European Sustainable Phosphorus Platform

SCOPE NEWSLETTER

1st White Ammonia and N-recovery Research Meeting (WARM), Brussels and hybrid, 7th June) 2023.

Showcasing N-recovery R&D. Links with EU policies and industry. Discussion of research conclusions and needs presented below.

Within EU Green Week, Brussels. Back-to-back to the 6th Power to Ammonia conference, Rotterdam 8-9 June 2023 NH3 Event.

Programme & registration www.phosphorusplatform.eu/NRecovery

V. 12/5/23

7th June 2023 Brussels & hybrid

White Ammonia Research Meeting

Contents

Proposed conclusions 2
- *Widespread and increasing potential* 2
- *Recovery of aqueous solutions incompatible with industrial recycling* 2

Summaries of selected publications 3

Our review of reviews 3

Membranes, dialysis, etc. 4
- *GENIUS full-scale membrane system* 4
- *Full scale N-recovery Yverdon-les-Bains* 5
- *LIFE pilot for N-recovery from air and liquid* 5
- *Membrane fouling in ammonia recovery* 6
- *Pilot wwtp digestate ammonia recovery* 6
- *Membrane contactor for N recovery* 7
- *Solar catalytic membrane cell* 7
- *Membranes plus microbial electrolysis cells* 8
- *Electrodialysis of landfill leachate* 8
- *Electrolytic N-concentration & stripping* 8
- *IEX + membranes + microbial protein* 8
- *Electrodialysis + microbial protein* 9
- *Capacitive deionisation (CDI) N-recovery* 9
- *Other membrane studies* 9

Adsorbents & ion-exchange 10
- *Ammonia capture by ionic liquids* 10
- *Full scale Ionic Liquid ammonia gas recovery* 12
- *NH_3 recovery from gas by ENILs* 12
- *Zeolite ammonia ion-exchange* 12
- *Fertiliser value of zeolite adsorbed N* 13
- *Testing zeolites for ammonia recovery* 14
- *12 t/day zeolite NH_4 removal from manure* 14
- *Ion-exchange from sludge drying condensate* 14
- *Geopolymers for ammonia adsorption & recovery* 15

Reacting ammonia with CO_2 16
- *Stripping to solid ammonium bicarbonate* 16
- *Conversion of adsorbed NH_3 and CO_2 to urea* 16
- *Wood biochar CO_2 – NH_3 trapping* 17

Nitrogen transformation 17
- *Conversion of nitrate to ammonia* 17
- *Enzyme ammonia release in sludge* 18

N-recovery from urine 18
- *N-recovery from source-separated urine.* 18

Biomass N-recovery 19
- *Microbial protein production* 19

Concentrations & conversions 20

ESPP members 20

Stay informed 20

Editorial

Following the first ESPP Workshop on Nitrogen Recovery (Jan. 2023, see SCOPE Newsletter n°145.), this new SCOPE Newsletter now summarises 80+ recent research publications on nitrogen recovery ("White Ammonia") worldwide, and proposes possible conclusions.

ESPP suggests that industry, farmer and societal needs for recycling should drive research: form of product, logistics. Our action on Nitrogen Recovery started by bringing together industry and downstream users and by showcasing ammonia stripping – recovery installations or NOx stripping.

*This first workshop found that there is increasing potential for stripping of ammonia, NO_x and N_2O from digestates, waste water treatment, industrial and combustion offgas, driven by air quality and greenhouse emissions obligations, but that **processes operational today mostly result in aqueous solutions, which make transport and logistics prohibitive, except for local use, and are not adapted to industrial recycling.***

This review of research publications confirms this, with a range of research approaches generating dilute ammonia streams (membranes, electrodialysis, adsorbents …). However, it also identifies other routes, which can generate products adapted to market needs, such as quality organic fertilisers, targeted biomass products.

*This Newsletter will input to ESPP's workshop on Nitrogen Recovery research: **WARM Brussels & hybrid 7th June 2023**.*

Robert Van Spingelen, ESPP President

Nitrogen Recovery

This SCOPE Newsletter summarises a **selection of nearly 80 recent science publications on nitrogen recovery**, with the aim of showing current state of the art in research and proposing conclusions on R&D needs.

Proposed conclusions

These proposed conclusions will be discussed at the White Ammonia Research Meeting (WARM) Brussels, 7th June

Widespread and increasing potential ….

Ammonia stripping and NO_x/NO_2 scrubbing are widespread and increasingly used technologies, with the development of anaerobic digestion for renewable methane production and with tightening limits on ammonia and N_2O/NO_x emissions.

Recovery of aqueous solutions incompatible with industrial recycling

However, ammonia stripping, NO_x/NO_2 scrubbing, and much of the current nitrogen recovery research, result in aqueous solutions of ammonia salts / ammonia water which are incompatible with industrial recycling:

✘ **Aqueous solutions are largely incompatible with industrial recycling** because of transport and logistics costs (except where local cheap thermal energy allows concentrating the liquid). This was clear at ESPP's first Nitrogen Recovery Workshop. However, aqueous solutions remain the direction of much of the research identified in this Newsletter.

Such aqueous ammonium (salt) solutions **can be sold locally to farmers**, **for local N recycling**.

✘ **Membrane** "concentration": results in ammonium salt **solutions of 1 – 5 %N** which pose the same problems. Membranes also pose questions of operational cost (energy and chemicals input, need for upstream filters, replacement, cleaning and maintenance) and in some cases fouling.

✘ The membranes used are often based on PTFE (polytetrafluorethylene = "Teflon"), a **"PFAS",** potentially targeted by the current EU proposed ban. It is needed to identify reliable, effective, low-fouling alternatives: other polymers, ceramic membranes.

✘ **Vacuum evaporation** for concentration: work is underway, but to date unproven on ammonia and energy efficiency in operational conditions needs to be determined.

A research challenge is **how to concentrate dilute ammonia water or salt solutions** with low energy consumption.

One route may be **mechanical vapour compression (MVC) / mechanical vapour recompression (MVR),** as in the Sedron Varcor process (several full scale units operational).

Several routes are identified which could potentially **recover N in a solid form, or as a gas**, rather than in aqueous solutions:

- **Easymining** (SCOPE 145), ammonia is recovered as solid struvite (magnesium ammonium phosphate). At present the struvite is redissolved to recycle the Mg and P back to the process, so resulting in an aqueous ammonia salt solution.
- **Reaction of ammonia to non-soluble nitrogen salts**, recovered as a solid, seems to be not investigated to date.
- **Adsorption / regeneration from liquid.** Zeolites or geopolymers can uptake around 2% N (by weight) from wastewater, but also uptake other elements. N-content is thus too low for use as a fertiliser, other than locally. Regeneration liquor for one case with geopolymers reached 9% N. However, for zeolites, regeneration by heat to c. 60°C can release ammonia gas. We found no studies on ammonia gas release from geopolymers.
- **Adsorption / regeneration from gas**. Significant recent research is underway designing and lab-testing specific ionic liquids (ILs) able to selectively adsorb ammonia from gases, with over 20% $N\text{-}NH_4$ adsorption, then release ammonia gas in regeneration by heating to e.g. 80°C. Full-scale IL units (80 and 130 million m^3gas/year) are operating on industrial offgas in China, recycling ammonia gas onsite back into industrial processes (L. Zhang et al., 2021, below).

Effects of water on ionic liquids may be critical, as offgas ammonia is usually humid.

A challenge would be to **recover pure ammonia gas from regeneration of these materials** (not mixed with N_2 or air flow), then clean the ammonia gas and compress it for transport. See Lemus et al. 2016 below.

Other routes for nitrogen recycling include:

- N2 Applied: **plasma technology** fixes N into and stabilises N in organic substrates.
- **Reaction with carbon dioxide**: this is a known process for production of urea or carbamate. CCm (see SCOPE Newsletter n°145, Yeh 2005) react ammonia with CO_2 and organic substrates to produce a stable organic N fertiliser, as well as fixing carbon.
- **Processing of separately collected urine** to recycled fertiliser products.

Summaries of selected publications

Our review of reviews

Review papers abound on nitrogen recovery and focus either on type of technologies, category of treated stream or global solutions to nitrogen issues. However, these mostly analyse research papers and so lead to theoretical rather than practical conclusions.

Ochs et al., 2023, compared different **scenarios for ammonia removal in dewatering liquors from anaerobic sludge digestion**: treatment of liquors from conventional anaerobic digestion and from anaerobic digestion with thermal hydrolysis as pre-treatment. This techno-economic analysis compared technologies such as deammonification in a continuous stirred tank reactor, nitrification/denitrification sequenced batch reactor and thermal ammonia stripping. This theoretical approach concluded that, despite its advantages such as N recovery and N_2O emission reduction, the stripping technology presented a whole-life cost much higher than biological solutions. The authors highlighted the need to reduce costs of N-stripping to allow broader application, and so wider possibilities for N-recovery.

Deng (Z.) et al. reviewed around **150 studies all using real (not synthetic) residual streams for analytical or experimental research into ammonia recovery**. The review analyses potential of different streams based categorisation by levels of ammonia, total nitrogen, suspended solids and chemical oxygen demand (COD); discusses possible uses of recovered ammonia, analyses potential processes for increasing ammonia concentration and recovery technologies and discusses possible adjustments of anaerobic digester parameters to optimise conversion of total nitrogen to ammonia.

Reviewing 107 literature sources, **Palakodeti et al.,** 2021, focussed on **column ammonia stripping from anaerobic digestate**. They concluded that, besides usual parameters such as temperature, pH and gas flow rates, the composition of the stripping gas can have a significant impact on ammonia removal. Various configurations linking the column and the digester and multiple columns designs are also discussed.

Chen et al., 2021, reviewed 161 references about **electrokinetic and stripping processes for ammonia removal and recovery from wastewater**. Yield and energy consumption per g N were compared for conventional, advanced, microwave-assisted and membrane contactors stripping processes, as well as electrodialysis, electrodeionisation, capacitive deionisation and bio-electrochemical systems. Despite technical challenges, they concluded that hybrid processes (integrating both types of technologies) displayed the potential to combine flexibility (regarding sources), high recovery ratio, relatively low energy consumption and cost-effectiveness (compared to conventional ammonia production).

Beckinghausen et al., 2020, compared different technologies for N recovery from wastewater from the efficiency and energy requirement viewpoints (104 references). **They concluded the lack of full-scale operating data** to support decision making and highlight the need for full-scale energy and economic analysis for each both existing and emerging technologies.

Pandey and Chen, 2021, carried out the same exercise and reached the same conclusions for livestock manure, **again concluding that there is a lack of long term operation and economic data**. They suggest that air stripping by direct aeration, thermal vacuum stripping and gas-permeable membrane can offer recovery efficiency and lower cost.

Montalvo et al., 2020, analysed the literature related to **carbon, nitrogen and phosphorous recovery from swine liquid waste** (118 references). They focussed first on algae biomass production, air stripping, membrane processes and struvite formation, as well as bioelectrochemical processes and adsorption.

Wu and Vaneeckhaute, 2022, investigated the **combination of stripping, adsorption and struvite precipitation** (124 papers reviewed). In their conclusion, the authors proposed to apply adsorbents for nitrogen recovery, such as activated carbon, metal organic frameworks and other nanostructured materials, as an alternative to the acid scrubber downstream of the stripping column.

Qin et al., 2023, reviewed (150 references) nitrogen up-concentration in domestic wastewater for improving N recovery, as current technologies are usually adapted to N-rich streams. **The paper summarises the challenges for application of selected technologies such as ion exchange and membranes**. (See a second paper by the same authors under "Adsorbents").

Xiang et al., 2020, classified various nitrogen removal technologies from wastewater based on their ammonia recovery potential. They drew conclusions for different wastewater streams.

Matassa et al., 2022, discussed **alternative pathways to decrease the use of synthetic fertiliser nitrogen, to enter a "post-Haber-Bosch mindset and era".** The first pathway proposed is to develop other forms of protein production processes than agriculture, such as microbially catalysed protein production. The second pathway proposed is nitrogen recovery, using technologies such as described in this Scope Newsletter, including the production of microbial proteins or microalgae, to be used as feed or food. Finally, a third pathway proposed is based on nitrogen-fixing abilities of microorganisms, to be then used in organic fertilisers. A final possibility could be to recycle organic nitrogen to energy in the ammonia – hydrogen economy.

