

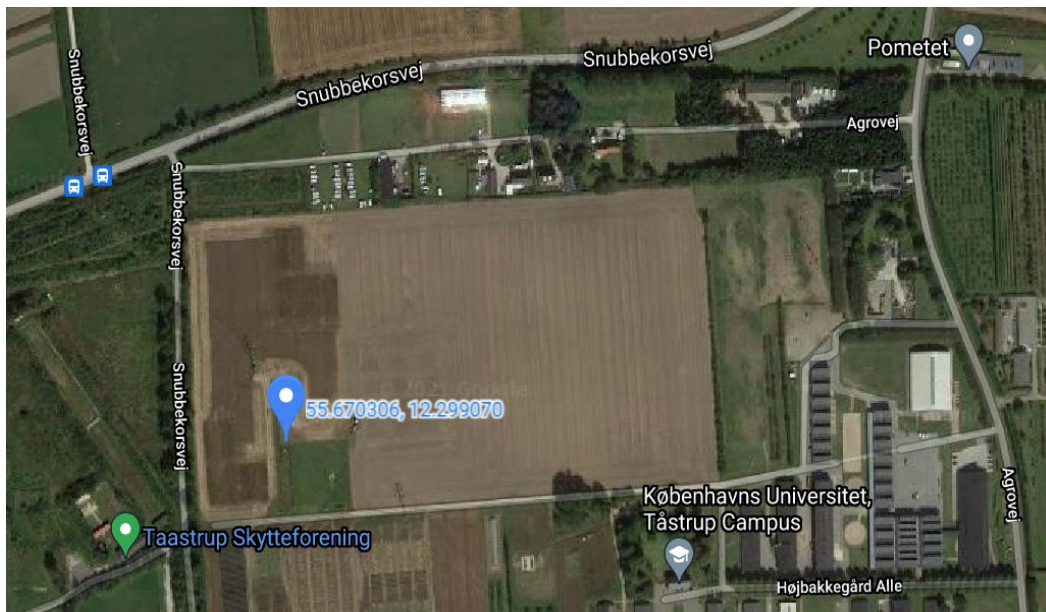
Zero-valent iron and zeolite filter

Location

Country: Denmark

City: Taastrup

Coordinates: 55.670306, 12.299070



Problem description

Intensive application of nitrogen fertilizers to agricultural fields results in high leaching of nitrate (NO_3^-) to the aqueous environment. Eutrophication with nitrate has strong attention both as part of the UN sustainability goals (United Nation Environmental Assembly (UNEA), 2019) and as part of water regulation, e.g. the EU Water Framework Directive (2015). The member states including Denmark has taken strong national actions to reduce nitrate leaching to surface and coastal waters. Runoff from agricultural land is regarded as the predominant source of nitrogen discharges to the aquatic environment (EEA, 2018). Moreover, also phosphate is transported from agricultural land to the aquatic environment, although in much lower quantities compared with nitrate. However, because of the low threshold phosphate concentration (25 - 50 $\mu\text{g P/L}$) initiating eutrophication, even low phosphate discharges of less than 1 kg P/ha/y is harmful to the aquatic environment.

Nitrate reduction to ammonium by zero-valent iron (ZVI) followed by ammonium retention by a cation exchanger would be an attractive way to recycle nitrogen, and reduce energy consumption for industrial ammonium (fertilizer) production. In addition such system would apply the concept of circular economy to nitrogen. With agricultural drainage water as major source of phosphate and nitrogen discharge to the environment, the aim was to develop a filtration system that can remove phosphate and nitrate, and recover ammonium from agricultural drainage water. Therefore, ZVI and the cation exchanger clinoptilolite were used as filter materials, with the ZVI filter part preceding the clinoptilolite trap.

Filter description

Season of 2019-2020: Field experiment

A field experiment was performed using a pilot scale filter system implementing the optimized features of a lab scale unit, but now 100 times larger, for treatment of water flows up to 1.2 L min^{-1} . The purpose of the field experiment was to monitor the performance of the much larger filter system *in situ* and to compare efficiency with the lab scale model. Like the lab filter, the field filter system comprised three units (Figs. 1, 2).

