

Article

Nitrogen Recovery from Swine Manure Using a Zeolite-Based Process

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Abstract: Intensive pig farming produces huge amounts of swine manure, which can cause regional nutrient imbalances and represent a potential source of soil and water pollution due to manure over-application. In order to improve nutrient stewardship, technologies for manure treatment and selective recovery of nutrients (especially ammonia) have to be developed to foster agriculture–food system sustainability. In the present study, a combined stripping and ion exchange process using natural zeolite (ion-exchanger-loop-stripping process) is tested for nitrogen recovery from swine manure to determine its technical feasibility in this novel field of application. Ammonium removal rates of 85 to 96% were achieved in pilot scale experiments with preprocessed manure (~500 L h⁻¹ after mechanical filtration; input concentration: ~1.3 g NH₄⁺ L⁻¹). NH₄⁺ was successfully transferred to a concentrated ammonium sulfate solution (final concentration: 66 g NH₄⁺ L⁻¹), with no significant transfer of other manure components. Hence, various utilizations of the product solution are possible, e.g., for industrial off-gas cleaning (DeNO_x) or as raw material for fertilizer production. Based on these findings, the ILS-process can be regarded as a promising option for nitrogen recovery from swine manure.

Keywords: nutrient recovery; manure processing; sustainable agriculture

1. Introduction

Intensification and industrialization of livestock raising generates huge amounts of swine wastes, which include an important quantity of nutrients, especially nitrogen and phosphorus compounds [1]. In 2019, Austria's livestock farmers produced around 4.7 million pigs [2]. Given an average manure production of ~0.5 m³ per pig and year [3], the overall quantity of swine manure is around 2.3 million m³ per year from pig fattening (pig breeding not included). Assuming the average amounts of nutrients in swine manure to be 2.5 kg NH₄⁺ m⁻³ and 0.65 kg P m⁻³ [4], the estimated potential of N and P in swine manure is around 4500 t N a⁻¹ and 1500 t P a⁻¹.

Due to its nutrient content, swine manure is widely used as a valuable fertilizer. Nevertheless, in some regions (e.g., southern Styria and the Murtal region), intensive pig farming has led to significant imbalances between nutrient demand for crop farming and the amount of available nutrients from locally produced manure [5]. Hence, huge amounts of swine manure have to be stored over certain periods of the year (i.e., manure storage capacities for at least 10 months are mandatory), which leads to significant additional cost. Although fertilizer utilization is strictly regulated in Austria, local over-application of manure has led to soil and water pollution by nitrate formation. Additionally, NH₃-losses from manure can degrade air quality and threaten human health [6], whereas N₂O-emissions from nutrient over supply can contribute to global warming and climate change [7]. As an important part of the new

Green Deal, the EU's "Farm-to-Fork" strategy poses ambitious objectives for agriculture–food system sustainability, including to reduce nutrient losses by at least 50% and fertilizer use by 20% by 2030, to improve nutrient stewardship [8]. Hence, alternative technologies to enable nutrient recycling and assist the management of the large amounts of generated manure are necessary.

Many different technologies for liquid manure processing are currently available. Biological processes comprise anaerobic ammonia oxidation processes and nitrification/denitrification, which are nutrient removal processes and do not allow for their recovery. Biological nutrient recovery can be enabled by bioelectrochemical processes (BE), microalgae- or duckweed-based processes (MA/DW), enhanced biological phosphorus removal (EBPR), as well as macrophyte-based constructed wetlands (WL) and hybrid processes. These recovery processes suffer from challenges at larger scales (BE), high costs (MA/DW) and the requirement of large land areas and high retention times (WL). A comprehensive review of biological nutrient removal and recovery from livestock manure is given by Zubair et al. [9].

Physical/chemical nutrient recovery processes involve membrane processes, struvite precipitation, stripping processes and the use of ion exchangers, for example zeolites. Hollow fiber liquid–liquid membrane contactors have been investigated to recover ammonia nitrogen from swine waste after previous treatments [10], with high recovery rates of 97–99% after 5 days of continuous processing [11]. Immersed gas permeable membranes have also been applied to swine manure [12] with average NH_3 -recovery rates of 81% when the pH of the manure was adjusted to nine [13]. The main disadvantages of membrane processes are obstruction and fouling, leading to high costs for membrane replacement and energy expenditures to maintain the necessary operating pressures [14]. Nevertheless, obstruction and fouling of gas permeable membranes can be effectively prevented when they are operated at low pressure [15]. Controlled formation of struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) has been used for N and P recovery from swine manure [16–18]. Reported removal rates for NH_4^+ were 23–29% and over 90% for PO_4^{3-} [19]. Major challenges for an economic struvite precipitation are the chemical costs for pH-adjustment and additional Mg-sources [14].

Air stripping by means of a turbulent mixing process was investigated as an ammonia removal technique to treat raw manure digestate: ammonia removal efficiencies of 88.7% were achieved after 24 h of treatment with NaOH as pH-control agent [20]. Liu et al. [21] stripped CO_2 from anaerobic digestate of swine waste to reduce the chemical demand for pH-adjustment and stripped NH_3 in a second step at a pH-value of 12.38 after lime addition to produce ammonium sulfate solution. The maximum NH_3 removal efficiency reached 96.78%. Liao et al. [22] also used aeration and air stripping for ammonia removal from swine waste and reported removal efficiencies of 90% depending on the air flow rates and liquid temperature, whereas Alitalo et al. [23] achieved removal rates of 59 to 86%. High operational costs for chemical pH-adjustment and potential environmental impacts due to odor emanations during aeration are the main drawbacks of stripping processes [14].

