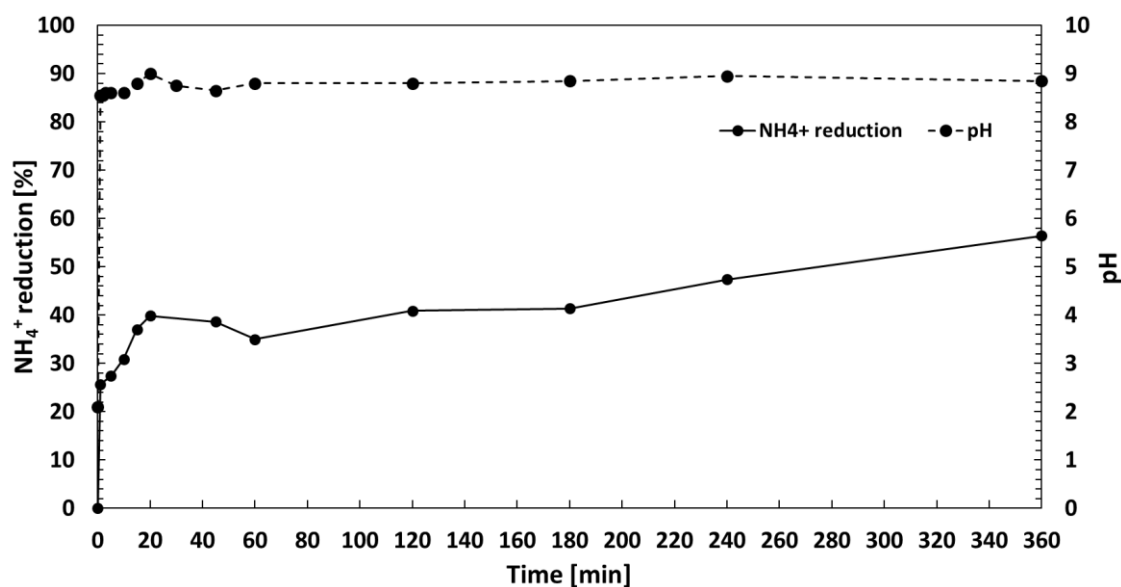


Fig. 4 Effect of time on the removal percentage of NH_4^+ . Sorbent dose was 20 g/L and initial NH_4^+ concentration was 100 mg/L at room temperature ($22 \pm 1^\circ\text{C}$)

Effect of temperature

Effect of temperature ($8-80^\circ\text{C}$) on the removal percentage of NH_4^+ is presented in Fig. 5. The sorbent dose used in the experiments was either 20 g/L or 50 g/L, treatment time was 4 h and initial NH_4^+ concentration 1000 mg/L. Experiments were conducted with several sorbent doses (20, 50, 100, 200, 500 g/L) but temperature did not have a clear effect on the removal percentage. The main conclusion is that NH_4^+ removal does not improve as temperature is increased up to $80 \pm 1^\circ\text{C}$. However, Yuan et al. (2016) reported that the NH_4^+ sorption capacity of analcime increased considerably as temperature was between $110-130^\circ\text{C}$. Therefore, experiments were conducted also at $90 \pm 1^\circ\text{C}$ and $120 \pm 1^\circ\text{C}$.