The nitrate reduction unit consists of a 120 cm long column with an internal diameter of 31.5 cm. This unit is packed with a 2/1 m/m mixture of ZVI and sand, with a total mass of 45 kg of ZVI, a pore volume (PV) of 35 L and water residence time of 35 min. In the second unit - the oxidation unit - air was pumped at a flow of 35 L min^{-1} using a Hailea AC Piston air compressor pump. In order to diffuse the air as micron-sized bubbles into the unit, the air pump was connected via silicone tube and air valve to a Hygger type aquarium bubble stone (10 cm diameter). Similar as in the laboratory experiment, retention of ammonium was achieved in the ammonium retention unit consisting of a 140 cm long column with an internal diameter of 31.5 cm. The bottom was filled with 20 kg filter sand followed by 70 kg of clinoptilolite. The PV of the retention unit was 45 L and the water residence time was approximately 45 minutes.

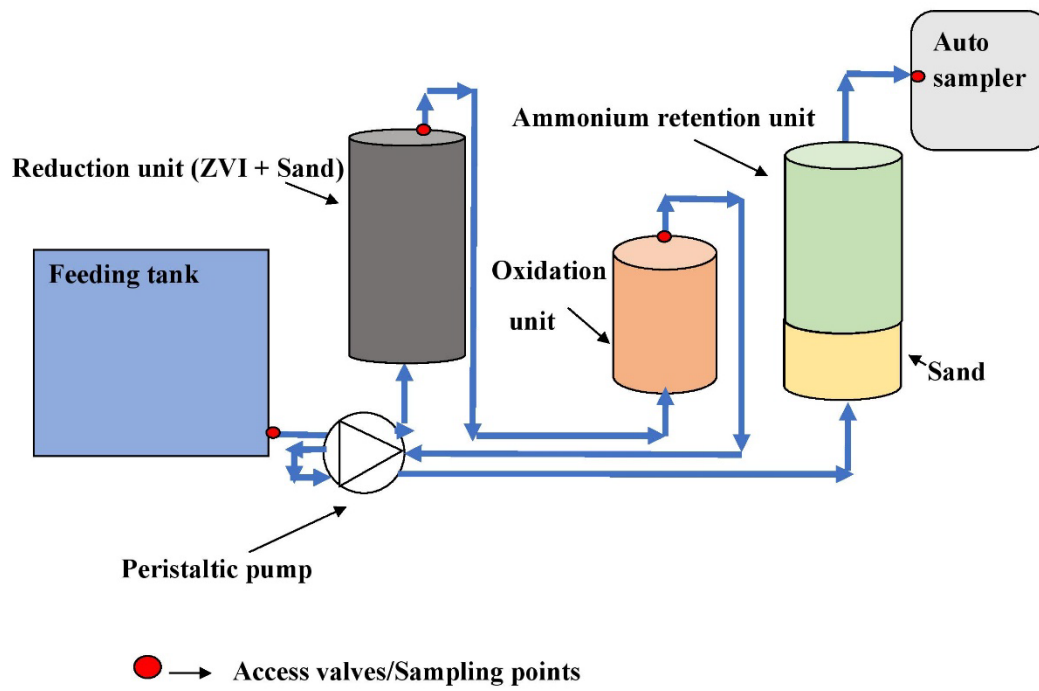


Fig. 1 - Schematic diagram of the laboratory ZVI filter system setup



Fig. 2: Photo of the ZVI filter system field experiment

Results

Field experiment

1. Reduction capacity

The filter system built in the field, based on the laboratory filter system model, was continuously operated for 1691 PVs. Inlet nitrate concentrations ranged between 2 and 8 mg L⁻¹ NO₃⁻N (= 9 and 35 mg L⁻¹ NO₃). The nitrate removal efficiency ranged between 72% and 100% (Fig. 3), while the average removal efficiency of the field filter system was 94%.

