

The ion-exchanger–loop-stripping process: ammonium recovery from sludge liquor using NaCl-treated clinoptilolite and simultaneous air stripping

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ABSTRACT

The technical feasibility of an ammonium recovery process ('ion-exchanger–loop-stripping') for sludge liquor from municipal wastewater treatment plants is examined. The proposed process combines ion-exchange on natural zeolites with simultaneous air stripping of ammonia to produce an industrial NO_x-removal agent. Column experiments with continuously recycled NH₄Cl-solutions and a real sludge liquor sample were conducted to determine basic ion-exchange kinetics of the applied clinoptilolite. Mass balances of consecutive loading/regeneration cycles show the positive influence of NaCl-pretreatment as well as simultaneous air stripping on the NH₄⁺-exchange capacities. Removal rates for NH₄⁺ between 61.5 and 84.6% were achieved at NH₄⁺-concentrations typical for sludge liquor (900 to 2,300 mg L⁻¹). Zeolite loadings ranged from 5 to 8 mg NH₄⁺ g⁻¹ after 90 min of loading. Regeneration rates were between 42.9 and 49.7%, but increased to 64.8% with simultaneous air stripping. A minimal decrease in the ammonium removal rate was observed as a result of matrix effects in sludge liquor (e.g. flocculants, competing ions). Liquid analyses showed a considerable phosphate-reduction in the sludge liquor sample after ion-exchange due to potential struvite or apatite precipitation. The obtained results enable a detailed design, scale-up and further optimization of the ion-exchanger–loop-stripping process in future.

Key words | ammonium recovery, natural zeolite, wastewater treatment

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INTRODUCTION

The anaerobic treatment of primary and secondary sludge from municipal wastewater treatment plants is a cost-effective way to reduce sludge amounts, stabilize biosolids and recover energy in the form of biogas. Hence, anaerobic digestion has gained considerable attention during the last years (McCarty *et al.* 2011) and is nowadays a common process at wastewater treatment plants larger than 20,000 population equivalents (PE).

Anaerobic sludge treatment leads to the formation of ammonia nitrogen (NH₄⁺-N) as a result of ammonification of organic nitrogen. Due to its high solubility the major share of ammonium (NH₄⁺) is found in the liquid phase of digestates (Fuchs & Drosig 2010); therefore high NH₄⁺ contents are present in the effluents deriving from mechanical sludge dewatering. Typical concentrations for the return flow from sludge treatment are in the range of 250 to 1,500 mg NH₄⁺ L⁻¹ (e.g. Fux & Siegrist 2004; Thornton

et al. 2007), but can also be higher depending on process parameters and input of additional substrates in the digestion tower (co-fermentation) as well as origin and type of the incoming wastewater.

NH₄⁺-concentrations in sludge liquors are usually higher than the effluent discharge limits. Further treatment of sludge liquors is therefore necessary, which is usually done by returning the liquid phase to the aerobic nitrification of the wastewater treatment plant. This approach is a practicable method to reduce ammonium without the need for additional installations. Nevertheless, high NH₄⁺-concentrations in the recycled liquors increase the ammonium loading in the nitrification basins and lead to higher costs for energy-intensive aeration. Together with urban expansion, increasing centralization and decreasing effluent threshold values the design capacity for NH₄⁺-removal of many wastewater treatment plants is currently being

approached and will be exceeded in future (Thornton *et al.* 2007). Many plants, especially those conducting co-fermentation of nitrogen-bearing residues, have to apply additional processes for ammonium removal from sludge liquor (sidestream treatment). Sidestream treatment is essential to decrease N-reversal rates and enable a more stable operation by minimizing the risk of impeding biological nitrification processes (Yenigün & Demirel 2013). Common sidestream treatment alternatives comprise both biological and chemical/physical methods.

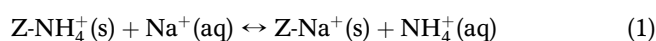
Biological sidestream treatment processes can be based on additional nitrification/denitrification (e.g. In-Nitri, BABE processes), nitritation and denitrification (e.g. SHARON process) or nitritation/deammonification (e.g. ANAMMOX, DEMON processes) (Ergas & Aponte-Morales 2014). Chemical/physical methods such as precipitation, air stripping and ion-exchange (Gupta *et al.* 2015) usually enable the selective recovery of ammonium, which can for example be used as a fertilizer (Verstraete *et al.* 2009). Revenues from nitrogen recovery facilitate economic efficiency of chemical/physical methods, whereas biological processes usually work with large volumes and high footprint areas and are often of limited economic feasibility. Furthermore, intermittent volumetric flow rates and varying ammonium concentrations typical for wastewater treatment sidestreams can decrease operation performance and stability of biological treatment methods. Given these advantages, increasing effort is currently being made to develop chemical/physical sidestream treatment processes.

Ammonium can effectively be removed from anaerobically treated effluents by struvite precipitation (Escudero *et al.* 2015). Depending on the effluent composition, this method usually requires the addition of magnesium and phosphorus to achieve optimal molar ratios for struvite formation as well as accurate pH adjustment and control (Uludag-Demirel *et al.* 2005). For a selective recovery, a subsequent separation of struvite is necessary. These aspects can result in high operating costs (Capodaglio *et al.* 2015).

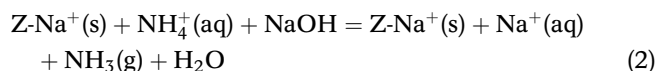
Operating and maintenance costs of air stripping for main wastewater streams are generally too high for economic operation. The high costs mainly derive from large amounts of chemicals required for pH adjustment and substantial installation sizes of the columns, compressors and pumps needed for aeration. Nevertheless, ammonia stripping was successfully applied for sidestream treatment at a couple of wastewater treatment plants with favorable boundary conditions, but scaling and accumulation of bio-solids in the stripping columns is still an unsolved problem (Gang 2001; Hofstetter *et al.* 2009).

