



Maria Celeste Gritti

Ammonia partitioning and recovery from industrial wastewater:
exploring precipitation, stripping, and sorption technologies

School of Water, Energy and Environment
Research Degree

PhD
Academic Year: 2020 - 2024

Supervisor: Dr Marc Pidou
Associate Supervisor: Professor Bruce Jefferson
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the degree of PhD

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Abstract

Circular economy in wastewater management is increasingly applied, with ammonia recovery playing a critical role. Established ammonia partitioning technologies, being precipitation, typically as struvite, stripping and scrubbing, and sorption, have been predominantly applied to manure, anaerobic digestate, urine and municipal wastewater. Industrial effluents also hold potential for ammonia recovery and have been increasingly targeted by research. These effluents comprise a wide category of wastewaters with diverse physicochemical characteristics, generated by different sectors, including food/drink processing, mining, agro-industrial processes, manufacturing, metallurgy, etc. Some of these effluents contain high ammonia loads alongside significant concentrations of ions, metals, and recalcitrant organic compounds, contributing to complex chemical compositions that can pose challenges for conventional recovery technologies. Despite the increasing focus on industrial wastewaters, there remains limited understanding of how to effectively select and operate recovery technologies, based on the effluent composition and desired recovery outcomes.

This research aimed to advance the understanding of how several physico-chemical factors impact the mechanisms enabling ammonia partitioning into gas, liquid and solid phases, in order to establish optimum transfer pathways. The key knowledge gaps addressed in this research were i) determination of main criteria for ammonia recovery technology selection for a range of industrial wastewaters, ii) understanding the feasibility and recovery performance of struvite precipitation and ammonia stripping at demonstration scale from distillery wastewater, iii) understanding and quantifying the impact of transition metals and acidic organic compounds on ammonia stripping, iv) assessment and comparison of ammonia separation performance via ion and ligand exchange media and influence of operation parameters (e.g. pH, buffer capacity, metal load, N concentration). The findings are utilised to generate an informed decision process for technology/strategy selection and the operational requirements and potential challenges posed by selected factors, with relevance for industry stakeholders, technology providers, and consultants. A specific focus was placed on distillery

wastewater as a case study, a sector concerned with ammonia management and potentially suitable for recovery, particularly in Scotland.

A review of the literature found that struvite precipitation is the most widely implemented method with industrial effluents, yet stripping and sorption processes may be preferred for their ability to deliver versatile, ammonia-rich solutions. The identified technology-selection criteria included the feed concentration of ammonia and competing cations, and the struvite formation potential. Based on the practical recommendations developed in this study, an ammonia recovery strategy for distillery wastewater was established, integrating anaerobic digestion with chemical precipitation and ammonia stripping coupled with scrubbing. The performance of this treatment train had never been tested before for filtered digestate of distillery effluent, addressing a key gap in understanding for full scale applications. Demonstration scale trials allowed to understand how the expected performance translated with real digested distillery wastewater and to validate its feasibility. The results demonstrated its technical viability, achieving 76% N removal and 80% P removal, while generating high-quality struvite and ammonia sulphate solution. Moreover, the findings highlighted the critical impact of pH and addressed operational challenges, improving readiness for full-scale application.

Beyond distillery effluents, this thesis examined broader challenges in industrial wastewaters treatment, addressing gaps identified in the literature review, relevant for a range of industrial wastewaters, including from metallurgy and agro/food processing. Specifically, the impacts of species found in some of these effluents, such as transition metals (as Ni, Cu, Zn) and organic, acidic compounds (as humic acids), on the stripping process were investigated. Results showed that elevated levels of such species can reduce ammonia availability for stripping, via complex formation and electrostatic interactions. This highlighted the need for mitigation strategies to maintain stripping efficiency with these streams. Additionally, the metal-ammonia bond potential was further explored to assess ligand exchange (LEX) sorption mechanism as alternative to ion exchange (IEX), a mechanism often limited by high concentrations of ammonia and competing

cations. Although various media have been tested in literature, comparative studies on their performance under different conditions are lacking, along with insights on how factors such as pH, transition metal and cations load can impact their mechanisms and effectiveness. In this study, two zinc-hybridised sorption media were tested and benchmarked against IEX media, in synthetic and real wastewaters (distillery, municipal). The results showed effective removal, although limited by self-inhibiting pH changes, with a zinc-hybridised media matching or exceeding IEX resin's performance only when pH 9-10 was maintained (75 meq N/g). pH, buffer capacity and Zn/Na loads were demonstrated to be critical factors to enable or limit IEX and LEX mechanisms. The findings established operational requirements for hybridized sorption media and provided research directions for further improvement.

Overall, this work advanced knowledge on the impact of key species on ammonia recovery technologies, with implications for industrial effluents treatment in general and distillery wastewater management in particular. The findings contributed to developing recommendations for selection and operation of ammonia partitioning strategies, optimizing metal-hybridized sorption media, and improving process feasibility for full-scale implementation.

Keywords: *ammonia recovery; industrial wastewater; distillery wastewater; chemical precipitation; stripping; ion exchange; ligand exchange; circular economy.*

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List of Abbreviations

AD	Anaerobic digestion
AEX	Anion exchange resin
AnMBR	Anaerobic membrane reactor
“AnMBR”	Permeate of anaerobic membrane reactor
AS	Ammonium sulphate
Avg	Average
BOD ₅	5-day biological oxygen demand
“CE”	Cranfield sewage works effluent
CEX	Cation exchange resin
Ch.	Chapter
COD	Chemical oxygen demand
CS	Cross section
D.L.	Discharge limits
DAP	Diammonium phosphate
DOC	Dissolved organic carbon
EC	European Commission
EDTA	Ethylenediaminetetraacetic acid
EtOH	Ethanol
FA	Free ammonia
FA*	Fulvic acids
FBR	Fluidised bed reactor
FO	Forward osmosis
G/L	Gas/Liquid flow ratio
HA	Humic acids
HFMC	Hollow fiber membrane contactors
HFO	Hydrated ferric oxide
IS	Ionic strength
IAP	Ion activity product
IC	Ion chromatography
ICP-MS	Inductively Coupled Plasma Mass spectrometer
IDA	Iminodiacetic acid
IEX	Ion exchange

K _{so}	Conditional solubility product
K _{sp}	Constant solubility product
LEX	Ligand exchange
M	Metal
MAP	Magnesium ammonium phosphate (struvite)
MaP	Macroporous
MiP	Microporous
NP	Nanoparticles,
n.a.	Non-available
N _r	Reactive nitrogen
Obj.	Objective
OC	Organic compounds
PCB	Printed circuit board
pK _a	Negative log ₁₀ of acid dissociation constant
“PP_Str”	AnMBR effluent treated with precipitation and stripping
Pr	Precipitation
q _f	Adsorption capacity
(r)	Real effluent
RO	Reverse osmosis
(s)	Synthetic solution
SA	Strong acid
S-DVB	Styrene-divinylbenzene
SEM-EDS	Scanning electron microscopy - Energy dispersive X-ray
SGS	Synthesis gas scrubber
SI	Saturation index
SSR	Supersaturation ratio
StDev	Standard deviation
Str	Stripping
SW	Spent wash
TAN	Total ammonia nitrogen
tbd	To be determined
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen

TOC	Total organic carbon
TP	Total phosphorus
TRL	Technology readiness level
TSS	Total suspended solids
UV-vis	Ultra-violet and visible regions
VM	Visual Minteq
VOC	Volatile organic compounds
VTs	Vacuum thermal stripping
WA	Weak acid
WB	Weak base
wpd	WebPlotDigitiser
WRRF	Water resource recovery facilities
WW	Wastewater
X	Generic cation
XRD	X-ray diffraction
η	Removal efficiency
θ	Coefficient of strippable ammonia
[]	Concentration

Chapter 1

1 Introduction

1.1 Background

Ammonia (NH_3) management is critical to enable a sustainable human life support system on Earth. Ammonia plays a direct role in the nitrogen (N) cycle and currently reactive nitrogen (Nr) flows are heavily perturbed by anthropogenic actions, posing a risk to the planet's resilience ¹. Atmospheric N_2 can be fixed via the energy-intensive Haber-Bosch process into Nr , in the ammoniacal form, which is commonly used in several agricultural and industrial applications, including as fertiliser ^{2,3}. It is projected that in 2050, about a third of man-made Nr will be fixed via the Haber-Bosch process (ca. 165 Tg N/year) ³, consuming 28-44 MJ/kg N ^{4,5}. Indeed, the demand of Nr is expected to rise, largely by the need of fertilisers to produce food for the increasing global population, but potentially also by the use of ammonia as fuel, for carbon capture and biofuel production ⁵. Part of the synthesised ammonia reaches wastewater (e.g. industrial, municipal) where it must be removed to protect the receiving water bodies. Losses of Nr to the environment can generate cascades of effects, disrupting ecosystem equilibria and fostering phenomena such as eutrophication and biodiversity reduction ⁶. Ammonia removal can be achieved via biological processes, such as nitrification/denitrification, converting it back to N_2 with a large energy footprint (42-45 MJ/kg N) ^{4,7}. Partial nitrification coupled to anaerobic ammonia oxidation has gained popularity as an alternative biological removal process with significantly reduced energy demand (22 MJ/kg N) ⁷. Nonetheless, both options are responsible for emissions of nitrous oxide (N_2O), a greenhouse gas with high global warming potential ($\text{GWP}_{100} = 273$) ^{4,8}. Additionally, biological processes are often characterised by low conversion rates and high sensitivity to toxic species and temperature variations, compared to physico-chemical processes ⁹. As such, the latter are expected to progressively replace the former to accomplish a better N management ¹⁰.

Aiming to improve the sustainability of the Nr cycle, ammonia recovery from wastewater has gained increasing interest in the past decades ⁷, especially via physico-chemical methods. This trend is aligned with the paradigm shift in the thinking where wastewater is now processed from water resource recovery facilities (WRRFs), in the context of the circular economy ^{11,12}. Struvite precipitation, ammonia stripping and scrubbing, and ammonium sorption are processes commonly used to separate and recover total ammonia nitrogen (TAN) from wastewater, exploiting physico-chemical mechanisms ^{13,14}. At the current state, their energy footprints can match or exceed the energy demand for biological ammonia removal and artificial synthesis ¹⁵. However, these recovery technologies can limit direct N₂O emissions and contribute to provide additional revenues e.g. via sale of recovered materials.

Many research efforts have already targeted nitrogen recovery from highly loaded streams, such as manure ^{16,17}, anaerobic digestate of agro-food waste and sludge ^{18–20} and human urine ²¹ (Figure 1-1). Research has also expanded to include municipal wastewater, despite its lower ammonia content ²². More recently, studies on ammonia recovery from industrial effluents have started to increase as well (Figure 1-1), with the potential to further support circularity-based nitrogen management. This is likely driven by the appeal to recover valuable products, reusable in industrial symbioses networks, but also by the increasing stringency of discharge standards ¹⁴. In fact, while large loads of ammoniacal nitrogen are still released with industrial effluents into water bodies, stricter measures will further push the implementation of effective removal processes ¹⁴. Depending on the sector, the ammonia content varies greatly in industrial wastewaters, likewise for the content of other nutrients (e.g. phosphorus, sulphur), heavy metals and organic substances ¹⁴. Interestingly, the application of anaerobic digestion, often used for agro-industrial effluents ²³, promotes the release of ammonia from organic N species ²⁴, making it more accessible for recovery.

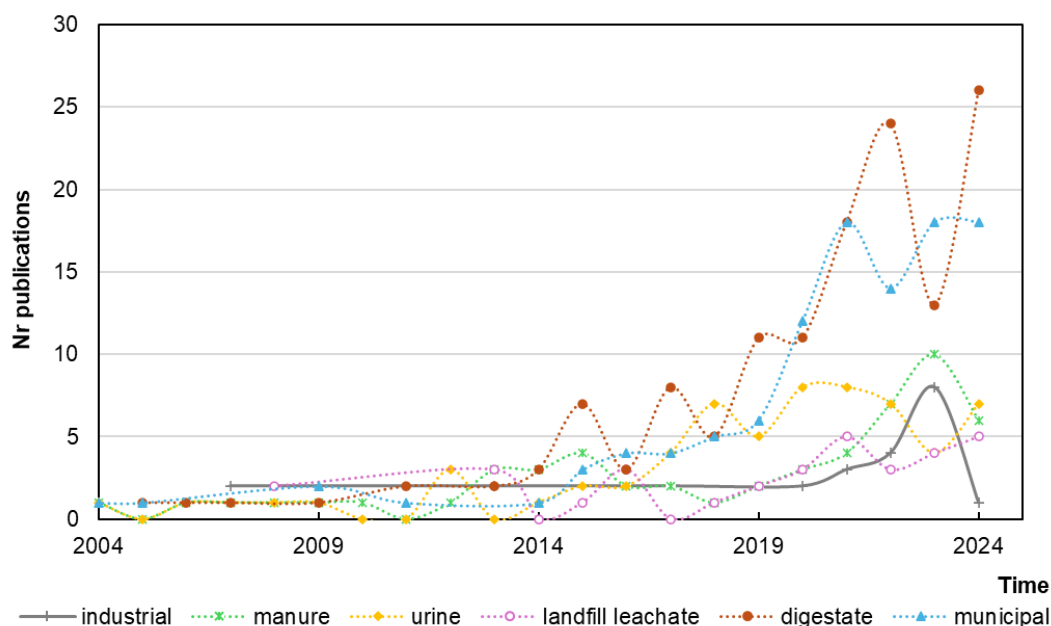


Figure 1-1. Publications (articles, reviews) on ammonia recovery, in English, available in Scopus for the period 2004-2024, as function of the targeted wastewater. Criteria: “ammon*” OR “NH*” AND “recovery” AND (specific wastewater type) AND NOT (other wastewaters) in title, abstract, and keywords.

This research focused predominately on ammonia recovery from distillery wastewater. Distillery wastewater is a promising candidate for resource-recovery worldwide and particularly in Scotland, as highlighted by recent analyses on the biorefining potential of this country ^{25,26}. Historically, distilleries were allowed to discharge partially treated or untreated effluents to the environment, however this has been changing for environmental protection ^{27,28}. Distillery wastewaters are increasingly treated with anaerobic processes to harvest biogas. This step releases high levels of ammonia and phosphate in solution, yet the recovery of such nutrients has been limited to only a few small scale studies ^{29–31}. In Scotland, distilleries located inland, mostly in rural areas, often opt to tanker their effluents to larger treatment centres, increasing costs and emissions. Distilleries on the coast are sometimes allowed to discharge process waters into the sea by the local environment agency. In both scenarios, the water characteristics promote the spontaneous formation of N- and P-containing struvite, causing a significant scaling challenge in the associated pipework, adding to the maintenance

requirements. Drivers of various natures exist for *in situ* nutrients removal, including i) reduction of effluent transport-associated costs and emissions, particularly relevant for rural areas ii) mitigation of scaling-caused costs, iii) compliance with increasingly stringent regulations. On top of the critical need for removal based on these drivers, there are also potential opportunities and benefits associated with recovery, including the valorisation of resources to be reused either in the proximate areas or at a broader scale fostering circularity. While there has been some work on treatment for removal, there is little insight on the potential for recovery ³², highlighting the need to focus research on this. Recovering ammonia and phosphate into fertilisers is likely to find limited application in some Scottish areas, with significant environmental vulnerability, but could be introduced on the market at national level. Moreover, recovered ammonium salt solutions and struvite could be used for other applications as well. Both removal alone or combined with recovery imply gains and disadvantages on the economic and environmental sides. It should be highlighted that exploration of nutrients recovery from distillery wastewater has been limited so far, especially at larger scale, showing a clear gap in understanding of the potential and feasibility.

Determining an ammonia recovery strategy for distillery effluents and other industrial wastewaters can be challenging for industry stakeholders and consultants, due to their composition and potential treatment limitations. Ammonia harvesting from industrial effluents can be realised via the above-mentioned technologies, although their performance is thought to be dependent on the wastewater physico-chemical characteristics. Currently, there are no detailed indications facilitating the selection and operation of such ammonia recovery technologies from industrial effluents, including distillery wastewater. Comparable guidelines exist for anaerobic digestate, mainly produced via degradation of organic waste such as sewage sludge, manure, crops residues and food waste ³³. Previous literature has reviewed physico-chemical and biological technologies to remove and recover nutrients, including nitrogen, from industrial effluents, using N concentration as main criterion to dictate the

suitability of technologies ³⁴. Nonetheless, besides the feed concentration ⁴, the overall water's matrix determines the suitability of a technology to effectively separate and harvest ammonia. To illustrate, pH, with temperature, is a key factor determining the fraction of ammonia/um ³⁵ and the speciation of other ions and compounds, such as phosphate and metals ^{36,37}. Competing ions such as calcium, sodium, and potassium can reduce both struvite precipitation ³⁶ and ammonium sorption ³⁸. Moreover, industrial wastewaters can contain different species able to bind ammonia/um and potentially posing a hindrance to the mentioned partitioning technologies, by sequestering the target compound. Examples of these are transition metals, complexing with ammonia ³⁷, and acidic organic compounds binding ammonium ³⁹. Their impacts on the partition technologies are still poorly understood, consequently, further research is required to clarify them. This will enable a more informed technology selection and operation for ammonia recovery from industrial effluents, including distillery wastewater.

1.2 Aim and objectives

The overall aim of this thesis is to critically evaluate the impact of the water matrix on the mechanisms controlling ammonia partitioning in complex fluids, so to establish a mean to identify the optimum transfer routes into gas, liquid, solid phases from industrial effluents, including digested distillery effluent. To do so, the major drivers for technology selection and operation were identified and integrated from literature into a set of recommendations. Furthermore, the specific impacts of chemical species (e.g. transition metals, acidic organic compounds) contained in some industrial effluents, such as from metallurgy, mining and agro/food processing, were experimentally assessed to expand the proposed guidelines. The actual performance of three partitioning processes was evaluated experimentally with a real case study water, being anaerobically digested distillery wastewater. This was performed by pilot scale testing of precipitation and stripping with scrubbing and with lab scale testing of emergent sorption media.

To deliver the overall aim the following objectives were set:

Objective 1: To review the literature to critically assess the drivers for ammonia partitioning technologies' use in industrial wastewaters and develop preliminary guidelines for their selection and operation based on the impact of water physicochemical properties.

Objective 2: To assess the viability and determine the performance of ammonia partitioning in real digested distillery wastewater, treated with an integrated system comprising chemical precipitation and air stripping, at demonstration scale. To determine and mitigate bottlenecks in real application, aiming to advance the technologies readiness levels (TRLs).

Objective 3: To elucidate the mechanisms of ammonia partitioning in water matrices containing selected transition metals and organic compounds, assessing and quantifying their impact on ammonia volatilisation during vacuum thermal stripping.

Objective 4: To determine the factors driving ammonia partitioning mechanisms in metal-hybridised sorption media. To compare their capacity and performance in real wastewaters, including distillery wastewater, with conventional ion exchange (IEX) media.

1.3 Thesis structure

The thesis is presented as chapters formatted as individual journal papers, in accordance with Cranfield University guidelines. The thesis comprises a literature review (chapter 2) and three technical papers (chapters 3, 4, 5). The links between the different thesis' objectives and chapters are depicted in Figure 1-2.

Maria Celeste Gritti was the lead author of all the chapters in this PhD thesis, with editing and revision provided by Dr Marc Pidou and Prof Bruce Jefferson. All experiments were designed, performed or supervised by Maria Celeste Gritti. The contribution of each chapter is presented below, along with the acknowledgement of external contributions.