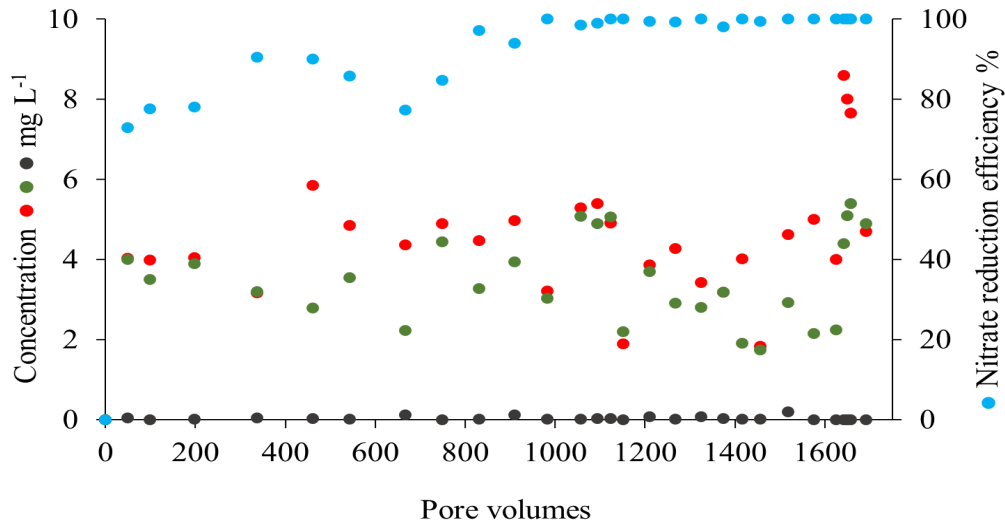


Fig. 3 – Nitrate reduction efficiency, nitrate to ammonium conversion and ammonium retention versus number of pore volumes in the field filter system. ● Nitrate reduction efficiency %; ● Nitrate-N reduced mg L⁻¹; ● Ammonium-N produced mg L⁻¹ and ● Ammonium-N outlet mg L⁻¹.

Measurements of pH in influent and effluent samples showed that outlet pH increased from 7.6 to 8.9, while the flow decreased over time, from 1.2 L min⁻¹ in the beginning of the experiment, to 0.2 L min⁻¹ at the end.

2. Oxidation of soluble iron(II)

Soluble iron(II) measured after the ZVI filter unit was found to be highly variable, with concentrations ranging between 0.5 and 9 mg L⁻¹. Like for the laboratory system, the oxidation unit showed almost 100% efficiency in iron(II) oxidation and removal (Fig. 4).