Several reports exist for the use of zeolites to remove and recover nutrients from swine manure: Huang et al. [24] used Mg-modified natural zeolite to promote struvite precipitation from simulated swine wastewaters. Ammonia-nitrogen and phosphate removal efficiencies reached 82% and 98%, respectively. Zeolite synthesized from fly ash was applied to anaerobically digested swine wastewater by Li et al. [25], achieving 74% nitrogen and 96% phosphorus sequestration. Lin et al. [26] evaluated the sorption kinetics and equilibria for ammonium separation from liquid swine manure through natural chabazite and determined the maximum sorption capacity at room temperature with 34.2 mg g^{-1} . Chabazite sorption also decreased soluble phosphorus, possibly by forming insoluble calcium phosphate. Penn et al. [27] tested various zeolites (main mineral: clinoptilolite) for their ammonium removal capacity from synthetic and natural swine manure. Ammonium removal was lower in batch-stirred compared to batch-shaken systems, suggesting that diffusion between particles was rate-limiting. Measured removal capacities were around $25 \text{ g NH}_4^+ \text{ kg}^{-1}$ zeolite. Montégut et al. [28] investigated the cation exchange properties for NH_4^+ and K^+ of three different zeolites (clinoptilolite, chabazite and NaX faujasite) in synthetic and natural swine manure. Chabazite and faujasite were found more efficient than clinoptilolite for trapping ammonium cations from natural manure. The feasibility

of using natural and NaCl-treated Australian zeolites to simultaneously remove excess nutrients from anaerobically digested swine manure was evaluated by Wijesinghe et al. [29]. Adsorption isotherms confirmed selectivity for K^+ over NH_4^+ by natural and sodium modified zeolites and ammonium removal was considerably reduced when there was simultaneous potassium uptake.

A zeolite based process combining ion exchange and simultaneous stripping of the zeolite regeneration fluid was developed by Ellersdorfer et al. [30,31] (ion-exchanger-loop-stripping process; ILS) and successfully applied for N-recovery from effluents of mechanical sludge dewatering (sludge liquor) at waste water treatments plants. Compared to conventional stripping processes, the ILS-process comprises lower chemical and energy demands and smaller installation sizes due to a selective preconcentration of ammonium via zeolite sorption, therefore leading to lower overall costs for N-recovery. An existing mobile pilot plant of the ILS-process was adapted and applied for trial runs to recover nitrogen from swine waste at a pig breeding facility in Austria. In comparison to sludge liquor, swine manure has higher ammonium and dry matter contents, therefore, trial runs are necessary to show the applicability and performance of the ILS process for this novel field of application. In the present study, the results of these pilot scale experiments are presented to prove the technical feasibility and possible limitations of the ILS-process using swine manure as input material. To the best of our knowledge, this is the first report of an on-farm pilot scale plant applying a combined zeolite/stripping technology for the treatment of swine manure.

2. Materials and Methods

Experiments to recover ammonium from pig manure were conducted using a pilot plant of the ILS-process (container facility; treatment capacity: 500–1000 L h⁻¹). The mobile plant was installed and operated at a pig breeding facility in southern Styria (Austria) during summer 2019. The pig breeding facility has a capacity of 500 breeding and 5000 fattening pigs leading to a total manure output of around 14,000 m³ per year. Two different types of manure were used for ammonium recovery in this study: separately collected manure from pig breeding (breeding manure) and mixed manure, a blend of breeding manure (~30%) and manure from pig fattening (~70%). The different manure qualities were either withdrawn from the breeding manure tank (total volume approx. 2000 m³) or from the mixed manure tank (total volume approx. 5000 m³) by means of a submerged pump, which was lowered to the pumpable manure zone in the containers (Figure 1).

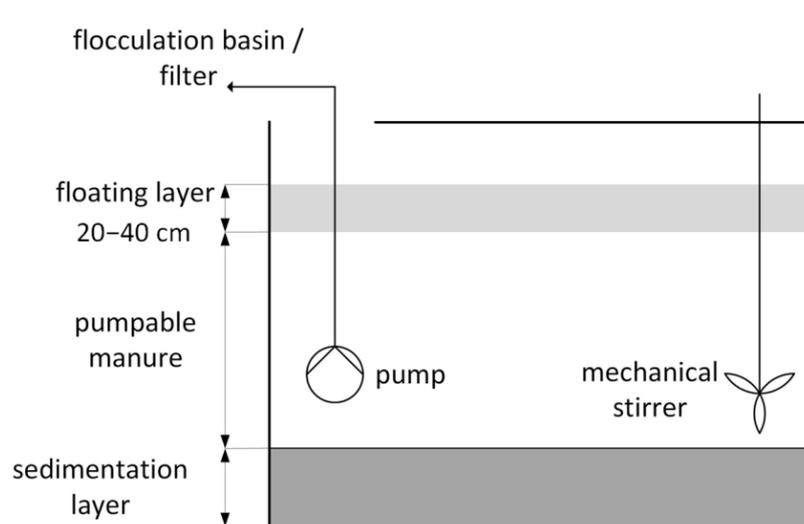


Figure 1. Illustration of the sample extraction from the mixed and breeding manure tanks.

The collected manure was processed either by simple filtration using bag filters (two subsequent stages: 200 μm and 100 μm) or flocculation using a 40 mass-% solution of FeCl_3 (industrial grade)

for pH-adjustment ($\text{pH} < 6$) together with commercially available flocculants (type 202 L, 0.5–1% solutions, Applied Chemicals International Group). Processing of manure was executed batch wise in mechanically stirred containers (1 m^3), which were also used as intermediate storage for manure supply of the pilot plant.

The pilot plant (Figure 2) consists of two ion exchange columns made of polypropylene (PP) and filled with approx. 100 kg zeolite each. Columns can be operated separately (single mode) or in series (serial mode). The liquid is pumped through the columns from the bottom to the top by means of centrifugal pumps. The zeolite bed in the columns is fixed between two sieve trays with a mesh size of 0.2 mm resting on perforated PP-plates to ensure a homogeneous liquid distribution over the columns cross-section. The pilot plant has two identical stripper and scrubber columns (both PP), equipped with packed structure material. Stripper and scrubber columns both comprise sumps to hold the regeneration (NaOH) and washing solutions (H_2SO_4) used for zeolite regeneration and ammonia scrubbing. Both sumps are equipped with a pH control. The regeneration solution is pumped from the stripper sump through the ion exchanger columns via a separate pipeline system passing a recuperative heat exchanger and a water heater (max. $80 \text{ }^\circ\text{C}$). The plant has two separate pipeline systems for water flushing and emptying of the ion exchanger columns to remove excess solutions.