Ammonium recovery by ion-exchange on organic resins and inorganic materials like natural and artificial zeolites as well as natural clays has been extensively studied in literature, mostly in batch experiments at ammonium concentrations below 100 mg L^{-1} (cf. Gupta *et al.* 2015). Natural zeolites, especially those containing clinoptilolite, are a very promising material for NH_4^+ -removal from wastewater due to their high treatment capacity, selectivity and removal efficiency, low costs and fast kinetics (Ames 1960, 1967; Mercer *et al.* 1970; Pabalan & Bertetti 2001; Wang & Peng 2010).

Nevertheless, ion-exchange whether on organic resins or inorganic materials is not economically viable as a result of the large amounts of salts (e.g. NaCl) needed for regeneration (Deng *et al.* 2014). The ion-exchange equilibrium for the regeneration of ammonium-bearing zeolite (Z) with Na-ions can be described as follows (Equation (1)):



Low concentrations of NH_4 in the regeneration fluid are required to increase regeneration rates by shifting the ion exchange equilibrium to the right hand side of Equation (1). Hence, large volumes of fresh regeneration fluids are needed, which can be avoided in processes that combine ion-exchange on natural zeolites with air stripping of the regeneration fluids. Air stripping of ammonia can efficiently be realized at alkaline pH-values between 10.8 and 11.5 – but it is highly dependent on air temperature and air/water ratios (Cheremisinoff 1995). By adding NaOH for pH adjustment to the regeneration fluid, ammonium is removed as NH_3 and ion-exchange is promoted (Equation (2)).



Sherman (1978) gave an overview of installations based on clinoptilolite including the ammonia removal and recovery process (ARRP), which combines ion-exchange and air stripping of the regeneration fluid (NaCl/NaOH) with acid scrubbing to recover $(\text{NH}_4)_2\text{SO}_4$. Large scale installations of this process began operation in California and Virginia in the late 1970s. ARRP was designed for nitrogen levels lower than 50 mg N L^{-1} to reach the maximum permissible values prior to discharge (Sherman 1984).

Recently, Deng *et al.* (2016) tested the simultaneous regeneration of exhausted zeolite applied for ammonium recovery from anaerobic membrane reactors at alkaline

pH by air stripping. By means of continuous-flow column studies they showed that the ammonium exchange capacity of the applied zeolite in NH_4Cl -solutions with input concentrations of 30 mg N L^{-1} considerably decreased with increasing regeneration frequency.

In Ellersdorfer (2012b) a process called ‘ion-exchanger-loop-stripping’ for nitrogen recovery from liquid digestates was proposed. It combines ammonium preconcentration on natural zeolites with simultaneous air stripping of a continuously recycled regeneration fluid (Figure 1). The obtained ammonium sulfate solution can directly be applied as an industrial NO_x -removal agent. According to Ellersdorfer (2012a), operating and investment costs of this process are reduced compared to conventional air stripping due to lower demands of energy and a significant size-reduction of the required stripping columns. Furthermore, problems due to scaling and bio-fouling of packing materials are prevented.

Studies regarding the ion-exchange performance of natural zeolites at NH_4^+ -concentrations typical for effluents from mechanical sludge dewatering ($1,000 \text{ mg NH}_4^+ \text{ L}^{-1}$ and higher) are currently missing in literature but are essential for the scale-up and potential implementation of the proposed process at wastewater treatment plants. In the present study, column experiments are conducted to determine ammonium separation and regeneration performance of natural clinoptilolite from NH_4Cl -solutions and real sludge liquor samples ($900\text{--}2,300 \text{ mg NH}_4^+ \text{ L}^{-1}$). On the basis of

loading and regeneration measurements as well as detailed mass balances, ion-exchange kinetics and the influence of simultaneous air stripping of ammonium on the regeneration performance are examined. The potential mechanisms of ion-exchange in real effluents are investigated by liquid analysis of treated and untreated sludge liquor samples.

METHODS

A solution reservoir, a mixing vessel (2,000 mL) and a glass column (diameter 5 cm, height 40 cm) filled with zeolite (Figure 2) were used for loading and regeneration studies. Natural zeolitic rock between 1 and 2.5 mm in size (clinoptilolite content 82–85%) was placed on a layer of glass beads (diameter 1 mm) between two porous glass filter plates to ensure a homogeneous liquid inflow. The liquid from the mixing vessel was pumped through the column from bottom to top to ensure a complete submersion of the zeolite particles in the solution. The overflow from the zeolite column was transferred back to the mixing vessel, whereby a continuous cycle of a defined solution volume was realized. The experimental setup corresponds to the planned operation mode of the ion-exchanger-loop-stripping, where a small volume of regeneration fluid is continuously recycled