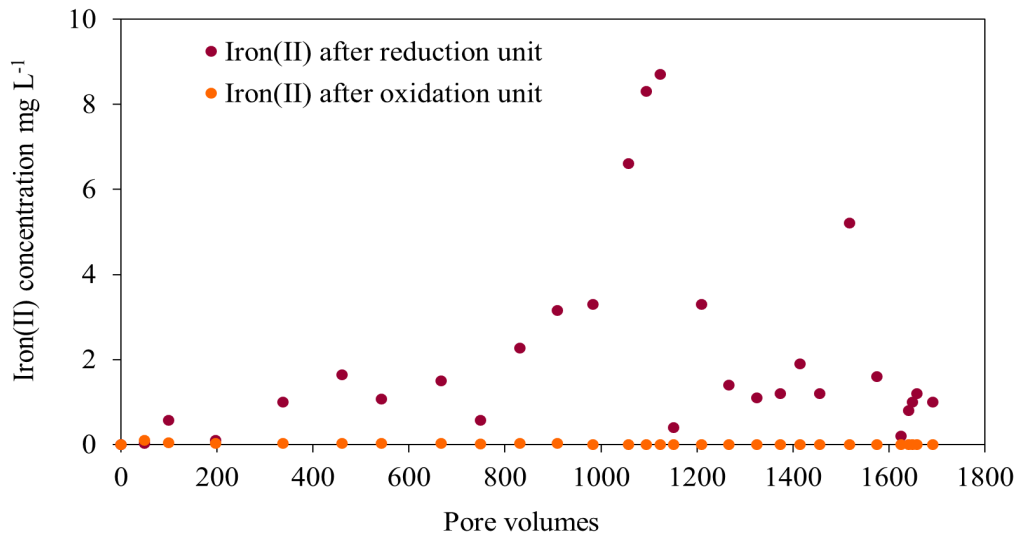


Fig. 4 - Concentration of ● iron(II) measured after the reduction unit and ● iron(II) measured after the oxidation unit for the field filter system as a function of passed pore volumes.

3. Stoichiometry

The first 400 PVs treated by the field filter system resulted in 95% conversion of nitrate to ammonium (Fig. 3). After this period, the conversion rate varied between 50% and 99% with an average of 70%.

4. Ammonium retention

The ammonium retention unit of the field filter system was able to retain approximately 99% of the ammonium formed by ZVI nitrate reduction, for the entire duration of the experiment (Fig. 3).

5. Phosphorus retention

The pristine phosphate concentration measured in the agricultural drainage water was low, with the highest concentration of 0.12 mg P L⁻¹. However, for the field experiment, the water in the feeding tank was spiked 2 times with phosphate, to reach phosphate concentrations of 0.5 mg P L⁻¹. This treatment was done in order to test the capacity of ZVI to retain phosphate. Very low concentration of phosphate was measured after the reduction unit, and no phosphate was found in the outlet samples, demonstrating a total retention of P onto the ZVI and iron oxides formed in the nitrate reduction process (Fig. 5).

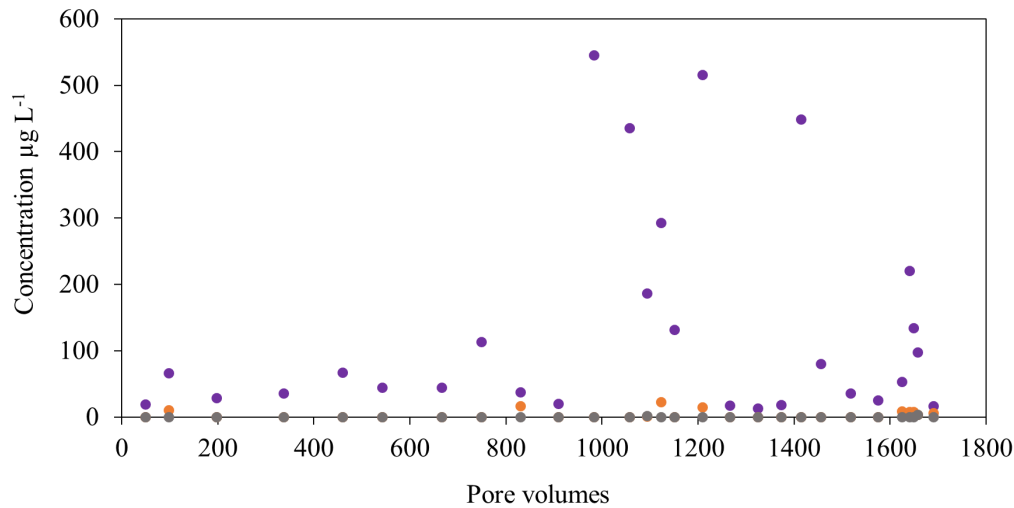


Fig. 5 - Phosphate concentration in the field filter as a function of passed pore volumes - ● Phosphate-P inlet; ● Phosphate-P after reduction unit and ● Phosphate-P after oxidation unit.

6. Corrosion products in the ZVI reduction unit.

After termination of the field experiment, the reduction unit of the field filter system was opened for visual inspection and sample collection. Visible green solids were present in the water from inside the reduction unit, and the ZVI material had a black-green color. Four samples of used filter material were collected from the upper part of the unit, between 10 and 20 cm from the outlet, as well as four samples of water with suspended solids.