See also the **review of some 200 recent publications on separated urine treatment** by **Larsen, Riechmann & Udert, 2021**, which covers stabilisation, concentration, nitrogen and phosphorus recovery, sanitisation and organic micropollutants..

"Techno-economic analysis of sidestream ammonia removal technologies: Biological options versus thermal stripping", P. Ochs et al., Environmental Science and Ecotechnology 13 (2023) 100220, https://doi.org/10.1016/j.ese.2022.100220

"Recovery and applications of ammoniacal nitrogen from nitrogen-loaded residual streams: A review", Z. Deng, N. van Linden et al., J. Env. Management 295 (2021) 113096 https://doi.org/10.1016/j.jenvman.2021.113096

"A critical review of ammonia recovery from anaerobic digestate of organic wastes via stripping", A. Palakodeti et al., Renewable and Sustainable Energy Reviews 143 (2021) 110903, https://doi.org/10.1016/j.rser.2021.110903

"Advanced ammonia nitrogen removal and recovery technology using electrokinetic and stripping process towards a sustainable nitrogen cycle: A review", T. Chen et al., Journal of Cleaner Production 309 (2021), https://doi.org/10.1016/j.jclepro.2021.127369

"From removal to recovery: An evaluation of nitrogen recovery techniques from wastewater", A. Beckinghausen et al., Applied Energy 263 (2020) 114616, https://doi.org/10.1016/j.apenergy.2020.114616

"Technologies to recover nitrogen from livestock manure - A review", Pandey and Chen, Science of the Total Environment 784 (2021) 147098, https://doi.org/10.1016/j.scitotenv.2021.147098

"Carbon, nitrogen and phosphorus recovery from liquid swine wastes: a review", S. Montalvo et al., Journal of Chemical Technology and Biotechnology (2020), https://doi.org/10.1002/jctb.6336

"Nutrient recovery from wastewater: A review on the integrated Physicochemical technologies of ammonia stripping, adsorption and struvite precipitation", H. Wu and C. Vaneeckhaute, Chemical Engineering Journal 433 (2022) 133664, https://doi.org/10.1016/j.cej.2021.133664

"Up-concentration of nitrogen from domestic wastewater: A sustainable strategy from removal to recovery" Y. Qin et al., Chemical Engineering Journal 451 (2023) 138789, https://doi.org/10.1016/j.cej.2022.138789

"New progress of ammonia recovery during ammonia nitrogen removal from various wastewaters", S. Xiang et al., World Journal of Microbiology and Biotechnology 36 (2020), https://doi.org/10.1007/s11274-020-02921-3

"How can we possibly resolve the planet's nitrogen dilemma?", S. Matassa et al., Microbial biotechnology (2022), https://doi.org/10.1111/1751-7915.14159

"State of the art of urine treatment technologies: A critical review", T. Larsen, M. Riechmann, K. Udert, Water Research X 13 (2021) 100114 https://doi.org/10.1016/j.wroa.2021.100114

Membranes, dialysis, etc

GENIUS full-scale membrane system

Nijhuis GENIUS triple membrane system treating all of the output digestate from > 80 000 t/y (ww, input) mixed manure co-digesters, Groot Zevert Vergisting (GZV), Beltrum, The Netherlands. Around 1/3 of N and 2% of P are recovered in reverse osmosis (RO). The RO "concentrate" solution contains around 0.8% N_{total}/ww (21% / DM), 0.015% P_{total}/ww (0.4% / DM) and 1.4% organic matter/ww (38% / DM).

The GZV biogas plant takes some 93 kt/y ww of input materials, mainly manure with some dairy and animal feed industry wastes and glycerine. These inputs had estimated overall average contents of around 0.71 % N/ww and 0.16 % P/ww. The final digester is operated at 52°C to ensure sanitisation. N and P concentrations in the digestate are 0.7 %N and 0.16 % P /ww.

This paper reports results of operation of the GENIUS digestate processing system, **treating nearly 100% of the GZV digestate, from September 2020 to February 2021**.

The GENIUS process starts with two cascaded decanters for solid-liquid separation, the first with magnesium chloride dosing (which will partly precipitate phosphate into the solid fraction as struvite), the second with polymer flocculant dosing. The solid fractions contain 1.2 – 1.5 % N_{total}/ww and 0.5 – 0.9 % P_{total}/ww. Following this, the liquid fraction is passed through a microfiltration membrane to further separate solids, then final purification by two reverse osmosis membranes (RO) with sulphuric acid dosing, followed by ion exchange to further purify water before discharge.

The system required weekly cleaning of the decanters and of the first RO membrane, and monthly cleaning of the microfiltration membrane (MF). To clean the MF membrane, 50% citric and 10% hydrochloric acid were used (0.01 and 0.1 kg/t digestate respectively). The first and second RO membranes have required replacement 1 – 2 times per year. The GENIUS system required around 20 kWh of electrical energy per tonne digestate treated.

The authors estimate that **GENIUS in this case reduces the mass-weighted average transport distance for products leaving the site by around 50%.**

Around 1/3 of the digestate N_{total} was transferred to the RO concentrate.

The N concentration in the RO "concentrate" (0.8% N_{total}/ww) is similar to the average in the digestate input to the GENUIS process (0.7% N_{total}/ww).

The EU Fertilising Product Regulation (FPR) requires a nitrogen content of 5% for PFC 1(C)(I)(b)(i) liquid inorganic macronutrient fertiliser or minimum 3%/ww organic carbon for PFC 1(B)(II) liquid organo-mineral fertiliser. **The RO**

“concentrate”, in which around 1/3 of the inflow nitrogen is recovered, cannot be classified as a “fertiliser” under the EU Fertilising Products Regulation because its nitrogen content /ww is too low for an inorganic fertiliser (0.8 %/ww compared to requirement of 5 %/ww. If the RO concentrate were (hypothetically) evaporated to a solid, its organic carbon content would also be much too high for an EU FPR Inorganic Fertiliser (organic carbon < 7.5% = 14% organic matter using the conversion coefficient of the FPR, compared to 38 % organic matter / DM in the RO “concentrate”).

“Performance of a full-scale processing cascade that separates agricultural digestate and its nutrients for agronomic reuse”, J. Van Puffelen et al. Separation and Purification Technology 297 (2022) 121501 DOI.

See also GENIUS process in ESPP-DPP-NNP Technology Catalogue http://www.phosphorusplatform.eu/techcatalogue

Full scale N-recovery Yverdon-les-Bains

Pürro & Gindroz (Yverdon-les-Bains municipal waste water treatment works 45 000 p.e., ALPHA WasserTechnik AG, Switzerland) have published results of full-scale stripping / scrubbing of ammonia from sewage sludge digestate centrate. The digestate can contain up to 20% of the works inflow ammonia load and returning this to the works inflow can deteriorate works biological functioning and increase greenhouse gas N_2O emissions.

The centrate pH is increased from below 7 to 9 – 10 and temperature is increased from 35°C to 50°C. This releases ammonia gas in solution which moves across a hydrophobic contactor membrane (polypropylene) into 96% sulphuric acid. 80% of ammonia in the centrate is recovered as ammonium sulphate.

The installation has been operating since early 2016, treating c. 4 m^3/h, that is around half of the sewage work’s digestate centrate.

Aqueous ammonium sulphate 35 – 50 gN-NH_4/l is produced (3.5 – 5 %N/ww). Since 2020, a concentration unit increases this to c. 8% N/ww. The ammonium sulphate is sold to farmers in a distance of around 50 km.

*“Stripping membranaire de l’ammoniaque”, Aqua & Gas n°1, 2018 (in French)*https://www.aquaetgas.ch/fr/eau/eaux-us%C3%A9es/ag2018-01_fa_p%C3%BCrro/

LIFE pilot for N-recovery from air and liquid

EU funded Ammonia Trapping project tested two mobile gas-permeable membrane pilots (with sulphuric acid downstream of the membrane) for a total of nearly two years recovering ammonia solution from livestock stable offgas and from manure/digestate liquors. Ammonia sulphate solutions at around 3 %N were recovered in both cases.

The **pilot for ammonia recovery from gas** was operated in continuous mode, treating c. 50 m^3/h air (6 – 20 gN-NH_3/m^3) from a pig stables and a chicken house. Expanded polytetrafluoroethylene (ePTFE, that is, PFAS) gas-permeable membranes were used. In both cases the pilot was **operated continuously for around 8 months**. The pilot was also operated for 1 ½ months treating offgas from a composter (c. 90 gN-NH_3/m^3). The final concentrations of nitrogen in the recovered ammonium sulphate solution was nearly 3 %N.

The **pilot for ammonia recovery from liquids** was operated in batch mode: batches of c. 6 m^3, ePTFE gas membrane, batch treatment duration 7 – 20 days, with membrane cleaning between batches when necessary. This pilot was operated first on **raw pig manure (without prior solid-liquid separation**, 22 – 72 g/l total solids) and then on **digestate (again without prior solid-liquid separation**, 32 - 76 g/l total solids, digester input mainly pig manure with some agricultural by-products).

A total of thirteen batches were tested, five with manure and eight batches with digestate.

The ePTFE membrane showed no fouling after two years of operation.

The reactor was aerated to maintain manure pH at 8.5 and acid was added when needed to keep the acid side of the membrane below pH 2.

Input ammonia nitrogen in both the manure and digestate was 0.1 – 0.5 %N-NH_3 (1000 - 5000 mgN/l). N-NH_3 removal was 15 – 50 % with 40 – 80 % recovery of removed N as ammonia sulphate solution (the remainder presumably being lost to air). Performance was significantly influenced by temperature.

A final ammonium sulphate concentration of up to 3.5 %N was achieved.

A later study presents 1.5 litre lab trials using synthetic wastewater to investigate the effects of operational conditions on the performance of this technology.

The **new EU-funded LIFE Green Ammonia project "Market technology based on membranes for the reduction of ammonia in livestock farms"** (here) aims to develop the technology to TRL 8-9, taking into account the results obtained in the Ammonia Trapping project above.

2021-1: “Effect of Acid Flow Rate, Membrane Surface Area, and Capture Solution on the Effectiveness of Suspended GPM Systems to Recover Ammonia”, M. Soto-Herranz et al., Membranes 2021, 11, 538. https://doi.org/10.3390/membranes11070538

2021-2: “Pilot Plant for the Capture of Ammonia from the Atmosphere of Pig and Poultry Farms Using Gas-Permeable Membrane Technology”, M. Soto-Herranz et al., Membranes 2021, 11, 859, https://doi.org/10.3390/membranes11110859

2021-3: “Reduction of Ammonia Emissions from Laying Hen Manure in a Closed Composting Process Using Gas-Permeable Membrane Technology”, M. Soto-Herranz et al., Membrane Technology. Agronomy 2021, 11, 2384. https://doi.org/10.3390/agronomy11122384

2022-1: “Evaluation of Different Capture Solutions for Ammonia Recovery in Suspended Gas Permeable Membrane Systems”, M.

Soto-Herranz et al., Membranes 2022, 12, 572, https://doi.org/10.3390/membranes12060572

2022-2: "Comparison of the Ammonia Trapping Performance of Different Gas-Permeable Tubular Membrane System Configurations", M. Soto-Herranz et al., Membranes 2022, 12, 1104, https://doi.org/10.3390/membranes12111104

"Effect of Operational Conditions on Ammonia Recovery from Simulated Livestock Wastewater Using Gas-Permeable Membrane Technology", B. Riaño, B. Molinuevo-Salces et al., (EU Interreg SYMBIOSIS_II), Membrane Technology. Environments 2022, 9, 70. https://doi.org/10.3390/environments9060070

"Ammonia Recovery from Digestate Using Gas-Permeable Membranes: A Pilot-Scale Study", B. Riaño et al. Environments 2021, 8, 133 https://doi.org/10.3390/environments8120133

"Pilot-Scale Demonstration of Membrane-Based Nitrogen Recovery from Swine Manure", B. B. Molinuevo-Salces, B. Riaño et al., (EU LIFE Ammonia-Trapping), Membranes 2020, 10, 270; https://doi.org/10.3390/10.3390/membranes10100270

EU LIFE Ammonia Trapping project website http://ammoniatrapping.com/

Membrane fouling in ammonia recovery

Lee et al. 2021 present wastewater ammonia membrane trials, with 6-day continuous operation at the lab scale (20 cm^2 membrane area) show that fouling problems depend on pH and generated ammonium sulphate solution up to 130 mgN-NH$_4$/l (0.1 % N/ww).