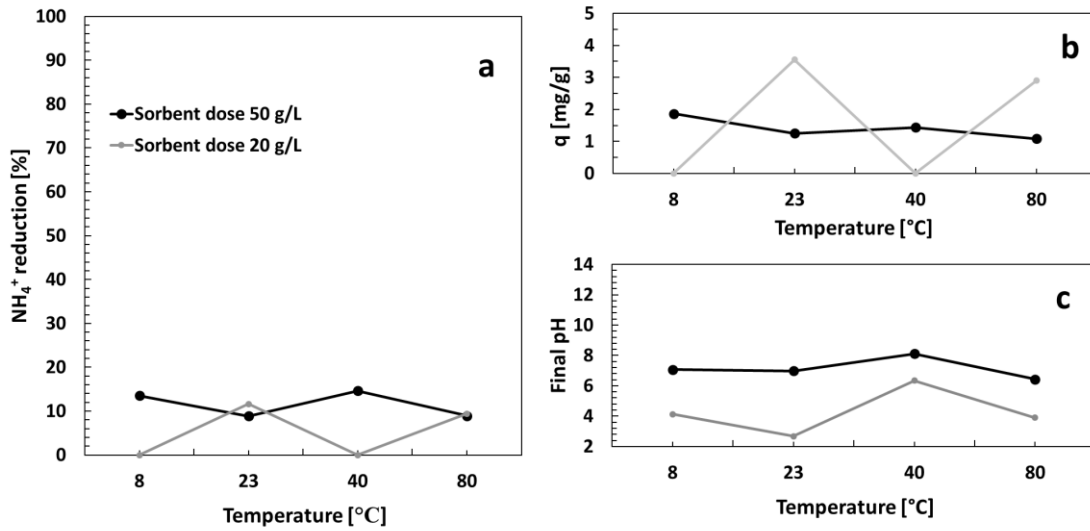


Fig. 5 Effect of temperature on the removal percentage (a) and sorption capacity (b) of NH_4^+ , and on the final pH value (c). Sorbent dose was 20 g/l or 50 g/L, initial NH_4^+ concentration 1000 mg/L, and treatment time 4 h

Concentration in analcime after ammonium uptake at different temperatures is presented in Fig. 6. Even though some ammonium was sorbed, the concentration was at most 0.5 m% at temperatures up to $90 \pm 1^\circ\text{C}$. However, at $120 \pm 1^\circ\text{C}$ the NH_4^+ sorption increased considerably up to 2.85 m% when sorbent dose was 10 g/L.

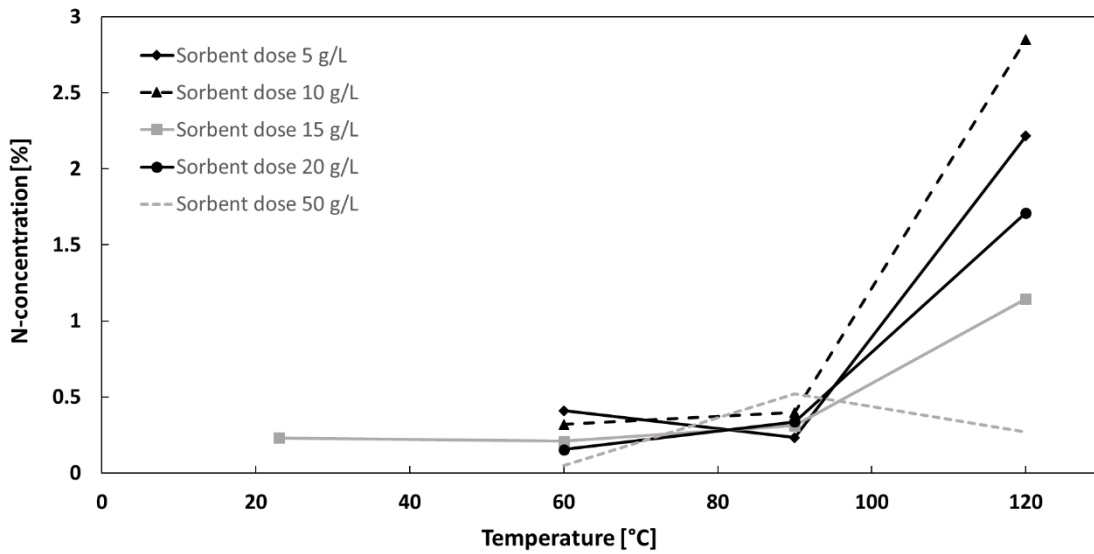


Fig. 6 Ammonium concentration in analcime after sorption at different temperatures and sorbent doses. Treatment time was 4 h and initial NH_4^+ concentration 1000 mg/L at $22 \pm 1^\circ\text{C}$ and $60 \pm 1^\circ\text{C}$ and 2 h at $90 \pm 1^\circ\text{C}$ and $120 \pm 1^\circ\text{C}$

Experiments with agricultural slurry

Sorption experiment results with agricultural slurry are presented in Fig. 7. In practice, no NH_4^+ removal was achieved at $8 \pm 1^\circ\text{C}$. The best removal percentage (around 30%) was achieved at room temperature with sorbent dose 500 g/L. Sorption capacity values (q) were small (below 3 mg/g) and they decreased as the sorbent dose increased. The pH remained below 7 in all cases, therefore no NH_4^+ losses should have occurred [25].