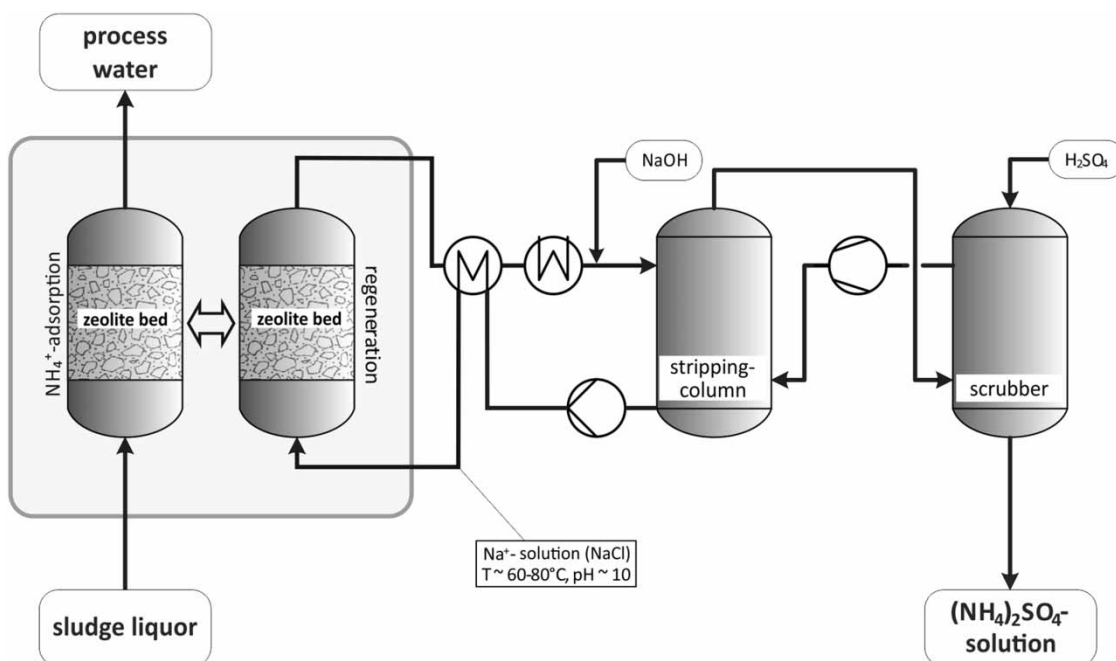


Figure 1 | Flow chart of the ion-exchanger-loop-stripping process.

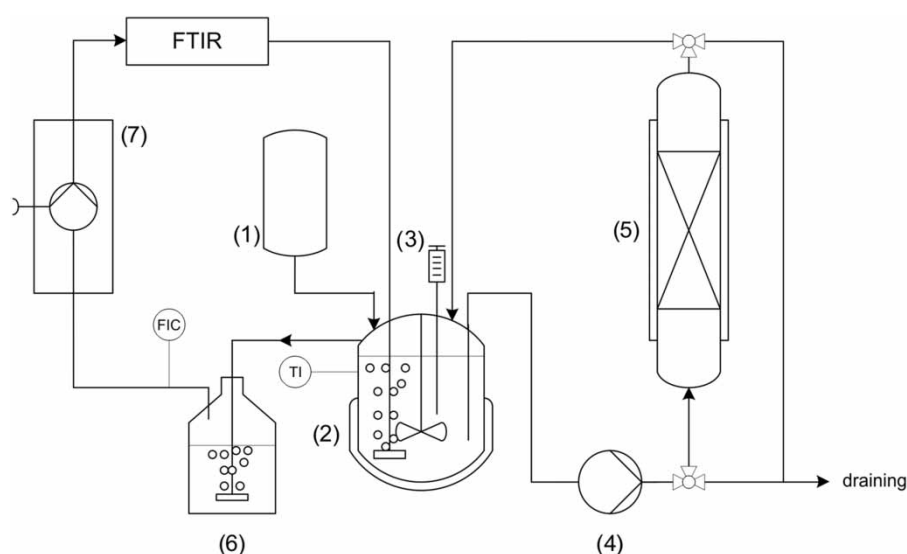


Figure 2 | Experimental setup: (1) solution reservoir, (2) mixing and stripping vessel, (3) sampling device, (4) gear pump, (5) zeolite column, (6) washing bottle, (7) gas sampling system for quantitative gas analysis (FTIR).

to ensure high ammonium concentrations and facilitate stripping performance.

Zeolite loading was performed with NH_4Cl -solutions of defined ammonium concentrations as well as sludge liquor samples from the wastewater treatment plant in Knittelfeld, Austria (70,000 PE). Concentrated NaCl -solutions were used to regenerate the exhausted zeolite. Ammonium concentrations of the applied solutions during loading and regeneration were determined in predefined time intervals by taking samples of 5 ml out of the mixing chamber. The samples were diluted with distilled water (1:10) and analyzed using an ammonia gas-sensitive combination electrode (ISE; type: NH 500/2, WTW) after pH adjustment to values above 10 with concentrated NaOH (32%). The pH measurements were conducted with a SenTix RJS-electrode (WTW).

Ammonia stripping was performed by aeration of the mixing chamber at pH-values above 10.5 adjusted with NaOH (32%), followed by a washing bottle with sulfuric acid (1,000 mL, 1 M H_2SO_4). Samples from the acidic solution were analyzed for ammonium using the Kjeldahl method. The residual ammonia concentration in the carrier gas, after the washing bottle, was measured with a mobile Fourier-transform infrared analyzer (FTIR; DX-4000, Ansyco) combined with a gas sampling device (SYCOS P-HOT, Ansyco). The gas stream was recycled to the mixing chamber after analysis.

Each of the tests consisted of varying pretreatments, loading and regeneration sequences. The zeolite bed was flushed between the cycles with distilled water to remove residual ammonium. Length and conditions of the cycles were varied as shown in Table 1. For the experiments 1b

and 2b, the zeolite samples from the previous runs 1a and 2a (after regeneration) were used.

Specific ammonium contents of the zeolite during loading (q_{LOAD}) were calculated by multiplying the differences between the initial and continuing NH_4^+ -concentrations in the solutions by the total solution volumes divided by the total amount of zeolite in the column (Equation (3)).

$$q_{LOAD} = \frac{(c_{0,LOAD} - c_{i,LOAD}) * V_{0,LOAD}}{m_{ZEO}} \quad (3)$$

q_{LOAD} : specific amount of NH_4^+ on zeolite during loading (mg g^{-1})

$c_{0,LOAD}$: initial NH_4^+ -concentration of the loading fluid (mg L^{-1})

$c_{i,LOAD}$: NH_4^+ -concentration of the loading fluid after certain time interval (mg L^{-1})

$V_{0,LOAD}$: total volume of loading fluid (L)

m_{ZEO} : total mass of zeolite in column (g)