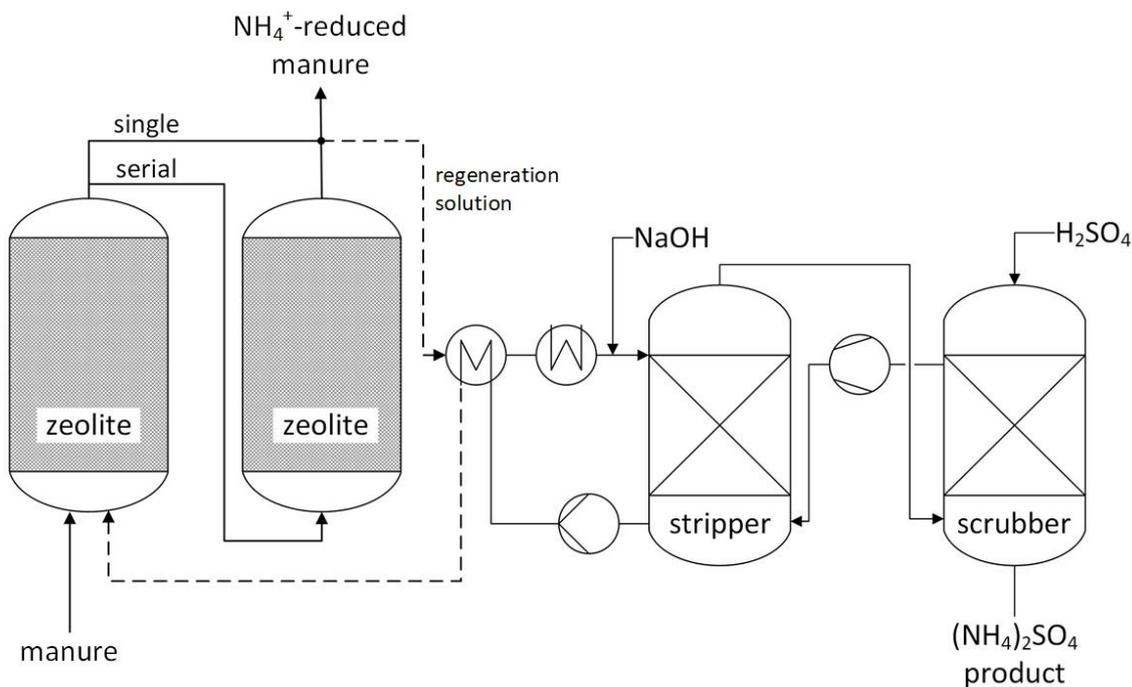


Figure 2. Principle flowchart of the ILS-pilot plant (treatment capacity: $500\text{--}1000 \text{ L h}^{-1}$) and the different operation modes of the ion exchanger columns (single/serial).

The experiments were conducted with natural zeolite from Slovakia (mainly clinoptilolite) with a particle size of 1 to 2.5 mm—a detailed mineralogical and chemical analysis of the zeolite is presented in Tschegg et al. [32].

Test runs consist of alternate loading and regeneration cycles: during loading, ammonium is removed from the manure via zeolite sorption. During regeneration, ammonium is desorbed from the zeolite by means of a concentrated NaOH -solution, which is continuously stripped over the whole regeneration cycle. Stripped ammonia is fixed with H_2SO_4 in the subsequent scrubber.

At the beginning of each test run, the storage tanks were filled with a sufficient amount of processed pig manure to ensure a continuous manure input quality throughout the respective test run. A sample was taken to determine the ammonium concentration (= input concentration) of the processed manure. During loading, manure was pumped through the ion exchanger columns at a flow

rate of 500 L h⁻¹ for 60 min in single mode (one ion exchanger column) and 180 min for the test runs in serial mode (two consecutive columns). Ammonium reduced manure was directly returned to the mixed manure tank. Samples from the outlet of the ion exchanger columns were analyzed for their NH₄⁺-concentration at defined times (after 5, 10, 15, 30 und 60 min in single and additionally after 90, 120, 150 und 180 min in serial operation). At the end of the loading cycles, the ion exchanger columns were rinsed with tap water (~10 min) and emptied to minimize the transfer of pig manure leftovers into the regeneration solution.

After loading, zeolite beds were regenerated with a sodium hydroxide solution (pH > 10) and a volumetric flow rate of 500 L h⁻¹ for 90 min in single and 120 min in serial operation. The regeneration fluid (~200 L) was produced by mixing a sufficient amount of NaOH (32%, technical grade) with tap water to adjust the pH-value in the solution to above 10. The regeneration fluid was heated to 60 °C before entering the stripping column for simultaneous ammonia removal. During stripping, the pH-value was permanently adjusted > 10 by adding additional doses of NaOH (32%) when necessary. Stripped ammonia was washed from the circulating gas using H₂SO₄ (pH < 2 at 60 °C) to produce (NH₄)₂SO₄ in the scrubber sump. The scrubbing solution was prepared using tap water (150 L) mixed with technical grade H₂SO₄ (40%) to an initial pH < 2. Additional H₂SO₄-doses (40%) were added when necessary, i.e., when pH-values increased to above 2. After each regeneration cycle, the remaining NaOH solution in the ion exchanger columns was returned to the stripper sump. The zeolite bed was again rinsed with tap water and emptied before the next loading process was started.