The primary effluent (input wastewater after de-gritting etc.) was from a municipal sewage works in Seoul and contained 30 – 40 mgN-NH$_4$/l. A PVDF (PFAS) hydrophobic gas porous membrane was used (pore size 0.22 µm, thickness 125 µm). The feed was adjusted to pH 9.2 or 11. Sulphuric acid (0.1 M) downstream of the membrane was used to trap ammonia.

Significant mineral fouling of the membrane showed after 6 days at pH 11 but not at pH 9.2. **Protein and lipid fouling was also identified at both pH**, coherent with other studies.

After 120 hours of continuous operation, ammonia sulphate concentration downstream of the membrane reached c. 130 mgN-NH$_4$ (0.01 N/ww).

Fouling of ammonia recovery membranes is also discussed in **Zarebska et al.** (2014, 2015) in lab-scale tests using real and synthetic pig manure. Organic fouling was identified as important (lipids, carbohydrates, proteins, carboxylates), as well as mineral deposits. After a week of operation, the ammonia separation membrane showed10 – 15 µm of fouling, resulting in a loss of membrane hydrophobicity. Possible solutions proposed included membrane cleaning with acid and alkali or cleaning agents, or ultrafiltration upstream of the membrane, but these would increase operating costs or possibly simply move the fouling problem to the upstream ultrafiltration membrane.

"Ammonia harvesting via membrane gas extraction at moderately alkaline pH: A step toward net-profitable nitrogen recovery from domestic wastewater", W. Lee et al., Chemical Engineering Journal 405 (2021) 126662, https://doi.org/10.1016/j.cej.2020.126662

"Fouling mitigation in membrane distillation processes during ammonia stripping from pig manure", A. Zarebska et al., J. Membrane Science 484 (2015) 119–132 http://dx.doi.org/10.1016/j.memsci.2015.03.010

"Ammonia recovery from agricultural wastes by membrane distillation: Fouling characterization and mechanism", A. Zarebska et al., Wat. Res. 56 (2014) 1-10 http://dx.doi.org/10.1016/j.watres.2014.02.037

Pilot wwtp digestate ammonia recovery

A 100 litre capacity membrane ammonia recovery batch pilot was tested for three months (24/7) fed with pre-filtered (200 µm) centrifuge dewatering liquor from sewage sludge anaerobic digestion at Gleisdorf municipal wwtp Austria. Ammonium sulphate solution 0.5% N was produced (5 gN-NH$_4$/l).

The pilot contact membrane unit had 14.5 m^2 of DCMD membrane (commercially available PTFE membrane, that is PFAS, pore size 0.45 µm).On one side, pre-filtered digestate liquor rich in ammonia was fed, with sodium hydroxide for pH adjustment, on the other side sulphuric acid was dosed, resulting in ammonia transfer across the membrane to generate ammonium sulphate solution. **The pilot was operated continuously for three months** in batch mode, with 100 litre input batches for 3 hour cycles (with the ammonium sulphate permeate not changed after each batch).

The wwtp sludge digestate liquor, from dewatering by centrifuge with iron and polyelectrolyte dosing, had 0.04 – 0.07 % ammonia nitrogen (0.4 – 0.7 gN-NH$_4$/l) and a total solids content of 0.7%.

In order to reduce membrane fouling, a 200 µm sieve filter was installed upstream of the pilot, reducing total solids to c. 0.1%. With this filter in place, membranes were cleaned only once in three months operation. Cleaning with water proved inadequate and mild acid was required to maintain performance (2% citric acid at 50°C for one hour).

Another challenge was sodium hydroxide consumption, probably water hardness in the digestate, which would imply operating costs and led to precipitation (of insoluble carbonates). These were removed in the filter, so preventing them causing membrane fouling.

Ammonium-N concentration reached c. 0.5% in the permeate after around 2 ½ days of continuous operation, that is treating around 1.8 m^3 of digestate.

The authors conclude that the membrane unit can recover **0.5 %N ammonium sulphate solution**, when operated at 38°C, using c. 14 kWh per kg N (low temperature thermal energy = 40°C), but this does not include energy cost of chemicals used (sodium hydroxide, acid for cleaning).

"Recovery of ammonia from centrate water in urban waste water treatment plants via direct contact membrane distillation: Process performance in long-term pilot-scale operation", E. Guillen-Burrieza et al., J. Membrane Science 667 (2023) 121161, https://doi.org/10.1016/j.memsci.2022.121161

"Vacuum membrane distillation multi-component numerical model for ammonia recovery from liquid streams", D. Scheepers et al., J. Membrane Science 614 (2020) 118399, https://doi.org/10.1016/j.memsci.2020.118399

Membrane contactor for N recovery

A pilot-scale membrane unit recovered ammonia sulphate solution up to 0.9% N from sewage sludge digestate liquor.

In the reactor (volume 300 litres), the input liquor is a stirred around six "contact membrane" modules, each containing on hundred membrane fibres (total membrane surface 21 m^2). Ammonia is transferred through the membranes to acids.

The pilot was operated continuously, with input flow rates of 24 to 48 l/h, and was **tested for one month at Viikinmäki sewage works, Finland** (treating sludge digestate liquor after aluminium salt + polymer P-removal and settling, then filtration through a bag filter), and on landfill leachate for four days, Finland. In different trials both PTFE (PFAS) and polypropylene membranes were tested, different flow rates and residence times, and different acids.

A smaller unit was previously tested on these substrates and on urine.

A maximum of 0,9 % N was attained in the recovered ammonium salt solution through the membranes (compared to 0.08 – 0.12% N in the sludge liquor), with 35% - 60% N-recovery (the remaining N remained in the treated liquor or was lost to the atmosphere, the objective here was to test conditions not optimise recovery). A higher N-recovery of 70% was achieved by NPHarvest (Kaljunen 2021 paper).

PTFE membranes (PFAS) showed better performance than PP but **both organic and inorganic fouling was noted**, with an increase in carbon, oxygen, phosphorus, calcium, silicon on the membrane. Sulfuric acid performed better than nitric or phosphoric acid. Information on contaminants and other ions present in the recovered ammonium salt solution can be found in the SvensktVatten 2022 report referenced (not yet available in English).

A 2023 paper (Högstrand et al.) performs the **Life Cycle Analysis (LCA) of the NPHarvest process, and of struvite precipitation + ammonia stripping**, concluding that benefits of both technologies were reductions in mainstream wwtp N_2O emissions and substitution of mineral fertilisers and that LCA hotspots for the NPHarvest technology were ammonia emissions (which could be resolved by air sealing, electricity and use of chemicals (NaOH, acid).

"Membrane contactor onsite piloting for nutrient recovery from mesophilic digester reject water: The effect of process conditions and pre-treatment options" R. A. Al-Juboori et al. Separation and Purification Technology 303 (2022) https://doi.org/10.1016/j.seppur.2022.122250

"Membrane Technologies for Nitrogen Recovery from Waste Streams: Scientometrics and Technical Analysis", A. Al-Juboori et al., Membranes 2023, 13, 15. https://doi.org/10.3390/membranes13010015

"Newly developed membrane contactor-based N and P recovery process: Pilot-scale field experiments and cost analysis" J. U. Kaljunen et al., J. Cleaner Production 281 (2021) https://doi.org/10.1016/j.jclepro.2020.125288

"Nitrogen Recovery from Landfill Leachate Using Lab- and Pilot-Scale Membrane Contactors: Research into Fouling Development and Membrane Characterization Effects", I. Righetto et al., Membranes 2022, 12, 837, https://doi.org/10.3390/membranes12090837

SvenkstVatten NPHarvest report n°2022-12, Högstrand et al., in Swedish https://vattenbokhandeln.svensktvatten.se/wp-content/uploads/2023/03/svu-rapport-2022-12.pdf

"Incorporation of main line impact into life cycle assessment of nutrient recovery from reject water using novel membrane contactor technology", S. Högstrand et al., J. Cleaner Production 408 (2023) 137227 https://doi.org/10.1016/j.jclepro.2023.137227

Solar catalytic membrane cell

Lab trial with synthetic salt solution suggests solar-driven four chamber photoelectrochemical cell with photovoltaic silver sulphur bismuth vanadium anode can concentrate ammonia solution.

The system was tested in continuous mode *for a total operating time of ????? hours ????,* with a c. 20 ml capacity cell and ammonium chloride solution. The Ag_2S-$BiVO_4$ photoanode (chamber 4) was manufactured by electroplating onto tin-doped glass and produces current when exposed to sunlight (electrons which flow to a titanium mesh cathode in chamber 2. Ammonia solution (NH_4^+) is fed into chamber 3, and ammonia ions are driven by the electrical potential into chamber 2 and chlorine ions Cl^- into chamber 4: *it is suggested that this degrades organics (phenol was tested, showing 93% breakdown to CO2) but the mechanism is not clarified: perhaps this is by release of chlorine gas?* The NH_4^+ ions entering chamber 2 cause pH increase, which drives ammonium through the gas permeable membrane into chamber 1, where sulphuric acid is dosed to generate ammonium sulphate solution. After ten cycles, ammonia is concentrated over 20x to c. **7 g/l ammonium sulphate (1.5 %N).**

Answers to???s not received from authors despite requests.

"A novel sustainable N recycling process: Upcycling ammonia to ammonium fertilizer from dilute wastewater and simultaneously realizing phenol degradation via a visible solar-driven PECMA system with efficient Ag_2S-$BiVO_4$ photoanodes", D. Fang et al. Science of the Total Environment 864 (2023) 161121 http://dx.doi.org/10.1016/j.scitotenv.2022.161121

Membranes plus microbial electrolysis cells

The objective is that microbes consuming organic carbon generate electron flows which drive ammonia across a cation exchange membrane to concentrate in the cathode compartment where the pH then favour further transfer of ammonia through a hydrophobic membrane into acid to generate aqueous ammonium salt solution.

In this paper, two different microbial electrolysis cell (MEC) configurations were tested lab scale (c. 1 litre volume), coupled to a PTFE (PFAS) hydrophobic membrane for ammonia recovery in sulphuric acid, generating ammonia sulphate solution. The MECs were inoculated with biofilm from a previously operated MEC to ensure presence of suitable microbes.

The MECs were operated for up to 190 days with synthetic solutions **and 100 days with diluted pig slurry digestate** (0.15% $N\text{-}NH_4$).

With digestate, ammonium removal efficiencies of maximum 23 % were achieved. **Average ammonia concentrations in the cathode compartment of 0.12 % $N\text{-}NH_4$ were achieved**. Ammonium recovery through the gas permeable membrane was variable depending on the cathode compartment pH.

"Hydrophobic membranes for ammonia recovery from digestates in microbial electrolysis cells: Assessment of different configurations" M. Cerrillo et al. Journal of Environmental Chemical Engineering 9 (2021) *https://doi.org/10.1016/j.jece.2021.105289*

Electrodialysis of landfill leachate

Lab trials of effects of calcium and magnesium ions on ammonium-N separation membranes in a 1-litre, 5-compartment electrodialysis cell with 2 bipolar, 1 cation exchange and 1 anion exchange membranes.

Sodium sulphate was loaded in the two electrode compartments and pure water in the acid and alkali compartments, then current was applied. Nearly 90% of ammonia in real landfill leachate was recovered as ammonium solution in the alkali compartment after 3 hours, so **reaching a concentration of around 2 $gNH_4\text{-}N/l$ (c. 2 %N),** similar to the concentration in the leachate. Tests with synthetic solutions showed that citric acid did not interfere with ammonium transfer, whereas magnesium and calcium both compete (migration rate: $NH_4^+ > Mg^{2+} > CA^{2+}$). Magnesium and even more so calcium tended to foul the membrane by forming calcite and magnesium hydroxide.