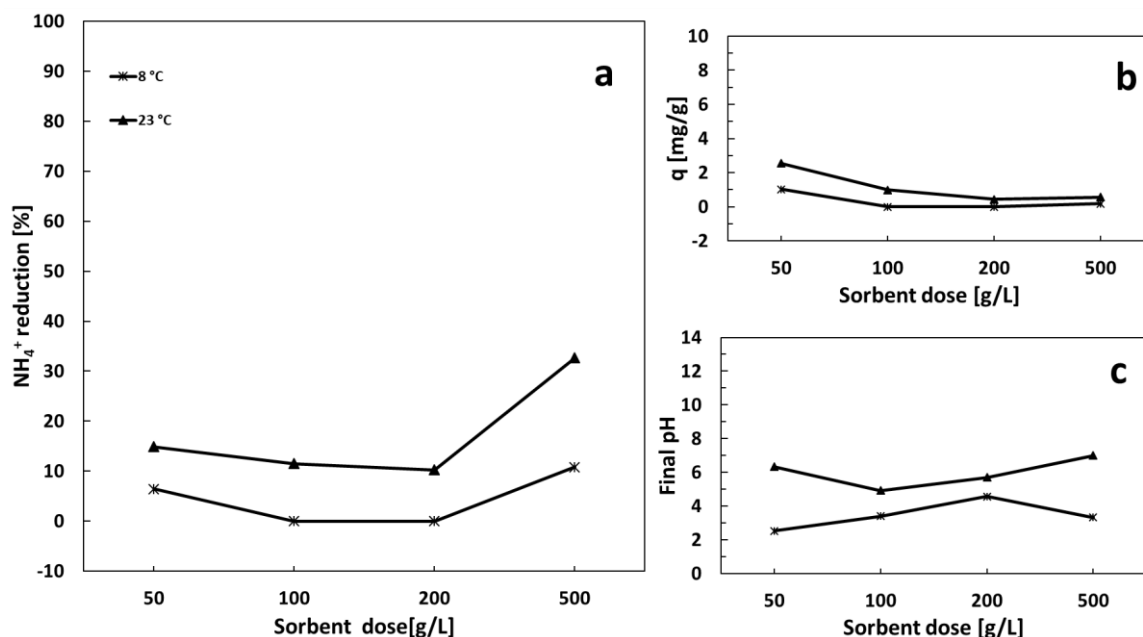


Fig. 7 Removal of NH_4^+ from agricultural slurry using different doses of analcime (50 g/L, 100 g/L, 200 g/L, and 500 g/L) at $8 \pm 1^\circ\text{C}$ and $22 \pm 1^\circ\text{C}$. Removal percentage of NH_4^+ (a); sorption capacity of NH_4^+ (b), and final pH (c). Treatment time was 4 h and initial NH_4^+ concentration was 176 mg/L

3.2 XRD analysis

Formation of ammonioleucite was confirmed by the XRD analysis of analcime after NH_4^+ uptake at 120°C (Fig. 8). This also explains why the effect of temperature was so high on the concentration of NH_4^+ in the used analcime. Previous studies have indicated that the $(\text{Si,Al})\text{O}_4$ framework of analcime is identical with the framework of ammonioleucite [26,27]. Since the ionic radius of NH_4^+ is 1.43 Å but the effective tunnel size of analcime is only 2.6 Å, NH_4^+ cannot pass through the tunnels at room temperature. Yamada et al. [26] suggested that the effective inside diameter of analcime is increased at high temperatures (above 100°C) as a result of lattice vibration, which enables the NH_4^+ to pass through the tunnel. Also, the increase of temperature causes the crystal water to escape from analcime and the NH_4^+ ion in the formed ammonioleucite takes the same site as water molecule in analcime structure [19,26]. These findings are confirmed also in our study. However, the results clearly indicate that some NH_4^+ is sorbed onto analcime also at lower temperatures but the presence of ammonioleucite was only confirmed after sorption at high temperatures.