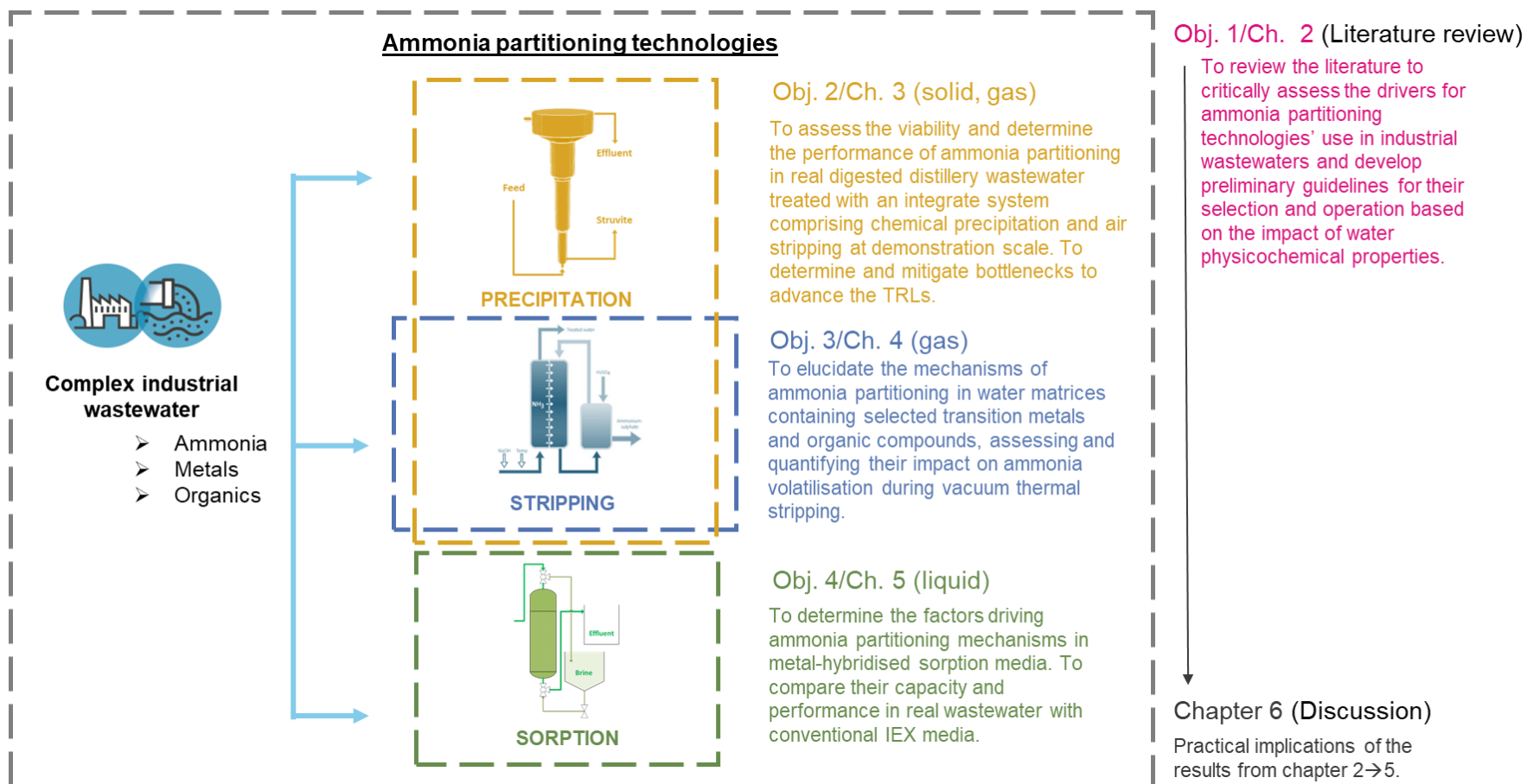


Figure 1-2. Thesis structure with objectives and related chapters.

Chapter 2 addresses objective 1. A systematic literature review demonstrated the current state of implementation of ammonia partitioning technologies with industrial effluents and highlighted drivers for their selection. Furthermore, the impact of wastewater physicochemical characteristics was reviewed to develop high-level guidelines for the selection and operation of ammonia partitioning technologies with industrial effluents. Knowledge gaps were identified which needed to be resolved in order to improve the guidelines. These structured recommendations were used to determine a strategy to recover ammonia, and phosphate, from digested distillery wastewater. – *M. C. Gritti, B. Jefferson, M. Pidou. A critical review on ammonia recovery from industrial wastewater. In preparation to be submitted to Environmental Technology Reviews.*

Chapter 3 focuses on the case study of distillery effluent treated for ammonia recovery. An integrated ammonia recovery system was selected, developed, tested and improved, at a demonstration scale at a whisky distillery (Tain, Scotland). The system integrated the previously existing anaerobic digestion treatment with struvite precipitation and ammonia stripping and scrubbing, addressing objective 2. The work evaluated the performance of the system at different operation conditions, including pH control, by quantifying its ammonia removal, against the theoretical expectations, and characterising the recovery products. Operational challenges were identified and mitigated, allowing to increase the readiness level of the technologies. The pilot plant design and commissioning was realised in collaboration with Aquabio Ltd. (UK), the industrial partner within the broader context of the Ultimate project (Horizon 2020, grant agreement N° 869318), under the supervision of Angel Sixto Aguilera Serrano. Christine Kimpton (Cranfield University, UK) carried out SEM-EDS and XRD analyses on the struvite samples. – *M. C. Gritti, A. S. Aguilera Serrano, B. Jefferson, M. Pidou. The impact of pH on the feasibility of recovering nutrients from distillery wastewater: a demonstration scale trial. In preparation to be submitted to Journal of Cleaner Production.*

Chapter 4 tackles objective 3, aiming to address some of the gaps identified in chapter 2, to further improve the preliminary guidelines. The impact of transition metal and recalcitrant, organic acidic compounds (e.g. humic acid) on ammonia partitioning via volatilisation was studied and quantified at lab scale, with synthetic solutions. The concentrations ranged of the tested species encompassed values found not only in distillery wastewaters, but also other industrial effluents (e.g. related to the metallurgical and mining sectors) to deliver a broader assessment for a wider range of industrial effluents. The mechanisms responsible for such effect and the conditions critical for ammonia removal were identified. The results identified the most impacting metal, presenting an opportunity for further research exploiting the metal-ammonia interaction. Zoi Brozou (Wageningen University, NL) performed some of the experimental work (tests and analyses) between February and June 2023, under the supervision of Maria Celeste Gritti. Christine Kimpton (Cranfield University, UK) carried out SEM-EDS and XRD analyses on powder samples. Nuannat Simmons supported with ICP-MS analyses. – *M. C. Gritti, Z. Brozou, B. Jefferson, M. Pidou. Impact of transition metals and humic acids on ammonia vacuum thermal stripping. Submitted to Journal of Environmental Management.*

Chapter 5 explores metal-ammonia interaction for ammonia recovery via zinc-hybridised sorption media, addressing objective 4. The work was conducted at lab scale in both synthetic solutions and real effluents. The results supported the identification of factors affecting the ammonia partitioning mechanisms (ion exchange and ligand exchange) in sorption media partially loaded with zinc in cationic form and hydroxide/oxide form. The critical conditions for each mechanism were explored. The capacity and performance of such media were benchmarked against the conventional ion exchange resin. This technology could further integrate into a nutrients separation strategy for distillery wastewater. Christine Kimpton (Cranfield University, UK) carried out SEM-EDS and XRD analyses on the media and powder samples. – *M. C. Gritti, B. Jefferson, M. Pidou. Ammonia removal via ion exchange and molecular adsorption on Zn-hybridised media. In preparation to be submitted to Journal of Water Process Engineering.*

Chapter 6 is an overall discussion of the key implications of this thesis' results for practical application. **Chapter 7** summarises the conclusions and presents opportunities for further research, stemming from the presented thesis's findings.

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Chapter 2

2 A critical review on ammonia recovery from industrial wastewater

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Abstract

The application of circular economy principles in wastewater management is gaining increasing importance. In this context, ammonia recovery from industrial effluents can provide a significant contribution. Industrial wastewaters vary widely in composition including ammonia content, depending on the sector, with some characterized by complex matrices containing high levels of ions, recalcitrant organic species, and heavy metals. Currently, there are no established guidelines in the literature for selecting and operating ammonia recovery technologies in industrial effluents. This study reviews the three most established ammonia recovery methods, precipitation (primarily as struvite), stripping processes, and sorption processes (ion exchange and adsorption), specifically in the context of industrial wastewater. A systematic assessment of the literature revealed that struvite precipitation was the most commonly applied and studied method in industrial wastewater, driven by the need to control spontaneous precipitation and by the well-studied operational parameters. Stripping processes emerged as the second most used approach, while sorption processes were underrepresented, possibly due to the high nitrogen load and complex matrices in such wastewaters affecting their performance. Despite this, stripping and high-capacity, selective sorption methods are expected to become predominant and complementary technologies, offering the ability to recover high-quality nitrogen products for various applications. In order to provide guidance for strategy selection and optimised operation, this study developed a set of recommendations, built on literature data informing about the impact of different

physicochemical factors on the technology performance. Moreover, knowledge gaps were identified, including the impact of organic compounds and heavy metals on the considered technologies.

Keywords: *ammonia recovery; industrial wastewater; stripping; precipitation; adsorption; ion-exchange*

2.1 Introduction

Ammonia plays a pivotal role in the terrestrial nitrogen cycle, which sustains human life on earth but has also become deeply unbalanced, crossing a planetary boundary ^{1,2}. Ammonia enters wastewater via different routes including organic matter decomposition in water (e.g. animal excreta, urban sewage, leachate, digestate), agricultural runoff, and by-products of industrial processes ^{3,4}. Ammonia recovery from water enables both protection of the receiving environment and its reuse, bypassing the long-established and energy-intensive process of conversion to gaseous molecular nitrogen and Haber-Bosch fixation into reactive nitrogen again ⁵. Consequently, for decades, research and industry have focused on developing methods to extract ammonia from water and benchmarking them against the standard processes, to foster the journey towards a circular and more sustainable economy ². The most established and researched separation methods for recovery are stripping processes ^{6,7}, precipitation, mostly as struvite, ⁸ and adsorption and ion exchange onto solid media ⁹. Besides these, other physico-chemical techniques have been explored, including membrane filtration and electrochemical systems. Nonetheless, their adoption is still limited. The former, e.g. via reverse or forward osmosis, separates total ammonia nitrogen (TAN) into either diluted streams (permeate) or complex matrices (brines) ^{6,10}. Electrochemical systems include electrodialysis, electrochemical cells and microbial cells ⁶. Despite being promising due to the limited chemical and energy demand, these are not fully established at large scale yet ^{11,12}. Furthermore, TAN uptake by biomass and subsequent upgrade/reuse has been assessed ^{7,9,11}, but, by nature, it is often less robust than abiotic processes ¹⁰.

Well-established ammonia harvesting methods have been thoroughly described in various reviews ^{13,14}. Their performance depends on multiple factors, including the wastewater chemical and physical properties. Previous studies proposed that such selection would be driven by the influent TAN concentration, directly impacting its cost effectiveness ^{4,15}. To illustrate, diluted streams such as

domestic wastewater (< 0.1 g N/L) should undergo biological treatment, whereas concentrated effluents (0.1 - 5 g N/L) could be treated with stripping and precipitation and for highly concentrated waters (> 5 g N/L) stripping and selective ion exchange could become economically viable ^{4,15}. For instance, Vaneeckhaute *et al.* ¹⁶ developed a decision-making algorithm tool to determine the most effective treatment configuration to harvest N and P fertilisers from digestate, accounting for selected physico-chemical characteristics. Although ammonia recovery from industrial wastewaters is increasingly encouraged ¹⁷, analogous guidelines for such effluents are not available in the literature, yet these would be useful considering the complexity and variety of these wastewaters. Such diversity is reflected also in their TAN loads, spanning from low (e.g. 0.1 - 20 mg TAN/L) to high levels (e.g. 600 - 5000 mg NH_3 /L) ^{3,9}, with the latter effluents being valuable candidates for direct recovery ¹⁷.

So far, research on ammonia harvesting has extensively targeted anaerobic digestate of agro-industrial effluents (e.g. manure) ^{8,18–20}, source-separated urine ^{21,22} and lately also municipal wastewater ^{23,24}. Only a few studies have reviewed ammonia recovery options from industrial streams, often focusing on specific processes e.g. membrane contactors ²⁵, stripping ²⁶, struvite precipitation ²⁷. Pedemonte and colleagues reviewed in 2017 the main biological and physico-chemical methods to remove and recover nutrients from industrial effluents, highlighting the role of the N concentration on the selection, but did not focus on the impact of the water matrix ^{15,28}. Xiang *et al.* presented the main ammonia recovery techniques used with different wastewaters, including industrial ones, and briefly reported cases where stripping and struvite precipitation have been used ³. Updated and extensive review and recommendations for choosing and operating N recovery technologies for industrial wastewaters is still missing. The macro-sector of industrial effluents is highly variable in terms of wastewater composition, depending on the industry, yet it distinguishes from other wastewater types by the occurrence, in some cases, of high contents of nutrients, recalcitrant organics, heavy metals, salt-forming species as chloride, sulphate, fluoride and other ions ¹⁷, all potentially impacting physico-chemical processes.

Consequently, this study aims to address these gaps in knowledge by first providing an overview of the current state of implementation of the three main N recovery processes from industrial effluents and highlighting well-established practices and identify areas of improvement. Furthermore, it aims to develop high-level guidelines for the selection and operation of these technologies from industrial wastewaters.

2.2 Materials and Methods

2.2.1 Dataset generation and processing

To assess the extent of implementation of precipitation, stripping and sorption processes with industrial effluents for TAN recovery, a systematic literature review was conducted. A dataset of scientific publications was generated via an advanced search with a specific string in the bibliographic database Scopus, including papers in English published between 1969 - 10th June 2024. The search output was based on the occurrence of keywords such as “recovery” and “ammonia/um” and terms related to different industrial sectors wastewaters and recovery technologies, in the papers’ title, abstract or keywords (search string details available in Appendix, section A.1). Stripping processes encompassed conventional stripping, distillation, membrane distillation, hydrophobic membrane contactors.

The systematic search yielded 918 scientific publications, which underwent screening and selection. The screening filtered for scientific papers reporting ammonia recovery from real or synthetic industrial effluents with stripping, distillation, transmembrane chemisorption, ammonium precipitation (e.g. as struvite), ion exchange or adsorption. Publications that were not accessible, had no DOI or were incomplete were excluded. As a result, 67 scientific articles were selected, with the addition of 7 articles, originally not included in the search output, but known to the authors for the relevance to the topic and meeting the selection criteria. The selected papers were analysed and the relevant data extracted and processed. When the required data was not explicitly reported in

the text, they were estimated from figures with an online image analyser tool (WebPlotDigitiser, “wpd”), calculations and unit conversions.

For the chart showing the influent TAN concentration as a function of technology and feed type (Figure 2-3), some of the values reported were retrieved from the same study e.g. when a range of values was reported in one study, the extremes of such range were included in the chart. When more than one type of wastewater was tested in the same study, the TAN values for each were reported. Standard deviations reported in the articles were excluded. For the chart displaying the best reported removal efficiency with the related influent TAN (Figure 2-5), if the latter was presented as a range in a paper, its average and standard deviation were used. When ">" or "<" was used to define a TAN value in a study, the absolute number was used. Studies where N removal efficiency or TAN content were not reported at sufficient level of detail were not included in the analysis.

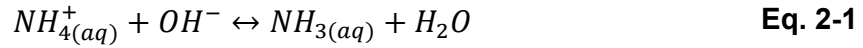
2.2.2 Recommendations for technology selection and operation

Indications on strategies for the selection and operation of N harvesting processes have been extracted from literature, elaborated and presented in a decision tree-type diagram, to facilitate their visualisation. Struvite precipitation, conventional stripping (air or vacuum) and sorption (ion exchange, adsorption) processes have been considered. Threshold values were used as indicative gates for path definition in the decision trees, when available. These were identified from qualitative and quantitative data from previous literature (peer-reviewed publications, handbooks) on N recovery technologies from any wastewater type, elucidating mechanisms, interactions and influence of several parameters on the process performance. The level of certainty of the quantitative indications was variable, with some being relatively certain (e.g. reported by different sources) and some others still having to be identified/clarified or being highly case-dependent. Such uncertainty was expressed by means of a colour grading system: green (relatively consolidated knowledge, as reported by ≥ 2 sources), yellow (one source reporting a certain value or information or a trade-

off value between different sources reporting comparable numbers), red (existing knowledge on the impact of a certain parameter, but no quantification).

2.3 Overview of ammonia partitioning technologies

Ammonia exists as an acid/base ion pair, with free, volatile ammonia (NH_3) and ionised ammonium (NH_4^+) in equilibrium (Eq. 2-1, Eq. 2-2 ^{29,30}):



$$[\text{NH}_3] = \frac{[\text{NH}_3 + \text{NH}_4^+]}{1 + \frac{[\text{H}^+]}{k_a}} = \frac{[\text{NH}_3 + \text{NH}_4^+]}{1 + 10^{pk_a - pH}} \quad \text{Eq. 2-2}$$

Where pk_a is the negative logarithm of the stoichiometric acid dissociation constant, dependent on temperature (Eq. 2-3) ²⁹.

$$pk_{a,T}^s = pk_{a,298}^s + 0.0324 \cdot (298 - T) \quad \text{Eq. 2-3}$$

Where T is the solution temperature (K) and $pk_{a,T}^s$ and $pk_{a,298}^s$ refer to the constant's value at the solution temperature and 298 K (9.2 ³⁰), respectively. Consequently, the fraction of free ammonia (FA) increases over rising pH and temperature (Figure 2-1).

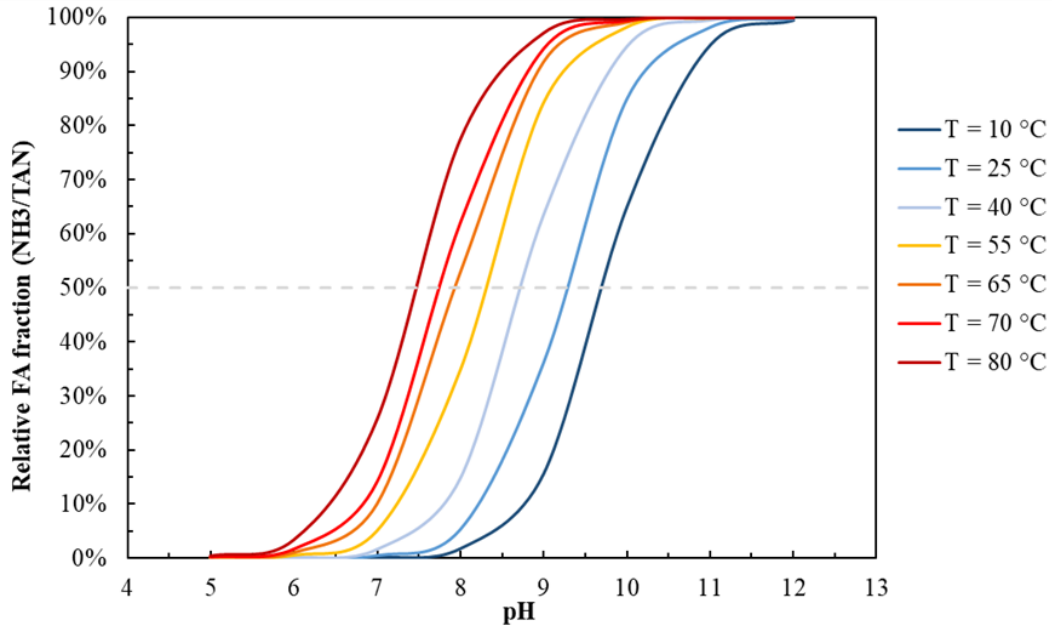


Figure 2-1. Fraction of free ammonia (FA, NH_3) over total ammonia nitrogen as function of solution pH and temperature, based on Eq. 2-2, Eq. 2-3 ²⁹.