"Recovery of ammonia nitrogen from landfill leachate using a biopolar membrane equipped electrodialysis system", C. Zhang et al., Water Science & Technology, 82.9, 2020 *https://doi.org/10.2166/wst.2020.438*

Electrolytic N-concentration & stripping

3-compartment electrodialysis cell was lab tested on real wastewater in combination with ammonia stripping and trapping in sulphuric acid.

CMI-7000 and AMI-7100 (gel polystyrene divinylbenzene) cation and anion exchange membranes separated the three cell compartments (anode, concentrate, cathode) to which current was applied. Synthetic wastewaters and real sludge digestate dewatering liquor were tested, fed continuously to the cathode chamber, where NH_4^+ was converted to volatile NH^3, then fed to the stripper where the ammonia was removed by air-bubbling. Ammonia was then trapped from the air in sulphuric acid. The liquor was then returned to the anode chamber, from which effluent was collected. The membranes ensured concentration of ammonium and of other ions in the central chamber (P, K, Na …). Over 90% N-removal was achieved from the real digestate liquor and over 85% recovery, but this was mostly in the concentrate (<5% in the stripping/trapping step). $NH_4\text{-}N$ concentration in the digestate liquor was c. 1 g/l, increased to 6 – 20 g/l in the concentrate.

"Efficient nitrogen removal and recovery from real digested sewage sludge reject water through electroconcentration", V. Koskue et al., J. Env. Chemical Engineering 9 (2021) 106286
https://doi.org/10.1016/j.jece.2021.106286

"Optimising nitrogen recovery from reject water in a 3-chamber bioelectroconcentration cell", V. Koskue et al., Separation and Purification Technology 264 (2021) 118428
https://doi.org/10.1016/j.seppur.2021.118428

IEX + membranes + microbial protein

Combinations of hollow fibre membranes, vacuum thermal ammonia stripping and a rotary evaporator were tested for nitrogen recovery from a 400 l/h zeolite-N ion exchange fed with secondary treated municipal wastewater.

The ion exchange system (IEX) was wastewater (after trickling filters from Cranfield University wastewater treatment plant) with 25 – 50 mg $NH_4\text{-}N/l$. The ion exchange reduced this to 3 mg $NH_4\text{-}N/l$. Repeated regeneration using 10% brine (sodium chloride = salt solution) resulted in an **ammonium solution of c. 900 mg $NH_4\text{-}N/l$ (0.09 %N).** Sodium hydroxide was then dosed to precipitate calcium carbonate, to prevent progressive fouling of the IEX. Regeneration using potassium chloride was also tested in municipal wastewater with 13 – 20 mg $NH_4\text{-}N/l$, resulting in an ammonium solution of c. 600 mg $NH_4\text{-}N/l$ (0.06 %N).

The regeneration brine contained high levels of chloride, but also magnesium, silicon and traces of heavy metals.

Ammonia separation from the regeneration brine was tested in different lab-scale systems (hollow fibre membrane contactor, vacuum thermal stripping processes, rotary evaporator), with in all cases sulphuric acid dosing, and the recovered ammonia sulphate solution was tested as feed for microbial protein production.

The membranes reduced the ammonia concentration in the regeneration brine down to 25 NH_4-N/l after 100 cycles (4 ½ hours).

Ammonia sulphate was recovered using thermal vacuum systems and air dried to produce an ammonium salt. It was also **tested as feed for a microbial protein reactor**, showing no significant difference in growth rate compared to use of a commercial mineral N fertiliser.

"Ammonia recovery from brines originating from a municipal wastewater ion exchange process and valorization of recovered nitrogen into microbial protein", S. Guida et al., Chem. Eng. J. 427 (2022) 130896 DOI.

Electrodialysis + microbial protein

Two papers present lab scale membrane electrodialysis cells for ammonia separation and testing of the resulting ammonia solution to feed culture of microbial protein.

Khoshnevisan et al. tested a lab-scale electrolysis cell (2 chambers each 0.2 l, 28-hour batch mode) using a sulphonic acid functionalised gel polystyrene membrane with organic fraction of municipal solid waste digestate liquor, cattle manure digestate liquor and urine. Sodium bicarbonate was used in the cathode chamber.

Nitrogen levels in the cathode chamber reached around 0.2 %N (around ten times lower than in the input liquors). Energy demand to produce this dilute N solution was around 10 – 15 kWh/kgN.

The recovered dilute ammonia solution (a mixture of ammonium, carbonate and sodium), with added phosphate (buffer) was **tested as the growth media for methanotrophic bacteria culture**, fed with a mixture of oxygen and methane. Bacteria grew well, up to 05 g/l cell dry weight and contained a range of essential amino acids.

Yang et al. lab tested a 0.34 litre electrolysis cell, in which **microbial protein was cultivated directly in the cathode chamber, fed by ammonia molecules passing across the membrane with the applied voltage**, and with injected carbon dioxide and hydrogen gas. Pure ammonium sulphate solution was used as test medium in the anode chamber (0.05 – 8 gN/l).

Bacterial growth up to 0.9 g/ cell dry weight (54% protein content) was obtained after 120 hours.

"Coupling electrochemical ammonia extraction and cultivation of methane oxidizing bacteria for production of microbial protein", B. Khoshnevisan et al., J. Env. Management 265 (2020) 110560, https://doi.org/10.1016/j.jenvman.2020.110560

"Self-sustained ammonium recovery from wastewater and upcycling for hydrogen-oxidizing bacteria-based power-to-protein conversion", X. Yang et al., Bioresource Technology 344 (2022) 126271, https://doi.org/10.1016/j.biortech.2021.126271

"Green electricity-driven simultaneous ammonia recovery and in-situ upcycling for microbial protein production", X. Yang et al., Chemical Engineering Journal 430 (2022) 132890, https://doi.org/10.1016/j.cej.2021.132890

Capacitive deionisation (CDI) N-recovery

CDI is an electrochemical technology based on the accumulation of ions on the surface of porous carbon electrodes, followed by desorption for recovery (by stopping or reversing the electric field), in a cyclic pattern. The ammonia is released into aqueous solution.

Different types of CDI cells operated in single-pass mode were tested in laboratory (0.001 litres, 0.002 l/minute flow, 1.2V, cycles of 2 x 8 minutes) for N removal and recovery in synthetic solutions and 0.45 µm filtered municipal wastewater (from the primary clarifier) from Kenkäveronniemi wwtp, Finland (2.4 mol NH_4/l = 33 g/l N-NH_4). Removal efficiency of ammonia was over 80% for the first operational cycle but fell to around 60% for the second cycle.

A challenge is that **N-recovery rates (below 5 %) were much lower than removal rates,** as desorption of ions is hindered due to possible irreversible reactions on the surface of the carbon electrodes. An oxygen functionalised AC cathode showed the best performance and time-dependent selectivity for ammonium.

No indications are given as to the nitrogen concentration in the recovery solution.

"Enhanced ammonium removal and recovery from municipal wastewater by asymmetric CDI cell equipped with oxygen functionalized carbon electrode", O. Pastushok et al. Separation and Purification Technology 274 (2021) https://doi.org/10.1016/j.seppur.2021.119064

"Nitrate removal and recovery by capacitive deionization (CDI)", O. Pastushok et al., Chemical Engineering Journal 375 (2019) 121943 https://doi.org/10.1016/j.cej.2019.121943

Other membrane studies

There are a number of recent publications testing membranes for ammonia separation from different waste water streams, in particular various manures or manure digestate liquid fractions.

Rodríguez-Alegre et al., 2023,lab tested 3^{M} Liqui-Cell EXF contact membranes (non-PFAS) at lab scale (1.4 m^2 membrane area, recirculation flow rate 0.5 l/min) using as input pig slurry after centrifuge then 280 µm filtration. Sodium hydroxide was dosed to adjust input pH and sulphuric acid was used downstream of the membrane. **Total N concentration increased from c. 0.4 % in the filtered slurry to around 1.4% downstream of the membrane**, phosphorus increased from 0.1% to around 0.5% and potassium from 0.2% to around 1.2%.

"Nutrient recovery and valorisation from pig slurry liquid fraction with membrane technologies", R. Rodríguez-Alegre et al., Sci. Total Environment 874 (2023) 162548, http://dx.doi.org/10.1016/j.scitotenv.2023.162548

Ward et al. tested onsite a pilot CEM and AEM (cation and anion exchange membranes) electrodialysis cell fed with sewage sludge digestate centrifuge dewatering liquor **at the Luggage Point wwtp, Brisbane, Australia**, after struvite precipitation.

The membranes were crosslinked copolymers with quaternary ammonium or sulphonic acid ion exchange groups, that is without PFAS.

The cell electrodialysis cell volume was 22 litres (7 m^2 membrane area), **treating 5 400 l of centrate in each 72 hour run, with acid cleaning of membranes between each run**.

After 72 hours, volume downstream of the cell increased by a factor of 5 (100 l water loss from the 5 400 l of treated centrate). **Nitrogen and potassium concentrations were increased from around 0.08 and 0.02 % in the input centrate to around 0.7 %N and 0.2% K in the electrodialysis output**.

Electrical consumption to generate this dilute solution was c. 5 kWh/kgN.

"Nutrient recovery from wastewater through pilot scale electrodialysis", A. Ward et al., Wat. Res. 135 (2018) 57e65, https://doi.org/10.1016/j.watres.2018.02.021

Mubita et al. review results of a range of membrane ammonia recovery studies carried out in the TKI Biovalor project. Authors are from Wageningen University & Research (WUR) and technology suppliers **Colubris, Nijhuis** and **Lenntech. Technologies** covered are electrodialysis with bipolar membranes (EDBM), transmembrane chemisorption (TMCS).

Generated ammonia salt solutions show concentrations of 0.8 – 3 %N.

"Ammonium recovery from residual aqueous Streams", T. Mubita et al., Wageningen WUR Report 2395, march 2023, https://doi.org/10.18174/588320

Van Linden et al. lab tested three different membranes using synthetic input feeds, in beaker-scale batch tests: gas-porous PTFE (PFAS) membrane, hydrophilic hybrid silica membrane, hydrophobic polydimethylsiloxane membrane. Only the PTFE membrane showed preferential transfer of ammonia compared to water (so effective ammonia concentration). In a further paper, again using synthetic input feeds (ammonia + carbonate solution), a lab-scale set-up was tested with ammonia recovery by vacuum membrane stripping. Ammonia was up up-concentrated from 10 gNH_3/l (0.8 %N) to 110 gNH_3/l (8.7 %N) and the recovered ammonia solution was used to fuel a solid oxide fuel cell.

"Selectivity of vacuum ammonia stripping using porous gas-permeable and dense pervaporation membranes under various hydraulic conditions and feed water compositions", N. van Linden et al., J. Membrane Science 642 (2022) 120005 https://doi.org/10.1016/j.memsci.2021.120005

"Ammonia - from pollutant to power. Removal and recovery of total ammoniacal nitrogen from residual waters for electricity generation", N. van Linden, Delft TU PhD thesis, 2022 https://doi.org/10.4233/uuid:756b1c69-83a8-4050-ab07-9627a998b6e6

"Fuelling a solid oxide fuel cell with ammonia recovered from water by vacuum membrane stripping", N. van Linden et al., Chemical Engineering J. 428 (2022) 131081 https://doi.org/10.1016/j.cej.2021.131081

Adsorbents & ion-exchange

Ammonia capture by ionic liquids

Reviews of over 100 papers (**Tian & Liu, 2020**) and over 90 papers (**Zhang L. et al. 2021**) explore the mechanisms of gaseous ammonia adsorption by specific ionic liquids (ILs), IL hybrid and IL composite materials. These are effective because of low vapor pressure, high chemical and thermal stability, adjustable acidity and selective gas dissolubility. Research has been ongoing for around a decade but is still at an early stage and offers considerable potential for ammonia uptake and then desorption for possible recovery.

Polar organic solvents can be used to take up ammonia from gas. Ionic liquids are based on organic solvents (often nitrogen containing, based e.g. on pyrimidine 3C-2N ring, imidazolium …), functionalized with selected cations and anions, including e.g. metals. Ionic liquids have larger hydrogen bond grids, enabling more gas capture, and high decomposition temperature and low vapor pressure, so avoiding losses in use.