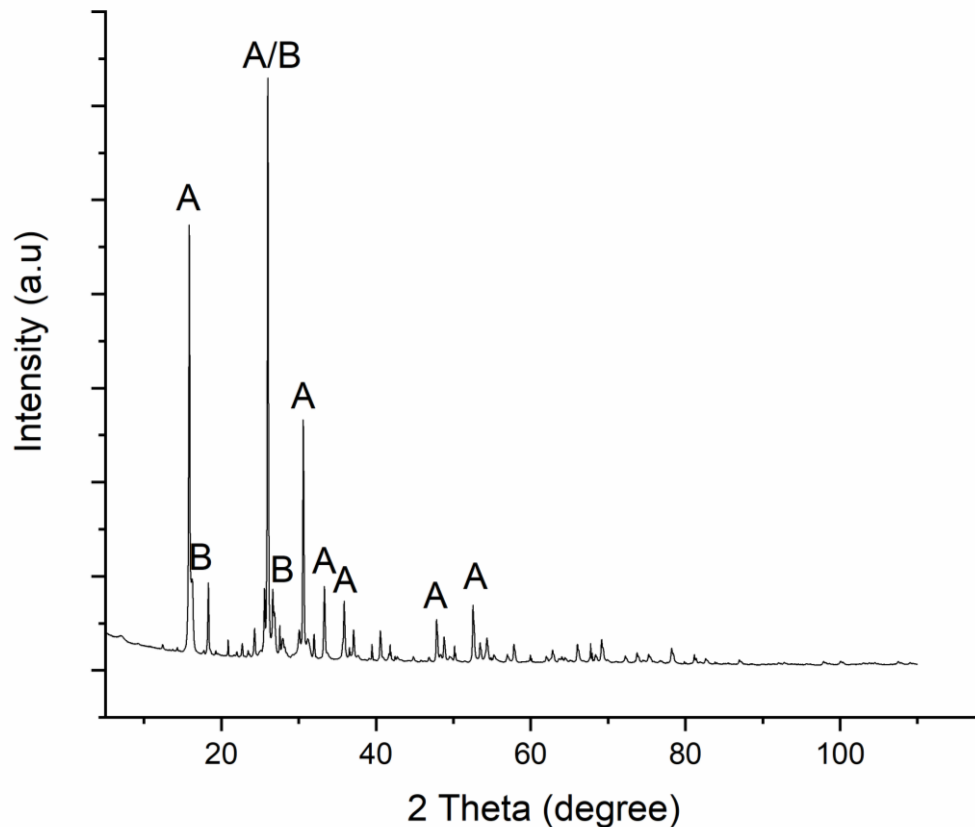


Fig. 8 XRD diffractogram of the analcime after sorption. A = analcime; B = ammonioleucite

3.3 Soil enhancer properties

Sequential leaching and aqua regia digestion results of the analcime before and after NH_4^+ uptake experiments are presented in Table 3. The leaching of Cd, Cr, Cu, Ni, Pb, and Zn was very low in the sequential leaching, which means that they are not bioavailable. However, As is quite soluble in the first fraction indicating it is bioavailable but it seems that the sorption reaction reduces the bioavailability of As. Still, all concentrations (aqua regia digestion) of the harmful elements (As, Cd, Cr, Cu, Ni, Pb, Zn) are well below the limit values of Finnish fertilizer decree [28]. Therefore, it would be possible to use analcime as a soil improver in Finland. However, also the nutrient concentrations (Ca, K, P) are low. The neutralizing value of the analcime before sorption was 5.5 Ca%, which is in line with the Ca concentration. Therefore, the ability of analcime to raise the pH of acidic soil is low compared to lime (neutralizing value typically between 30–40 Ca%).

Table 3 Sequential leaching and aqua regia digestion results of the analcime before and after NH_4^+ uptake (mg/kg) and a comparison to the limit values of Finnish Fertilizer decree [28]

	Ca	K	P	As	Cd	Cr	Cu	Ni	Pb	Zn
Before sorption										
F1	660	460	80	9.0	<0.08	<0.4	1.9	<0.2	<0.6	1.7
F2	560	300	30	1.1	<0.08	<0.4	0.5	<0.2	<0.6	0.4
F3	1000	460	410	1.4	<0.08	0.7	1.3	<0.2	0.9	1.9
F4	450	480	210	<0.8	<0.10	<0.5	1.7	<0.3	<0.8	1.3
Aqua regia	6850	4700	850	16	<0.3	60	30	21	3.8	70
After sorption										
F1	100	140	28	3.8	<0.08	<0.4	1.3	0.1	<0.6	0.9
F2	730	390	5.1	0.5	0.2	<0.4	1.1	0.4	<0.6	0.3
F3	2200	970	730	4.1	0.4	<0.4	3.1	0.3	<0.6	2.4
F4	690	650	170	<0.8	<0.10	0.8	0.1	0.6	<0.8	1.1
Aqua regia	6270	3280	1060	15	1.4	68	45	19	4.1	100
Limit value (mg/kg) field fertilizers/forest fertilizers	-	-	-	25/40	1.5/25	300	600/700	100/150	100/150	1500/4500