Free ammonia is volatile and can desorb from water, reaching an equilibrium between its partial pressure in the gas phase (P_a , atm) and its concentration in the liquid phase (C_a , mol/L). For diluted solutions (≤ 0.1 M), such equilibrium is described by a coefficient in Henry's law (H_{PC} , atm L/mol) (Eq. 2-4). The coefficient is generally expressed in the dimensionless form (H_d), determined knowing the temperature T (K) and the ideal gas constant R (0.082057 atm L/ K mol) (Eq. 2-5) ³¹.

$$H_{PC} = \frac{P_a}{C_a} \quad \text{Eq. 2-4}$$

$$H_d = \frac{H_{PC}}{RT} \quad \text{Eq. 2-5}$$

H_d is 0.0006 for ammonia at 20°C, but it is affected by temperature as described by the van't Hoff equation (Eq. 2-6) ³¹.

$$H_{d,T_2} = H_{d,T_1} \exp \left[\frac{-\Delta H_{dis}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right] \quad \text{Eq. 2-6}$$

Where T_1 and T_2 indicate the two temperatures (K), and ΔH_{dis}° is the standard enthalpy change of dissolution in water (J/mol) (36120 for NH_3 at 20°C). Depending on its form, ammonia/um can be separated and harvested from the solution in different ways.

2.3.1 Partitioning to the gas phase

Ammonia volatilisation is a well-established process exploited to extract uncharged NH_3 from the liquid to the gas phase, driven by a concentration gradient. According to the two-film theory and assuming the resistance to ammonia transfer is all on the liquid side, the flux of ammonia mass transfer is described with Eq. 2-7 ³¹.

$$J_A = K_{ov} \cdot \left(C_L - \frac{C_g}{H_d} \right) \quad \text{Eq. 2-7}$$

$$\frac{1}{K_{ov}a} = \frac{1}{k_la} + \frac{1}{H_d k_g a} \quad \text{Eq. 2-8}$$

Where J_A is the flux of ammonia through the gas-liquid interface ($\text{mg/m}^2 \text{ s}$), C_L and C_g are the concentration of ammonia in the bulk liquid (mg/L) and in the bulk gas phase (mg/L), respectively. Multiplying the overall ammonia mass transfer coefficient (K_{ov} , m/h) by the specific surface area a ($1/\text{m}$) yields the overall constant of mass transfer rate $K_{ov}a$ ($1/\text{h}$). K_{ov} combines the mass transfer coefficients for the liquid (k_l , m/h) and gas phases (k_g , $1/\text{h}$) (Eq. 2-8) ³¹. The mass flow of ammonia ($\frac{dM}{dt}$, mg/h) is determined knowing the contactor's volume (V , m^3) (Eq. 2-9) ^{31,32}.

$$\frac{dM}{dt} = K_{ov}a \cdot \left(C_L - \frac{C_g}{H_d} \right) \cdot V \quad \text{Eq. 2-9}$$

K_{ov} is influenced by the air density, viscosity and velocity, ammonia diffusivity in air, and temperature of the liquid and the gaseous phase ³². The free ammonia

concentration in the bulk (C_L) is promoted by increasing pH and temperature (Figure 2-1), with the latter inversely affecting the ammonia saturation concentration and feed viscosity ^{29,33}. Accordingly, pH and temperature are key parameters in enabling ammonia stripping. pH control during operation is envisaged, as the pH decreases as the stripping process progresses ³⁴ due to protons release ³⁵, loss of buffering by CO₂ stripping or precipitations ³⁶. To increase the surface area available for the transfer of ammonia, volatilisation (or stripping) is often carried out in tall columns containing packed material. The liquid is sprayed onto the media via nozzles, while a carrier gas flows counter-current with the ammonia transferring from the gas-liquid interface ³¹. Alternatively, thermal stripping and distillation rely on the volatilisation of ammonia by boiling and so do not necessarily need a carrier gas ^{29,37}. Applying a vacuum lowers the required temperature and so the heating-related energy demand ²⁹. The volatilised ammonia can then be captured by absorption in acid traps or condensation by cooling ^{35,38}. Often packed scrubbers are used, similar to stripping towers, recirculating acid solutions in batch to absorb NH₃ from the gas phase. Sulphuric and phosphoric acid are preferred, yielding ammonium sulphate or phosphate solutions, yet nitric, hydrochloric, acetic acid can be used as well ³⁹. The desorbed ammonia can be recovered also as pressurised gas ⁴⁰ or in a concentrated aqueous form via condensation ⁴¹. The latter form can have many applications, depending on its quality (e.g. concentration, contamination), which is affected also by the influent's composition ⁴¹.

Although effective, stripping packed columns are sensitive to total suspended solids (TSS), causing blockages and thus requiring solids separation ⁴² (e.g. <0.06% ⁴³), and have large land footprints. To mitigate these, alternative configurations have been tested such as turbulent feed mixing with ⁴⁴ or without aeration ³⁴, both without packing material, or semi-batch jet loop reactors ⁴⁵ and water-sparged aerocyclone reactors ⁴⁶. The concept of stripping can be extended to separation technologies relying on gaseous ammonia volatilisation from the liquid phase, thus including some membrane-based processes. Membrane distillation exploits a physical hydrophobic barrier between the feed and the

permeate, with the vapor pressure gradient generating a driving force for the transfer of NH_3 ⁴⁷. Membrane distillation can occur via direct contact, vacuum, air gap or sweep gas ⁴⁸, with NH_3 being absorbed or condensed. Liquid-liquid hydrophobic membrane contactors can also be used to harvest ammonia, transferring ammonia from an alkalised stream to an absorbing solution on the permeate side e.g. acid or aqueous solution ⁴⁸. Membrane-based processes have the advantage of a modular and compact configuration ^{25,47}, but are limited by membrane wetting and fouling ²⁵ and water carryover ³³. Previous publications reviewed different processes exploiting ammonia partitioning to the gas phase, including air and vacuum stripping ^{49,50}, membrane contactors ⁵¹ and membrane distillation ⁴⁸.

Solution pH and temperature are key parameters determining the fraction of available NH_3 , nonetheless other factors can impact stripping processes, especially with packed towers. These have been highlighted in Table 2-1, which indicates also thresholds reported in literature or trade-off values from figures available in different studies. Nonetheless, the full set of references for these information and values is available for consultation in Appendix Table A-1. To illustrate, suspended solids, scaling agents, some organic compounds, transition metals and carbonates can influence the process performance. Scaling agents could include for instance struvite and phosphate salts ⁵², sulphate and carbonate salts ⁴⁵, metal oxides ⁴⁵, elemental sulphur ⁵³. Previous literature advised that further research was needed to elucidate whether and how organics contained in complex matrices can bind TAN ⁵⁴, which could potentially impact stripping. Furthermore, metals, especially transition ones, can complex with ammonia ⁵⁵, potentially hampering volatilisation ³⁸. Nonetheless, no clear understanding of critical levels has been proposed yet. Transition metals and organic species, both dissolved and particulate, can be found in various industrial streams ^{56,57}, thus these potential hindrances should be further assessed.

Table 2-1. Selected parameters/steps impacting ammonia stripping operation. Key references are shown (KR), and further details and complete list of references can be found in the supplementary information (Table A-1).

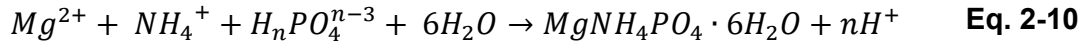
Parameter/step	Impact/threshold value
pH	Main affecting parameter. Should be $\geq 9.5-10.0$, depending on the temperature. KR ⁵⁸ CO ₂ stripping is an effective measure to reduce costs associated with pH increase, especially if molar ratio $\text{NH}_4:\text{HCO}_3 \leq 1$. KR ⁵⁹
Temperature	$T \geq 50^\circ\text{C}$ promotes stripping, and should be optimised with pH. If cheap heat is available, it should be exploited for thermal stripping. KR ⁴⁴
Pressure	An optimum combination of pressure and temperature should be used to maximise removal and selectively transfer ammonia, over water and volatile organics. KR ^{29,60}
[TAN]	Increasing [TAN] promotes the driving force and the stripping rate, but does not significantly affect the removal efficiency, provided sufficient time is allowed. For economic feasibility, it should be $\geq 0.5-1 \text{ g N/L}$. KR ¹⁶
[TSS]	The concentration should be $\leq 0.06\%$, to reduce maintenance needs caused by clogging in packed towers. KR ⁴⁴
[Scaling agents]	Scaling agents should be removed if have high supersaturation ratio (SSR), to avoid clogging of stripping equipment (e.g. struvite, oxides, carbonates-based minerals). KR ³⁴
[Organic compounds]	Volatile organics can affect the purity of the end-product, which is mitigated using alkaline traps. Some organic compounds could bind NH_4^+ and lower TAN removal. No critical thresholds have been determined yet. KR ⁶¹
[Transition metals]	Transition metals can complex with NH_3 and affect its stripping. No critical thresholds have been determined yet. KR ^{55,62}
Recovery ^a	Water carryover should be minimised (e.g. with demisters) and the concentration of AS should be $\approx 40\%$ (w/w) to minimise costs for crystals precipitation and dewatering. Scrubbing liquor should have $\text{pH} < 4$ to maintain driving force. KR ^{63,64}

^a In the case of stripping and acid scrubbing to form ammonium sulphate (AS).

From an economic perspective, the TAN concentration in the feed could affect the feasibility of the stripping processes, with more loaded streams being preferred, but no final consensus on the minimum TAN content for viability has been reached (more details in Appendix Table A-1).

2.3.2 Partitioning to the solid phase

Precipitation is a physical-chemical process allowing the separation of solutes from the solution via the formation of solid species. Precipitation applied for ammonia capture is mostly based on N-struvite formation and recovery, since most of the other ammonium salts have higher solubilities ²³. N-struvite or ammonium magnesium phosphate hexahydrate (MAP), $MgNH_4PO_4 \cdot 6H_2O$, is a white mineral salt with orthorhombic crystal structure and low solubility in water (0.018 g/100 mL, 25°C) ⁶⁵ (Eq. 2-10). Although other types of struvite analogues exist, such as the potassium, K, and sodium, Na forms, and other divalent cations can react with struvite (e.g. Cu^{2+} , Ni^{2+} , Pb^{2+} , Mn^{2+}), MAP has generally greater stability, making it a suitable method to separate ammonium ⁶⁶. Moreover, N-struvite precipitation has a fast reaction rate, requires a simple operation and the solid-liquid segregation is obtained via settling and/or filtration.



Where $n = 0/1/2$. When the concentrations', or activities', product (i.e. $[Mg^{2+}] \cdot [NH_4^+] \cdot [PO_4^{3-}]$) is greater than the mineral's constant solubility product (Ksp) (thermodynamic constant), the solution is supersaturated and precipitation occurs. Ksp values have been determined in the range $3.89 \cdot 10^{-10}$ and $8.46 \cdot 10^{-15}$, as influenced by the solution's temperature, pH, and ionic strength ^{65,67,68}. Doyle and Parsons indicated a range of 9.4 - 13.26 for struvite pKsp ⁶⁹ and Siciliano *et al.* highlighted the variability of Ksp values found in literature, at different temperatures (10-60°C) ⁶⁶. A range of pH values, 8.0-10.7, was reported for struvite minimum solubility, and generally higher pH lowers the struvite solubility, resulting in a greater precipitation potential ⁶⁹. In solutions with high ionic strength (e.g. with [ionic species] > 10^{-3} M), saturation is better described by

the conditional solubility product (K_{so}) considering the species' activities ^{65,69}. Furthermore, K_{so} is specific for a pH value, in contrast to K_{sp} which is suitable to any pH ⁶⁹. The ions' activities are determined by their activity coefficients γ , influenced by the temperature and the ionic strength I ⁶⁷, as described by the Davies approximation of the Debye-Huckel equation ⁶⁹ (Eq. 2-11).

$$\log \gamma = AZ^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad \text{Eq. 2-11}$$

Where A is the Debye-Huckel constant (0.509, at 25°C) and Z the valence. The driving force for precipitation is expressed by the supersaturation ratio (SSR) and the saturation index (SI) (Eq. 2-12 ^{65,67}, Eq. 2-13 ⁷⁰).

$$SSR = \left(\frac{a_{Mg^{2+}} \cdot a_{NH_4^+} \cdot a_{PO_4^{3-}}}{K_{so}} \right) = \frac{IAP}{K_{so} \text{ or } K_{sp}} \quad \text{Eq. 2-12}$$

$$SI = \log \frac{IAP}{K_{sp}} = \log[(a_{Mg^{2+}})(a_{NH_4^+})(a_{PO_4^{3-}})] - \log K_{sp} \quad \text{Eq. 2-13}$$

Where a is the species activity and IAP is the ion activity product. Importantly, the extent of struvite precipitation is limited by the lowest activity among the ionic species involved in the reaction (often magnesium or phosphate), due to the mineral's equimolar Mg:N:P proportions ⁶⁷. Such ratio must be optimised and both Mg and P can be spiked in wastewaters containing high N loads ⁶⁶. Excess Mg can mitigate the impact of interfering ions (e.g. carbonates), but can also lead to undesired precipitation of $Mg(OH)_2$ and Mg-phosphate minerals. Different Mg:P, N:Mg and N:P molar ratios have been reported in literature as ideal (more details available in Appendix Table A-2) and such operational conditions are often case-dependent, given the impact of competing ions ⁶⁶.

pH is responsible for changes in the activities of the struvite components, e.g. favouring NH_4^+ over NH_3 , hence affecting the SSR ⁶⁹. Different pH operational ranges have been reported, generally between 7 and 10.5, but the optimum operation value depends on the wastewater chemistry and should be a trade-off between removal efficiency, product purity and quality (e.g. crystal size) ⁷¹.

Struvite formation is characterised by a nucleation stage (crystal formation) and crystal growth until equilibrium ⁶⁹. In a supersaturated solution, both phases are triggered, but high supersaturation levels can favour primary nucleation over growth/agglomeration into bigger particles ⁷². To promote crystals agglomeration SSR is controlled and struvite is precipitated mainly in fluidised bed reactors and stirred reactors ⁶⁵. MAP precipitation mechanisms, challenges and advantages have been illustrated in previous reviews ^{66,73}. Besides pH and molar ratios, other water characteristics can affect struvite precipitation, such as temperature, suspended solids, ionic strength, foreign ions, organic matter. The impacts of these parameters are summarised in Table 2-2, providing specific or trade-off threshold values gathered from scientific literature. The extensive set of references for these data and values are listed in Appendix Table A-2. Other ions in solutions can heavily impact the process performance ⁷¹, which could become critical in industrial effluents often characterised by high loads of different ions. So called “foreign ions” can lengthen the time of induction and crystal growth, covering surface active sites and/or sequestering required components ⁶⁵. Moreover, by reacting with other species and co-precipitating, they lower the purity of the product, e.g. calcium, Ca, forming hydroxyapatite, calcium phosphate and calcium carbonate ^{65,74}. Some industrial effluents can also contain significant levels of heavy metals such as Cu, Pb, Zn ⁵⁶ and organic species ⁵⁷, which can negatively affect struvite formation and purity (Table 2-2). Interactions between organic compounds and foreign ions, including metals, and their effect on struvite recovery should be further investigated, as their combination might lead to a mitigated impact ^{75,76}.

Struvite precipitation was considered for concentrated effluents with 0.1-5 g N/L ¹⁵, although its economic feasibility is questionable ⁴. Potentially, struvite precipitation can be applied to any ammonia-containing wastewaters to harvest N, if the molar ratios and the supersaturation level have suitable values or are adjusted accordingly. Often N recovery requires dosing of phosphate and magnesium, which could become economically unsustainable with effluents containing a high ammonium load and with high N:P and N:Mg ratios. Thus, bulk

N harvest in the form of struvite is recommended for waters containing N and P in a molar ratio relatively closer to unity. Examples reported in literature include effluents from fertiliser production with N:P of 0.1 ⁷⁷, semiconductor 0.8-1.1 ⁷⁸, cheese processing 1.4 ⁷⁹, cochineal processing 1.5 ⁸⁰, aquaculture 3.3 ⁸¹. Magnesium deficiency could be tackled by using cheap sources of Mg, such as magnesite and seawater ⁶⁶. Moreover, to further reduce such chemicals' costs, struvite dissolution and recycling of Mg and P have been investigated ⁸².

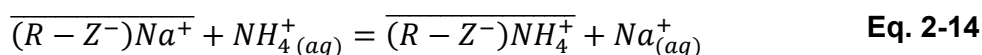
Table 2-2. Selected parameters impacting struvite precipitation. Ratios are presented as molar. Key references are shown (KR), and further details and complete references list can be found in supplementary information (Table A-2).

Parameter	Impact/threshold value
pH	Main affecting parameter. Should be 8.5-9.5 , to promote formation and limit precipitation of other compounds. KR ⁶⁵
Temperature	T should be ≤ 30-35°C to promote struvite removal and purity. KR ⁸³
N:P	Should be a case-specific determination, but generally: 4-6:1 to improve product purity and 1:1.1-1.5 to favour removal efficiency. KR ^{66,84}
N:Mg	Should be a case-specific determination, but generally: ≥ 1:1.2 to promote removal. KR ⁶⁶
Mg:P	Should be a case-specific determination, but generally: 1.5-1.7:1 to favour removal. KR ^{84,85}
SSR	SSR must be > 1 to allow precipitation. Should be < 3-6 to promote aggregation and pellets growth. KR ⁶⁵
[TSS]	The concentration should be ≤ 1 g/L , to enable precipitation and maintain purity of precipitates. KR ¹⁶ Crystals seeding can promote crystal growth and limit scaling.
[Metals]	Transition metals can complex with NH ₃ , reducing the precipitation rate and can contaminate the precipitates. Other metals such as Al, Fe can sequester PO ₄ . Mg:N:P molar ratios can be adjusted to overcome these hindrances. No critical thresholds have been determined yet. KR ⁸⁶
[Ca]	Ca:Mg should be < 1:1 and Ca:P < 0.5-1:1 , to increase struvite purity and enable precipitation. KR ^{68,87}

[K], [Na]	Both K and Na can compete with NH ₄ , delay struvite induction time and co-precipitate. No critical thresholds have been determined yet. KR ^{88,89}
[SO ₄], [F], [CO ₃]	SO ₄ delays induction time in struvite formation and F inhibits struvite crystallisation (N:SO₄/F ≤ 0.2), which can be mitigated by dosing excess Mg. Carbonates can co-precipitate with struvite, lowering the product purity. No critical thresholds have been determined yet. KR ^{65,90,91}
[Organic compounds]	Some organic species can inhibit and delay struvite formation. Critical thresholds for citric and succinic acid were N:OC 1.5-3:1. KR ^{71,92}

2.3.3 Partitioning to the liquid phase

Ion exchange and adsorption processes exploit the interaction of a target species in solution, such as TAN, with an insoluble media, to selectively separate it. The target species can then be released in a purer liquid phase by regeneration of the solid media. Adsorption and ion exchange operate under different mechanisms, although the actual application processes share similarities ⁹³, and will be collectively referred to as “sorption processes” in this study. Adsorption can occur via physisorption, fast and reversible, chemisorption, involving chemical bonding between species, and ionosorption ⁹³. Example media for adsorption include zeolites, biochar and metal oxides ^{94,95}. Ion exchange selectively targets ions, which are replaced in the solution by the counter-ions electrostatically held to the functional groups of the media, maintaining the electroneutrality ^{93,96} (Eq. 2-14).



Where *R* is the solid media matrix, holding the negatively charged co-ions *Z*[−]. Ion exchangers can be organic/polymeric media, such as cross-linked polyelectrolytes resins functionalised with specific chemical groups ⁹⁶. Inorganic materials such as zeolite minerals can separate TAN via both exchange of cations in their structure and adsorption, driven by electrostatic attraction and chemisorption ⁹⁵. Generally, zeolites have greater selectivity for NH₄⁺, while polymeric exchangers are indicated to remove large loads of N, due to their greater capacity and rapid regeneration, but are more expensive ^{97,98}. Sorption

processes can be described with adsorption isotherms, indicating the distribution of the target species in the liquid and solid phases at a certain temperature ⁹⁶. The most utilised isotherm models are the Freundlich (Eq. 2-15) and Langmuir equations, here shown in the linear form (Eq. 2-16) ³¹.