To determine the zeolite loading during regeneration (q_{REG}), the amounts of ammonium in the regeneration fluid and in the washing bottle are subtracted from the final specific loading obtained in the previous loading sequence (Equation (4)).

$$q_{REG} = q_{LOAD,final} - \frac{(c_{i,REG} - c_{0,REG}) * V_{0,REG}}{m_{ZEO}} - \frac{(c_{i,STRIP} - c_{0,STRIP}) * V_{0,STRIP}}{m_{ZEO}} \quad (4)$$

Table 1 | Pretreatment, loading and regeneration conditions during the experiments

		1a	1b	2a	2b	3	4
Zeolite mass in column	g	250	250	350	350	350	350
Bed volume	cm ⁻³	330	330	460	460	460	460
Flow rate	L h ⁻¹	24	24	24	24	24	24
	BV ^a min ⁻¹	1.21	1.21	0.87	0.87	0.87	0.87
Pretreatment							
Solution		–	–	NaCl	–	NaCl	NaCl
Concentration	g L ⁻¹	–	–	175	–	175	175
pH	–	–	–	7.0–7.5	–	7.0–7.5	7.0–7.5
Total volume	L	–	–	1	–	1	1
Duration	min	–	–	120	–	60	90
Loading							
Solution		NH ₄ Cl	NH ₄ Cl	NH ₄ Cl	NH ₄ Cl	NH ₄ Cl	sludge liquor
Feed concentration (analyzed by ISE)	mg NH ₄ ⁺ L ⁻¹	915	947	916	922.5	2292.5	1,060
pH	–	4.5–5.0	4.5–5.0	4.5–5.0	4.5–5.0	4.0–4.5	8.5–9.0
Total volume	L	2	2	2	2	2	2
L/Z ratio ^b	mL g ⁻¹	8	8	5.7	5.7	5.7	5.7
Duration	min	90	90	90	90	60	90
Regeneration							
Solution		NaCl	NaCl	–	NaCl	NaCl/NaOH	NaCl
Simultaneous stripping		no	no	–	no	yes	no
Concentration	g L ⁻¹	100	150	–	175	150	150
pH	–	7.0–7.5	7.0–7.5	–	7.0–7.5	10.5–11	7.0–7.5
Total volume	L	1	1	–	1	1	1
L/Z ratio ^b	mL g ⁻¹	4	4	–	2.9	2.9	2.9
Duration	min	60	60	–	120	90	60

^aBed volume.^bRatio of the volumetric amount of loading/regeneration fluid to the mass of zeolite in the column.

q_{REG} : specific amount of NH₄⁺ on zeolite during regeneration (mg g⁻¹)

$q_{LOAD,final}$: final specific amount of ammonium on zeolite after loading (mg g⁻¹)

$c_{i,REG}$: NH₄⁺-concentration of the regeneration fluid after certain time intervals (mg L⁻¹)

$c_{0,REG}$: initial NH₄⁺-concentration of the regeneration fluid (mg L⁻¹)

$V_{0,REG}$: total volume of regeneration fluid (L)

$c_{i,STRIP}$: NH₄⁺-concentration in the washing bottle solution after certain time intervals (mg L⁻¹)

$c_{0,STRIP}$: initial NH₄⁺-concentration in the washing bottle solution (mg L⁻¹)

$V_{0,STRIP}$: total volume of H₂SO₄ in washing bottle (L)

The depiction of q_{LOAD} and q_{REG} during the loading/regeneration cycles results in the specific NH₄⁺-loading and regeneration characteristics for the different experimental runs. Mass balances were calculated by using the initial and the final concentrations in the liquids together with the total solution volumes. The ammonium amounts for the loading and regeneration cycles were balanced separately. To determine the influence of ion-exchange on natural zeolites on the composition of sludge liquor, samples of the original and the treated sludge liquor (experiment 4) were analyzed for Cl⁻, SO₄²⁻ and PO₄³⁻ (ion chromatography), as well as Ca²⁺, Mg²⁺, K⁺ and Na⁺ inductively coupled plasma mass spectroscopy), total and carbonate hardness, biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC).

RESULTS AND DISCUSSION

Loading and regeneration characteristics/kinetics

The first experimental run (Figure 3 (1)) consisted of two consecutive loading and regeneration sequences. In the first sequence (Figure 3 (1a)) a final loading of $5 \text{ mg NH}_4^+ \text{ g}^{-1}$ zeolite was reached after 90 minutes. Ion-exchange equilibrium during 60 minutes of regeneration was obtained at $2.5 \text{ mg NH}_4^+ \text{ g}^{-1}$. Despite this residual ammonium loading, the uptake and regeneration capacity of the zeolite packing was somewhat higher in the second sequence (Figure 3 (1b)). An additional amount of 5.5 mg g^{-1} of ammonium was adsorbed, which resulted in a final loading of 8 mg g^{-1} . An amount of $3.5 \text{ mg NH}_4^+ \text{ g}^{-1}$ was exchanged during regeneration in the second sequence of this run compared to 2.5 mg g^{-1} in the first sequence. The increased uptake and recovery of NH_4^+ may be the result of an enhanced ion-exchange capacity after regeneration with NaCl-solution caused by Na^+ -replacement of the natural cation loading (homoionization, cf. Englert & Rubio 2005). Pretreatment of the zeolite with NaCl was therefore applied in any further experiment.