Tian & Lu identify IL's able to adsorb up to around 3% ammonia (40 $mgNH_3/gIL$) whereas Zhang et al. find **some studies showing ILs with >20% N adsorption.** The ILs can be fixed into structures or particles.

Ammonia can be desorbed from the IL by heating to temperatures 80°C – 200°C for different ILs.

However, for ILs showing rapid and effective NH_3 uptake due to reaction with metal ions, desorption may less effective.

Ammonia can be taken up by ILs by occupying voids between cations and anions, or by covalent chemical reactions (either with acidic groups or complexation with metal ions). Performance of ILs depends on absorption capacity, uptake rate, selectivity for ammonia, temperature and water sensitivity. Water can compete for ammonia absorption sites.

Tian & Lu note that cost of ILs and environmental impacts of production are also identified as possible obstacles. Work is needed on toxicity and biodegradability of certain ILs.

"IL analogues" such as phenol or azole-glycerol based solvents (such as ammonium thiocyanate NH_4SCN) may offer simpler and cheaper production, using more readily available inputs.

Tian & Lu identify as challenges to implementation: developing better performing ILs taking into account temperature and water resistance, cost of IL synthesis, ensuring safe and sustainable chemistry; gas processing system costs and IL fixing, validation of multiple ammonia absorption and regeneration and effective recovery of ammonia in a useful form during IL regeneration.

The review by **L. Zhang et al.** presents work on and discusses ammonia adsorption mechanisms of many different types of Ionic Liquid (certain studies quoted analysed several hundred ILs), including: "conventional", hydroxyl-functionalised ILs, protonic ILs, metallic ILs, multiple-site ILs, deep eutectic solvents. **Ammonia adsorption rates of up to gNH_4/gIL (24%N)** are identified for some halogenated ILs or up to 18%N for non-halogenated ILs. Il-based materials, (supports such as silica gels or carbon nanospheres or capsules, composites) are presented. Full-scale industrial installations using ILs for ammonia gas separation and recycling are presented (see below).

ESPP notes that IL ammonia adsorption and regeneration performance could be reduced if treating ammonia in the presence of water or other impurities.

Zeng et al., 2019, 2020, tested at lab scale (1 cm diameter tube) ammonia absorption and desorption by ionic liquid loaded with different metals (copper, nickel, cobalt) fixed in porous silica gel.

The ionic liquid used was the commercially available halogenated solvent (1-butyl-3-methylimidazolium chloride Bmim-Cl). Cobalt Bmim-Cl showed the highest ammonia absorption, 10 % (per g IL) in 15 minutes. Ammonia was completely desorbed by heating to 80°C in nitrogen flow, with no detectable loss of ammonia absorption capacity in five regeneration cycles.

This work continues in **Zhan et al. 2020** and **S. Zheng et al., 2023**.

Zheng et al. 2023 tested composites of dried composites composed of ILs supported on porous molecular sieves, then dried.

Four different hydroxyl ammonium protic ILs (HAPILs, all fluorinated) were tested lab scale (3g samples per test). Up to 9% adsorption (gN / g composite) was achieved from a mixture of ammonia with N_2. Good selectivity was also demonstrated when tested with on a gas flow containing CO_2.

Ammonia was released (into a flow of N_2) simply by heating to 80°C showing good recyclability (regeneration) over six cycles.

Deng et al. 2019 et **Zhong et al. 2019 (1, 2)** tested different eutectic solvents (melt at a lower temperature than does either component) at lab scale for ammonia adsorption and desorption.

Deng et al. 2019 tested glycerol (hydrogen donor) with eight different N-containing azoles (hydrogen receptor), combined to give eutectic solvents at lab scale (c. 3 g of solvent).

All eight tested eutectic solvents showed efficient and reversible adsorption, with glycerol-triazole giving the best results with nearly 12 % ammonia uptake (g uptake / g solvent). As above, performance could be reduced in presence of water or impurities.

Zhong et al. 2019 (1,2) tested halogenated eutectic solvents (choline chloride + urea, phenol or ethylene glycol) at lab scale (40 cc + 100 cc chambers).

Ammonia uptake of up to 16% (g uptake / g solvent) were achieved and effective ammonia desorption and solvent reuse up to ten cycles.

"Ammonia capture with ionic liquid systems: A review", J. Tian & B. Liu, Critical Reviews in Environmental Science and Technology (2020), http://dx.doi.org/10.1080/10643389.2020.1835437

"An Overview of Ammonia Separation by Ionic Liquids", L. Zhang et al., Ind. Eng. Chem. Res. 2021, 60, 6908−6924, https://doi.org/10.1021/acs.iecr.1c00780

"Efficient adsorption of ammonia by incorporation of metal ionic liquids into silica gels as mesoporous composites", S. Zeng (Shaojuan) et al., Chemical Engineering Journal 370 (2019) 81–88 https://doi.org/10.1016/j.cej.2019.03.180

"Ionic liquid–based green processes for ammonia separation and recovery", S. Zeng et al., Current Opinion in Green and Sustainable Chemistry 2020, 25:100354, https://doi.org/10.1016/j.cogsc.2020.100354

"Process Simulation and Optimization of Ammonia-Containing Gas Separation and Ammonia Recovery with Ionic Liquids", G. Zhan, S. Zeng et al., ACS Sustainable Chem. Eng. 2021, 9, 312−325 https://dx.doi.org/10.1021/acssuschemeng.0c07242

"Porous multi-site ionic liquid composites for superior selective and reversible adsorption of ammonia", S. Zheng et al., Separation and Purification Technology 310 (2023) 123161 https://doi.org/10.1016/j.seppur.2023.123161

"Efficient and reversible absorption of NH_3 by functional azole–glycerol deep eutectic solvents", D. Deng et al., New J. Chem., 2019, 43, 11636, https://doi.org/10.1039/c9nj01788g

2019-1: "Solubilities of ammonia in choline chloride plus urea at (298.2–353.2) K and (0–300) kPa", F-Y. Zhong et al., J. Chem. Thermodynamics 129 (2019) 5–11, https://doi.org/10.1016/j.jct.2018.09.020

2019-2: "Phenol-Based Ternary Deep Eutectic Solvents for Highly Efficient and Reversible Absorption of NH_3", F-Y. Zhong et al., ACS Sustainable Chem. Eng. 2019, 7, 3258−3266, http://dx.doi.org/10.1021/acssuschemeng.8b05221

Full scale Ionic Liquid ammonia gas recovery

In the review cited above, **L. Zhang et al. 2021** presents two full scale installations using ionic liquids to separate/remove ammonia from mixed gas streams and recover ammonia gas for onsite recycling.

An 8 million m^{3}gas/year full-scale pilot gas separation unit, operated from 2012 *(until ???? date stopped ??? or still operating today ???)* on ammonia synthesis purge gas, in Sichuan, China. This uses IL's to selectively adsorb ammonia, leaving hydrogen and nitrogen gas, with over 99% ammonia adsorption (taking ammonia down to < 45 ppm, compatible with input to membrane hydrogen separation). The desorption process is energy efficiency because the ILs have low heat capacity and no heat is lost to evaporation (as for water stripping). *The recovered ammonia is recycled back into the ammonia production line ?*

A second 130 million m^{3}gas/year installation was built in 2018 in Shaanxi, separating ammonia from offgas of an ammonium molybdate production unit. The recycled ammonia is returned to the production. This technology has reduced wastewater release by around 24 ml/y. The 2021 paper reports steady operation already for two years *and the installation is continuing to operate today ???.*

"An Overview of Ammonia Separation by Ionic Liquids", L. Zhang et al., Ind. Eng. Chem. Res. 2021, 60, 6908−6924, https://doi.org/10.1021/acs.iecr.1c00780

NH$_3$ recovery from gas by ENILs

Encapsulated ionic liquids (ENILs), in a fixed-bed column of hollow, porous, carbon-silicon microparticles, were tested at lab scale for ammonia capture and possible recovery from gas streams. The ENILs were regenerated by heat (130°C or 200°C) under nitrogen flow.

Three specifically designed ENILs were tested* (two fluorinated, one not). They were impregnated into carbonaceous microspheres. Impregnation was by dissolving in acetone, soaking into the microspheres, then vacuum evaporation of the acetone at 60°C.

The hollow core mesoporous shells of carbon were produced (**Alonso-Morales et al**. 2013) via silica templates. These were produced by precipitating silica spheres from tetraethoxysilane, calcining these, then impregnating them with phenol and formaldehyde and catalysing polymerization.

The impregnated microspheres were tested in a 4mm diameter x 5 cm long lab-scale column with a 50 – 250 mg of microspheres, with throughflow of 20 ml/minute of nitrogen – ammonia gas mixtures at test temperatures of 30 – 60 °C.

These tests aimed to evaluate the ammonia sorption capacity, and no data is reported on the % reduction achieved in ammonia in the throughflow gas, nor to what level ammonia could be reduced. The ENILs showed high sorption capacity and mass transfer and low sensitivity to temperature.

The ENILs showed good regeneration, by heating to 130°C or 200°C (depending on the thermal stability of the different ENILs) with nitrogen throughflow, but this would generate a gas mixture of nitrogen and ammonia, for which no recycling route is proposed.

The authors indicate that further work is underway, not yet published, recovering a nearly pure ammonia gas stream, using vacuum (0.1 bar). Ongoing work also suggests that ionic liquids regeneration can be optimised by combining pressure and temperature changes. Installation of more than one fixed bed can enable continuous operation. Cheaper supports for the ionic liquids can deliver performance for ammonia capture, robustness and lower costs (see work on Supported Ionic Liquid Phase SILP sorbents for CO$_2$ capture, **Santiago et al**., 2019 here)

**1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate, choline bis(trifluoromethylsulfonyl)imide and tris(2-hydroxyethyl)methylammonium methylsulfate.*

"Ammonia capture from the gas phase by encapsulated ionic liquids (ENILs)", J. Lemus, J. Palomar et al., RSC Adv., 2016, 6, 61650–61660 https://doi.org/10.1039/c6ra11685j

"Preparation of hollow submicrocapsules with a mesoporous carbon shell", N. Alonso-Morales, J. Palomar et al., Carbon 59 (2013) 430-438 http://dx.doi.org/10.1016/j.carbon.2013.03.036

Zeolite ammonia ion-exchange

Qin et al. (2023) lab tested zeolites for reversible ammonia adsorbents (ion-exchange) from municipal waste water.

The lab zeolite reactor was batch, volume 4 litres, and the input was municipal waste water after chemically-enhances primary treatment from Bailongggan wwtp. The zeolite was a natural mineral, commercially available, from Jinyun County (Zheijiang Province, China), containing aluminium, silicon, calcium, sodium and other alkali or alkaline-earth metals. The zeolite bed was regenerated using concentrated sodium nitrate solution, resulting in **ammonium nitrate solution with total N content 0.02 – 0.04 %**, containing also magnesium and calcium which were periodically removed by precipitation.

This ammonium nitrate solution was nitrified (biological nitrification reactor) then concentrated by electrodialysis (up to 0.1 – 0.2 %N) and finally evaporated to sodium nitrate crystals.

Godifredo et al. also tested clinoptilolite (natural zeolite, 300 – 1200 µm particle size) and Purolite SSTC60 strong acid cation exchange resin (SAC) for ammonia adsorption from AnMBR permeate.

Tests were carried out using the permeate (outflow downstream of the membrane) of an AnMB (Anaerobic

Membrane Bioreactor) treating real sewage The permeate was free of solids and contained 29 mg N-NH_4/l and 67 mg COD/l.

The clinoptilolite showed uptake of 7 – 9 mgN-NH_4/g zeolite, that is **a resulting N-loaded zeolite with 0.7 – 0.9 %N by weight**.

Presence of cations (Ca, Mg) reduced the zeolite N uptake by up to 22% whereas presence of organic matter increased the N uptake, possibly linked to a reduction in surface tension.

Studies on zeolite regeneration and ammonia release will be carried out in future work.

Sheikh et al. (LIFE Necovery, Spain) tested the adsorption of ammonia by clinoptilolite zeolite, then regeneration to release an ammonia solution, which was then passed through hollow-fibre liquid-liquid membrane contactors (HF-LLMC) into phosphoric acid, producing ammonium phosphate solution.