Scanning Electron Microscopy (SEM) analysis of the used ZVI filter material showed the formation of small (nano and micro sized) green rust (GR) (a layered metal hydroxide, $\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{CO}_3 \cdot 2\text{H}_2\text{O}$) particles located on ZVI particle surfaces with tabular single crystals aggregated to form a "flower-like" structure (Fig. 6).

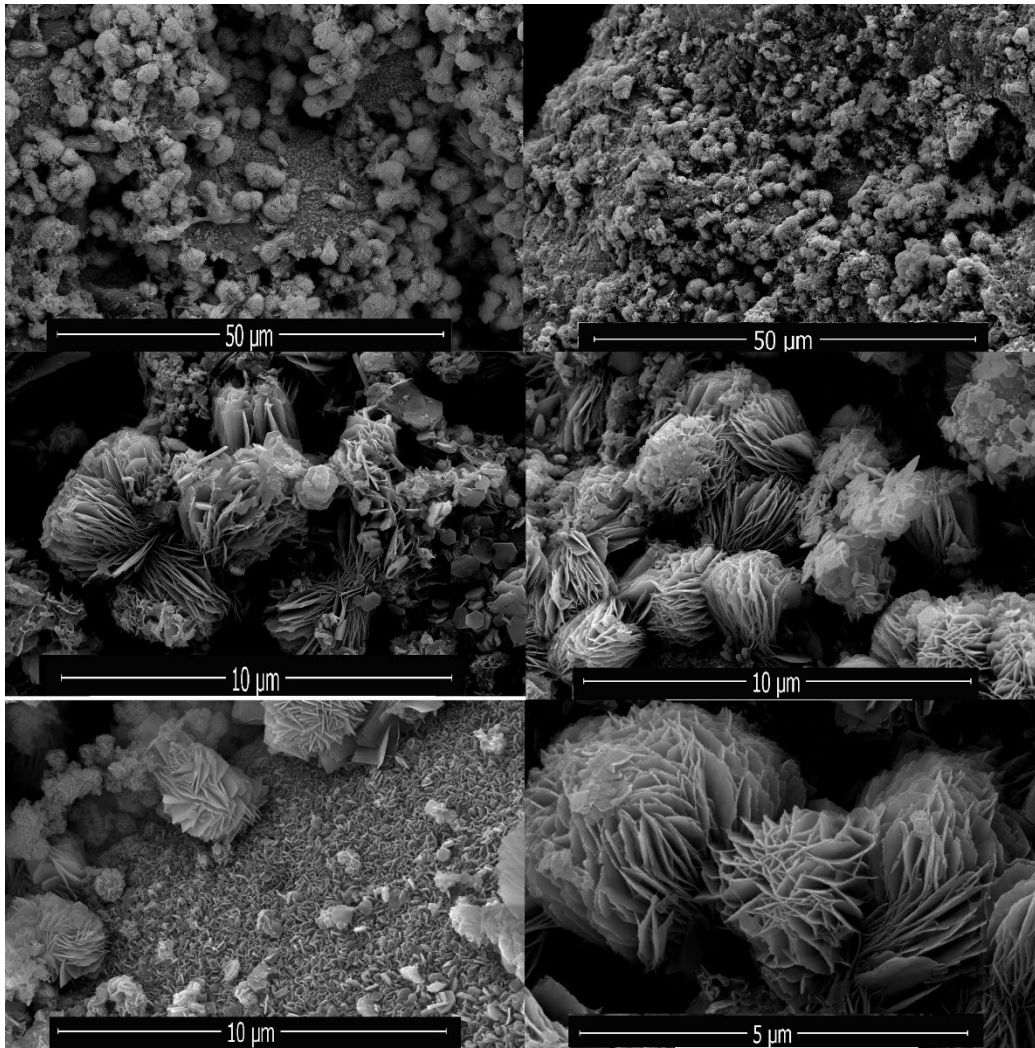


Fig. 6 - SEM images of GR flower-like structure for a sample from the top 10 to 20 cm of the ZVI filter unit in field experiment.