In the second run (Figure 3 (2)) two consecutive loadings followed by one regeneration sequence were applied on NaCl-pretreated zeolite. The zeolite amount was increased from 250 to 350 g, which reduced the specific flow rate from 1.21 to $0.87 \text{ bed volume (BV) min}^{-1}$ and the L/Z ratio (ratio of volumetric amount of loading/regeneration fluid to mass of zeolite) from 8 to 5.7 mL g^{-1} at the same absolute flow rate (24 L hr^{-1}). The specific NH_4^+ -contents of the zeolite after the first (4.5 mg g^{-1}) and second loading sequence of run 2 (8 mg g^{-1}) were nearly the same as with intermediate regeneration in the first run. Nevertheless, the absolute amount of ammonium removed from the solution was

significantly higher in loading sequence 2a compared to loading sequence 1a due to NaCl-pretreatment and lower L/Z ratio. The overall specific uptake capacity after two consecutive loadings in run 2 was considerably lower (8 mg g^{-1}) than with intermediate regeneration in run 1 (10.5 mg g^{-1}), and so was the overall regeneration (4 mg g^{-1} compared to 6 mg g^{-1}). Thus, an operation mode permanently changing between loading and regeneration sequences favors higher ammonium separation and recovery.

In both runs 1 and 2, the specific ammonium content of the zeolite obtained around 80% of the final values within the first 40 minutes of the loading sequences. Ion-exchange equilibrium during regeneration was approached after 30 min when ammonium removal from the zeolite dramatically decreased. The specific loading reduction of the zeolite during regeneration was only around 50% in every regeneration sequence of run 1 and 2.

Continuous air stripping of the regeneration fluid was applied in experimental run 3 (Figure 4 (3)). Zeolite was loaded at a higher incoming concentration of ammonium ($2,300 \text{ mg NH}_4^+ \text{ g}^{-1}$) resulting in a significantly higher specific loading of $8 \text{ mg NH}_4^+ \text{ g}^{-1}$ after 60 minutes. Hence, the incoming concentration is a major influence factor regarding the attained loading of the zeolite. Regeneration resulted in a decrease of the specific loading to 4.5 mg g^{-1} without stripping (considering only NH_4^+ in the regeneration fluid) and 2.9 mg g^{-1} when absorbed ammonia in the scrubbing bottle was included. Air stripping therefore significantly reduces the residual loading on the zeolite. At the beginning of regeneration, the influence of air stripping was only small but it increased after 20 minutes, when ammonium concentrations in the regeneration fluid were higher. Finally the regeneration rate of ammonium was approximately 35% higher with simultaneous stripping.

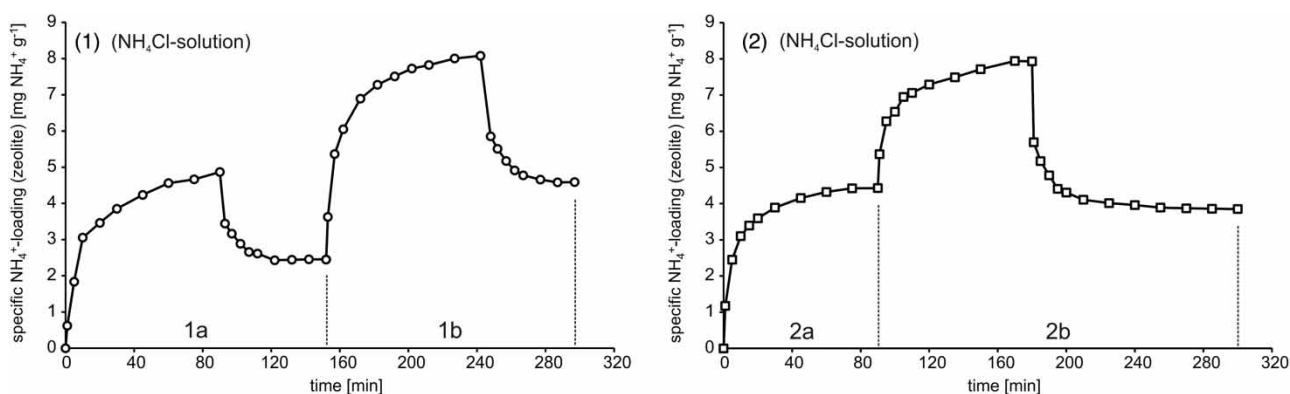


Figure 3 | Specific ammonium loading/regeneration characteristics on natural clinoptilolite; (1) untreated zeolite (250 g; L/Z ratio: 8 mL g^{-1} , flow rate: 1.21 BV min^{-1}), NH_4Cl -loading ($900 \text{ mg NH}_4^+ \text{ L}^{-1}$), NaCl-regeneration; (2) NaCl-pretreated zeolite (350 g; L/Z ratio: 5.7 mL g^{-1} , flow rate: 0.87 BV min^{-1}), NH_4Cl -loading ($900 \text{ mg NH}_4^+ \text{ L}^{-1}$), NaCl-regeneration.