Tests were carried out at the lab scale (c. 30 l/h) to adsorb ammonia from the secondary treatment effluent from a pilot activated sludge plant treating municipal wastewater (c. 5% N-NH_4). The natural clinoptilolite zeolite (particle size 800 – 1 200 µm) was activated using 0.1 mol/l NaOH.

The zeolite column could reduce ammonia in the wastewater to below 1 mg N-NH_4 (0.1% N), with breakthrough volumes of around 100 bed volumes. Nine cycles through to breakthrough were tested, with closed loop regeneration using NaOH, suggesting that **the zeolite could be regenerated at least seven times**.

Zeolite regeneration resulted in ammonium solutions of around 0.35% N (0.25 mmol/l).

With 0.4 mol/l phosphoric acid, **the membrane contactor system generated up to 0.2% N solution** downstream of the membranes (Fig. 7).

"Nitrogen recovery from wastewater as nitrate by coupling mainstream ammonium separation with side stream cyclic up-concentration and targeted conversion", Y. Qin et al., Chemical Engineering Journal 455 (2023) 140337, https://doi.org/10.1016/j.cej.2022.140337

"Zeolites for Nitrogen Recovery from the Anaerobic Membrane Bioreactor Permeate: Zeolite Characterization", J. Godifredo, J. Ferrer, A. Seco, R. Barat, Water 2023, 15, 1007. https://doi.org/10.3390/w15061007

"Ammonia recovery from municipal wastewater using hybrid NaOH closed loop membrane contactor and ion exchange system", M. Sheikh et al., Chemical Engineering Journal (2023) https://doi.org/10.1016/j.cej.2023.142859

Also review of membrane systems: "Efficient NH3-N recovery from municipal wastewaters via membrane hybrid systems: Nutrient-Energy-Water (NEW) nexus in circular economy", M. Sheikh et al., Chemical Engineering Journal 465 (2023) 142876 https://doi.org/10.1016/j.cej.2023.142876

Fertiliser value of zeolite adsorbed N

Natural clinoptilolite zeolite and oak wood biochar were used to adsorb nitrogen from liquid fraction of manure digestate, then tested as nitrogen fertilisers in 70-day ryegrass pot trials. The N-enriched clinoptilolite showed plant biomass production and N uptake comparable or better than synthetic fertiliser, whereas the N-enriched wood biochar was less effective.

The clinoptilolite zeolite from Turkey contains mainly silicon and aluminium, with also >0.5% iron, sodium, potassium, calcium, magnesium. Particle size was 1 – 3 mm.

The zeolite removed 40 – 90 % of ammonium, 40 – 80 % potassium and 60 – 80 % orthophosphate from liquid fraction of digestate from a centralised biogas plant.

Preconditioning of the zeolite by loading sodium ions, by soaking in salt brine, did not result in lasting increases in ammonia uptake.

The zeolite uptake of N was 0.9 – 2.1 % (9 – 21 mgN/g zeolite) and around 0.5 – 1.2 % K. This would mean that 200 - 400 kg of zeolite would be needed to remove ammonia from one tonne of liquid fraction of manure digestate (@ 4000 mgN-NH_3/l) and that 10 - 20 tonnes of zeolite/hectare would have to be applied to bring 200 kgN/ha.

The N-enriched zeolite and biochar were tested in the pot trials at the same N dosage as for comparison synthetic fertiliser (equivalent to 150 or 450 kgN/ha.

N-loaded zeolite showed considerably better growth and plant N-uptake than control (no N dosage), and comparable or better than synthetic N-fertiliser (ammonium nitrate). N-loaded biochar performed only slightly better than control (no N dosage) and significantly less well than synthetic fertiliser.

"Recovery of nutrients from the liquid fraction of digestate: Use of enriched zeolite and biochar as nitrogen fertilizers", N. Kocatürk-Schumacher et al., J. Plant Nutr. Soil Sci. 2019, 182, 187–195 https://doi.org/10.1002/jpln.201800271

"Nutrient recovery from the liquid fraction of digestate by clinoptilolite", N. Kocatürk-Schumacher et al., Clean Soil Air Water 45, 2017, https://doi.org/10.1002/clen.201500153

"Does the combination of biochar and clinoptilolite enhance nutrient recovery from the liquid fraction of biogas digestate?", N. P. Kocatürk-Schumacher et al., Environ. Technol. 38, 1313–1323, 2017, https://doi.org/10.1080/09593330.2016.1226959

Testing zeolites for ammonia recovery

Two zeolites and two cationic resins were assessed for ammonia uptake, selectivity and regeneration capacity. Tests showed that throughflow experiments were necessary (not only batch). Trials with municipal wastewater treatment plant effluent showed c. 90% ammonia removal with 6 minute contact time and 80 – 90% yield in regeneration over 7 cycles.

Tests were lab-scale in 13 mm diameter, 1.3 m columns with 0.6 m bed height. A natural zeolite from Italy (mixture of Chabazite and Philippsite) showed to be most effective. Tests assessed exchange capacity, sensitivity to ammonia and regeneration yield. Regeneration was ensured by back-washing with water then with ten bed volumes of sodium chloride (salt) or potassium chloride. As with other techniques proposed, this would result in a very dilute ammonia salt solution (no data are provided on the concentration of the solution generated).

The authors conclude that continuous flow testing is necessary to generate reliable data, that is not only batch trials, that the **natural zeolite is robust and effective at ammonia removal from municipal wastewater enabling a high regeneration yield after up to 7 cycles**. Notably, the zeolite continued to function well through a saltwater intrusion.

"Ammonium recovery from municipal wastewater by ion exchange: Development and application of a procedure for sorbent selection", D. Pinelli et al., J. Environmental Chemical Engineering 10 (2022) 108829 https://doi.org/10.1016/j.jece.2022.108829

12 t/day zeolite NH_4 removal from manure

A mobile 500 l/h continuous pilot, consisting of two zeolite columns (bed volumes of 100 kg each) and columns for sodium hydroxide (for zeolite regeneration) and sulphuric acid ammonia recovery, was tested on a pig farm in Austria, fed with liquid manure from raw manure decantation, after mechanical filtration.

The inflow manure had 1500 – 3500 mg/l ammonia, significant potassium (700 – 3000 mg/l), low phosphorus (50 – 300 mg/l) and presence of sodium, calcium, magnesium …

Natural zeolite clinoptilolite (from Slovakia), a mineral containing calcium, sodium, potassium, aluminium and silicon, particle size 1 – 2.5 mm, was used to trap ammonia. **The zeolite was regenerated using salt brine** (sodium chloride), then ammonia was stripped to gas by heating to 60°C and dosing alkali (sodium hydroxide). Finally the ammonia was recovered in sulphuric acid, to produce sodium sulphate solution.

Ammonia removal of 85 – 95 % was achieved with double-column operation. The zeolite regeneration solution showed ammonia concentration of around 130 mg/l. After a total operating time of 30 days, **ammonia concentration in the final product had reached 66 g-NH_4/l (c. 5%** N/ww ammonia sulphate solution), with low levels of other ions: 140 mg/l sodium, 1600 mg/l iron, 370 mg/l zinc …

In a previous paper by the same authors, the clinoptilolite zeolite was batch tested unmodified and loaded with calcium or with sodium, in lab-scale (20g) batch tests for ammonia removal from landfill leachate. The sodium modified clinoptilolite showed to be most effective.

The authors conclude that these tests demonstrate that clinoptilolite could be an effective route to remove ammonia nitrogen from liquid manure and to store it for recycling as a fertiliser, or to recover nitrogen after zeolite regeneration. In these tests, **up to c. 2% by mass nitrogen was adsorbed in the zeolite**. For use of the N-loaded zeolite as a fertiliser, such levels of nitrogen would imply significant bulk transport, but this is not important if the process is on-site regeneration for N-recovery. These tests did not aim to maximise nitrogen loading.

"Nitrogen Recovery from Swine Manure Using a Zeolite-Based Process", M. Ellersdorfer et al., Processes 2020, 8, 1515; https://doi.org/10.3390/pr8111515

"Ammonium Sorption from Landfill Leachates Using Natural and Modified Zeolites: Pre-Tests for a Novel Application of the Ion Exchanger Loop Stripping Process", D. Vollprecht et al., Minerals 2019, 9, 471; https://doi.org/10.3390/min9080471

"Impact of concentrated acid, base and salt pretreatments on the characteristics of natural clinoptilolite and its ammonium uptake from model solution and real effluents", K. Stocker et al., Microporous and Mesoporous Materials, 2019, 288; https://doi.org/10.1016/j.micromeso.2019.06.015

Ion-exchange from sludge drying condensate

Lab-scale trials ion-exchange trails, using synthetic test solutions of ammonium acetate, resulted in an ammonium potassium phosphate salt solution of nearly 0.007%N (70 mgN/l).

The synthetic test solution contained concentrations of ammonium acetate (c. 2.5% N-NH_4, 9% acetate CH_3COO^-) found in condensate from the sewage sludge drying of the ENDEV process, upstream of and integrated into the ENDEV PAKU process at the Rovaniemi wwtp, Finland, see ESPP Technology Catalogue, contains

Synthetic ammonium acetate solution at this concentration was used for initial lab tests, then for a lab-scale pilot (bed 12 cm diameter, 42 cm high) using the commercial ion-exchange resin from Finex (CS16GC). The resin bed was regenerated using 2 molar K_3PO_4 solution, then washed to removed excess potassium nitrate. Seven regeneration cycles were tested. After around eleven bed volumes of synthetic condensate were fed over the ion exchange, nitrogen concentration in the regeneration solution reached around 0.007%N, but after this many bed volumes ammonia removal efficiency had fallen to only around 60%. *This comes from fig. 4. However, S5 seems* *to suggest up to 10 mgN/l = 1%N for a potassium phosphate regeneration volume of one BV. But is this sufficient to regenerate the IEX ???*

Answers to???s not received from authors despite requests.

The final product is an N P K solution, but with an N:K ratio of 0.04 – 0.26:1, which means that nitrogen concentration is too low for use other than as a K – P fertiliser, so that the nitrogen is not significantly being recycled.

"Recovery of Ammonium from Biomass-Drying Condensate Via Ion Exchange and Its Valorization as a Fertilizer", J. Song et al., Processes 2023, 11, 815, https://doi.org/10.3390/pr11030815

Geopolymers for ammonia adsorption & recovery

Geopolymers are synthetic amorphous aluminosilicates (so with similar chemistry to zeolites), produced from e.g. metakaolins (aluminosilicate source). They have been successfully tested for ammonia adsorption from wastewater and regeneration releasing the ammonia.

Luukonen et al. 2017 indicates that geopolymers are obtained at low temperatures (< 100°C) by reaction between an alkaline activator (concentrated aqueous solution of, e.g., alkali hydroxide and/or silicate) and solid aluminosilicate precursors (such as metakaolin, fly ash or waste materials containing silicon and aluminium). They have an amorphous to semi-crystalline 3D network, while zeolites are crystalline. Geopolymers can be a cost-effective adsorbent for wastewater treatment, adsorbing cations by ion exchange. with **good mechanical properties and robustness adapted to repeated adsorption/desorption cycles**.

Samarina et al. 2019 conclude that geopolymer ammonia adsorption capacity is equal or higher than typically used zeolites such as clinoptilolite, morderite or wollastonite).

Medri et al. (2022) compared **synthetic metakaolin potassium – aluminium – silicate geopolymer** (see Papa 2022) to natural zeolite (of volcanic origin, from Italy), for ammonia adsorption from synthetic wastewater and real wastewater (high salinity, spiked with ammonia to 40 mgN-NH_4/l) at lab scale (adsorbent bed: 0.2 l volume, 60 cm height) and then regeneration using potassium chloride then potassium nitrate, releasing a mixture of ammonium nitrate and potassium nitrate solution (with negligible sodium concentration)..

Uptake of ammonia reached 0.85 % per mass dry geopolymer.

The regeneration solution was 0.075 %N/ww, but half of this nitrogen came from the supplied potassium nitrate.

Luukkonen et al. and Franchin, et al. synthesised geopolymers and tested them for ammonia removal from synthetic and real wastewaters, and demonstrated regeneration and ammonium solution release using salt brine and sodium hydroxide. A selection of their papers are summarised here.