Updates from drainage seasons 2021 – 2023

As mentioned above the ZVI corrodes with the formation of ochrous products that eventually may clog the ZVI unit. Also ochreous products from the oxidation unit may pass on to the zeolite unit and impair its function. Finally, the zeolite part needs regeneration when it has become saturated with ammonium.

In 2022 we conducted lab experiments to find a suitable reagent that can remove the corrosion products from the used ZVI material to recover its hydraulic and reactive properties. Oxalic acid, citric acid and HCl were tested followed by lab testing of nitrate reduction. The citric acid resulted in best performance and highest recovery of the nitrate reduction capacity. In these tests it was also observed that traces of oxygen poisons nitrate reduction and hence that oxygen is first reduced before nitrate reduction commences. With these tests it was decided to

regenerate the ZVI unit of the field filter. 80 L of 0.5 mol/L citric acid was circulated through the filter over a period of 4 hours at a flow of 2 L/min. The leachate was collected and the filter reassembled. The filter was now used for a new round of drainage water filtration (47 days) at a flow of approximately 1 L/min, and with a similar monitoring program as described above. Results are presented in Fig. 7. The nitrate reduction slowly increased on start-up of the filter demonstrating that the filter first had to consume the oxygen in the system before nitrate reduction was optimal. No phosphate was seen in the outlet of the filter unit at any time.

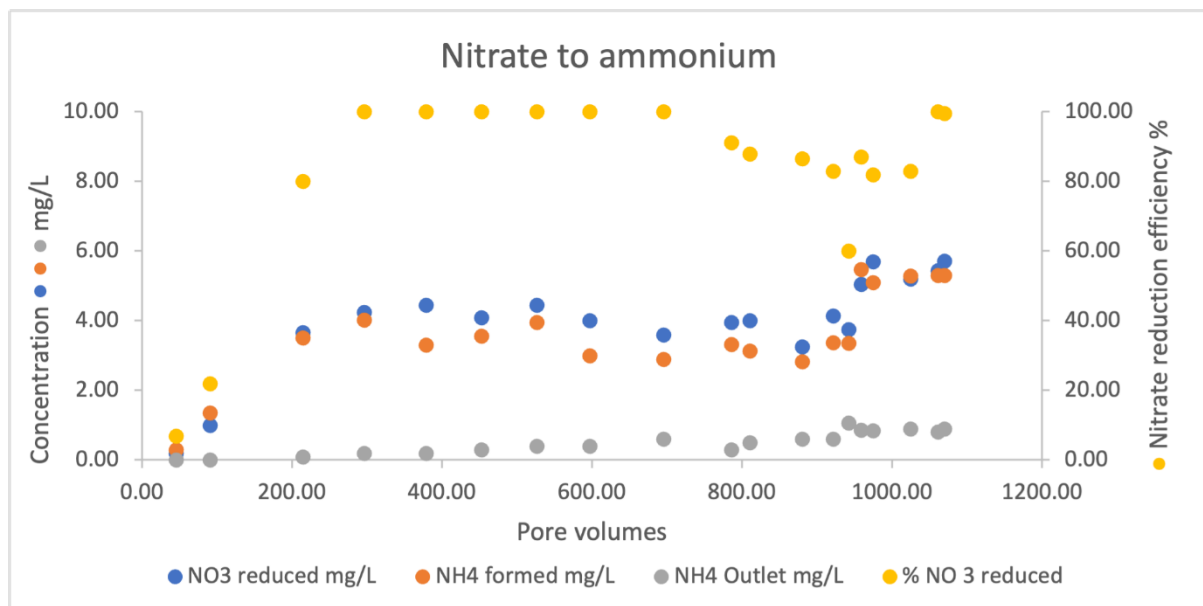


Fig. 7 – Nitrate to ammonium reduction efficiency and ammonium retention in the zeolite unit after regeneration of the field ZVI unit using citric acid. Run time 47 days at a flow of 1 L/min . Also the efficiency of Fe(II) oxidation in the oxidation unit was monitored. Almost all Fe(II) got oxidized throughout the testing period, but with a little carry over of iron to the zeolite unit probably affecting its performance.