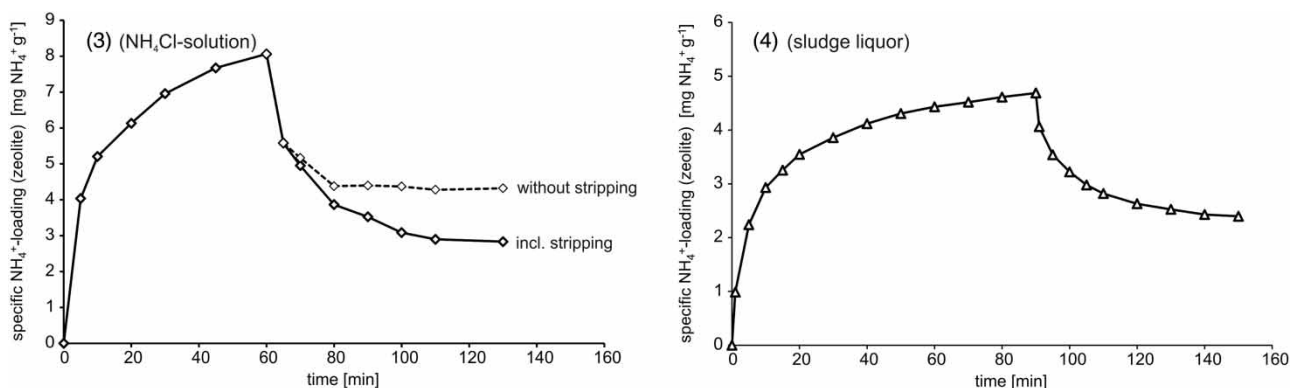


Figure 4 | Specific ammonium loading/regeneration characteristics on natural clinoptilolite; (3) NaCl-pretreated zeolite (350 g; L/Z ratio: 5.7 mL g^{-1} , flow rate: 0.87 BV min^{-1}), NH_4Cl -loading ($2,300 \text{ mg NH}_4^+ \text{ L}^{-1}$), NaCl/NaOH-regeneration (pH = 10.5–11); (4) NaCl-pretreated zeolite (350 g; L/Z ratio: 5.7 mL g^{-1} , flow rate: 0.87 BV min^{-1}), sludge liquor ($1,060 \text{ mg NH}_4^+ \text{ L}^{-1}$), NaCl-regeneration.

Regeneration rates can be further enhanced for example by increasing the volumetric flow rate of air and heating to increase mass transfer rates for ammonia from the liquid to the gas phase. Ammonia concentrations in the stripping gas were below detection limits ($<1 \text{ ppm}$) after the washing bottle, indicating an instantaneous ammonium sulfate formation in the washing fluid.

Ammonium exchange characteristics and specific uptake were not influenced by the use of sludge liquor (Figure 4 (4)). Incoming concentrations of $1,060 \text{ mg NH}_4^+ \text{ L}^{-1}$ resulted in 4.7 mg g^{-1} ammonium loading after 90 minutes, which corresponds to sequence 2a with NH_4Cl -solution at $900 \text{ mg NH}_4^+ \text{ L}^{-1}$ under similar experimental conditions. The obtained regeneration rate was comparable to that of the synthetic solutions; hence no influence of competing ions or further matrix effects (e.g. flocculants, total dissolved solids, TOC) on the ammonium exchange characteristics were detectable.

Mass balances

Mass balances reveal that $1,216.7 \text{ mg}$ of initial ammonium were exchanged during loading sequence 1a, resulting in a removal rate of 66.5% (Figure 5 (1a)); 604.6 mg were regenerated with NaCl-solution, corresponding to a regeneration rate of 49.7%. The overall recovery rate accounted for 33.0%. Around 50% of the total ammonium remained on the zeolite after regeneration. In the following sequence 1b the removal rate considerably increased compared to sequence 1a (80.6%) by reason of homoionization. The overall ammonium loading on the zeolite was nearly doubled in sequence 1b, but the regeneration rate decreased to 42.9% due to equilibrium reasons based on higher ammonium concentrations in the regeneration fluid. The overall recovery

rate was slightly higher in this sequence (34.6%) owing to the elevated loading of the zeolite and the higher absolute amounts of recovered ammonium. The residual NH_4^+ on the zeolite after regeneration indicates that there is still a significant potential for further recovery.

A removal rate of 84.6% was obtained in the second trial run (Figure 5 (2)), which was by far the highest of all loading sequences caused by NaCl-pretreatment and lower L/Z ratio. Removal rate dropped to 66.5% in the consecutive loading sequence without intermediate regeneration. Residual ammonium contents of the zeolite were still high after regeneration and the overall recovery rate was lower (34.3%) compared to the first experiment (39.5%). Although an intermediate regeneration increases the overall amount of recovered ammonium, regeneration appears to limit ammonium recovery in both trial runs 1 and 2.

Higher NH_4^+ -concentrations during loading in trial run 3 decreased the removal rate from 84.6% to 61.5% (Figure 5 (3)). The influence of concentration levels on the ammonium removal rate at constant L/Z ratios is evident. Even though the specific ammonium exchange was the highest of all conducted experiments (8.1 mg g^{-1} ; cf. Figure 3 (4)), increased zeolite loading does not fully balance the higher ammonium amounts in the loading fluid. Hence, the NH_4^+ -concentration of the incoming fluid is a key parameter for the adaption of the zeolite bed volume to achieve removal rates higher than 80%.

Simultaneous air stripping was applied in experiment 3 to shift equilibria for enhanced NH_4^+ -recovery (Figure 5 (3)). Both the regeneration rate and the overall recovery of ammonium increased to 64.8% and 39.9%, which were by far the highest values of all experiments. The quantity of ammonium on the zeolite after loading and the recovered NH_4^+ -amount in the regeneration solutions are nearly the same in runs 2b and 3