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e) \quad \text{Eq. 2-15}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \quad \text{Eq. 2-16}$$

Where q_e and C_e are the equilibrium adsorption capacity (mg TAN/g media) and concentration (mg TAN/L), respectively. q_m is the maximum adsorption capacity (mg TAN/g media). K_F is the Freundlich constant (mg/g), related to the binding affinity of TAN to the media's site, whereas n is related to the reaction's intensity (g/L). K is linked to the energy of adsorption (L/g). Both adsorption and ion exchange are controlled by diffusion of the target species and are often applied in fixed bed columns with their performance determined by the media's capacity and selectivity ⁹⁶. The capacity depends on the number of available interactions sites on the media and can be expressed as mass of retained species per mass/volume of media (g/g or g/L) or as equivalent per mass/volume of media (eq/g or eq/L) for ion exchangers ⁹⁶. Capacity can be improved by material conditioning e.g. with thermal, chemical (acid/base/salt) treatment ^{38,99,100}. Selectivity describes the preferential uptake of one species over others and depends on several factors, including the species' valences, hydrated ionic radii and concentrations ⁹⁶. Another key element enabling a positive performance is the ability of the TAN-loaded media to be regenerated, restoring its capacity and extracting the separated target species. This can be realised with different methods, including thermally and, most commonly, chemically by means of regenerant brines ¹⁰¹. Such brines are typically highly concentrated salt solutions (e.g. NaCl, KCl), contacted with the exhausted media to induce the displacement of the sorbed ammonium ^{101,102}. The media regeneration may become a limiting step in sorption processes, affecting also the overall recovery and the final product TAN concentration ¹⁰³. Hence, spent brine clean-up and reuse are

encouraged, and previous studies tested membrane contactors ¹⁰⁴ and vacuum thermal stripping ³⁸, the latter also combined to struvite precipitation ¹⁰⁵, to extract ammonia.

Adsorption and ion exchange mechanisms, bottlenecks and strengths have been reviewed in previous studies ^{23,94}. The advantages include a small space requirement, simplicity and rapidity of operation ²³, and the double function of concentrating ammonia from a dilute solution ¹⁴ and separating it into a simpler matrix, easier to use or process downstream. Nonetheless, their application at full scale is still limited ^{8,23}, when compared to stripping and precipitation.

Sorption processes are sensitive to several parameters, including suspended solids, competing cations, anions, and organic compounds. Table 2-3 summarised these impacts and related thresholds values reported in scientific literature, with Appendix Table A-4 illustrating the complete set of references for this data. Removal of suspended solids is often required to avoid clogging of the fixed bed systems ¹⁰⁶. Na, K, Ca, Mg are commonly found in complex industrial matrices at variable levels and can compete with NH_4^+ for the negatively charged groups of the media. This results in lower media ammonium capacity ²³ and shorter breakthrough time ¹⁰⁷. Furthermore, the sorbed competing ions can be transferred to the regenerant brine, requiring a further processing step prior use e.g. CaCO_3 precipitation to separate Ca ¹⁰⁸. Also heavy metal cations, such as iron, can compete with NH_4^+ for the media's active sites ⁹⁹ but less studies are available on their impact. Research is constantly investigating new media and strategies to improve the capacity and selectivity ²³, to make this process more competitive and suitable for TAN harvesting. Ligand exchange media has been explored in recent years, as a potential alternative to overcome the limited selectivity of ion exchange ¹⁰⁹, by exploiting the interaction of fixed metals with strong Lewis acid behaviour and strong ligand NH_3 ¹⁰¹. Initial results for this emerging adsorption technology are promising in terms of TAN-selectivity versus K^+ , when compared to conventional media ¹⁰⁹. Furthermore, organic compounds can also influence sorption processes, but the available research presents conflicting outcomes, with some studies suggesting they enhance sorption while

others reporting a reduction in removal ^{110,111}. Further investigation is needed, particularly for effluents with high organic loads, to better understand these effects.

In terms of TAN content-handling capacity, sorption processes are often applied for ammonium accumulation from diluted streams, such as municipal wastewater ^{23,104}. Previous literature advised they would be suitable even for wastewaters with 2-5 g TAN/L ^{14,15}, although impacted by increased operational expenses driven by the limited media capacity ³⁹. Indeed, some studies testing ion exchange (IEX) processes on high N-load waters are available in literature (some examples provided in Appendix Table A-3), yet their viability with streams containing high N and ions levels, such as digestate or industrial effluents, requires further demonstration ^{98,112}.

Table 2-3. Selected parameters impacting NH₄⁺ sorption processes. Selected key references (KR) are shown, with further details and complete references list can be found in supplementary information (Table A-4).

Parameter/ Step	Impact/threshold value
pH	For NH ₄ ⁺ sorption, ideal pH is 5-7 , to favour the charged form and limit protons competition. KR ¹¹¹
Temperature	T = 25-30°C promotes sorption on zeolite. IEX processes are generally tolerant to wide temperature ranges. KR ¹¹³
[TSS]	The concentration should be < 1.5 g/L , to limit clogging of media bed and backpressure. KR ¹⁰⁶
[Cations]	Cations compete with NH ₄ ⁺ for sorption sites, with different selectivity series depending on the IEX media, reducing the separation efficiency. KR ⁹⁸
[Heavy metals]	As cations, can compete with NH ₄ ⁺ , yet less studies are available, leaving unclear their position in the selectivity series. KR ⁹⁹
[Anions]	Anions can reduce NH ₄ ⁺ exchange capacity in zeolites, affecting the solution surface tension and the access to the media pores. No critical levels have been determined. KR ^{113,114}

[Organic compounds]	Some acidic organic species can promote NH_4^+ sorption by lowering surface tension, whereas in other studies were reported to reduce the media exchange capacity. KR ^{110,113}
[TAN]	Overall, the technology is better suited for more diluted streams. E.g. $[\text{TAN}] \leq 0.8\text{-}1 \text{ g/L}$ can maintain high driving force, but also control operational costs. KR ^{103,115}
Regeneration Brine	A trade-off between media regeneration and [TAN] dilution in the brine is needed. Brine clean up, especially via stripping, is recommended to improve the economic viability of the system. KR ^{103,116}

2.4 TAN recovery in industrial effluents

2.4.1 Industrial wastewater types and influent concentrations

The dataset of the systematic search encompassed 35 different sources of industrial wastewater (Figure 2-2 a), showing how the interest in harvesting ammonia has become transversal across substantially different industrial sectors. The potential value for recovery is large, considering the high ammonia concentrations in these streams (Figure 2-3) and the annual volumes of wastewater generated by the responsible sectors e.g. manufacturing, chemical products, agricultural, mining/metallurgy, food processing, all producing more than 700 Mm³/year, only in the European Union ((Figure 2-2 b).

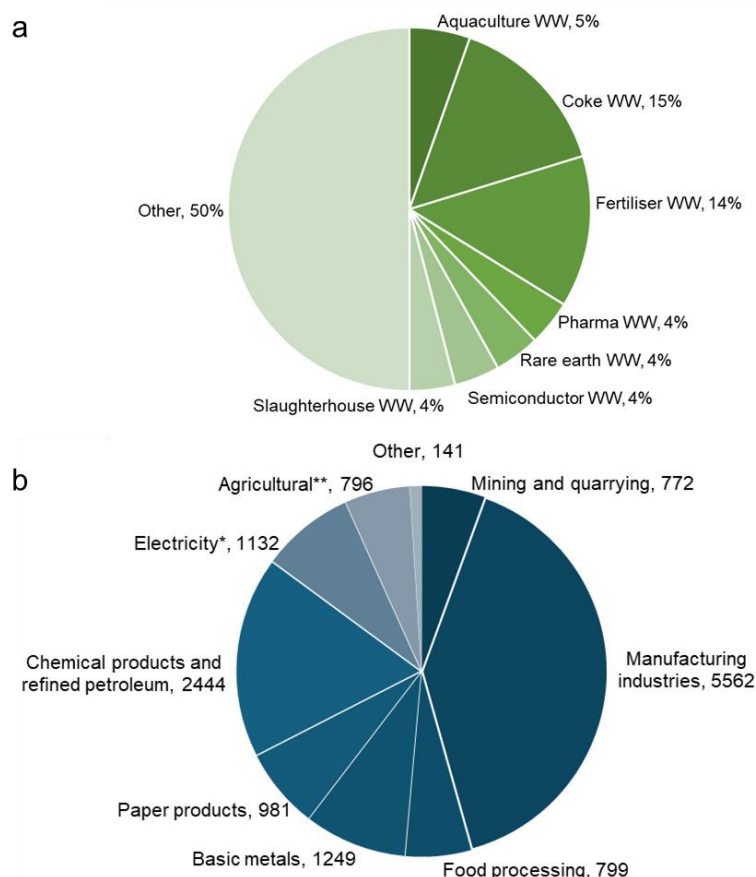


Figure 2-2. a) Distribution (%) of industrial wastewater types in the analysed dataset. Labels referred to types with ≥ 3 studies. b) Wastewater production (million m³/y) in the European Union as function of the industry sector in 2019 ¹¹⁷. *electricity generation and distribution, **including from fisheries and forestry.

Additional, but less commonly considered, sources for ammonia recovery include: tannery ¹¹⁸, whiskey distillery ¹¹⁹, food processing ¹²⁰, textile printing ¹²¹, fellmongery ¹²². More details on these are available in Appendix, Table A-5. Fertiliser manufacture and coke processing effluents were the most represented, with 10 (14%) and 11 (15%) studies, respectively. Both streams were treated with all three considered methods, with precipitation being the most implemented (Figure 2-3). Sorption technologies were applied in the coke-processing streams with the lowest TAN concentrations, ≤ 447 mg N/L ^{123,124}, whereas precipitation was used even in highly concentrated waters ≥ 3500 mg N/L ^{125,126}. Likewise, fertiliser wastewater with TAN ≤ 822 mg/L was treated only with sorption

processes ^{77,127}. Interestingly, only in one study, this industrial water underwent stripping ¹²⁸, and struvite precipitation was largely the preferred option, which could be explained by the co-presence of ammonium and phosphate in many fertiliser factory effluents. Also with other wastewater types, precipitation has been the predominant technique, whereas stripping testing has been limited in comparison. To illustrate, slaughterhouse effluents were treated to recover struvite in two cases ^{129,130}, while only in one recent work ammonia was separated by volatilisation ¹³¹. A similar trend was observed for rare-earth elements processing wastewater, where micro-wave-heating stripping was tested only recently ¹³², compared to struvite ^{133,134}.

Some types of effluents were treated uniquely with one process type (Figure 2-3). Semiconductors processing wastewater underwent struvite precipitation in three studies, with comparable concentrations (169-179 mg TAN/L), with the choice being driven by the high levels of phosphate (83-360 mg P/L). Furthermore, effluents from NH_4NO_3 , NH_4Cl and NH_3 synthesis were all treated with sorption, with $\text{TAN} \geq 800$ mg/L, exploiting the advantage that the media regeneration brine, loaded with NH_4^+ , could be reused directly in the manufacturing steps after sufficient concentration and avoiding costs associated with the brine clean-up ¹³⁵⁻¹³⁷. Finally, in four different studies, aquaculture wastewater was almost always treated with a sorption process, possibly explained by the low influent TAN content (≤ 24 mg/L) less suitable for stripping.

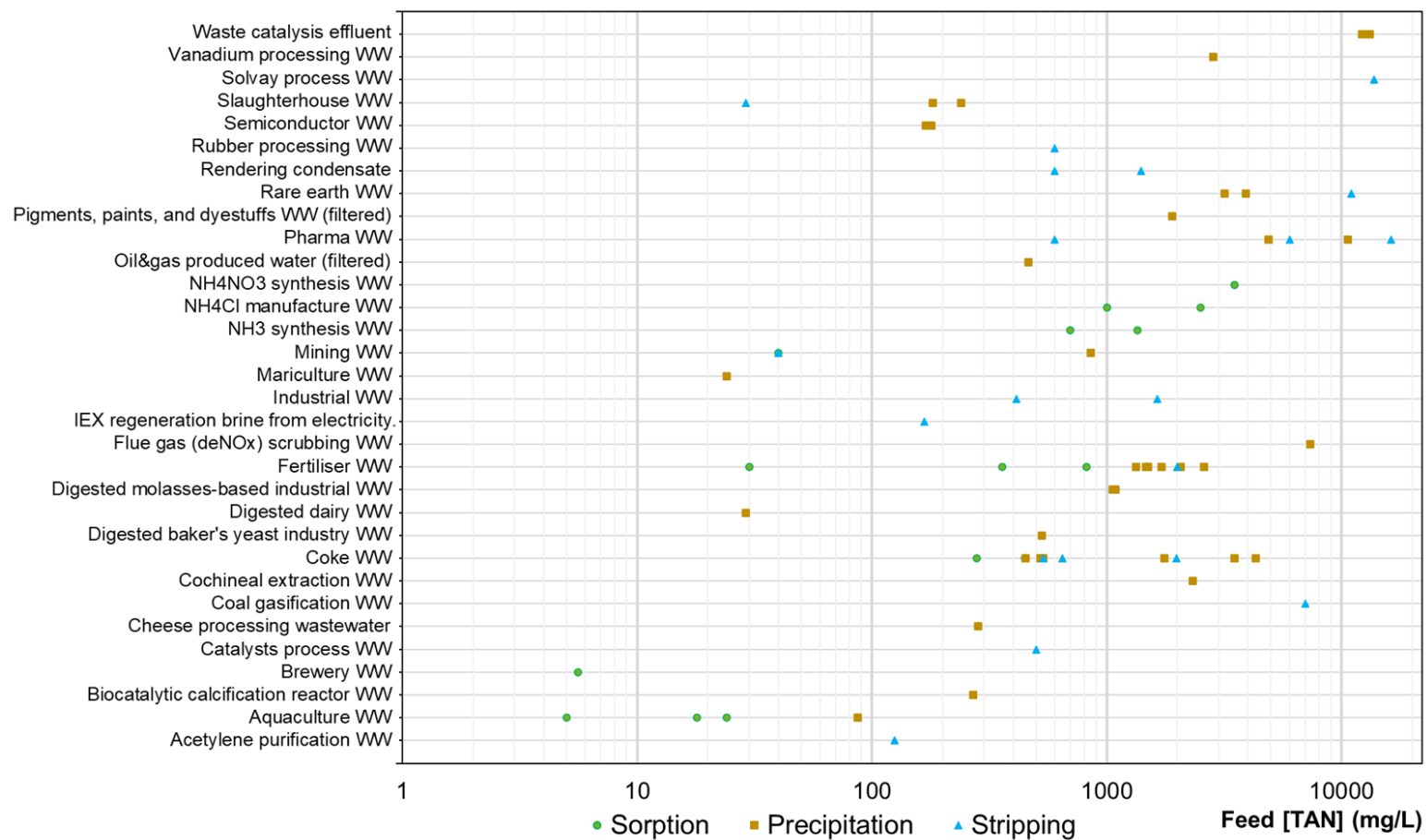


Figure 2-3. TAN content in real industrial effluents reported in the dataset, as function of N recovery technology and wastewater type. When a range of TAN was reported, both extremes were depicted.

The feed concentration of ammonia across the reported studies ranged between 5 and 23941 mg TAN/L (Figure 2-4). IEX/adsorption studies had the concentration smallest ranges, for both synthetic (10-5000 mg N/L) and real wastewaters (5-3500 mg N/L), which was consistent with the general trend of using this technology for lower N loads.

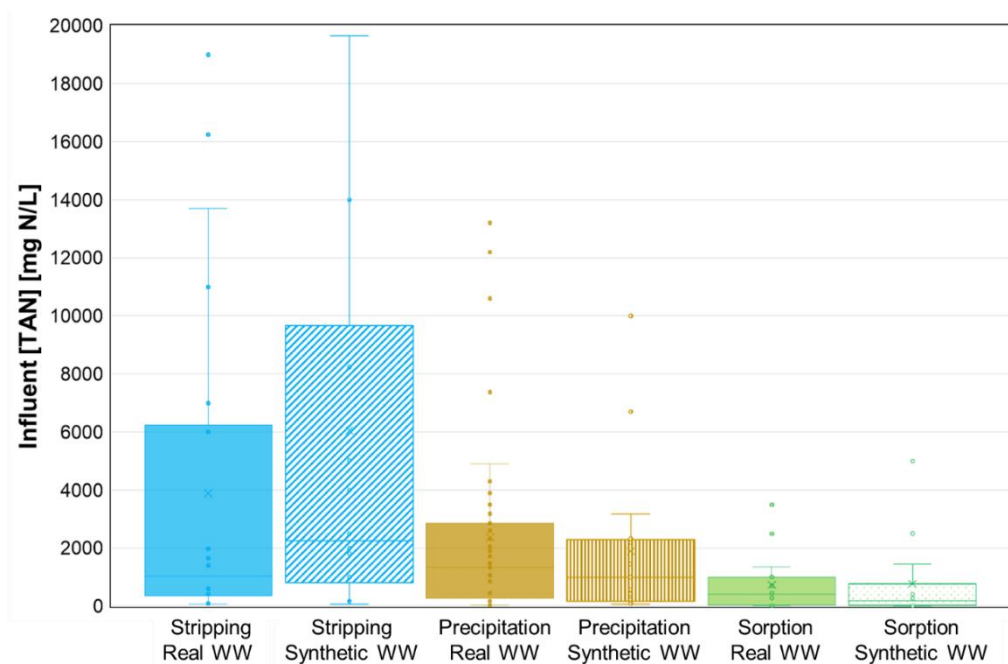


Figure 2-4. Ranges of influent TAN concentration used in the dataset's studies, as function of the adopted technologies and type of feed (synthetic, real). The medians were excluded from the quartiles calculations.

Precipitation and stripping applications on real wastewaters covered comparable ranges (8-13208 mg N/L and 62-19000 mg N/L, respectively) indicating their overlapping capabilities and the flexibility in treating both low and high strength streams. Stripping processes had the largest and highest interquartile ranges (middle 50% of observations), 411-6000 mg N/L for real and 812-9676 mg N/L for synthetic solutions, showing that these technologies have been tested for various conditions, including higher loads. For precipitation, the interquartile TAN ranges of real and synthetic wastewaters were comparable. Overall, stripping and precipitation appeared to have proportionate capacity, both treating even heavily concentrated TAN streams. IEX/adsorption processes positioned as a

complementary technology, applied for lower strength streams (interquartile ranges 29-1000 mg N/L for real effluents and 54-995 mg N/L for synthetic), enabling the application of stripping and precipitation technologies by increasing the feed concentration in more simple matrices. Improving the capacity and selectivity of the media could further expand their potential to deal with more concentrated and complex wastewaters. A few studies advocated for testing sorption processes on this type of streams, such as leachate, digestate, sludge dewatering streams ^{103,112}, and industrial effluents ^{98,138}, reflecting the associated challenges.

In addition to the feed ammonia concentration, the practicality and ease of implementation of some technologies also played a significant role in determining their selection over others. Precipitation, mainly as struvite, was applied in 49% of the studies as a standalone process and in additional 8% in combination with stripping or sorption. The spontaneous precipitation of struvite in wastewater, especially after anaerobic digestion ⁶⁹, provides a compelling driver for this pathway. Moreover, this process is considered to be straightforward and simple to operate, allowing to harvest a product that is directly usable ¹³⁹, besides being a well-established technology ⁶⁶. The second most-reported processes were stripping based, representing 24% of the papers when used alone and further 6% in co-application with sorption and precipitation. Sorption processes were the least represented choice (18% standalone, 4% in combination), likely due to some of the bottlenecks discussed in section 2.3.3. Nonetheless, in the last decades research on these processes has increased, indicating growing interest, with more than half (8) of the sorption studies being published between 2017 and 2024.

2.4.2 TAN separation performance and identified challenges

Most of the considered publications reported significant removal efficiencies, with levels generally above 60%, and with 74% of the studies achieving greater than 85% efficiency (Figure 2-5).