Eventually the flow decreased and the system clogged. The filter was disassembled. Fig. 8 shows part of the dismantled filter demonstrating the corrosion of the ZVI material, in particular at the inlet where highest nitrate and oxygen concentrations appear.



Fig. 8 – Corroded ZVI material stained brownish-red by the ochreous material at the inlet of the ZVI filter

For the drainage season 2022-23 the filter was rebuilt, but now with a new ZVI material from Höganäs AB. The filter was tested for a 40 day period from late March 2023 to May 2023. Other units and conditions were similar. The performance of the filter was similar as seen before, but with a somewhat poorer performance of the Höganäs material compared with ZVI filings that were used for the initial testing of the filter, see Fig. 9. The nitrate reduction efficiency dropped already after 25 days. Also the zeolite filter performance was poorer which could be attributed to a malfunctioning oxidizing unit. Hence some Fe(II) was carried onto the zeolite filter where it sorbed to the zeolite and partly oxidized decling the ammonium retention performance of the zeolite.

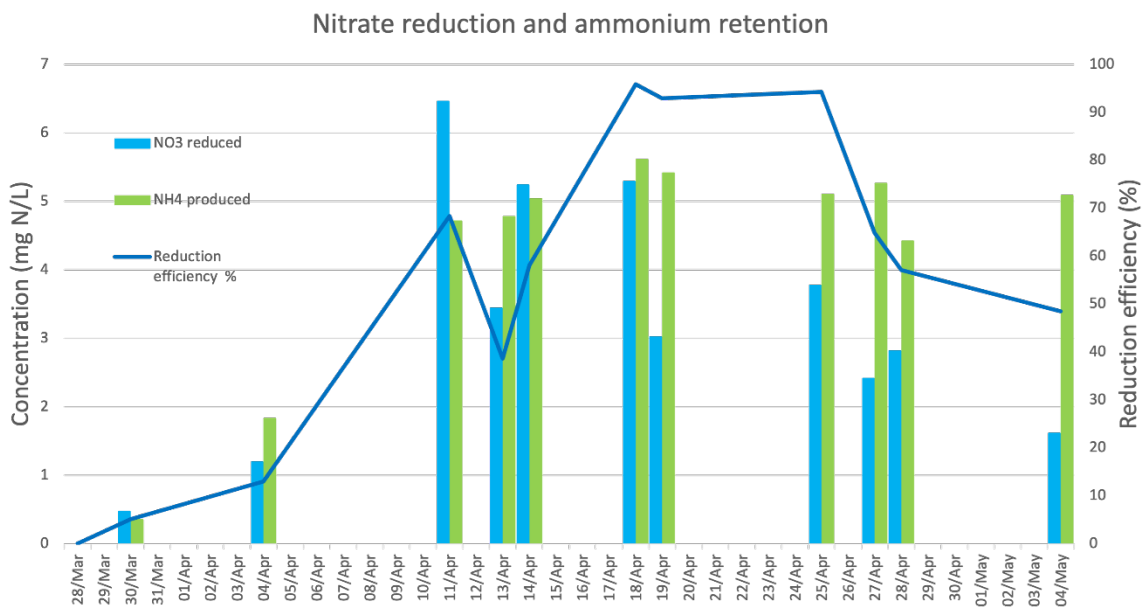


Fig. 9 – Nitrate to ammonium reduction efficiency for the field filter with the ZVI unit packed with Höganäs ZVI.

Also for this filter we tested regeneration using 0.5 M citric acid. This worked equally well as for the first regeneration. Thus, the flow was increased and nitrate reduction efficiency re-installed. In the period following the regeneration, the nitrate concentration in the inlet water was very low and hence the inlet water was spiked with nitrate. The spiking experiments showed there was no warming up time and spiked nitrate was immediately reduced in the ZVI filter again demonstrating the filter's ability to cope with variable nitrate inlet concentrations.