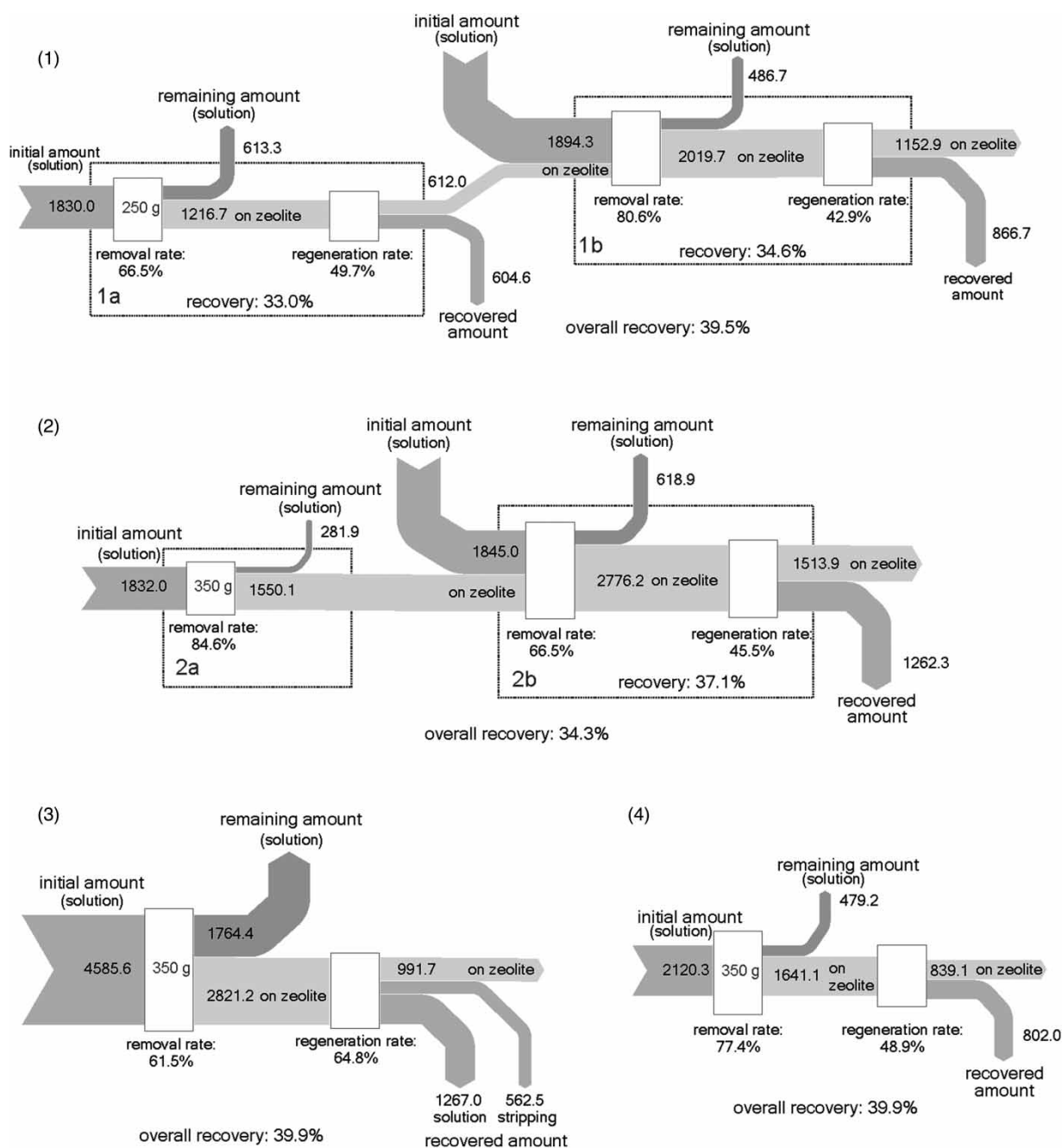


Figure 5 | Mass balances and ammonium recovery rates (values in mg): (1, 2) NH₄Cl-solutions and different operation modes, (3) NH₄Cl-solution and simultaneous air stripping, (4) sludge liquor.

(2,776.2 and 2,821.2 mg on zeolite; 1,262.3 and 1,267.0 mg in solution). The higher regeneration rate in run 3 is therefore a consequence of the additional NH₄⁺-amount recovered by air stripping (562.5 mg). The quantity of remaining ammonium on the zeolite is reduced by the same proportion; therefore air stripping decreases residual NH₄⁺-loadings and provides higher overall recovery rates.

Ammonium ion-exchange in sludge liquor (Figure 5 (4)) showed only a small decrease in the removal rate to a value of 77.4% compared to 84.6% in run 2 under similar conditions with NH₄Cl. This decrease may derive from competing ions or other components (e.g. flocculants) in sludge liquor, which influence NH₄⁺-uptake. Nevertheless, regeneration rate (48.9%) and overall recovery rate

(37.7%) are comparable to the other experiments without air stripping; hence no major limitations for ammonium removal from sludge liquor were identified.

Influence of ion-exchange on sludge liquor composition

As seen in Table 2 ammonium ions in sludge liquor were primarily exchanged by Na^+ followed by Ca^{2+} and small amounts of Mg^{2+} . Potassium in sludge liquor decreased during the exchange experiments, which may be a result of the higher selectivity of clinoptilolite for K^+ over NH_4^+ and Na^+ (Ames 1960; Ulmanu 2012). Hence, some of the cation positions might be blocked with potassium, which could result in a future decrease of the ammonium exchange rate after several subsequent loading/regeneration steps. The pH-value increased during $\text{NH}_4^+/\text{Na}^+$ ion-exchange due to the formation of higher dissociated NaOH.

Besides variations in the cation composition, some changes regarding the anion content were detected. There is a small increase in the Cl^- -concentration after ion-exchange, which may derive from salt residues on the zeolite from NaCl-pretreatment. Only a minor decrease in SO_4^{2-} was observed but a major decrease in the phosphate concentration occurred. This PO_4^{3-} -reduction could partially be a result of a mechanical filtering effect of the zeolite bed, as TOC values decreased during the experiment and phosphate is typically enriched in the separated biosolids (Lin

et al. 2015). PO_4^{3-} -reduction due to precipitation of insoluble substances by reaction of phosphate with some exchanged cations from the zeolite may also be possible. Mitrogiannis *et al.* (2017) describe the formation of surface layers of (hydroxy)-apatite ($\text{Ca}_5(\text{OH}, \text{Cl}, \text{F})(\text{PO}_4)_3$) on Ca-bearing zeolites in artificial PO_4^{3-} -solutions, but in the presence of NH_4^+ in supersaturated solutions struvite ($\text{MgNH}_4(\text{PO}_4)_3 \cdot 6\text{H}_2\text{O}$) precipitation is also likely to happen (Bouropoulos & Koutsoukos 2000). According to Battistoni *et al.* (1997), struvite formation is favored in anaerobic liquors due to the inhibiting effect of Mg^{2+} and bicarbonate ions on (hydroxy)-apatite formation. Hermassi *et al.* (2016) showed, that P-removal on zeolites synthesized from fly ash proceeds through two main mechanisms: (1) surface complexation with AlOH and FeOH functional groups in fly ash zeolite and (2) the formation of brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) instead of hydroxyapatite due to the influence of the zeolite crystal structure.