The release of NH_4^+ from analcime was studied by shaking the sample in distilled water (stages 1–2) and in 0.1 M NaCl solution (stages 3–10). Release of NH_4^+ was around 315 mg/kg in first stage, which then reduced to less than 75 mg/kg in stage 2 (Fig 9.). With NaCl, the release of NH_4^+ was fast at first (around 1200 mg/kg), decreased constantly in stages 4-7, and then settled to around 70–100 mg/kg in stages 8–10. Results confirm that the NH_4^+ uptake was mostly caused by sorption and even though the conditions used here do not represent chemical composition of soil solution, they do confirm that analcime releases NH_4^+ slowly during a long period of time. Because of the low NH_4^+ concentration (Fig. 6), analcime does not have much value as an ammonium fertilizer as such but it could be used as a component in fertilizers to control the ammonia release in soil as Souza et al. [29] suggested for clinoptilolite. A reduction of up to 50% to the ammonia volatilization from urea in soil was achieved as clinoptilolite was pelletized with urea. As the enzymes in soil decompose urea, the part of the NH_4^+ that is not instantly needed for plant growth is captured by clinoptilolite and analcime could be used in a similar way. In this case, analcime could be mixed directly to soil without the previous NH_4^+ sorption. As urea or other NH_4^+ containing fertilizer was applied on the field, analcime could capture part of the NH_4^+ and release it gradually.

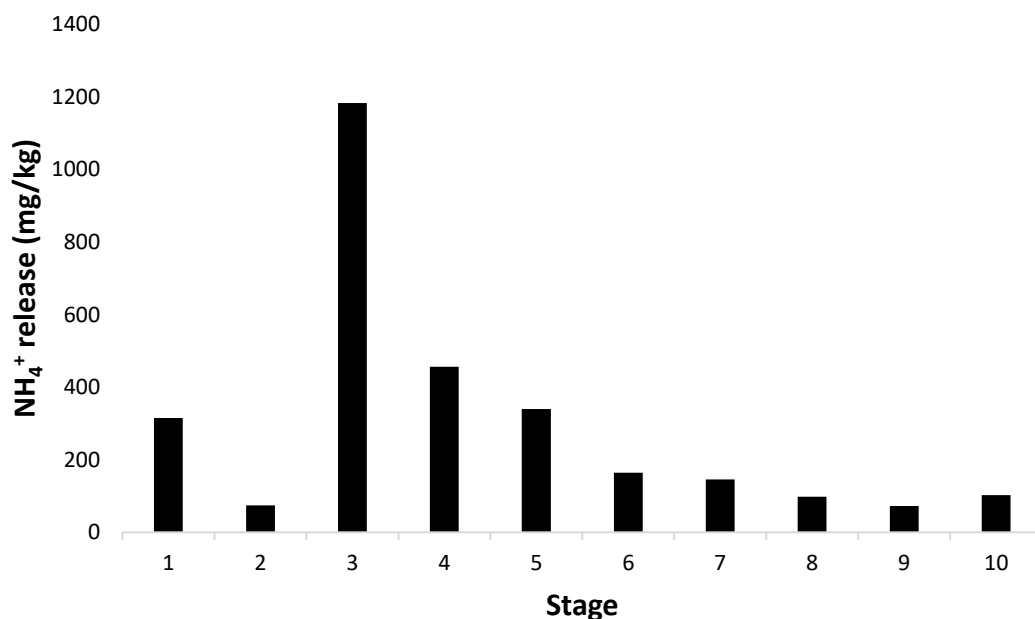


Fig. 9 NH₄⁺ release during leaching test. Distilled water was used in stages 1–2 and 0.1 M sodium chloride in stages 3–10

4. Conclusions

The use of industrial process based analcime to uptake NH₄⁺ from synthetic wastewater and real agricultural slurry via sorption for soil enhancer purposes was studied in this paper. NH₄⁺ sorption reaction was fast but the concentration of NH₄⁺ in analcime was low (0.5 m%) at temperatures up to 90 ± 1°C. However, results indicate that NH₄⁺ uptake was mostly caused by sorption and analcime releases NH₄⁺ slowly during a long period of time. Therefore, analcime does not have much value as ammonium fertilizer but it could be used to control the ammonia release in soil. In this case, analcime could be mixed directly to soil without NH₄⁺ sorption. As urea or other NH₄⁺ containing fertilizer was applied on the field, analcime could capture part of the NH₄⁺ and release it gradually. However, this should be confirmed with field tests.

Acknowledgements

This work was done under the auspices of the Waterpro project (Leverage from the European Union (EU), European Regional Development Fund (ERDF) project no: A74635; granted by Central Ostrobothnia, Northern Ostrobothnia and Kainuu Regional Councils) and LionLi project (private funding). The authors would also like to thank Maa- ja Vesiteknikan Tuki Ry for financial support.

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