Financial aspect

Cost efficiency and applications.

Recovery of nitrogen as described above provides a principle for lowering the environmental impact. Moreover, ammonium desorption and re-use can reduce the cost of reactive nitrogen production and apply the concept of circular economy to nitrogen. Although this could be an ideal solution to re-cycle nitrogen, the economic implications of a ZVI filter use should be addressed.

Estimating the construction, maintenance and materials costs of a filter system capable to filtrate nitrate in the annual discharge of drainage water from 1 hectare (approx. 2000 m³), having an average nitrate-N concentration of 10 mg L⁻¹, results in a total cost up to 35 € kg⁻¹ N reduced, over a projection/depreciation period of 10 years (Table 1). As the current market price of N is around 0.3 € kg⁻¹ for ammonia fertilizers, the cost of the recycled N is very high. However, compared with other nutrient removal techniques used for environmental protection, the cost is at a similar level (Table 2). Denitrification in constructed mini wetlands has an average cost of about 30 € kg⁻¹ N removed (Gachango et al., 2015). In addition, the ZVI filter technology is also a perfect filter for trapping phosphorus, with a retention efficiency of 100%. This could add to the cost-efficiency of the ZVI filter system, as the cost for removing P could reach 1000 € kg⁻¹ P for alternative filter solutions (Gachango et al., 2015). Nonetheless, this type of filter system could be used for small communities or green house production facilities for filtrating water containing higher concentrations of fertilizers, pesticides or heavy metals.

Table 1: Cost-efficiency calculation in €/kg N reduced, over a depreciation period of 10 years with 0% rate of interest.

	Price	Amount needed/ha/year (2000 m ³ drainage water – 10mg/L NO ₃ ⁻ -N; approx. 20 kg NO ₃ ⁻ -N)	Price/ha/year	Cost/year over 10 years period
ZVI	0.85 €/kg	72 kg	62 €	62 €
Zeolite (reusable material)	2.5 €/kg	500 kg	1250 €	125 €
Establishment (reusable material)	2000 €		2000 €	200 €
Maintenance/year	300 €		300 €	300 €
Total			3612 €	687 €
Total cost €/kg N reduced over 10-year projection				34.3 €

Table 2: Comparison of ZVI filter system cost effectiveness with other related measures.

Nutrient removal measures	Costs € per kg of reduced N
ZVI filter system (materials + establishment + maintenance)	Up to 35 €
Surface flow constructed wetlands	Up to 30.6 €
Buffer zones	Up to 34.9 €
Catch crops	Up to 41.6 €

The ZVI filter costs are from own calculations (Table S3), while the costs of all the other measures are adapted from Gachango et al. (2015).

Conclusion

Both laboratory and field experiments proof the principle of the ZVI - zeolite coupled filter system comprising reduction of nitrate and recovery of ammonium from agricultural drainage water. Main conclusions are:

- An average of 70% conversion ratio of nitrate to ammonium.
- High performance even with relatively short retention times of 35 - 45 min, and low NO₃⁻ concentrations
- Almost 100% retention of ammonium in zeolite enabling reuse of the recovered ammonium.
- The ZVI filter system works at variable nitrate concentrations and it has a high efficiency also at low temperature.

- ZVI surface corrosion by nitrate and oxygen reduction results in green rust formation which further facilitates nitrate to ammonium conversion and increases the reduction capacity of the filter system.
- Retention of phosphate in the filter system is complete.
- The limiting factor for the sustainability of the ZVI filter system is related to the formation of passivation layers and reduction in permeability. The ZVI filter can be regenerated using flushing with citric acid while the zeolite unit can be regenerated using sodium chloride. Regeneration with citric acid reinstalls the hydraulic conductivity and the nitrate reduction efficiency.
- Oxygen in the inlet water consumes ZVI and competes with nitrate for reduction.

Consequently, these findings can represent the starting point of a promising removal and recovery filter technology for both N and P and can be an important way to reduce energy consumption for industrial ammonium production and to apply the concept of circular economy to nitrogen.