Input material characterization, i.e., breeding manure and mixed manure, was performed in detail by means of wet sieving and drying of the sieve residues at 105 °C (Chair of Process Technology and Industrial Environmental Protection, Montanuniversität Leoben, Austria). Samples of the regeneration and scrubber solutions were taken at the beginning and at the end of the entire experimental runs directly from the stripping/scrubbing sumps to identify a potential transfer of slurry components to these solutions. Where necessary, the samples were acidified with concentrated H₂SO₄ and stored temporarily to be analyzed by the same means as the input material. Chemical analysis was conducted at the Chair of Waste Processing Technology and Waste Management, Montanuniversität Leoben, Austria and comprised cation (Na, K, Ca, Mg) and heavy metal quantification (Pb, Ni, Cd, Cr, Zn, Fe) by ICP-MS (ÖNORM EN ISO 17294-2). Furthermore, ammonium (NH₄⁺) was quantified in these samples using a photometric method (DIN 38406-5); nitrate (NO₃⁻), nitrite (NO₂⁻) and orthophosphate (PO₄³⁻) were determined via ion chromatography (DIN EN ISO 10304-1). Total organic carbon (TOC) was measured by catalytic oxidation at 680 °C (DIN EN 1484-3). Total nitrogen (TN)-determination comprised oxidative conversion of N-compounds to nitrogen oxides (EN 12260). Dry matter contents (DM) were determined by drying at 105 °C and loss on ignition (LOI) at 550 °C (ÖNORM EN 15935). On-site determination of ammonium concentrations in manure samples was done with a photometer (Macherey-Nagel PF-12; ammonium test kits Nanocolor[®] ammonium 200) after filtration with 0.45 µm syringe filters. Selected samples were acidified (H₂SO₄) and analyzed at the Chair of Process Technology and Industrial Environmental Protection (Montanuniversität Leoben) via Kjeldahl method using boric acid and HCl (0.1 M)/Tashiro's indicator for titration in order to verify the reliability of the on-site photometric method.

The NH₄⁺-removal rate (A (%)) is calculated via the trapezoidal integral of the difference between the inlet and outlet concentrations normalized to the inlet concentration over the whole loading cycle (see Formula (1)).

$$A = \int_0^t \frac{c_{0,LOAD} - c_{i,LOAD}}{c_{0,LOAD}} * \frac{1}{t} dt \quad (1)$$

A ...NH₄⁺-removal rate (%);

c_{0,LOAD} ... NH₄⁺-input concentration of the processed manure (mg NH₄⁺ L⁻¹)

c_{i,LOAD} ... NH₄⁺-concentration at the outlet of ion exchanger columns at t = i (mg NH₄⁺ L⁻¹)

t ... elapsed time (min)

3. Results

3.1. Manure Quality and Composition

Table 1 shows the composition of the two different manure qualities used for the experiments. Mixed manure comprises significantly higher ammonium and total nitrogen concentrations, which is a result of the different conditions during pig breeding and pig fattening. During pig fattening, higher feeding and nutrient dosing (i.e., more intensive farming conditions) lead to increased nutrient amounts in mixed manure. Some amounts of nitrate and nitrite can be found in mixed manure, whereas these components were not detected in breeding manure. pH-values are nearly the same for both manure qualities, but cation concentrations, PO_4^{3-} as well as TOC and LOI are considerably lower in breeding manure, which is again due to the different farming conditions. Measured TN values in mixed manure are lower than the measured ammonium concentrations, which may be a result of sample inhomogeneity.

Table 1. Composition of breeding and mixed manure used in this study (LOD: limit of detection; TN: total nitrogen; TOC: total organic carbon; DM: dry matter; LOI: loss on ignition).

Parameter		LOD	Breeding Manure	Mixed Manure
NH_4^+	mg L^{-1}	0.05	1500	3500
NO_3^-	mg L^{-1}	13	<13	94
NO_2^-	mg L^{-1}	13	<13	110
TN	mg L^{-1}	-	2600	3100
Na^+	mg L^{-1}	0.2	200	400
K^+	mg L^{-1}	0.1	690	3010
Ca^{2+}	mg L^{-1}	2	98	250
Mg^{2+}	mg L^{-1}	0.02	56	15
PO_4^{3-}	mg L^{-1}	0.5	52	270
pH	-	-	7.4	7.3
TOC	mg L^{-1}	0.5	396	2100
DM	%	-	0.4 ¹	4.8 ¹
LOI	%	0.1	38.1	66.2

¹ at the particular sampling point (pump inlet; cf. Figure 1).

A significant difference can be identified in terms of dry matter (DM) contents: DM of breeding manure is 0.4% and therefore very low compared to mixed manure with 4.8% of dry matter. This is a direct consequence of the type of animal husbandry during pig fattening (operation, litter usage etc.). It has to be mentioned, that these DM-contents are only valid for the intermediate layer of pumpable manure in the tanks (Figure 1), which was used for the ammonium recovery experiments.

In order to obtain more information about the particle size distribution of the dry matter in mixed manure, wet screening experiments were conducted (Table 2). Two samples of mixed manure were taken directly from the manure tank during the test runs and analyzed: the results show only small differences between the individual sieve fraction amounts and indicate a high homogeneity of the samples in regard to particle size distribution. The amount of particles smaller than $45 \mu\text{m}$ is very high (>78 and 79%), whereas the other particle size fractions ($45\text{--}1000 \mu\text{m}$) are nearly evenly distributed. Hence, a major share of the DM in the pumpable zone of the mixed manure tank is composed of very small particles, which is important information for subsequent manure processing.

Table 2. Particle size distribution of mixed manure (wet screening).