In a 2016 paper, they produced the geopolymer by condensing metakaolin with sodium hydroxide, then crushing to particles.

After initial lab batch tests, a through-flow steel pilot (volume 5.2 l, height 0.6 m, flow rate c. 45 l/h) was **tested for 24 hours using landfill leachates** (raw and filtered/treated, 620 and 55 mg-NH_4/l).

The tests conclude that the geopolymer can adsorb around 21 mgN-NH_4/ (**c. 1.7 % N by weight**), that is nearly 50% more than a zeolite tested for comparison (clinoptilolite-heulandite).

Regeneration of the geopolymer was tested in the lab batch tests, using pure ammonia solutions with pH adjustment (not landfill leachate). Over 80% of the adsorbed ammonia could be released to solution using 0.2 M NaCl and 0.1 M NaOH for regeneration.

In a 2017 paper, similarly produced geopolymer was tested in the same steel pilot using outflow treated discharge from the Jämsä municipal wastewater treatment plant, Finland, after tertiary and UV treatment, containing around 40 mgNH_4/l.

In this case, ammonia adsorption by the geopolymer was **around 2.5% N/weight** in pure ammonia solution but lower in real wastewater treatment plant effluent. 30 – 80% ammonia removal from the real effluent was achieved, depending on bed contact time, with removal improving after a first and second regeneration of the geopolymer, achieving reduction to 4 mgNH_4/l.

The regeneration solution reached 120 mgNH_4/l (c. 9% N).

In a 2020 paper, the geopolymers were produced using 3D-printing (direct ink writing using a metakaolin ink) to give a highly permeable structure.

"Optimization of the metakaolin geopolymer preparation for maximized ammonium adsorption capacity", T. Luukkonen et al., 2017, Journal of Materials Science, 52, 9363-9376, http://dx.doi.org/10.1007/s10853-017-1156-9

"Metakaolin-based Geopolymers for Removal of Ammonium from Municipal Wastewater", T. Samarina et al., 2019, Proceedings of the 5th World Congress on New Technologies (NewTech'19), Paper No. ICEPR 195, http://dx.doi.org/10.11159/icepr19.195

"Ammonium removal and recovery from municipal wastewater by ion exchange using a metakaolin K-based geopolymer", V. Medri et al., Water Research 225 (2022) 119203 https://doi.org/10.1016/j.watres.2022.119203

"Metakaolin geopolymer characterization and application for ammonium removal from model solutions and landfill leachate", T. Luukkonen et al., Applied Clay Science 119 (2016) 266–276, http://dx.doi.org/10.1016/j.clay.2015.10.027

"Removal of ammonium from municipal wastewater with powdered and granulated metakaolin geopolymer", T. Luukkonen et al., Environmental Technology, Volume 39, 2017 - Issue 4, https://doi.org/10.1080/09593330.2017.1301572

"Removal of ammonium from wastewater with geopolymer sorbents fabricated via additive manufacturing", G. Franchin et al., Materials and Design 195 (2020) 109006 https://doi.org/10.1016/j.matdes.2020.109006

Salam et al. (2021) synthetised geopolymers and a hybrid zeolited geopolymer (Z/G) from natural kaolinite and diatomite and demonstrated at lab scale in batch tests their capacity to uptake ammonia and phosphate from sewage, groundwater and synthetic solutions.

Ammonia uptake of over 50 mg NH_4 per gramme of zeolited geopolymer (c. 4 % N) was achieved at pH8 (c. 2.5 % N for non-zeolited geopolymer). Somewhat lower uptakes of phosphate (when expressed as %P) were obtained at pH 3-6. In real wastewater, the ammonium and phosphate uptake were significantly deteriorated by competing ions such as chloride, carbonate, sulphate and nitrate.

"Synthesis of zeolite/geopolymer composite for enhanced sequestration of phosphate (PO_4^{3-}) and ammonium (NH_4^+) ions; equilibrium properties and realistic study", Salam et al., J. Environmental Management 300 (2021) 113723 https://doi.org/10.1016/j.jenvman.2021.113723

Sanguanpak et al. (2021) synthesised porous geopolymers by calcining kaolin to generate metakaolin (containing silicate and aluminium) then reacting with sodium silicate, sodium hydroxide and a foaming agent. This was then tested lab scale (batch, 0.25 l volume) for ammonium removal and regeneration in synthetic solution and in discharge from an anaerobic reactor treating piggery wastewater, in comparison to natural clinoptilolite zeolite.

Ammonium removal was better with the synthetic geopolymer than with zeolite, and better with higher air foam content (0 – 15%). **Up to 47 mgNH_4/g (c. 4% N) was achieved by the 15% air foam geopolymer** (at pH 6.4, 30°C, 24 h contact time). 80 - 85% ammonia removal from the piggery wastewater was achieved (initial ammonium concentration 75 – 200 mg/l), nearly twice as high as with zeolite.

The geopolymer was regenerated (3 cycles) using 0.2 M NaCl and 0.3 M NaOH (loss of ammonia removal efficiency of only around 5%).

"Porous metakaolin-based geopolymer granules for removal of ammonium in aqueous solution and anaerobically pretreated piggery wastewater", S. Sanguanpak et al., Cleaner Production 297 (2021) 126643 https://doi.org/10.1016/j.jclepro.2021.126643

Sundhararasu et al. (2022) lab tested three sodium zeolite geopolymers synthesised from analcime (a sodium aluminium silicate) and metakaolin (an aluminium silicate), activated with sodium hydroxide, sodium silicate and potassium silicate. The tests used synthetic ammonium solution, initial concentration 40 mg, with continuous flow (3 cm diameter 0.5 cm bed height).

Ammonium uptake achieved was around 1.3 -3.3 mg NH_4/lg (0.1 – 02.6 %N). **Ammonium adsorption capacity was not significantly decreased after two regenerations** with NaCl and NaOH.

"Column Adsorption Studies for the Removal of Ammonium Using Na-Zeolite-Based Geopolymers", E. Sundhararasu et al., Resources 2022, 11, 119. https://doi.org/10.3390/resources11120119

Reacting ammonia with CO_2

Stripping to solid ammonium bicarbonate

Negative pressure steam stripping of landfill leachate, followed by scrubbing to ammonia water then carbon dioxide dosing to precipitate crystalline ammonium bicarbonate.

Landfill leachate (Laogang Municipal Landfill, shanghai, China, 0.25% N-NH_4) was heated to 60-65°C then stripped of ammonia in a negative steam-pressure pilot plant (8-10 m^3/d at 80-85°C), from which ammonia water was recovered both in the steam condenser and in the vacuum pump system. *This resulted in ammonia water with concentration approx. ???? %N.* This was sent to a carbonation tower (injection of pure CO_2) resulting in **precipitation of crystallised ammonium bicarbonate**. After 8 days, concentration in the carbonisation tower reached 6% N and ammonium bicarbonate crystals started to form and could be extracted by centrifuge. The carbonisation tower was operated in batch mode, with the accumulated liquor returned to the ammonia recovery tower after 11 days. N removal from the landfill leachate reached 74-90 % *of which approx. ???? % was recovered as ammonium bicarbonate.*

Answers to???s not received from authors despite requests.

"Recovery of NH3-N from mature leachate via negative pressure steam-stripping pretreatment and its benefits on MBR systems: A pilot scale study" J. Xiong et al. Journal of Cleaner Production 203 (2018) https://doi.org/10.1016/j.jclepro.2018.08.285

Conversion of adsorbed NH_3 and CO_2 to urea

At lab scale, ammonia from (pure) ammonia solution and/or carbon dioxide (gas or solution) were adsorbed into hollow silica microspheres, then reacted by heating to generate urea.

Hollow silica spheres of diameter 55 – 160 nm were synthesised by sol-gel process using solvent, sodium hydroxide, water, surfactant, alkane, alcohol, amine and a silane. Uptake of ammonia from (pure) aqueous ammonia solutions was tested, as was uptake of copper (from copper acetate solution) and of carbon dioxide (from CO_2 gas and from water through which CO_2 had been bubbled.

Urea was generated in the nanospheres after uptake of copper, ammonia and carbon dioxide, by heating at 30 – 100 °C for 5- 42 hours. **Final levels of up to 15% urea, that is c. 7 %N (per g final dried spheres) were achieved**.

"Conversion of Recovered Ammonia and Carbon Dioxide into Urea in the Presence of Catalytically Active Copper Species in Nanospaces of Porous Silica Hollow Spheres", T. Umegaki & Y. Kojima, ACS Appl. Mater. Interfaces 2023, 15, 5109−5117, https://doi.org/10.1021/acsami.2c17560

Wood biochar CO_2 – NH_3 trapping

At the lab scale, pyrolysed oxidised maple wood chips were effective in trapping ammonia and then CO_2 and then again ammonia, whereas pyrolysed human latrine waste did not perform effectively.

The wood chips were pyrolysed at 500°C then oxidised in hydrogen peroxide for 25 days, then rinsed and dried. The human latrine waste was pyrolysed only, not treated with hydrogen peroxide.

The pyrolysed oxidised wood chips and the pyrolysed latrine waste were exposed to different sequences of: ammo nia, then CO_2, then ammonia; or CO_2 then ammonia.

Results showed that, for the pyrolysed oxidised wood chips:

- inherently present nitrogen compounds were effective in adsorbing CO_2,
- uptake of CO_2 was improved by prior uptake of NH_3,
- after exposure to CO_2, more ammonia could be taken up
- ammonia uptake was 0.8 %N (per weight of material) before CO_2 exposure, then an additional 0.5 % after one CO_2 exposure and a further 4% after a second CO_2 exposure **(total 1.2 % weight N uptake).**

NH_3 adsorption by the pyrolysed latrine waste was low. The authors suggest this was because of potassium bicarbonate precipitation.

The paper contains considerable information concerning nitrogen species, surface properties and surface chemistries.

ESPP suggests *that the lab tests presented leave many questions open concerning possible use of this method for adsorbing ammonia from an offgas or stripping flow, but that the paper does provide* ***interesting background surface chemistry information on the route of co-fixing CO_2 and ammonia to substrates****, which is also the route used in the CCm process (see SCOPE Newsletter n°145, summary of ESPP 1st N-recovery workshop).*

A second paper shows similar results, with **up to 1.1% per mass nitrogen uptake with wood biochar**, but much lower N uptake for dairy manure biochar. The manure biochar already contained over 2% N and only took up < 0.1% per mass additional N.

Six week pot trials with marigold, radish and tomato showed plant growth and N-uptake from the N-enriched wood biochar as high or better than from mineral fertiliser (urea, with the same N dosage), whereas results were lower with the manure biochar (figs.1 and 2 in 2021 paper).

"Sequential Ammonia and Carbon Dioxide Adsorption Pyrolyzed Biomass to Recover Waste Stream Nutrients", L. Krounbi et al., ACS Sustainable Chem. Eng. 2020, 8, 7121−7131, https://dx.doi.org/10.1021/acssuschemeng.0c01427

"Plant uptake of nitrogen adsorbed to biochars made from dairy manure", L. Krounbi et al., Scientific Reports (Nature Portfolio), (2021) 11:15001, https://doi.org/10.1038/s41598-021-94337-8

Nitrogen transformation

Conversion of nitrate to ammonia

Lab-scale polymer electrolyte membrane (PEM) cell using pure nitrate solutions shows efficient conversion of nitrate in solution to ammonia in solution.

Bunea, Ampurdanes, et al. report trials using pure potassium nitrate solution at 0.02, 0.05 and 0.1% N. A Nafion membrane (PFSA/PTFE, that is PFAS) allows transport of H^+ ions, so application of electricity induces $NO_3^- \rightarrow NH_4^+$ or N_2 at one side and $H_2O \rightarrow$ oxygen at the other side. Iridium was used as catalyst for water electrolysis and various metals were test as catalysts for nitrate breakdown, the most effective being ruthenium towards NH_3. 93% nitrate conversion was achieved in 8 hours, with 94% faradaic efficiency and energy efficiency up to 15%. The second cited paper addresses conversion to N_2 rather than to NH_3.

Li et al. also report lab tests using electroreduction (with pulses of electrolysis) in a Nafion membrane cell to convert nitrate to ammonia. A copper (II) polypyrrole phthalocyanine tetrasulfonate polymer gel was used as a catalyst, producing ammonia from both nitrate and nitrite at pH neutral conditions.