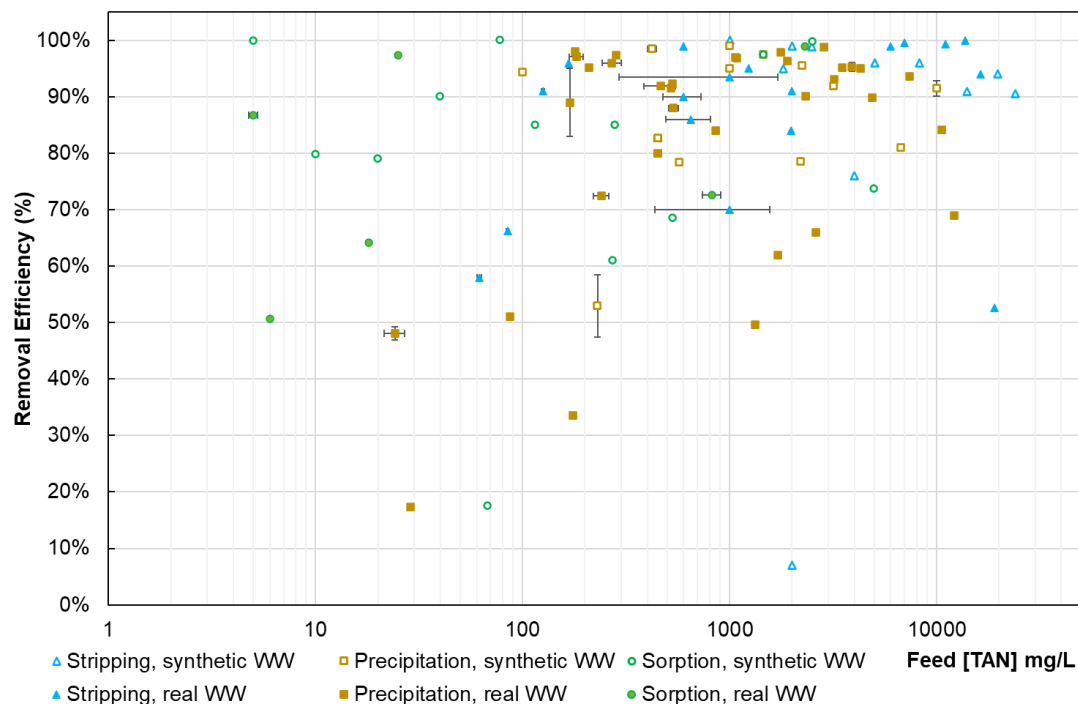


Figure 2-5. Best reported removal efficiencies as function of influent TAN load (log scale), technology type, wastewater type (actual=full, synthetic=void).

No clear impact of the feed TAN content on the removal efficiency could be observed, because the analysed studies operated in different settings and only the performances at optimised conditions were considered. A few of the selected studies assessed the effect of increasing influent [N] on the process performance. In cases of NH_3 volatilisation-based processes (mainly membrane-based), TAN concentration did not have a critical role on the removal in the tested conditions^{140–142}. In contrast, with struvite formation and separation, increasing ammonium concentration, with comparable Mg:N:P, led to higher removal efficiency^{70,78,143}. With sorption processes, the influent TAN load was beneficial for zeolite and palygorskite capacity, but also caused a decrease in removal, at fixed adsorbent content^{124,144} and a fast media saturation⁷⁷.

Several studies reported limitations with real matrices, providing insights on the technology-wastewater compatibility. For instance, the majority of the studies reporting less than 60% removal were associated with precipitation processes (Figure 2-5). In most of these cases, the ambition was to recover both P and N

and thus the operation was not optimised for TAN removal only ^{81,145–147}. McIntosh and colleagues identified several factors causing low TAN removal via precipitation in dairy processing wastewater, including high N:P molar ratio, additional release of NH_4^+ by microbial degradation and competing co-precipitation of hydroxyapatite, with the latter being solvable by optimising the Mg:P ratio ¹⁴⁷. Further challenges reported during struvite precipitation were linked to the impact of other species, particularly competing cations. Excess K^+ promoted the formation of potassium struvite, over ammonium struvite, in cheese processing and fertiliser wastewaters ^{79,148}. Sodium and calcium competed with Mg^{2+} and NH_4^+ for phosphate in yeast factory and oil and gas effluents ^{74,149}, forming sodium struvite and Ca-based precipitates, with the double effect of reducing the fraction of available phosphate and lowering the recovery product's purity. To limit this, Ca removal via CaCO_3 precipitation was proved to be an effective pre-treatment ⁷⁴.

Anions were also reported to limit struvite formation, with sulphate and carbonate competing for Mg^{2+} and NH_4^+ ^{70,150}, similarly to fluoride, F, sequestering magnesium into MgF_2 ^{78,90,148}. The effect of fluoride ions can be mitigated by creating conditions more favourable for struvite formation, e.g. via dosing excess Mg ⁹⁰ and optimising the chemicals mixing intensity ⁷⁸. Furthermore, SiO_2 in wastewater from fertiliser and fluorosilicate acid processing reduced struvite crystals nucleation and growth by binding Mg, with high TAN and Mg concentrations decreasing this hindrance ¹⁵¹. Finally, organic compounds were reported to negatively impact struvite precipitation. To illustrate, phenols and quinoline in synthetic coke wastewater sequestered Mg and reduced TAN removal ¹⁵², whereas Fenton oxidation and removal of organics in dyes effluent improved the purity of the struvite that formed and TAN reduction ¹⁵³.

Low efficiencies in stripping-based processes were few and related to specific cases where ammonia recovery was not optimised, such as membrane distillation of a concentrated $(\text{NH}_4)_2\text{SO}_4$ solution ¹⁵⁴, capillary column stripping of slaughterhouse wastewater ¹³¹, and membrane contactors separation of ammonia from synthetic coke wastewater ¹⁵⁵. Matrix-related hindrances were

mainly reported for membrane-based stripping technologies. To illustrate, organic fouling and mineral scaling were observed in membrane contactors treating natural rubber wastewater and filtered catalyst factory effluent, mitigated by base and acid cleaning, respectively ^{141,156}. Likewise, wetting agents in rendering condensate impacted membrane contactors, but could be controlled with hexane and water cleaning ¹⁵⁷.

In sorption studies the impaired TAN removal was sometimes associated with the media's limited capacity (zeolites, mordenites, metakaolin geopolymers), exacerbated by co-existing cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , competing with NH_4^+ in effluents from mining, aquaculture, cheese production ^{79,158–160}. This confirmed the need for sorption media with greater capacity and selectivity. Ca and Mg were also linked to the formation of struvite and Ca-based precipitates crystals covering the biochar surface and limiting TAN sorption in fertiliser wastewater ⁷⁷. Numviyimana et al. exploited this phenomenon to use zeolite surface not only for TAN adsorption from cheese processing water, but also as platform for struvite crystals growth ⁷⁹, whereas Koe et al. efficiently combined zeolite sorption of NH_4^+ with Mg^{2+} release for precipitation with PO_4^{3-} in aquaculture effluents ¹⁶⁰. Finally, anions were also reported to have impacted the TAN removal efficiency by adsorption on MgO nanoparticles and in-situ precipitation, with chloride, Cl^- , causing the largest drop from 100 to 60% ¹⁶¹.

2.4.3 Recovery products

The type of harvested N products can be another criterion for technology selection. Key reported recovery products included ammonium struvite and ammonium sulphate solution. Struvite recovery is a popular form to precipitate ammonium, given its spontaneous formation and its suitability as a slow-release fertiliser for both N and P ¹⁴⁹. Nonetheless, its commercial value as fertiliser is limited (Table 2-4) and research is looking at increasing its value proposition by using it as a fire-retardant ¹⁶². A few studies reported ammonium precipitation in less common forms such as $\text{Fe}(\text{NH}_4)(\text{OH})_4$, $(\text{NH}_4)\text{Al}(\text{SO}_4)_2$, and NH_4MgCl_3 , with applications as fertiliser and in chemical or food industries ^{161,163,164}.

Ammonium sulphate solution and crystals are often recovered as result of stripping. This product is commonly proposed as a fertiliser, although it can be used also as flame retardant and in the food/chemical industry ¹⁶⁵. In other studies, the stripped ammonia was recovered as ammonium nitrate and diammonium phosphate (DAP) ^{166,167}, both applicable as fertilisers, the former with a high explosive risk. Their use as fertiliser is still relatively limited (< 8%), compared to urea representing 48% of the global N consumption for fertiliser ¹⁶⁸. Some studies reported the recovery of ammonia into a solution by condensation ¹⁶⁹ or absorption in water ^{132,154}. This is the most versatile form of recovered TAN, suitable for a range of uses, including precipitation and formation of salts (e.g. by reacting with an acid), fuel ⁴¹ or substrate for biomass growth ³⁸. Use of ammonia for direct energy generation or as vector of hydrogen has been increasingly explored ²⁰, and, likewise, production of high-value biomass, as single cell protein, from alternative sources of nutrients could become central to the circular economy ¹⁷⁰. Several sorption processes enabled the recovery of TAN as ammonium nitrate and ammonium chloride in regeneration brines, which in some cases could be reused within the industrial sites, as in the case of N-processing facilities ^{127,135,136}. Direct use of adsorbed ammonia has also been reported using N-loaded biochar and zeolites as fertiliser ^{77,144}.

The values of different TAN based products is reflected in their prices (Table 2-4). Struvite, generally, is sold at lower price compared to ammonium sulphate (87 USD/ton and 521 USD/ton, respectively) ¹⁷¹, although the values ranges available in literature are large, especially for struvite. Together with the economic feasibility, local demand and legislation ^{50,172} and the end product's price, its versatility, and thus value, should also be considered when evaluating which technologies to apply.

Table 2-4. Indicative prices of TAN-based recovery products. AS= ammonium sulphate. DAP= diammonium phosphate. MAP= ammonium struvite.

Product	Price (USD/ton)	Reference
Ammonium nitrate	560	173a
Ammonium sulphate	521 - 533	173a, 171
AS solution (21%)	521	174b
N solution (30%)	359	173a
Anhydrous NH ₃	851	173a
DAP	502-611	173a, 171
MAP	87-2579	69,162,171
Microbial protein	2325	175b

^a average US farm prices for 2014. ^b conversion EUR-USD.

Distinct separation pathways allow for the recovery of different, but interconnected products from industrial effluents (Figure 2-6). Stripping processes have greater versatility in terms of end-products, with the possibility to generate ammonium salts solutions, which can be further processed to obtain a solid product via evaporation, and aqueous ammonia solution allowing a wide range of applications. The choice between such applications depends on the solution's purity, which in turn affects the overall product quality, value and marketability. Furthermore, extraction of NH₃ solution from ammonium salt solution is also a possible option, e.g. via basification and membrane distillation¹⁵⁴.

With sorption processes, some N-loaded materials can be directly reused as fertiliser/soil amendment¹⁴⁴, but their cost-effectiveness and market demand should be assessed (Figure 2-6). Likewise, regeneration brine can be reused in-situ¹³⁶ or by other stakeholders. Brine clean-up via stripping or precipitation processes would in fact raise the costs to a level whereby mainly the purity of the end-product can be a significant driver for selecting this strategy. The advantage

of N-rich brines is a lower matrix complexity and a higher N concentration, compared to the original feed, making it an interesting candidate for recovery of a purer ammonia product via stripping/precipitation, while achieving brine restoration. Precipitates of struvite or ammonium minerals and salts can be directly used and increasing their purity could improve their competitiveness in the market, e.g. by minimising Ca/Mg deposits, organics contamination, and metal content ^{176,177}. Alternatively, struvite can be thermally, chemically or microwave- decomposed to recycle Mg, releasing NH_3 ^{178,179}, which can be recovered in another form e.g. ammonium salt solution ¹⁵².

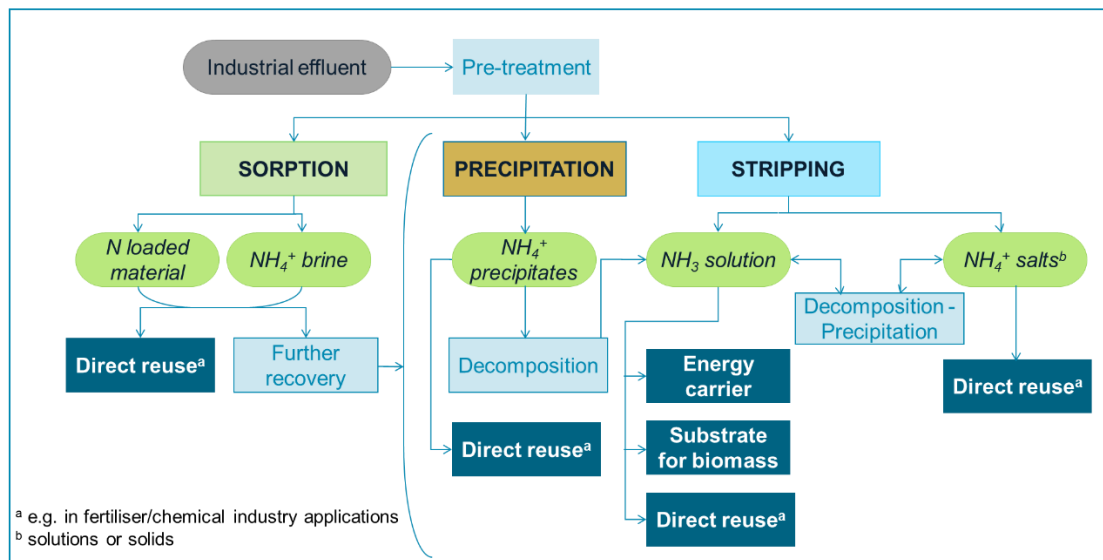


Figure 2-6. Potential TAN separation routes and end-products with reviewed technologies.

2.5 Guidelines for TAN recovery technologies selection and operation

Based on the reviewed literature (Table 2-1, Table 2-2, Table 2-3), a guideline for selecting and operating technologies to recover TAN from industrial effluents is presented. For this purpose, it is essential to consider not only the wastewater characteristics, but also the specific goals of the application. In this study, two main criteria were selected: maximising N removal and optimising product purity and quality (Figure 2-7). The key decision gates are based on: 1) critical factors

for selection, directly impacting process feasibility, 2) factors interfering with the operation, but potentially mitigated 3) convenience factors, favouring a particular process over another (Table 2-5, reporting available numerical thresholds, and with further details and references in Appendix Table A-1, Table A-2, Table A-4).

A central criterion in the technology selection is the value of the recovered product. Stripping and sorption can yield concentrated solutions of ammonia/um, which can be further processed for various applications. In contrast, precipitated struvite, while being a directly reusable fertilizer product, has limited market applications, influenced by competition from commercial products and local demand. The feed ammonia concentration is also a decisive element, determining whether stripping ($\geq 0.5\text{-}1\text{ g N/L}$) or sorption processes ($< 0.5\text{-}1\text{ g N/L}$) are best suited, in terms of economic viability. Struvite is applicable at any concentration, provided that dosing of chemicals to optimise components ratios and manage competing species is economically viable. Indeed, struvite precipitation is recommended mainly in cases where it would spontaneously form ($\text{SSR} > 1$) and where its recovery can prevent clogging issues downstream. Finally, the levels of competing cations (X) are a key factor hampering both struvite precipitation and ammonium sorption, whereas stripping is generally more robust towards these conditions. This can be addressed with the use of sorption media with high capacity and selectivity and the optimisation of Mg:N:P molar ratios for struvite. This is particularly relevant for industrial effluents, which can contain significant concentrations of cations, including heavy metals, but also anions, organic compounds, suspended solids ¹⁷. Most of these contaminants can interfere with the processes and thus warrant dedicated management (Table 2-5). Suspended solids affect all three processes, for instance causing clogging in sorption media beds and packed towers. Their effect on struvite formation and purity is negative at high content (e.g. above 1 g TSS/L), whereas a moderate amount can serve as a source of crystals seeds. Anions, especially those sequestering struvite-forming cations, can hamper precipitation but, reportedly, also reduce ammonium sorption efficiency. Organic compounds can inhibit struvite formation and contaminate the precipitates. With sorption and stripping,

the impact of acidic organic compounds on NH_4^+ is still unclear and requires additional investigation. Heavy metals, including transition ones, are detrimental for both precipitation and sorption, as responsible for cation competition and reducing the purity of struvite or media regeneration brine. Transition metals, moreover, can sequester ammonia, thus their impact on the recovery processes should be evaluated. Although stripping processes are more robust in handling high concentrations of cations and anions, the potential for interference by metals and acidic organic compounds must be investigated. In particular, these factors could reduce the ammonia removal, without critically compromising the end-product purity, and could be addressed during the design phase. All the mentioned species should be removed until below critical levels, if technically and economically possible, to enhance the overall performance.

Finally, other site-specific conditions can influence the convenience of a technology, such as the availability of waste heat/hot feed, favouring stripping, and the start feed pH, determining the $\text{NH}_3/\text{NH}_4^+$ form. Likewise, the presence of carbonate alkalinity can be leveraged to strip CO_2 , raising the pH as needed ¹⁸⁰. Moreover, although a pH increase can favour the precipitation of minerals such as calcium carbonate, CO_2 stripping directly impacts the carbonates system, reducing the overall amount of bicarbonates and carbonates that can form precipitates contributing to scaling ^{45,63}.

Table 2-5. Factors to consider for ammonia partitioning technologies selection and operation with industrial effluents.

1) Critical factors for selection	
Product value	Ammonia/um solution, obtained via stripping or sorption, can have more applications than precipitated struvite.
TAN content	→ High [TAN] (≥ 0.5 -1 g N/L) favours stripping viability → Low [TAN] (< 0.8 -1 g N/L) is preferable for sorption processes → Any [TAN] is suitable for struvite precipitation, if other ions-competition and co-precipitation are limited, and molar ratios are suitable
Content of competing cations N:Na/K/Ca/Mg (X) Struvite SSR	→ Stripping can handle feeds with low N:X → IEX sorption is inhibited by low N:X and the product quality is reduced. Alternative: media with high selectivity and capacity → Struvite precipitation is inhibited by low N:X, specifically with high levels of Na, K, Ca (Ca:Mg and Ca:P should be $< 1:1$) → If > 1 , struvite can precipitate → Between 1 and 3-6 favours struvite pellets growth
2) Interfering factors impacting operation	
TSS content	→ > 0.6 g/L and 1.5 g/L are detrimental for stripping and sorption processes, respectively → < 1 g/L is recommended for struvite precipitation
Anions content	→ Anions can affect surface tension and reduce sorption performance → SO_4 , F, CO_3 can sequester struvite-forming ions and co-precipitate (critical threshold $\text{N}:\text{SO}_4/\text{F} \leq 0.2:1$). Mitigation includes optimising Mg:N:P dosing, CO_2 stripping
Heavy metals	→ Transition metals potentially affecting stripping processes, by complexing NH_3 → Metals can compete with NH_4^+ or can sequester NH_3 → Can impair struvite precipitation and contaminate product, but can be mitigated by Mg:N:P optimisation
Organic compounds	→ Potentially affecting stripping processes, by binding TAN → Specific effect of acidic organic compounds on sorption media to be assessed (conflicting results in literature) → Some organic compounds can impair struvite precipitation and contaminate product
3) Conveniency factors	
Heat	→ High feed temperature and/or available waste heat favours stripping viability ($T \geq 50^\circ\text{C}$)
pH	Critical in determining TAN form, should be optimised for each process. Yet, high initial pH can be exploited for stripping (≥ 9.5 -10) / struvite (8.5-9.5)
Alkalinity level	If $\text{NH}_4:\text{HCO}_3 \leq 1$, carbonates can be stripped to increase the pH

With stripping, suspended solids content should be reduced to below 0.06%, where possible (Figure 2-7). Likewise, high concentrations of organic compounds could impact ammonia volatilisation, reducing the removal performance. Potential mitigation measures, if viable, could include hydrothermal oxidation, effective in organics removal to some extent, but less effective for ammonia oxidation in mild conditions ¹⁸¹. To increase the product purity from stripping processes, precise control of pH, temperature, and airflow/vacuum is recommended to promote ammonia transfer and limit water carryover. Furthermore, volatile organic compound (VOC) transfer should be mitigated. For acidic compounds, this could be achieved with an alkaline trap ⁶¹, whereas for neutral compounds separation via activated carbon sorption or selective membranes could be helpful ¹⁸².