Particle Size (μm)	Particle Size Distribution (%)	
	Run 1	Run 2
<45	79.0	78.0
45–90	3.1	2.5
90–250	5.7	7.2
250–500	3.7	3.2
500–1000	4.6	4.3
>1000	3.9	4.8
	100	100

3.2. Manure Processing

Preliminary experiments with small amounts of both manure qualities showed, that a simple, two-stage mechanical filtration (filter bags) was applicable for breeding manure but not for mixed manure due to nearly instant clogging of the filter elements. Hence, filtration of larger amounts of material for pilot plant experiments was only practicable for breeding manure. Small-scale flocculation tests (1 L) revealed that pH-adjustment and flocculation was possible for both manure qualities in the small-scale test setting. Nevertheless, things changed completely in larger scale (IBC-tanks; 1000 L manure): whereas batch-wise flocculation of breeding manure was successful, processing of mixed manure was not satisfactory regarding liquid purity and solid separation. Due to the high buffering capacity of mixed manure, large quantities of FeCl_3 were required for pH-adjustment (approx. 20–25 L 40% FeCl_3 for 1 m^3 of mixed manure). In addition, there was an enormous foam formation during pH-adjustment, which was a result of the development of gaseous CO_2 from the bicarbonate buffer system. A considerable over-dosage of flocculants did not lead to stable floc formation or repeatable flocculation results. Nevertheless, a sufficient amount of liquid phase could be produced ($\sim 2 \text{ m}^3$) in order to conduct two pilot test runs with flocculated mixed manure. However, the processing of mixed manure by flocculation proved not to be an operationally or economically feasible option for manure processing in that specific case.

3.3. Ammonium Removal

Figure 3 shows the obtained ammonium removal rates in single column experiments together with the NH_4^+ -input concentrations of the applied manure. Flocculated mixed manure comprised higher ammonium concentrations ($\sim 2500\text{--}3500 \text{ mg L}^{-1}$) compared to floccled or filtered breeding manure. Ammonium removal rates were around 40% for mixed manure. Significantly higher removal rates were achieved for breeding manure (input concentrations $\sim 1300 \text{ mg NH}_4^+ \text{ L}^{-1}$), starting with 67.2% in the first run. Stable removal rates between 85.8 and 90.3% were achieved during the following experimental runs. These results show that the removal rates in mixed manure are only half of that in breeding manure, which is a result of the higher concentrations of ammonium in mixed manure. Higher removal rates for mixed manure may be achieved by adjusting the zeolite to liquid ratio and increasing the amount of ion exchange material in relation to the treated liquid volume, either by larger columns or serial operation of several columns. A statistical test (*t*-test, two sided, confidence interval: 0.975) was executed to exhibit differences in the ammonium removal performance for floccled and filtered breeding manure. The values 67.2 and 80.9 were excluded from this test, as these values represent the start-up-phase. Results show, that there are no statistically significant differences in the ammonium removal performance between floccled and filtered breeding manure.

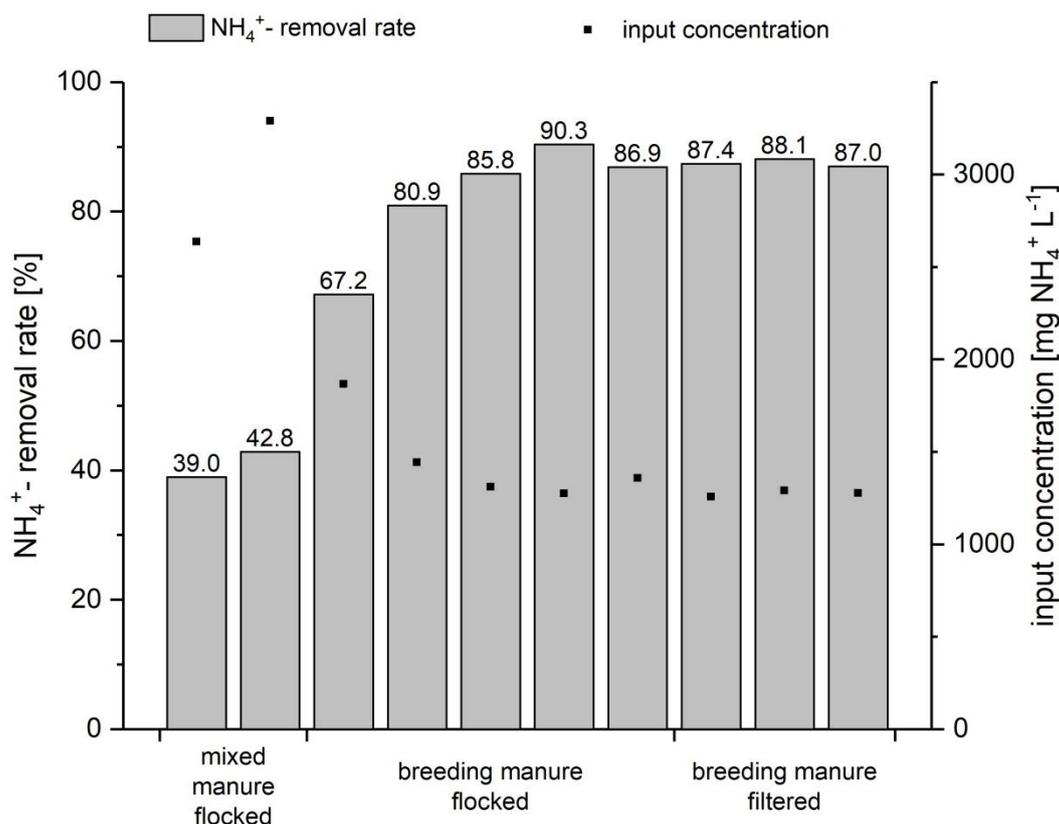


Figure 3. Ammonium removal rates (%) and input concentrations ($\text{mg NH}_4^+ \text{L}^{-1}$) of different manure qualities after preprocessing (single column operation).

Pilot plant operation was possible with filtered breeding manure over three cycles without noticeable constraints, e.g., blockage of zeolite columns or filters leading to decreased ammonium removal rates. Hence, simple mechanical filtration seems to be a suitable procedure for breeding manure preprocessing.