CONCLUSIONS

Column experiments in the present paper showed that ammonium recovery from synthetic solutions and real sludge liquor samples is possible. Natural clinoptilolite successfully removed NH_4^+ at concentrations from 900 to 2,300 $\text{mg NH}_4^+ \text{L}^{-1}$, which presents a typical range for ammonium in sludge liquor of wastewater treatment plants. Ion-exchange equilibria were reached after 30 minutes during regeneration and after 90 minutes during loading, when solutions are continuously recycled. Typical ammonium loadings were between 4 and 8 $\text{mg NH}_4^+ \text{g}^{-1}$ zeolite depending on the experimental conditions. Pretreatment with NaCl, increasing NH_4^+ -concentrations in the loading fluids and decreasing L/Z ratio significantly increased the quantities of removed NH_4^+ . However, single-step recovery of ammonium with NaCl-solutions is limited to a maximum recovery rate of around 50% of the zeolites loading capacity due to equilibrium reasons. Regeneration turned out to be the limiting step for ammonium recovery.

Simultaneous air stripping of the regeneration fluid at pH-values above 10.5 significantly reduced the amounts of residual ammonium on the zeolite and higher rates of ammonia recovery were obtained. Enhancing the stripping rates for NH_3 from the regeneration fluid, for example by heating the regeneration fluid, modifying liquid-to-gas ratios, further pH adjustment and the use of well-engineered

Table 2 | Sludge liquor composition before and after ion-exchange on NaCl-pretreated natural clinoptilolite

Parameter	Sludge liquor (exp. 4)	
	Input	After ion-exchange
NH_4^+ (mg L^{-1})	1,060	239.6
pH (-)	8.1	9.3
Na^+ (mg L^{-1})	87.9	958
K^+ (mg L^{-1})	234	126
Ca^{2+} (mg L^{-1})	32.2	138
Mg^{2+} (mg L^{-1})	2.89	18.6
Total hardness (mg L^{-1})	0.92	4.21
Carbonate hardness (mg L^{-1})	5.73	4.82
SO_4^{2-} (mg L^{-1})	276	247
PO_4^{3-} (mg L^{-1})	115	9.32
Cl^- (mg L^{-1})	127	170
TOC (mg L^{-1})	225	146
BOD_5 ($\text{mg O}_2 \text{L}^{-1}$)	120	136
COD ($\text{mg O}_2 \text{L}^{-1}$)	416	361

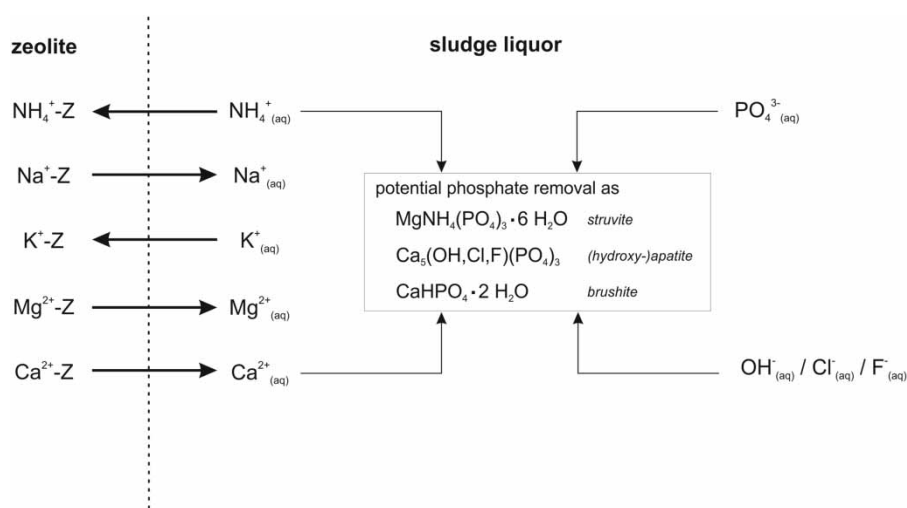


Figure 6 | Principle mechanisms of ion-exchange in sludge liquor on NaCl-pretreated clinoptilolite.

stripping columns is a promising way to further increase recovery rates.

Ammonium in sludge liquor was mainly exchanged by sodium, calcium and to smaller extent magnesium when NaCl-pretreated zeolite was used. Potassium was partially removed from the liquid phase. Analyses of sludge liquor before and after ion-exchange revealed a small increase in pH-values and significant removal of phosphate as a potential result of struvite or apatite (surface) precipitation. The probable mechanisms for ion-exchange in sludge liquor using NaCl-pretreated clinoptilolite are shown in Figure 6.

Based on the present study, the proposed ion-exchanger-loop-stripping process may present a viable option for ammonium recovery from sludge liquor of wastewater treatment plants at NH_4^+ -levels of 900 mg L^{-1} and higher. Analyses of sludge liquor before and after ion-exchange show indications for a potential phosphate removal by precipitation of insoluble P-phases like struvite, (hydroxy-)apatite or brushite, but further experiments have to be conducted to investigate the mechanisms in detail. For future applications, direct regeneration and stripping with NaOH-solutions may be an alternative to NaCl-bearing fluids to further reduce chemical demands and simplify the process. Nevertheless, typical NaCl-solutions used for zeolite regeneration comprise Na^+ -concentrations of 1 mol L^{-1} and above, which is equivalent to NaOH-solutions with pH-values around 14. At these highly basic pH-values, problems due to desilication and partial dissolution of the zeolite can arise. Hence, further investigations regarding the long-term influence of high pH-values during regeneration on the stability and uptake capacity of the

ion-exchanger bed have to be conducted. Furthermore, the influence of competing ions like K^+ or other sludge liquor components (e.g. flocculants) has to be investigated in detail.

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