To enhance the quality of struvite precipitates (Figure 2-7), it is advised to reduce calcium, metals, and organic compounds to levels enabling precipitation. Calcium interference can be mitigated by various strategies, such as dosing excess magnesium and phosphate, prior controlled brushite precipitation ⁷¹, EDTA chelation and CaCO_3 precipitation ^{67,68}. Ideal struvite supersaturation ratios (SSR) for removal and pellets growth, typically between 1 and 3–6, can be achieved by controlling pH, temperature, and dilution. Struvite precipitation can also serve as a pre-treatment, followed by stripping or sorption to maximize recovery and meet discharge limits. For lower-strength wastewaters (< 0.5–1 g N/L), struvite should be applied if the SSR is above 1 and particularly in wastewaters containing high levels of competing cations (X), if selective, high-capacity sorption media is unavailable. In such cases, dosing magnesium and phosphate to compensate for competing cations and achieve a molar ratio of Mg:P of 1.2–1.5:1 will not significantly increase operational costs, as the additional reagents are proportional to the low nitrogen content in the feed.

If a sorption process is selected (Figure 2-7), it is recommended to reduce suspended solids to below 1.5 g TSS/L. The critical levels of heavy metals will depend on the selectivity series of the media used, which may warrant their

removal or the use of NH_3 selective and high capacity media. Moreover, pH and temperature should be optimized to favourable conditions, e.g. within the range of pH 5-7 and temperatures of 25-30°C for NH_4^+ sorption. The recovered N-rich brine can be reused on-site or further processed for clean-up via stripping once concentrations exceed 0.5-1 g N/L.

To illustrate the application of these processes, the case of distillery wastewater can be considered. This wastewater typically undergoes anaerobic digestion, resulting in a heated stream ($\approx 37^\circ\text{C}$) with high levels of ammoniacal nitrogen (e.g. 1260 mg TAN/L) and phosphate (e.g. 400 mg P/L), but relatively low magnesium levels (e.g. 36 mg Mg/L) ¹¹⁹. The solids content in the anaerobic bioreactor can be effectively reduced through membrane ultrafiltration ¹⁹. Due to the tendency for struvite to spontaneously precipitate in such effluents, a combined approach is recommended, integrating two of the reviewed key processes, aiming to achieve high combined removal and recovery. Thus, a struvite precipitation unit is advised as first step. Following, the P-depleted stream still contains a significant ammonia load (exceeding 0.5-1 g N/L), which can be efficiently extracted through stripping and recovered via acid absorption, yielding a concentrated nitrogen solution. If the stripping unit effluent does not meet the discharge requirements, it can undergo further treatment via sorption processes. In this flowsheet, according to the provided recommendations and known characteristics of the distillery wastewater, it is recommended to assess the impacts of competing cations (such as sodium, potassium, calcium), recalcitrant acidic organic compounds, and copper, all contained in distillery effluent ¹⁸³, on both processes' performance and product quality. For reference, a diagram of the flowsheet presented here is available in Chapter 3, Figure 3-1.

2.6 Concluding remarks

The results from the systematic literature review showed that ammonia recovery has gained interest transversally to substantially different industrial sectors, particularly in fertilizer manufacturing and coke processing, the most frequently targeted streams. Struvite precipitation emerged as the most implemented technique to recover ammonium from industrial effluents. However, from a

product value perspective, alternative options such as recovering ammonia solutions from stripping or regeneration brines from sorption are encouraged. The second most implemented option involved processes exploiting ammonia volatilisation. Both partitioning methods were applied to wide ranges of feed N concentrations. In contrast, sorption processes were underrepresented in the dataset and were typically applied at lower ammonium concentrations, likely due to the uncertain compatibility with complex matrices containing competing ions and high N loads. Currently, sorption processes are positioned as a complementary technology to stripping and precipitation, suitable for concentrating ammonium from diluted waters into a purer brine and polishing pre-treated effluents. Future research improving media's sorption capacity and selectivity and demonstrating their viability with high strength wastewaters could broaden the range of applications for sorption technologies. Based on the reviewed literature, a set of guidelines has been developed for the selection and operation of N recovery processes for industrial effluents, considering the wastewater characteristics and their effect on the overall technology performance. Further investigation on the impact of organic compounds, heavy metals (especially transition), and foreign ions on the reviewed processes is recommended. Indeed, these species can be found in some industrial effluents at high loads, and while there has been some evidence of their effects on these technologies, a clear understanding of key levels enabling a positive performance remains lacking.

Appendix A

Search string used in Scopus: *TITLE-ABS-KEY ((("recover*" OR "recycl*") W/3 ("N" OR "NH*" OR "ammoni*" OR "nitrogen" OR "struvite")) AND (("*industr*" OR "*chemical*" OR "tanner*" OR "leather*" OR "min*" OR "quarr*" OR "oil*" OR "fuel*" OR "petro*" OR "paper*" OR "*pulp*" OR "solvent*" OR "textile*" OR "*food" OR "beverage*" OR "brewer*" OR "distiller*" OR "steel*" OR "iron" OR "cok*" OR "meat" OR "fish*" OR "slaughter*" OR "dair*" OR "dye*" OR "paint*" OR "manufactur*" OR "fertili*" OR "process*" OR "semiconductor*" OR "produced water" OR "rare-earth" OR "rare earth") W/5 ("wastewater*" OR "water*" OR "stream*" OR "effluent*" OR "residual*")) AND ("IEX" OR "ion exchange" OR "ion-exchange" OR "adsorption" OR "stripping" OR "distillation" OR "contactor*" OR "HFMC*" OR "GPHM*" OR "ammonium sul*" OR "ammonium carbonate" OR "ammonium nitrate" OR "struvite" OR "precipitation" OR "crystalli*" OR "magnesium ammonium phosphate" OR "MAP")) AND (LIMIT-TO (DOCTYPE , "ar") OR LIMIT-TO (DOCTYPE , "re")) AND (LIMIT-TO (LANGUAGE , "English"))).*

Only articles and reviews in English were screened, conference papers were excluded. The screening was performed by reading the abstracts and the papers and selecting with the following criteria. Eligible populations: real wastewater from a range of industrial activities, or synthetic solutions simulating industrial effluents, or synthetic solutions used in tests delivering findings applicable to real industrial wastewaters. Geographic boundary: the whole Planet. Eligible interventions: ammonia stripping and distillation processes (including transmembrane chemisorption), ammonium salts precipitation (e.g. struvite), ion exchange/adsorption processes carried out to recover N. Only scientific papers treating ammonia recovery by means of at least one selected technology, falling in the three processes categories, were retained. Eligible language: English.

Table A-1. Selected factors impacting ammonia stripping (mainly air/vacuum stripping processes) and related threshold values. ^a
Refers to ammonium sulphate (AS) recovery product. η indicates the removal efficiency, tbd indicates no certain value has been determined. ^a if AS is the desired recovery product.

Parameter	Impact / threshold values	Reference
pH		
To $\uparrow \eta \rightarrow \geq 10$ ~ temperature	pH is the main affecting parameter and using highly alkaline feeds (10.5 – 11) would consume less energy than heating and applying higher air flow rates (packed tower). Yet, > pH 10 the improvement in removal is less significant.	58
To $\downarrow$ costs $\rightarrow \approx 9.5-10.5$	pH > 10.5 increases operation expenses, but does not significantly improve removal	184
	pH = 12-12.5 enables “cold stripping”, at room temperature	185
pH adjustment		
To $\downarrow$ costs $\rightarrow$ CO ₂ stripping if NH ₄ :HCO ₃ ≤ 1	High carbonates alkalinity can buffer pH changes and increase the base demand to raise the pH, thus it should be exploited to increase the pH via stripping	44,180
	Molar ratios NH ₄ :HCO ₃ ≤ 1 are suitable for CO ₂ stripping, to increase the pH and buffer stripping-induced acidification	59,186
	4-6 g CaCO ₃ /L in anaerobic digestate suffice for chemical-free pH increase	16
Temperature (T)		
To $\uparrow \eta \rightarrow \geq 50^{\circ}\text{C} - 70^{\circ}\text{C}$	Operating at 60-70°C allows to lower pH increase requirement (8.3)	59
	Operating at 80°C allows to lower pH increase requirement (9.5)	36
	From 20/35°C to 50/55°C: high increase of removal efficiency/K _{La} transfer coefficient	44,45
	From 20/35°C to 50/55°C: limited increase of removal efficiency	58
$\downarrow$ costs	Cheap heat availability should be exploited for thermally induced stripping	23,44,63,187
	Operating at 80°C (favoured with cheap heat availability) allows to utilise smaller unit size, compared to lower temperature (e.g. 40°C)	63
Pressure (P)		
	A trade-off between T and P (vacuum) should be used to maximise removal and control the transfer of water and VOCs, affecting the product purity	29,60
TSS (in packed tower)		
$\rightarrow$ [TSS] < 0.06%	[TSS] should be removed to be prior operation to limit future maintenance needs, at least below 1%	42,44

Parameter	Impact / threshold values	Reference
	[TSS] $\leq$ 0.06% for packed towers	43
	[TSS] $\leq$ 0.05% in thermal stripping	188
Organic compounds		
	Some organic compounds could impact N removal, binding NH_4^+ ; thus, above threshold (tbd), their removal is recommended	61
	Volatile organic compounds can be stripped and recovered with ammonia, lowering the product quality, but can be mitigated by using alkaline traps or activated carbon	29,36,41,61,182,189
[Heavy metals]		
	Transition metals can complex with NH_3 and affect TAN stripping time. Moreover trace metals contamination in ammonia condensate was reported. If > certain level (tbd), they should be removed, if possible	38,55,191
[Scaling agents]		
	Scaling agents can precipitate on the surface of the packed towers and/or membranes, creating clogging issues and higher pressure drops, such as struvite, ferrous oxide, magnesium oxide, carbonates minerals.	34,45,52
[TAN]		
Impact on η	Stripping efficiency (and k_{ov}) is nearly independent from the feed [TAN], when it is controlled by gas film diffusion, whereas higher NH_3 load increases the driving force and the stripping rate.	45,46
Economic feasibility → $\geq 0.5\text{-}1$ g N/L	[TAN] should be > 5 g N/L	4
	[TAN] should be > 2 g N/L	23,180
	[TAN] should be > 1-1.5 g N/L	187
	[TAN] should be > 400-500 mg/L	16
	[TAN] 20-70 mg/L would not have economic viability (e.g. municipal WW)	24
Recovery		
To $\uparrow \eta$	Scrubbing liquor pH ^a should be kept < 4 to maintain the driving force	64
To $\downarrow$ costs and $\uparrow$ product purity	The concentration of [AS] ^a should be approx. 40% (w/w), minimising the risk of crystallisation and the water to be removed downstream	63
	Water and heat transport to the scrubber liquor should be avoided, to lower the solubility of AS and using less resources to harvest AS crystals. Demisters and condensation traps can be used.	29,61

Table A-2. Selected factors impacting ammonium struvite precipitation and recovery. η indicates the removal efficiency, tbd indicates no certain value has been determined.

Parameter	Impact / threshold values	Reference
pH		
Optimum for η → pH = 8.5-9.5	8.5-9.5	65
	7-9	15
	8.7	87
	8.5-9.5, to promote fast reaction time	192
To ↑ product purity	8-10.5, to limit the precipitation of other compounds	71
	7.5-9.5 to limit precipitation of other compounds	65,67,87,192
Temperature (T)		
To ↑ η and purity → T ≤ 30-35°C	Between 14.5 - 35°C, no critical effect	193
	< 25°C would be beneficial	66
	Increasing from 20°C to 30°C increases yield by small extent	84
	Should be < 35°C, to lower the solubility	83
	Increasing from 25 to 37°C alters crystalline structure and promotes conversion to newberyte	65
N:P molar ratio		
To ↑ P recovery and product purity → N:P = 4-6:1	4:1	84
	6:1 to improve product purity	16
To ↑ η → N:P = 1:1.1-1.5	1:1.3; 1:1.1 (yet, it should be a case by case determination)	66
	1:1.5	55
N:Mg molar ratio		
To ↑ N η → N:Mg=P = 1:1.2	From 1:1.1 up to 1:2 (yet, it should be a case by case determination)	66
	1:1.2	55
Mg:P molar ratio → 1.5-1.7:1		
	1.5:1 to promote the reaction yield	84
	1.7:1 to favour P removal and maintain struvite quality	192
	≤ 4:1 to maintain struvite precipitates' purity	66
Supersaturation ratio 1 < SSR < 3-6		
	SSR > 1 to enable precipitation	65,69,85

Parameter	Impact / threshold values	Reference
	Should be kept low to decrease struvite particle size	84,192
	Low SSR induce growth and aggregation of polyhedral crystal growth, whereas above 3.4 crystals become small, needle- and dendritic-like	192
	$1 \leq \text{SSR} \leq 2.5$ promotes particles size ≥ 3.5 mm	85
	$2 \leq \text{SSR} \leq 6$ promotes crystals agglomeration	194
[TSS]		
To $\uparrow$ η and purity $\rightarrow <1$ g/L	≤ 1 g/L to promote MAP formation and purity	16,82,195
	Particulate matter can slow down the precipitation rate, but also act as nuclei for crystal growth	75
	In the range 1-3 g/L, no significant negative impact reported for removal, but purity of precipitates was reduced	196
Crystals seeding		
	Seeding can promote crystals growth and limit scaling	197
	Seeding can limit scaling, even with high SSR	72
Ionic strength (IS)		
	High ionic strength can reduce ions availability for MAP	65
	IS > 0.145 M impacted the purity of precipitates	68
Heavy metals		
N:M (tbd)	Transition metals can complex with TAN, slow down crystal growth and precipitation rate, and contaminate precipitates	55,86,198
	Mg=P:N should be 1.2-1.5:1 to favour NH_4^+ sequestration in struvite, rather than metal complexes (pH 9), but Cu still co-precipitates ($\text{N/Cu} \geq 3\text{-}6\text{:}1$)	55,86
	High N:P (e.g. 11:1) favours PO_4 reaction with TAN, rather than metals (Cu, Zn, Cr)	199
	Al and Fe sequester PO_4 and should be removed when possible	16
Calcium		
To enable MAP precipitation and $\uparrow$ product purity $\rightarrow \text{Ca:Mg, Ca:P} < 1\text{:}1$	Ca:Mg < 1:1	68,87,200,201
	Ca:Mg < 0.2-0.5:1	67,202
	Ca:Mg < 1.67:1	88
	Ca:P < 0.5:1	87
	Ca:P < 1:1	203
Potassium		

Parameter	Impact / threshold values	Reference
N:K (tbd)	Low N:K and high MKP saturation degree can cause competition with NH_4 . N:K 3-5:1 did not critically hamper removal	88,204
Sodium		
N:Na (tbd)	At 0.6:1, Na-based impurities co-precipitated with struvite	89
	At 0.05–0.02:1 delayed induction time	91,205
Sulphate, fluoride, carbonates		
N:SO ₄ /F ≤ 0.2:1	N:SO ₄ 0.2-0.06:1 delayed induction time	91,205
N:CO ₃ and Mg:F (tbd)	F can sequester cations, such as Mg. Mg:P =1.8:1 allows to mitigate this (pH 9.5)	206
	N:F ≤ 0.2-0.3:1 inhibited struvite formation (N:Mg 1:1)	90
	N:F did not hamper struvite formation, when sufficient mixing was provided	78
	HCO ₃ , CO ₃ can generate impurities by co-precipitation and slow down struvite formation	65,67
	CO ₃ co-precipitation was not favoured due to slower kinetics	207
Organic compounds		
N:OC (tbd)	Organic compounds (e.g. acetate, citric acid, humic substances, EDTA, succinic acid) can inhibit/delay struvite precipitation or alter its morphology and should be controlled below tolerated concentration (tbd)	71,75
	N:OC 3.0-1.5:1 molar ratio decreased struvite removal (citric/succinic acid). N:OC 1.5:1 did not hamper struvite removal (acetic acid)	92
	To minimise impact of dissolved organic matter (e.g. humic substances/organic acids), pH= 9.5 – 10.5	75,92
	Phenols and melanoidins lower removal efficiency and struvite purity	208,209
	Citric, succinic and acetic acids can inhibit struvite removal	92,199,207
	N:acetate 0.5:1 molar ratio had no impact on struvite induction time	91

Table A-3. Wastewater type and influent N concentration ([N]_i, mg/L), treated with ion exchange and adsorption processes. AD= anaerobic digestion. RO= reverse osmosis filtration.

Effluent	[N]_i	Source	Effluent	[N]_i	Source
AD treated municipal WW	27	⁹⁷	Sludge liquor	1060	¹⁰³
AnMBR-RO permeate	467	²¹⁰	Swine manure	1300	²¹¹
Manure AnMBR-RO permeate	270	²¹²	WW dewatering centrate	500-1500	¹⁰⁶
Effluent of AD and oxygen stabilisation	800	²¹³	Diluted leachate	200-3750	²¹⁴

Table A-4. Selected factors impacting TAN partitioning via NH_4^+ sorption. η indicates the removal efficiency, tbd indicates no certain value has been determined.

Parameter	Impact / threshold values	Reference
pH		
To $\uparrow \eta$	6-7 for NH_4^+ sorption	215,216
→ pH =5-7	5-7 for NH_4^+ sorption	111
	4-6 for NH_4^+ sorption	104
	6-8, to limit proton competition and NH_3 loss	97,138,212
Temperature		
To $\uparrow \eta$ → 25-30°C	IEX processes are tolerant to wide temperature ranges	217
	Thermal desorption can be used for media regeneration	101
	Better efficiency at 25°C rather than 45°C (zeolite)	113
	Better capacity at 25°C rather than 55°C (zeolite)	218
	Best removal efficiency at ~30°C, in range ~5-60°C (zeolite)	219
TSS		
To $\downarrow$ impact on capacity and maintenance needs → < 1.5 g/L	To minimise hindrance, should be < 0.4% DM	211
	< 2 g/L	14
	< 1.5 g/L to avoid backpressure	106
	TSS of 5.9-4.7 g/L can clog a part of the sorption media column, affecting the removal	220
Foreign ions		
Commonly found cations (X). → N:X (tbd)	Some media preferentially bind Ca and Mg over NH_4	107,221
	Some media preferentially bind Na and K over NH_4	113,214,221
	Exchange materials have different selectivity series, thus are differently influenced by the cations present in wastewater	98
Heavy metals → N:M (tbd)	Heavy metals (e.g. Fe) compete with NH_4	99,222
Anions (A) → N:A (tbd)	Cl, PO_4 , SO_4 , CO_3 reduced NH_4 exchange capacity (zeolite), by affecting surface tension in solution and reducing access of NH_4 to the media's pores (N:A = 0.8-2.1:1)	113,114
	The extent of the zeolite's capacity reduction by NO_2 , NO_3 , SO_4 , $\text{HPO}_4/\text{H}_2\text{PO}_4$ was non-significant (N:A = 0.2:1)	223

Parameter	Impact / threshold values	Reference
Organic compounds		
N:OC (tbd)	Citric acid releases protons competing with NH ₄ (zeolite)	110
	Humic acid reduced ammonium exchange capacity (N:HA 1:2.5 mass based, with palygorskite)	224
	Humic acid caused limited reduction in TAN removal (N:HA 1:1 mass based, with IEX resin)	111
	Oxalic, malic and citric acids improved ammonium capacity, reducing surface tension (zeolite)	113
TAN		
Suitable range → < 0.8-1 g/L	≤ 2 g/L	14
	≥ 5 g/L can be suitable for selective ion exchange	15
	Often applied with diluted WW (e.g. 0.5-50 mg/L)	15,23,104,225
	IEX applied with relatively concentrated WWs (0.8-1 g N/L)	115
	Increasing [TAN] improves the driving force, media's uptake rate and capacity, but decreases the η if the media:TAN load ratio is not optimised	103,215
Regeneration brine		
To ↓ costs	Alkaline regenerant (pH 9-12) can be used to lower brine salt concentration (with zeolite)	102,107,226
	The same brine can be reused multiple times, before clean-up	225
	Spent brine should be cleaned up, for reuse	104,227
To ↑ η	Simultaneous regeneration and brine clean up via stripping can maintain high driving force	103,116,228
To ↑ product quality	A trade-off between regeneration efficiency and product dilution should be met	210,229

Table A-5. Industrial effluents and relative ammonia feed concentrations ([TAN]) treated for ammonia removal, not included in the dataset. Concentrations reported as NH_4^+ or NH_3 were converted to TAN.