The increase in the removal rates during the six experiments at the beginning (from 39 to 90.3%) is a typical effect of multiple NaOH-regeneration due to the formation of a mainly Na-bearing zeolite with favorable ion exchange conditions for NH_4^+ [33]. Furthermore, the ammonium removal rate is strongly influenced by the input concentration and, respectively, the amount of zeolite in relation to the amount and ammonium concentration of the input material. NH_4^+ -removal rates from flocced breeding manure in serial operation with two subsequent columns (= doubled mass of zeolite) are presented in Figure 4. Removal rates decrease greatly with increasing operation time for the single column (K1; measured at its discharge), e.g., from 85.8% (60 min) over 64.2% (120 min) to 49.8% after 180 min at $c_0 = 1310 \text{ mg NH}_4^+ \text{L}^{-1}$. In serial operation (K1 + K2), the ammonium removal of the second column measured at the discharge of column two compensates the decreasing removal rates in column one and increases the total ammonium removal to 96.4% (60 min), 94.4% (120 min) and 84.6% after 180 min. Experiments show, that the removal rates in serial operation are approx. 10%-points higher after 60 min compared to the single column.

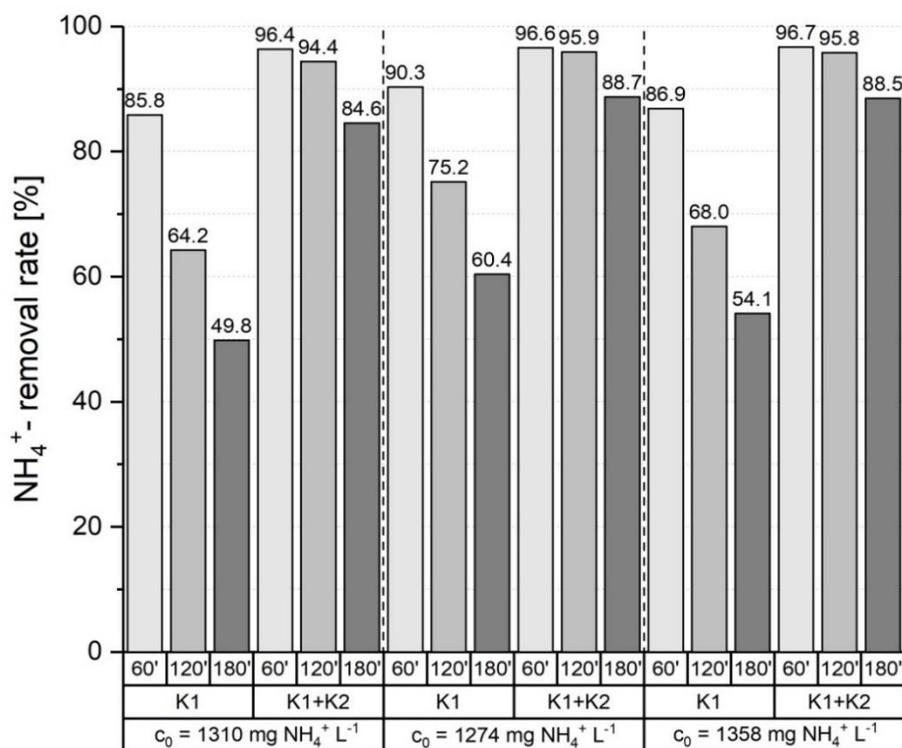


Figure 4. Ammonium removal rates (%) from and input concentrations c_0 after different operation times for single (K1) and serial column operation (K1 + K2) using flocced breeding manure.

By doubling the mass of zeolite in serial mode, the possible operating time at ammonium removal rates > 85% is tripled. This illustrates the importance of adjusting the amount of zeolite as a function of the input concentration and amount of liquid to be processed. Further investigations regarding the optimization of zeolite quantities for different manure qualities and nitrogen contents will be conducted in future.

3.4. Ammonium Recovery and Quality of Regeneration/Product Solutions

The chemical composition of the regeneration and product solution at the end of all batch experiments are presented in Table 3. The regeneration fluid is in direct contact with zeolite and exchanges sodium ions with corresponding zeolite cations, which derive either from the natural cation loading (e.g., Ca^{2+} , Mg^{2+}) or from manure components (e.g., NH_4^+ , K^+). Over the whole experimental series, a small increase in the potassium concentration was observed in the regeneration fluid, whereas no significant differences were measured for Ca^{2+} - and Mg^{2+} -concentrations. Ammonium concentrations increased oppositely to sodium, which is the driving cation for NH_4^+ -exchange. No significant transfer of heavy metals into the regeneration fluid was identified.

Table 3. Chemical composition of the product and regeneration solution at the beginning and end of the experimental runs.

Parameter	LOD	Regeneration Solution		Product Solution		
		Start	End	Start	End	
NH ₄ ⁺	mg L ⁻¹	0.05	1.3	130	21	66,000
Na ⁺	mg L ⁻¹	0.2	23,200	3630	130	140
K ⁺	mg L ⁻¹	0.1	8.0	280	4.0	3.5
Ca ²⁺	mg L ⁻¹	2	5.0	2.5	86.1	50.9
Mg ²⁺	mg L ⁻¹	0.02	0.1	0.2	18.4	12.1
PO ₄ ³⁻	mg L ⁻¹	0.5	31	1.8	1.1	2.0
pH	-	-	13.0	10.3	0.08	1.8
TOC	mg L ⁻¹	0.5	5.9	236	4.57	43.0
Pb	µg L ⁻¹	10	25	<10	<10	18
Ni	µg L ⁻¹	20	<20	120	23	32
Cd	µg L ⁻¹	10	<10	<10	<10	<10
Cr	µg L ⁻¹	20	<20	<20	42	<20
Zn	µg L ⁻¹	100	960	<100	430	370
Fe	µg L ⁻¹	100	350	1180	1360	1590

The product solution comprises a very high concentration of ammonium at the end of the whole series (~66 g L⁻¹) without any significant changes regarding cation content or heavy metal transfer compared to the starting solution. Given its chemical composition, the product solution is well suited for industrial off-gas cleaning, when nitrogen levels are to be reduced in the respective agricultural area, or can be used as a raw material for fertilizer production, if nitrogen should be selectively recycled as a nutrient.