ESPP notes *that such a processes may be of interest to increase potential ammonia recovery from wastewaters containing dissolved nitrogen in different forms. However, they generate a dilute ammonia / ammonia salt solution, and that application to real wastewater containing nitrates is likely to result in problems of competing compounds (reacting with the H^+ ions) and membrane / catalyst fouling.*

"Electrified Conversion of Contaminated Water to Value: Selective Conversion of Aqueous Nitrate to Ammonia in a Polymer Electrolyte Membrane Cell", S. Bunea et al., ChemSusChem 2022, 15, e202102180 https://doi.org/10.1002/cssc.202102180

"PEM Electrolysis-Assisted Catalysis Combined with Photocatalytic Oxidation towards Complete Abatement of Nitrogen-Containing Contaminants in Water", J. Ampurdanés, S. Bunea, A. Urakawa, ChemSusChem 2021, 14, 1534–1544 https://doi.org/10.1002/cssc.202002828

"Pulsed Nitrate-to-Ammonia Electroreduction Facilitated by Tandem Catalysis of Nitrite Intermediates", P. Li et al., J. Am. Chem. Soc. 2023, 145, 6471−6479 https://doi.org/10.1021/jacs.3c00334

Enzyme ammonia release in sludge

Enzymes are identified to release of non-dissolved nitrogen to ammonia in thermophilic composting.

Tests used Malaysia shrimp aquaculture pond sludge, dewatered to 19% DM by centrifuge. Enzymes tested were lysozyme, protease (from Streptomyces griseus), collagenase and phospholipase. Sludge hydrolysis was tested by incubation with the enzyme at 37°C for up to 90 mins. After incubation, the sludge was mixed with sawdust and composted lab-scale, at 60°C for 10 days, aerated by air-flow with ammonia trapping in sulphuric acid from the outflow air.

The most effective enzyme was protease, which **decreased final (after composting) non-dissolved N from 46% to 22% of total N (compared to 81% before composting).**

Without enzyme, around 20% of total N was lost with air flow in composting, with enzyme this increased to around 40%.

ESPP comment: *this study suggests that* ***use of enzymes could increase potential for ammonia recovery from compost or digestate by releasing organic N forms to ammonia****.*

"Effect of enzymatic pre-treatment on thermophilic composting of shrimp pond sludge to improve ammonia recovery", S. Kamal et al., Environmental Research 204 (2022) 112299 *https://doi.org/10.1016/j.envres.2021.112299*

N-recovery from urine

N-recovery from source-separated urine.

A range of different approaches have been tested to recover nitrogen from source-separated urine.

Urine is largely sterile, has low levels of organics and nitrogen at c. 0.4 – 1.1 %N, principally as urea. The challenges for N-recovery are therefore separation of the N from other elements (P, K, Na, S), **conversion or stabilisation of urea to a stable N form and concentration**. Levels of contaminants such as pharmaceuticals must be verified if not separated/removed.

Riechmann et al., 2021, increased the pH of fresh urine to 12-13 with calcium hydroxide. Phosphorous was precipitated as calcium phosphate. The high pH stabilised urea (main N form in fresh urine), preventing conversion to ammonia and so loss to air. Attempts to then concentrate the remaining N solution by blown air evaporation were initially successful, but in longer trials showed 80% loses of ammonia to air (captured by activated carbon), probably because of CO_2 exposure. After these losses, the remaining N was concentrated to c. 2.6%.

Zuo et al., 2022, lab-tested for over five months a two-step system with a biological reactor used to partially nitrify the urine (converting urea to nitrite) then a chemical reactor converting to ammonium nitrate. The biological reactor was operated in 8 hour cycles (7 hours aerated with air, 50 minutes settling to allow removal of the nitrite liquor). The chemical reactor was aerated with oxygen, with hydrochloric acid dosed to pH 3 (from c. pH 6 in the urine). The final ammonium nitrate solution had a low concentration of c. 0.6 % N.

Yu et al., 2021, review membrane technologies for urine resource recovery, considering membranes driven by chemical potential, external pressure, vapour pressure, electric fields. They emphasise the need to first stabilise urine, to prevent urea loss as ammonia, by either increasing pH to 12 – 13 or by urease enzyme inhibitors or electrochemical treatment. Little information is provided concerning the concentrations of ammonia solutions generated, but these appear to be typically very dilute (<1% N). Energy consumption and membrane fouling are identified as challenges for these processes.

Moharramzadeh et al., 2022, tested urease inhibitor (peracetic acid) and progressive freeze concentration at lab scale, but using synthetic urine only (with urease enzyme). Freeze concentration was tested with coolant at -4 to -12°C and time 7 hours. The input urine had 15 g/l urea (c. 0.7% N). Freeze concentration achieved 5x concentration, with output 2.1% N.

Häfner et al., 2023, tested nitrified urine fertilisers and human faecal compost in field trials on cabbage, with three different soil types, comparing yields to use of vinasse as organic fertiliser and analysing uptake of pharmaceuticals (Carbamzepin) from the urine and faecal fertilisers. They conclude that the nitrified urine fertilisers gave promising yields.

See also the review of urine treatments by **Larsen et al. 2021** referenced in the "reviews" chapter above.

"On-site urine treatment combining Ca(OH)2 dissolution and dehydration with ambient air", M. Riechmann et al., Water Research X 13 (2021) 100124 https://doi.org/10.1016/j.wroa.2021.100124

"Recovery of ammonium nitrate solution from urine wastewater via novel free nitrous acid (FNA)-mediated two-stage processes", Z. Zuo et al., Chemical Engineering Journal 440 (2022) 135826 https://doi.org/10.1016/j.cej.2022.135826

"Membrane technologies in toilet urine treatment for toilet urine resource utilization: a review", C. Yu et al., 2021, RSC Adv., 2021, 11, 35525 https://doi.org/10.1039/D1RA05816A

"Stabilization and concentration of nitrogen in synthetic urine with peracetic acid and progressive freeze concentration", S. Moharramzadeh et al., J. Env. Chem. Engineering 10 (2022) 107768 https://doi.org/10.1016/j.jece.2022.107768

"Recycling fertilizers from human excreta exhibit high nitrogen fertilizer value and result in low uptake of pharmaceutical compounds", F. Häfner, A. Krause et al., Front. Environ. Sci. 10:1038175, *https://doi.org/10.3389/fenvs.2022.1038175*

Biomass N-recovery

Microbial protein production

A few lab-scale studies, only, are available on production of single cell protein as a route to nitrogen recovery, by using wastewater as growing medium providing nutrients for microbial protein.

This differs from use of algae for wastewater treatment and nutrient removal / recovery (see ESPP input to EU consultation on algae, 2021, here).

If microbial protein is grown directly in e.g. wastewater or manure digestate, then **questions of safety will need to be addressed:** possible concentration of heavy metals, pharmaceuticals or other organic contaminants, sanitary safety) as well as **regulatory questions** (Animal By-Product status, End-of-Waste status, end-use application regulations) and possible downstream user resistance.

There may be fewer concerns if ammonia is stripped from the wastewater/digestate then used as feed for the microbial protein production (see e.g. Guida et al., above), either directly (as dilute gas / water vapour) or after conversion into dilute ammonia salt aqueous solution.

A summary update on microbial protein production fed by waste streams is provided by Zhou et al., 2023 (covering applications for aquaculture feed), including microbial protein production by bacteria, fungi and algae, and use of starch residue, sugar industry molasses, fruit processing pomace, oil cake residue, liquor production vinasse, biogas slurry and offgases (CO_2, CO, NH_3).

Banks et al. provide an information update of industrial implementation of microbial protein production. The global market for such protein for human food products (only) is over 20 billion €. Another key market is for aquaculture feed. Use of methane (natural gas) or hydrogen as inputs face cost and supply challenges, and the use of offgas or waste CO_2 and ammonia are identified as offering potential. The Netherlands Power-to-Protein project (www.powertoprotein.eu) is cited as using wastewater ammonia, but the authors conclude that this only achieved <30% of intended hydrogen transfer to the microbial cells and the project website suggests no recent progress.

Verbeek et al. present theoretical modelling of microbial protein production using manure digestate ammonia and biogas / CO_2. In the theoretical cases modelled, this could be economically positive with a hypothetical price for of digestate nutrient removal and assuming high-value of the microbial protein produced, e.g. for aquaculture feed. The ammonia is assumed to be stripped from liquid fraction of digestate then recovered as ammonium sulphate and used to feed microbial protein production along with biogas methane or CO_2 after biogas combustion.

Zhang et al. lab tested growth of single-cell protein in chicken manure slurry using yeasts. The chicken manure contained c. 4 500 mgN-NH_4/l and was diluted to 1 000 mgN-NH_4/l, heat sterilised, acid dosed to adjust to pH 7.3 and then glucose was added before yeast inoculation. After four days of culture, nearly 13 g/l of cell dry weight containing 36% protein was reached (in further work pending publication, up to 40 g/l cell dry weight is reached).

Ding et al. lab tested growth of single-cell protein in chicken manure slurry using yeast. The chicken manure slurry contained c. 5000 mgN-NH_4/l and was tested as after microfiltration and heat sterilisation, with dosing of various readily available carbon sources. pH dropped with fermentation, and was maintained at the optimal pH 5.5 be addition of further manure slurry. Phosphorus showed to be limiting yeast growth, and addition of sodium phosphate enabled increased production. Yeast biomass of up to c. 15 g/l cell dry weight was obtained after 3 days, with protein content up to around 50%

"Generation of microbial protein feed (MPF) from waste and its application in aquaculture in China", Y-M. Zhou et al., J. Env. Chem. Engineering 11 (2023) 109297 https://doi.org/10.1016/j.jece.2023.109297

"Industrial production of microbial protein products", M. Banks et al., Current Opinion in Biotechnology 2022, 75:102707, https://doi.org/10.1016/j.copbio.2022.102707

"Assessing the potential for up-cycling recovered resources from anaerobic digestion through microbial protein production", K. Verbeek et al., Microbial Biotechnology (2021) 14(3), 897–910, https://doi.org/10.1111/1751-7915.13600

"The production of single cell protein from biogas slurry with high ammonia-nitrogen content by screened Nectaromyces rattus", L. Zhang et al., 2021 Poultry Science 100:101334, https://doi.org/10.1016/j.psj.2021.101334

"Ammonia nitrogen recovery from biogas slurry by SCP production using Candida utilis", H. Ding et al., J. Env. Management 325 (2023) 116657, https://doi.org/10.1016/j.jenvman.2022.116657

Concentrations & conversions

Units of measurement: % = g/100 ml. molar (M) = mol/l.

- **ammonium sulphate** $(NH_4)_2SO_4$ = **21 %N**
- **ammonium nitrate** NH_4NO_3 = **35 %N** (but if generated by recovering stripped ammonia using nitric acid, then only half of this N is recycled, the other half comes from the intrant nitric acid)
- **ammonia** (NH_4 as present in ammonia water) = **79 %N**
- **urea** $CO(NH_2)_2$ = 47 %N

E.g. a 10% ammonium sulphate aqueous solution = 2.1% N.

For reference, a “liquid inorganic macronutrient (nitrogen) fertiliser” must contain **minimum 5% N under the EU Fertilising Products Regulation** (PFC 1(C)(I)(b)).

Saturated solutions: **ammonium sulphate** c. 43% (@ 25°C) (link**), ammonium nitrate** c. 68% (@ 25°C) (link**)**

Other conversions:

1 g/l NH_4 = 0.78 mg/l N = 0.056M N (or NH_4) = 0.08% N

1% N = 0.7M N (or NH_4) = 10 g/l N = 12.8 g/l NH_4

1M N = 1.4% N

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1st White Ammonia and N-recovery Research Meeting (WARM), Brussels and hybrid, 7th June 2023.

Showcasing N-recovery R&D. Links with EU policies and industry. Discussion of research conclusions and needs presented below.

Within EU Green Week, Brussels. Back-to-back to the 6th Power to Ammonia conference, Rotterdam 8-9 June 2023 NH3 Event.

Programme & registration https://www.phosphorusplatform.eu/NRecovery

7th June 2023
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