	[TAN] g/L	Source
Struvite precipitation		
7-Aminocephalosporanic acid WW	1.13	230
Digested Nylon-66 salt WW	0.55	231
Leather tanning industry WW	0.2 - 0.6	118
Digested whiskey pot ale	1.26	119
Simulated digested distillery WW	0.8	209
Textile printing WW	0.02 - 0.59	121
Stripping processes		
Textile printing WW	0.02 - 0.59	121
Coke WW	2.5	232
Digested blue crab processing WW	2.3	120
Adsorption processes		
Fellmongery WW	0.56 – 0.94	122

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Chapter 3

3 Nutrients recovery from AnMBR treated distillery wastewater: a demonstration scale trial

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Abstract

Distillery effluents contain high loads of nitrogen (N) and phosphorus (P), whose accessibility for recovery is further unlocked by anaerobic digestion pre-treatment, releasing them in ammonia and phosphate forms. For distilleries, particularly in Scotland, the necessity to manage their nutrients load in environmentally sensitive areas can provide an opportunity to expand their contribution and revenue in circular collaborations. Nonetheless, nutrients recovery from distillery wastewater has often been overlooked or addressed either via direct wastewater application to arable land or by using such effluents as feed in biotechnological applications to produce specific molecules e.g. lipids, proteins. In the literature on distillery wastewater, reports of ammonia or phosphate harvesting into pure, simple and versatile forms, such as ammonium sulphate solution and struvite, are sparse or limited to small scale tests. Ammonium salts solutions and phosphate minerals can be reused for different applications, depending on their quality, with fertilising being the most recognised so far. While anaerobic digestion of distillery effluents has gained popularity, its operation in membrane bioreactors (AnMBR) is promising, but not fully established yet. Currently, there is a gap in understanding the viability and performance of established nutrients recovery processes, such as ammonia stripping with scrubbing and struvite crystallisation, in real distillery wastewater,

at demonstration scale. This research aimed to assess these and to understand the potential impact of distillery wastewater's background inorganic and organic components that could inhibit the processes.

This study assessed the feasibility of the proposed treatment train at demonstration scale (12 m³/d) comprised of a fluidised bed reactor generating struvite pellets of up to 5 mm, a stripping packed tower and an ammonium sulphate solution. The integrated system achieved high removal (>70%) of ammonia-N (76%) and phosphate-P (80%), by controlling pH, magnesium dosing and temperature, critical factors enabling/limiting the processes. pH impacted the removal performance for both nutrients, the size of the struvite pellets and the concentration of the ammonium sulphate solution. It was determined that the location of the pH adjustment was critical to enable an effective use of the combined systems and avoid precipitation in unwanted locations. This study demonstrated the feasibility of recovering nutrients in high quality products from digested, filtered distillery wastewater, providing a proof of concept and operational insights for replication at larger scale and further performance improvement.

Keywords: *ammonia recovery; distillery wastewater; industrial wastewater; stripping; struvite precipitation; circular economy.*

3.1 Introduction

Recovering resources, such as nutrients, from wastewater is set to become an essential element of the circular economy associated to wastewater ¹. Industrial effluents are increasingly treated as sources of harvestable nutrients, due to their typically high loads ². Among these, distillery process water is an interesting candidate for recovery of resources, as it contains large amounts of nitrogen (N) (5-7 g/L), phosphorus (P) (0.8 g/L) and organic carbon (C) (110-190 g COD/L, 50-60 g BOD₅/L), locked in a complex matrix which requires treatment ^{3,4}. Furthermore, the alcohol fermentation sector has increased over the last decades ⁵, and is responsible for a large production of wastewater, with 8-13 L of effluent generated per L of ethanol ³. Despite containing heavy metals (e.g. Cu, Zn, Pb, Fe, Cr), phenols, complex organic molecules such as melanoidins ^{3,4}, yet this water has been used also for fertigation ⁴. The high organics levels are generally reduced via anaerobic processes ³, enabling biogas recovery and unlocking N and P content into the accessible forms of ammonia/um and phosphate, respectively ⁶. The partially treated wastewater can be discharged in the environment e.g. estuaries, upon granted permits, or further processed with both biological and physicochemical methods to reduce the loads of organics and nutrients to meet the legislative requirements ^{7,8} which become ever-stringent. The valorisation of such nutrients has been investigated at lab/small pilot scale for different applications, such as soil amendment, fertiliser, substrate for biomass often processed to harvest specific compounds such as microbial lipids, fatty acids, chlorophyll and carotenoids for biofuel, feed, food applications (examples available in Appendix Table B-1). There have been only few cases of nutrients extraction in simple, versatile and purer forms from distillery effluents, although this strategy would allow more options for their use. This can be achieved by a range of technologies, whose selection depends on different criteria, such as the effluent composition and the treatment target (removal, product quality) (Chapter 2). The most commonly implemented technologies for direct recovery of ammonia from wastewater are precipitation of struvite (magnesium ammonium phosphate, MAP), stripping and scrubbing, and sorption processes, relying on physico-chemical pathways ^{9,10}.

This work targeted distillery effluents and specifically used the case study of a whisky distillery located on the eastern coast of Scotland. At this site, distillery wastewater is treated in an anaerobic membrane bioreactor (AnMBR), a promising technology not extensively established yet. The AnMBR effluent is currently discharged into the sea, with a permission from the local Environmental Agency, similarly to other distilleries located on the coast. Factories located inland face stricter regulations, being surrounded by sensitive ecosystems, and often incur high costs to tanker their effluents from rural areas to large treatments plants. Discharge limits can be compared to the typical requirements indicated in the Urban Wastewater Treatment Directive (e.g. 0.7 mg TP/L and minimum 87.5% removal, 10 mg TN/L and minimum 80% removal) ¹¹. With increasing promotion of circular approaches in Scotland ^{12,13}, and regulations expected to become more stringent for both nutrients and greenhouse gases emissions, more distilleries are considering *in situ* nutrients removal and recovery. While more insights are available about conventional nutrients removal, knowledge and assessments about nutrients recovery from this wastewater are sparse.

Struvite crystallisation and stripping with scrubbing were selected to recover phosphate and ammonia. Struvite precipitates spontaneously in water due to a low solubility product when the suitable conditions are met ¹⁴, as in the case of digested distillery wastewater ¹⁵. Together with other scaling agents, this causes blockages and equipment failure and thus inflates maintenance needs. Therefore controlled struvite removal achieves both protection of downstream equipment from scaling and recovery of a mineral fertiliser. N removal via struvite is often limited by P and Mg levels ¹⁵, thus the residual ammonia can be partitioned to a gas phase by stripping and absorbed in sulphuric acid, forming ammonium sulphate, which can be used as fertiliser but also to store ammonium for other applications ¹⁶. Local valorisation of these products would depend on the surrounding demand ¹⁷, especially for fertilisers determined also by legislation and extent of arable land, but could be further expanded beyond Scottish borders, on a National level context.

Combinations of these technologies have been tested on other streams such as urine ¹⁸ and effluent from vanadium extraction ¹⁹, but have not been assessed with the AnMBR effluent of distillery wastewater. Such effluent has the advantage to be virtually solids-free, but has a complex matrix, containing also recalcitrant organics, competing ions and metals. The identified scientific gap revolves around the understanding of how the performance of these established processes translates for this wastewater, at demonstration scale, in terms of nutrients removal and product quality. Struvite recovery from actual digested distillery effluent was reported by a few studies mainly at small scale ^{6,20,21}, whereas Kumari and colleagues explored struvite formation in a synthetic analogue, indicating that phenols, melanoidins and calcium were detrimental to the reaction ^{22,23}. To our knowledge, no previous studies have experimentally assessed the feasibility of ammonia stripping from distillery digestate. For both processes, pH is expected to exert a critical impact on species partitioning and thus removal and products composition. Therefore, the aim of this work is to validate the feasibility and effectiveness of ammonia and phosphate removal (>70%) and recovery with struvite precipitation and ammonia stripping and scrubbing from digested distillery effluent at demonstration scale, evaluating their advantages and challenges. The resulting intellectual contribution consists in the understanding of these technologies' performance in a novel context i.e. AnMBR permeate of distillery effluents and large scale. In particular, fresh insight into potential operational and water chemistry-based challenging will inform definition of future research needs.

3.2 Materials and Methods

3.2.1 Distillery wastewater

Distillery wastewater produced at a Scottish whisky distillery underwent anaerobic treatment in a mesophilic, ultrafiltration membrane bioreactor (AnMBR), delivering approximately 313 ± 65 m³/d permeate ($n=256$). During testing, the variability in the permeate quality was limited, with the differences occurring between two campaign seasons being due to changes in the AnMBR operation. During the testing period, the permeate contained on average $760 \pm$

143 mg TAN/L and 256 ± 39 mg PO₄-P/L. Detailed characterisations of the distillery wastewater before and after anaerobic digestion are available in the Appendix (Table B-2 and Table B-3).

3.2.2 Pilot units

The pilot units were built and operated on the distillery site (Figure 3-1). The struvite crystallisation unit was a fluidised bed reactor (FBR), with a recirculation loop. The unit was ca. 5 m high and had several sections with increasing diameter from bottom to top (from 0.15 to 1 m). The reactor was fed from the bottom with the AnMBR permeate mixed with the recirculation flow, to generate up-flow velocities of 0.0027-0.1172 m/s to maintain suspension of the precipitates bed. Pumps (A-98474873-10000003 and A-98360653-10000005, Grundfos, Leighton Buzzard, UK) and flowmeters (SM8120 and SM9100, IFM, Derby) were used to control the feed and recirculation flows. 4 M MgCl₂ (Omex Environmental, King's Lynn, UK) was dosed to elevate the Mg/P molar ratio from 0.28 ± 0.05 in the feed to 0.5-1.1. pH was monitored online in the reactor (core), in the feed and in the recirculation flow and was adjusted by dosing 9.1 M NaOH (TAN international, Perth, UK). Initial tests led to the modification of some design features: the NaOH dosing point was moved from the pipework to the base of the reactor to avoid uncontrolled precipitation upstream of the FBR, and the chemicals mixing was improved by using orifice plates creating turbulence. Different pH values were assessed along the testing campaign, for periods of 2-9 days, with more details available in Appendix Table B-4). At the base of the reactor, crystals nucleated and were pushed upward to the top of the unit. As these agglomerated into larger pellets, they gradually stratified along the vertical axis of the FBR, with larger and heavier particles accumulating at the base.

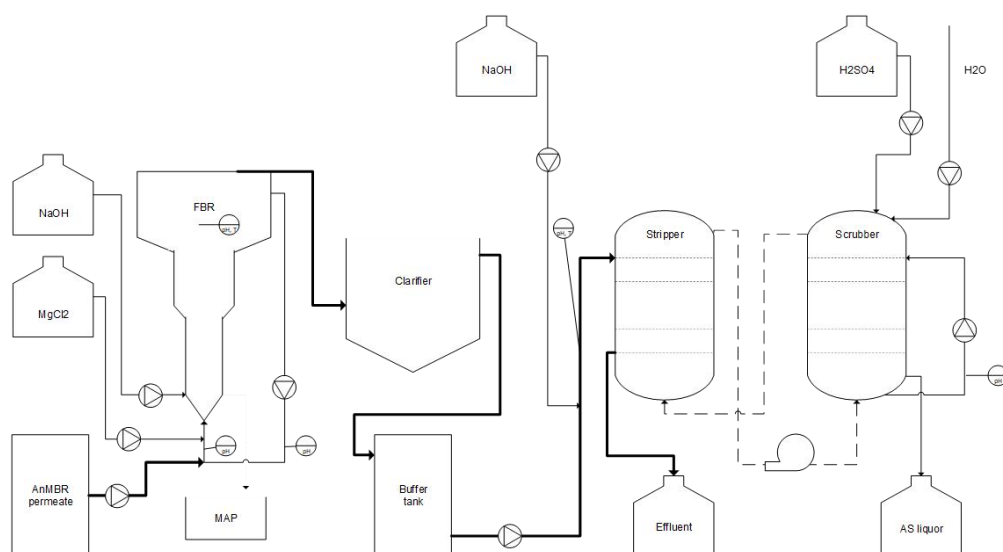


Figure 3-1. Above, flowsheet of the pilot scale treatment train treating digested distillery wastewater, comprising a fluidised bed reactor, ammonia stripping and scrubbing columns. Below, actual pilot scale treatment train, built and operated on site.

From the FBR base, struvite could be harvested, collected into 50 μm filter bags. A harvest event started with the isolation of the base and core sections of the FBR, to collect only the largest pellets and leave smaller seeds within the reactor. Such process was realised manually, by briefly interrupting the FBR operation (<10 minutes). Harvests were performed at the end of periods testing specific conditions or for maintenance. In the top section the up-flow velocity was ca.

0.0027 m/s (operating at 0.5 m³/h with a recirculation ratio of 14) and it was estimated that particles with size $\geq 70 \mu\text{m}$ would be retained. The FBR had a working volume of approximately 0.76 m³, a treatment capacity of 0.66 L permeate/L reactor h, and the hydraulic retention time was ≈ 6 minutes. The effluent overflowed at the top of the reactor into a clarifier (1.96 m diameter, overflow rate 0.166 m³/m² h) which collected fines potentially carried over from the FBR. The clarifier effluent was sent into a buffer tank, feeding into the stripping unit. Sampling ports were used to collect samples of the FBR feed and effluent, recirculation and reactor liquors at different heights. The temperature of the AnMBR permeate was on average $39 \pm 2^\circ\text{C}$. Temperature was not controlled in the FBR and it was monitored within its core, with values of $31 \pm 3^\circ\text{C}$ in autumn and $35 \pm 2^\circ\text{C}$ in summer, during stable periods. As the temperature in the FBR was not controlled and was subjected to external factors, it could reach maximum of 38°C and minimum of 24°C . The latter temperature was due to the use of cooled permeate left standing in the feed buffer tank for few hours when the systems were restarted after downtime due to maintenance.

The ammonia stripping was conducted in a packed tower (ca. 5.4 m high, 0.9 m diameter) containing 1.6 m³ of 25 mm polypropylene pall rings (Forbes Norfolk, UK) (Figure 3-1), without vacuum application. The FBR effluent was fed from the top of the tower (0.5 m³/h), with hydraulic residence time of approximately 47 seconds (specific liquid hold-up 0.009 m³/m³), while counter-current air was blown from the bottom, to facilitate ammonia desorption and transfer to the gas phase. A blower (CMVpro 400, Colasit, Spiez, CH) and a pump (A-98474873-10000003, Grundfos, Leighton Buzzard, UK) were used. 15 cm thick mesh demisters were used to limit water carryover in the gas stream in the stripper and scrubber. The pressure drop was estimated to be 64 Pa/m by VFF-Software 14.1 (VFF GMBH&Co, Ransbach-Baumbach, DE). The stripping effluent left the unit at its base and was discharged into the general AnMBR permeate tank before disposal. The ammonia-rich air was blown into the bottom of a scrubber packed tower (ca. 5.3 m high, 0.9 m diameter), where a 0.5-0.7 M sulphuric acid solution was recirculated, counter-current, by a STN 40 pump, (CDR, Bollate, IT) to form ammonium sulphate. The scrubber contained 1.6 m³ of 25 mm polypropylene pall

rings, with a 2.5 m height. The air recirculation was a semi-closed loop, to minimise cooling by fresh air and CO₂-derived scaling in the tower ²⁴. pH was monitored in the feed and in the scrubber liquor. 9.1 M NaOH could be dosed in the feed, prior to entering the stripping column to reach the target pH. The sulphuric acid solution was formed by dilution of 5.3 M H₂SO₄ (TAN international, Perth, UK) to a ratio of 1:6 with tap water. Feed temperature entering the stripping column was monitored, but not controlled, except during specific, short-term tests using additional heating elements in its feed tank (reaching up to 34±2°C). During stable operation, the intrinsic heat of the AnMBR permeate was exploited, although with losses, with an average stripping feed temperature of 32±1°C. Nonetheless, during specific tests, the feed temperature was reduced down to 20±3°C, cooled down in the feed tank during maintenance. The specific pH-temperature combinations were used to estimate the fractions of free ammonia in the feed.

3.2.3 Operation

Both units were operated with a feed flow of 0.5 m³/h. The FBR was operated continuously and the recirculation flow was 7 m³/h, yielding a recirculation ratio of 14. The stripping unit was also operated in continuous mode, whereas the scrubber was operated in batch, with the end of the batch dictated by reaching a set pH target in the scrubber liquors (pH 5.5) as recommended by the manufacturer. The gas flow rate was 2500 m³/h. The gas/liquid ratio (G/L) was approximately 5000 for the stripper and 139 for the scrubber. At least one set of samples was collected daily for analyses and/or visual inspection of the precipitates, during operation of the two units. A set included feed and effluent of the FBR, effluent of the stripping unit, scrubber liquor and samples from the FBR sections (base, core, middle, top). The grab sampling approach allowed to monitor some key parameters during steady operation. Nonetheless, the operation stability was highly influenced by all the potential variations in the wastewater and this approach had the limitation of potential mismatches between influent and effluent, also due to potential residence times dealignments.

Precipitates samples were collected from the harvests and stored in sealed vials and liquid samples were stored at 4°C, analysed on site for specific parameters (concentrations of TAN, PO₄-P, Mg, pH), and shipped in refrigerated boxes to Cranfield University for further analyses. The impact of pH (7.0-9.5) on the removal efficiencies and the recovered products quality was assessed, for periods of 1-9 days each (further details in Appendix Table B-4).

3.2.4 Analytical methods

pH in the samples was measured with pH meters Titralab AT1000 (Hach, Manchester, UK) with a Intellical PHC805 probe (Hach, Manchester, UK), and 3510 (Jenway, Stone, UK) with InLab expert Pro sensor (Mettler Toledo, Canada). Electrical conductivity (EC) in the samples was determined with a Jenway conductivity meter 4310 (Stone, UK). Temperature, EC, and pH were monitored online, by means of S400 series probes in the feeds and recirculation and a PG13.5 probe in the FBR, connected to a MXD75 multi parameter process instrument (all purchased from LTH, Luton, UK).

Concentrations of chemical species were measured in total samples. To minimise the potential interference of fines during the measurements, the supernatant of settled samples was used. TAN, PO₄-P, Mg, COD concentrations were determined with standard cell tests (Hach, Manchester, UK and Supelco, Merck, Gillingham, UK) and spectrophotometers DR3900 (Hach, Manchester, UK) and Spectroquant Nova 60 (Merck-Millipore, Darmstadt, DE). Metals concentrations were determined with PerkinElmer's NexION® Inductively Coupled Plasma Mass spectrometer (ICP-MS), after sample acidification with HNO₃ (Normatom®, 67-69%, for trace metal analysis, VWR International Ltd., Poole, UK) and dilution with ultra-pure water. Ions concentrations were measured with ion chromatography (IC): for cations, a Dionex ICS-900 IC and a Dionex IonPac (CS12A) columns were employed (Thermo Fisher Scientific, UK), with 0.026 mM methanesulfonic acid as eluent and 0.98 M tetrabutylammonium hydroxide regenerant phase; for anions, a Dionex ICS-1600 IC and a AS 9HC columns were utilized, with 9 mM Na₂CO₃ mobile phase.