4. Conclusions

The technical feasibility of ammonium removal from pig manure using the ILS-process was successfully demonstrated. Removal rates of > 85% (single column) and > 96% (serial columns) were accomplished in pilot scale experiments. An essential criterion for the use of the ILS process is a sufficient level of solid separation (<0.4% DM; <200 µm) due to potential blockage of the zeolite columns. Nevertheless, the requirements for the purity of the liquid phase are significantly lower than, for example, in the membrane processes, making the ILS-process a promising option for nitrogen recovery from manure. In addition, the purity requirements for preprocessed manure may be reduced by adaptation of future ILS-plant configurations, especially regarding the zeolite columns (e.g., use of coarser grain sizes and further adaptations for harsh environments). Hence, an appropriate and cost-efficient separation method, i.e., a two-stage mechanical process with vibrating screens and subsequent filtration, to avoid the addition of pH-adjusting chemicals and expensive flocculation agents, has to be developed to enable a feasible overall process for nitrogen recovery from pig manure. These aspects will be clarified in future investigations.

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References

- Mallin, M.A. Industrialized Animal Production—A Major Source of Nutrient and Microbial Pollution to Aquatic Ecosystems. *Popul. Environ.* **2003**, *24*, 369–385. [[CrossRef](#)]
- Federal Institute of Agricultural Economics. Pigs—Gross Domestic Production, Slaughter Weight, Export, Calculated Domestic Sales (Schweine—Bruttoeigenerzeugung, Schlachtgewicht, Außenhandel Schweinefleisch, Kalkulierter Inlandsabsatz). Available online: <http://www.agraroeconomik.at/index.php?id=338&L=1> (accessed on 3 November 2020).
- Chamber of Agriculture in Lower Saxony. How Much Manure Do Fattening Pigs Produce? (Wieviel Gülle produzieren Mastschweine?). Available online: <https://www.lwk-niedersachsen.de/index.cfm/portal/1/nav/753/article/30422.html> (accessed on 3 November 2020).
- Bavarian State Research Center for Agriculture. Nutrient Content of Organic Fertilizers at the Time of Application (Nährstoffgehalte organischer Dünger zum Zeitpunkt der Ausbringung). Available online: https://www.lfl.bayern.de/mam/cms07/iab/dateien/basisdaten_20190131_5.pdf (accessed on 3 November 2020).
- Feichtinger, F.; Dersch, G.; Fank, J.; Robier, J. Nitrogen fluxes on arable land in the Murtal with regard to groundwater-friendly management (Stickstoffflüsse auf Ackerland des Murtales in Hinblick auf grundwasserverträgliche Bewirtschaftung). In Proceedings of the 2nd Environmental & Ecological Symposium 2010, Raumberg-Gumpenstein, Austria, 2–3 March 2010; Lehr- und Forschungszentrum für Landwirtschaft Raumberg-Gumpenstein. pp. 37–42.
- Xu, R.T.; Pan, S.F.; Chen, J.; Chen, G.S.; Yang, J.; Dangal, S.R.S.; Shepard, J.P.; Tian, H.Q. Half-Century Ammonia Emissions from Agricultural Systems in Southern Asia: Magnitude, Spatiotemporal Patterns, and Implications for Human Health. *Geohealth* **2018**, *2*, 40–53. [[CrossRef](#)] [[PubMed](#)]
- Tian, H.; Xu, R.; Canadell, J.G.; Thompson, R.L.; Winiwarter, W.; Suntharalingam, P.; Davidson, E.A.; Ciais, P.; Jackson, R.B.; Janssens-Maenhout, G.; et al. A comprehensive quantification of global nitrous oxide sources and sinks. *Nature* **2020**, *586*, 248–256. [[CrossRef](#)] [[PubMed](#)]
- European Commission. A Farm to Fork Strategy for a Fair, Healthy and Environmentally-Friendly Food System: Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. COM/2020/381 Final. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52020DC0381> (accessed on 9 November 2020).
- Zubair, M.; Wang, S.; Zhang, P.; Ye, J.; Liang, J.; Nabi, M.; Zhou, Z.; Tao, X.; Chen, N.; Sun, K.; et al. Biological nutrient removal and recovery from solid and liquid livestock manure: Recent advance and perspective. *Bioresour. Technol.* **2020**, *301*, 122823. [[CrossRef](#)] [[PubMed](#)]
- Vecino, X.; Reig, M.; Bhushan, B.; Gibert, O.; Valderrama, C.; Cortina, J.L. Liquid fertilizer production by ammonia recovery from treated ammonia-rich regenerated streams using liquid-liquid membrane contactors. *Chem. Eng. J.* **2019**, *360*, 890–899. [[CrossRef](#)]
- Dube, P.J.; Vanotti, M.B.; Szogi, A.A.; García-González, M.C. Enhancing recovery of ammonia from swine manure anaerobic digester effluent using gas-permeable membrane technology. *Waste Manag.* **2016**, *49*, 372–377. [[CrossRef](#)]
- Oliveira Filho, J.D.; Daguerra-Martini, S.; Vanotti, M.B.; Saez-Tovar, J.; Rosal, A.; Perez-Murcia, M.D.; Bustamante, M.A.; Moral, R. Recovery of Ammonia in Raw and Co-digested Swine Manure Using Gas-Permeable Membrane Technology. *Front. Sustain. Food Syst.* **2018**, *2*. [[CrossRef](#)]
- García-González, M.C.; Vanotti, M.B. Recovery of ammonia from swine manure using gas-permeable membranes: Effect of waste strength and pH. *Waste Manag.* **2015**, *38*, 455–461. [[CrossRef](#)]
- Montalvo, S.; Huiliñir, C.; Castillo, A.; Pagés-Díaz, J.; Guerrero, L. Carbon, nitrogen and phosphorus recovery from liquid swine wastes: A review. *J. Chem. Technol. Biotechnol.* **2020**, *95*, 2335–2347. [[CrossRef](#)]
- Molinuevo-Salces, B.; Riaño, B.; Vanotti, M.B.; Hernández-González, D.; García-González, M.C. Pilot-Scale Demonstration of Membrane-Based Nitrogen Recovery from Swine Manure. *Membranes (Basel)* **2020**, *10*. [[CrossRef](#)]
- Huang, H.; Yang, J.; Li, D. Recovery and removal of ammonia-nitrogen and phosphate from swine wastewater by internal recycling of struvite chlorination product. *Bioresour. Technol.* **2014**, *172*, 253–259. [[CrossRef](#)] [[PubMed](#)]
- Nelson, N.O.; Mikkelsen, R.L.; Hesterberg, D.L. Struvite precipitation in anaerobic swine lagoon liquid: Effect of pH and Mg:P ratio and determination of rate constant. *Bioresour. Technol.* **2003**, *89*, 229–236. [[CrossRef](#)]

18. Amini, A.; Aponte-Morales, V.; Wang, M.; Dilbeck, M.; Lahav, O.; Zhang, Q.; Cunningham, J.A.; Ergas, S.J. Cost-effective treatment of swine wastes through recovery of energy and nutrients. *Waste Manag.* **2017**, *69*, 508–517. [[CrossRef](#)] [[PubMed](#)]
19. Ye, Z.-L.; Chen, S.-H.; Lu, M.; Shi, J.-W.; Lin, L.-F.; Wang, S.-M. Recovering phosphorus as struvite from the digested swine wastewater with bittern as a magnesium source. *Water Sci. Technol.* **2011**, *64*, 334–340. [[CrossRef](#)]
20. Limoli, A.; Langone, M.; Andreottola, G. Ammonia removal from raw manure digestate by means of a turbulent mixing stripping process. *J. Environ. Manag.* **2016**, *176*, 1–10. [[CrossRef](#)]
21. Liu, L.; Pang, C.; Wu, S.; Dong, R. Optimization and evaluation of an air-recirculated stripping for ammonia removal from the anaerobic digestate of pig manure. *Process Saf. Environ. Prot.* **2015**, *94*, 350–357. [[CrossRef](#)]
22. Liao, P.H.; Chen, A.; Lo, K.V. Removal of nitrogen from swine manure wastewaters by ammonia stripping. *Bioresour. Technol.* **1995**, *54*, 17–20. [[CrossRef](#)]
23. Alitalo, A.; Kyrö, A.; Aura, E. Ammonia stripping of biologically treated liquid manure. *J. Environ. Qual.* **2012**, *41*, 273–280. [[CrossRef](#)]
24. Huang, H.; Xiao, D.; Pang, R.; Han, C.; Ding, L. Simultaneous removal of nutrients from simulated swine wastewater by adsorption of modified zeolite combined with struvite crystallization. *Chem. Eng. J.* **2014**, *256*, 431–438. [[CrossRef](#)]
25. Li, J.; Zhang, Z.; Khunjar, W.; Zhao, K. Enhanced nutrient sequestration from swine wastewater using zeolite synthesized from fly ash integrated with surface amendment technique. *Fuel* **2013**, *111*, 57–65. [[CrossRef](#)]
26. Lin, H.; Wu, X.; Zhu, J. Kinetics, equilibrium, and thermodynamics of ammonium sorption from swine manure by natural chabazite. *Sep. Sci. Technol.* **2016**, *51*, 202–213. [[CrossRef](#)]
27. Penn, C.J.; Warren, J.G.; Smith, S. Maximizing ammonium nitrogen removal from solution using different zeolites. *J. Environ. Qual.* **2010**, *39*, 1478–1485. [[CrossRef](#)] [[PubMed](#)]
28. Montégut, G.; Michelin, L.; Brendlé, J.; Lebeau, B.; Patarin, J. Ammonium and potassium removal from swine liquid manure using clinoptilolite, chabazite and faujasite zeolites. *J. Environ. Manag.* **2016**, *167*, 147–155. [[CrossRef](#)] [[PubMed](#)]
29. Wijesinghe, D.T.N.; Dassanayake, K.B.; Scales, P.; Sommer, S.G.; Chen, D. Removal of excess nutrients by Australian zeolite during anaerobic digestion of swine manure. *J. Environ. Sci. Health A* **2018**, *53*, 362–372. [[CrossRef](#)] [[PubMed](#)]
30. Ellersdorfer, M. The ion-exchanger-loop-stripping process: Ammonium recovery from sludge liquor using NaCl-treated clinoptilolite and simultaneous air stripping. *Water Sci. Technol.* **2018**, *77*, 695–705. [[CrossRef](#)] [[PubMed](#)]
31. Lubensky, J.; Ellersdorfer, M.; Stocker, K. Ammonium recovery from model solutions and sludge liquor with a combined ion exchange and air stripping process. *J. Water Process Eng.* **2019**, *32*, 100909. [[CrossRef](#)]
32. Tschegg, C.; Rice, A.H.N.; Grasemann, B.; Matiasek, E.; Kobulej, P.; Dzivák, M.; Berger, T. Petrogenesis of a Large-Scale Miocene Zeolite Tuff in the Eastern Slovak Republic: The Nižný Hrabovec Open-Pit Clinoptilolite Mine. *Econ. Geol.* **2019**, *114*, 1177–1194. [[CrossRef](#)]
33. Englert, A.H.; Rubio, J. Characterization and environmental application of a Chilean natural zeolite. *Int. J. Miner. Process* **2005**, *75*, 21–29. [[CrossRef](#)]

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