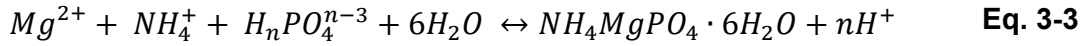
The harvested precipitates were dried at room temperature under a fume hood for ≥ 45 h and then analysed with different methods. They were ground into a powder, compressed on an aluminium frame and characterised with X-ray diffraction (XRD) spectrum, utilising a SIEMENS D5005 diffractometer and Diffrac Eva software (scan time 1 h, scan angles $10^\circ 2\theta$ to $90^\circ 2\theta$). Moreover, the outer surface of the precipitates and their cross-sectional area (when feasible) were characterised with scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDS) (Tescan Vega 4, large chamber, Kohoutovice, Czech Republic) to assess their morphology and elemental composition. Furthermore, the precipitates were dissolved in 1 M HNO_3 solution (Normatom®, 67-69%, for trace metal analysis, VWR International Ltd., Poole, UK), diluted with ultrapure water and analysed for concentrations of TAN, $\text{PO}_4\text{-P}$, COD and metals as described above. The selection of metals to analyse in the precipitates (B, Si, K, Ca, Mn, Fe, Ni, Cu, Zn, Sr, and Ba) was based on the fact that some of these were dosed as micronutrients in the AnMBR, whereas copper is released by the stills, while elements like Ca and K are naturally present in the permeate. Most of these metals are also known foulants to RO membranes, whose application was studied as further treatment reuse within the Ultimate project (not part of this thesis). Understanding their fate in struvite would partially inform about the potential downstream scaling risk. Other metals such as Cr, Hg, Pb, As, and Cd were not analysed as the composition was not initially assessed against EU/UK standards, however further analysis to evaluate compliance is warranted.

3.2.5 Data analysis

The struvite supersaturation ratio in the reactor was determined at the different tested conditions, with the ion activity product (*IAP*) determined via a chemical equilibria model software, Visual Minteq (version 3.1) (Eq. 3-1 to Eq. 3-3 ^{25–27}).

$$SSR = \frac{IAP}{K_{sp}} \quad \text{Eq. 3-1}$$

$$IAP = \gamma_{Mg}[Mg^{2+}] \cdot \gamma_{NH_4}[NH_4^+] \cdot \gamma_{PO_4}[PO_4^{3-}] \quad \text{Eq. 3-2}$$



Where K_{sp} is the constant solubility product of struvite at equilibrium ($10^{-13.26}$, ²⁸), affected by temperature ²⁵. Ions' activities depend on the activity coefficient γ . The purity of the precipitates was estimated, assuming that N can only precipitate as struvite ²⁹ (Eq. 3-4).

$$Purity (\%) = \frac{N \text{ content } (\frac{g N}{g Pr})}{\frac{14.0067 g N}{mol N}} \cdot \frac{245.41 g MAP}{mol MAP} \cdot 100 = \frac{g MAP}{g Pr} \quad \text{Eq. 3-4}$$

Where $N \text{ content}$ was retrieved from the SEM-EDS analyses of the precipitates (Pr). MAP is struvite.

3.2.6 Mass balances

The actual mass balances of the nutrients across the treatment train were based on the best N and P removal and recovery efficiencies measured throughout the testing campaign and applied to real wastewater data. It was assumed that all precipitated P-minerals and MAP were fully harvested from the FBR or clarifier (100% recovery efficiency). N removal as MAP was determined based on the removed P moles and the N/P % wt. proportions obtained via SEM-EDS analyses.

Theoretical mass balances were determined for comparison. Nutrients removal in the FBR was estimated by using Visual Minteq, ("modelled" output) and by a theoretical mass balance ("simulated" output), assuming equimolar removal of P, Mg, TAN and assuming that all other chemical species remained in solution, for ease of calculations. The software received as input the reactor's water physicochemical profile, obtained from analytical data (e.g. pH, temperature, ions concentration) and estimates from the mass balance calculations accounting for

the applied recirculation flow, the $MgCl_2$ dosing, and the measured P removal. It was assumed only struvite would precipitate, as other mineral species, despite showing high supersaturation ratios (SSR), could have slower precipitation kinetics^{30,31}.

The ammonia stripping performance was estimated by means of VFF-Software 14.1 (VFF GMBH&Co, Ransbach-Baumbach, DE) and based on literature^{32,33}, for given scenarios with inputs including the water temperature T (K), pH, influent $[TAN]_0$, gas/liquid volumetric ratio (2500 m³/h : 0.5 m³/h), column sizing (2.5 m packed bed height, 0.95 m diameter), packing material (Polypropylene Pall rings 25 mm). The software estimated the HTU (height of transfer unit, mm), the gas and liquid side mass transfer coefficient (k_l , k_g , respectively, m/s), the Henry coefficient at the specific temperature (H_p , kPa). Other required parameters were calculated, knowing the packed height L (mm), T (K), pH . Based on the data, the TAN removal efficiency η (%) of the system was determined (Eq. 3-5). Eq. 3-6 to Eq. 3-9 were utilised to calculate parameters in Eq. 3-5. The data was used to estimate also the volumetric mass transfer coefficient $K_{ov}a$ (1/s) for the tested system (Eq. 3-10).

$$\eta = \frac{C_0 - C_e}{[TAN]_0} \quad \text{Eq. 3-5}$$

$$C_e = C_0 \cdot \frac{1}{\exp(NTU \cdot \left(\frac{S-1}{S}\right)) - \frac{1}{S}} \cdot \frac{S-1}{S} \quad \text{Eq. 3-6}$$

$$C_0 = [TAN]_0 \cdot FA \quad \text{Eq. 3-7}$$

$$FA = \frac{1}{(1 + 10^{pk_{a,T}^S - pH})} \quad \text{Eq. 3-8}$$

$$pk_{a,T}^S = pk_{a,298}^S + 0.0324 \cdot (298 \text{ K} - T) \quad \text{Eq. 3-9}$$

$$K_{ov}a = \frac{1}{\frac{1}{k_l a} + \frac{1}{k_g a \cdot H_a}} \quad \text{Eq. 3-10}$$

Where, C_0 and C_e are the free NH_3 concentration at the start and end of the stripping run, respectively. η was estimated assuming the initial TAN concentration ($[\text{TAN}]_0$) was only removed via NH_3 stripping. NTU is the number of transfer units (-), S is the stripping factor (-), FA is the fraction of free ammonia in the TAN concentration. $pk_{a,T}^s$ and $pk_{a,298}^s$ are the negative logarithms of the stoichiometric acid hydrolysis constant of ammonium at specific T and 298 K (9.25). K_{ov} is the overall liquid mass transfer coefficient (m/s), a is the wetted surface area of packing (1/m) and H_a is the adimensional Henry coefficient (L H_2O / L air) ³².

3.3 Results

3.3.1 Fluidised Bed Reactor performance

The pH in the FBR had a substantial effect on phosphate removal, reaching approximately 80% above pH 8.9 (Figure 3-2), corresponding to an effluent $\text{PO}_4\text{-P}$ concentration of 45-53 mg/L (further details in Appendix Figure B-1).

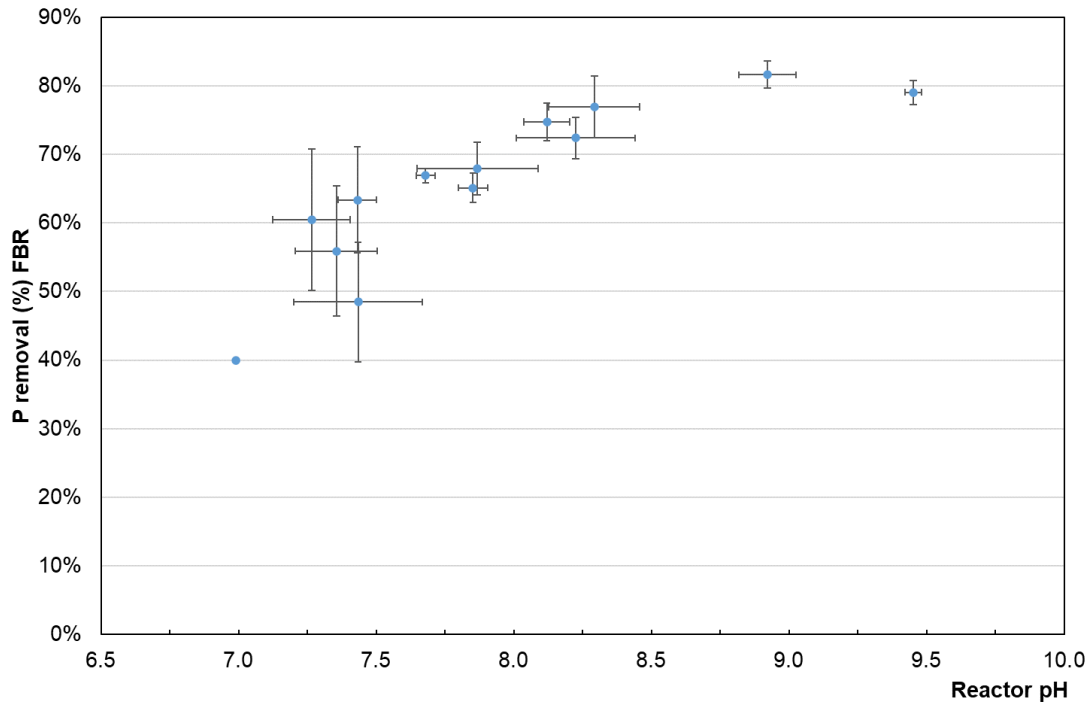


Figure 3-2. $\text{PO}_4\text{-P}$ removal as function of the pH in the reactor (core section).

Mg and TAN were removed, in most cases in similar proportions to PO₄-P (Table 3-1), suggesting that struvite precipitation was a major mechanism of their removal.

Table 3-1. Removal rate of PO₄-P, Mg, TAN (mol/h) from solution and TAN removal efficiency (%) in the FBR, as function of pH in the reactor (core) and Mg dosing rate (mg Mg dosed per L of feed to treat).

pH reactor	Mg dosing	P	Mg	N	N removal
-	mg/L	mol/h	mol/h	mol/h	%
6.99	-	1.8	1.7	-	-
7.27 ± 0.14	113	2.5 ± 0.6	2.8 ± 0.4	3.0 ± 0.5	12±1
7.36 ± 0.15	113	2.3 ± 0.4	2.4 ± 0.1	2.9 ± 0.4	5±11
7.43 ± 0.07	113	2.6 ± 0.4	2.9	2.2 ± 0.9	8±2
7.68 ± 0.03	113	2.8 ± 0.1	2.9 ± 0.2	2.7	10
7.87 ± 0.22	113	2.9 ± 0.2	2.7 ± 0.0	2.4 ± 1.9	7±8
7.85 ± 0.05	120	2.7 ± 0.1	2.8 ± 0.2	1.9 ± 0.8	7±3
8.12 ± 0.08	120	3.1 ± 0.2	3.0 ± 0.2	3.8 ± 3.8	13±10
8.1	150	2.0 ± 0.2	3.9 ± 0.1	3.0 ± 1.7	10±4
8.1	180	2.2 ± 0.0	4.9 ± 0.1	2.7 ± 1.6	11±6
8.23 ± 0.22	113	3.0 ± 0.1	2.8 ± 0.2	3.0 ± 0.9	6±6
8.29 ± 0.16	120	3.1 ± 0.2	3.2 ± 0.2	3.5 ± 1.8	13±6
8.92 ± 0.10	120	3.2 ± 0.4	3.2 ± 0.2	4.2 ± 2.0	18±9
9.45 ± 0.03	120	3.2 ± 0.2	3.4 ± 0.1	4.2 ± 2.1	17±6

Slight discrepancies in the 1:1:1 molar proportions can be ascribed to co-precipitation of other minerals and/or NH₃ losses. In fact, at higher pH values 8.9 ± 0.1 and 9.5 ± 0.0, the number of moles of TAN extracted were greater compared to P and Mg, indicating that other removal pathways occurred. The additional moles were consistent with losses due to volatilisation, as the fraction of NH₃ increased at higher pH (Eq. 3-8). Nonetheless, the maximum TAN removal was limited to 18±9% (pH 8.92 ± 0.10) and 17±6% (pH 9.45 ± 0.03), as it was present in a significant excess compared to PO₄-P. Furthermore, additional dosing of Mg seemed to only have limited impact on P removal, within the tested conditions at

pH 8.1. To illustrate, raising the Mg dosing rate from 120 to 180 mg Mg/L feed led to an effluent [P] of 43 ± 4 mg P/L compared to 66 ± 6 mg P/L, but the overall number of moles removed was also decreased (Table 3-1), due to lower initial [P] concentrations in the feed (261 ± 10 mg P/L vs 174 ± 7 mg P/L) during these trials. On the other hand, Mg removal rate increased, suggesting that the excess Mg moles precipitated forming other minerals.

3.3.2 Stripping performance

In the stripping step, ammonia removal rose upon pH increase (Figure 3-3), following the trend of free ammonia fraction in most cases. Although the results suggest this trend, confidence in the values could be influenced by the grab-sampling limitations.

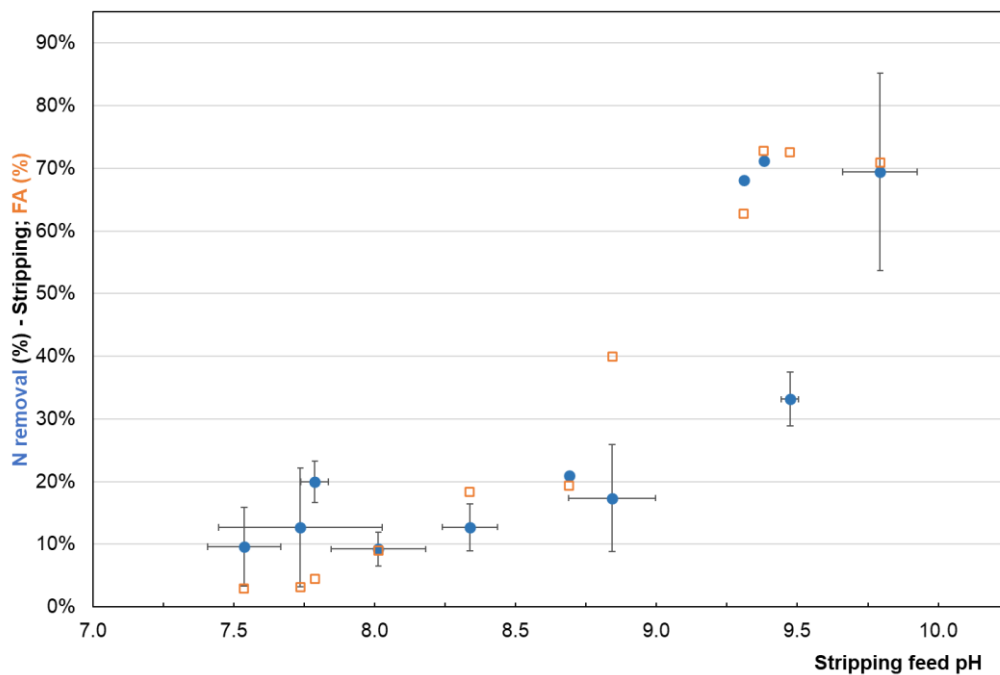


Figure 3-3. TAN removal in the stripping unit (circles) and relative free ammonia (FA) fraction (squares), as function of feed pH. FA was determined accounting also for the specific feed temperature.

The maximum removal of 71% was reached at pH 9.38 and a temperature of $34 \pm 2^\circ\text{C}$, obtained during a test at the end of the testing campaign. Moreover a removal of $69 \pm 16\%$ was reached at $20 \pm 3^\circ\text{C}$ and $\text{pH } 9.79 \pm 0.13$, during a test at the beginning of the trial period. In one test, where the pH was adjusted to 9.47

± 0.03 the removal levels was unexpectedly low at $33 \pm 4\%$ N, despite a high feed temperature of $31 \pm 1^\circ\text{C}$ resulting in high FA (73%). The discrepancy was accounted for by a temperature reduction within the stripper unit promoted by the outdoor air temperature and the air blown in the stripping unit. Preliminary lab scale tests indicated that 90% TAN removal was obtained at 65°C (data not shown). At the best performance, the pilot plant's effluent TAN concentration was 186 mg N/L (with further details available in Appendix Figure B-2).

To understand the impact of the integration between the FBR and the stripper unit, two different pH adjustment strategies were used. First, the pH was increased in the stripping feed to reach values ideal for ammonia volatilisation (i.e. > 9.25). Such operation resulted in a high TAN removal ($69 \pm 16\%$), but also caused significant scaling issues in the pipework downstream of the NaOH dosing point, as the FBR performance was not optimised yet and the scaling potential in the FBR effluent was still high. To avoid this, the pH was then only corrected in the FBR, specifically designed to precipitate minerals and minimise downstream scaling, aiming to gradually reach pH conditions suitable for ammonia stripping. Finally, when the P removal in the FBR plateaued at approximately 75-80% (≥ 8.1), it was assumed that most scaling agents had precipitated and the pH was further controlled in the stripping feed (raising pH to 9.3-9.4). Operating at such conditions achieved approximately 70% N removal without equipment clogging, demonstrating the feasibility of the combined system. Enabling a robust pH control was fundamental for the process performance, as it directly affected the fraction of free ammonia and thus the TAN removal rate, which at $\text{pH } 8.51 \pm 0.07$ was $1.9 \pm 0.4 \text{ mol N/h}$, at $\text{pH } 8.90 \pm 0.14$ was $3.4 \pm 1.3 \text{ mol N/h}$, at $\text{pH } 9.38$ reached 16.4 mol N/h , and up to 21.1 mol N/h at $\text{pH } 9.79 \pm 0.13$. An increase in ammonia removal would be directly reflected in the N concentration in the scrubber liquor.

Only a small fraction of the initial $\text{PO}_4\text{-P}$ load seemed to be removed in the stripping unit (in most cases $\leq 6\%$), with the bulk having been separated upstream via struvite recovery. COD removal appeared relatively limited, although with high

variability ($\leq 17\pm 11\%$), and comparable to literature values (10-30%³⁴), ascribable to volatile organic compounds (VOC) losses³⁵.

3.3.3 Recovery products

Within the FBR unit, mineral precipitates stratified along its vertical axis, depending on their size, which was assessed by visual inspection of samples. The fraction of fines and larger pellets in each section of the reactor changed with increasing operation pH (Figure 3-4).

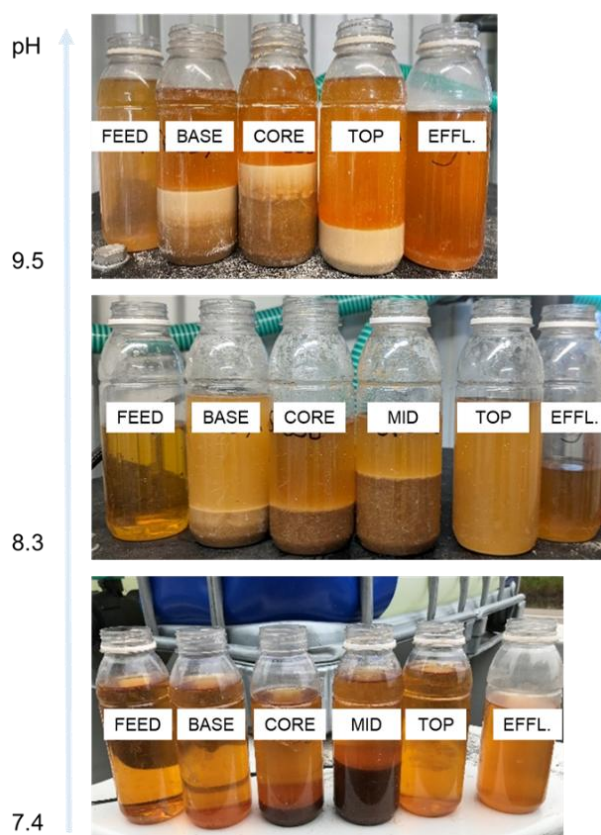


Figure 3-4. Samples showing the stratification of mineral precipitates along the vertical axis of the FBR, from bottom (base) to top, with pH changes in the reactor. Effl.= effluent.

The development of fine particles in the reactor rose as the pH increased. At a reactor pH 7.4, no visible fines were present in the FBR nor its effluent, whereas fines particles became visible from pH 8.1-8.3 in all sections of the reactor and in the effluent. At pH 9.45, the volume of fines matched the volume of larger particles in the FBR's base and became significant in the top section and in the

effluent (Figure 3-4). The estimated struvite SSRs were 2.5 (pH 7.4), 3.5 (pH 7.7), 7.6 (pH 8.3), 13.4 (pH 8.9), 16.8 (pH 9.5), driving the differences in pellets quantity and size (Figure 3-5).

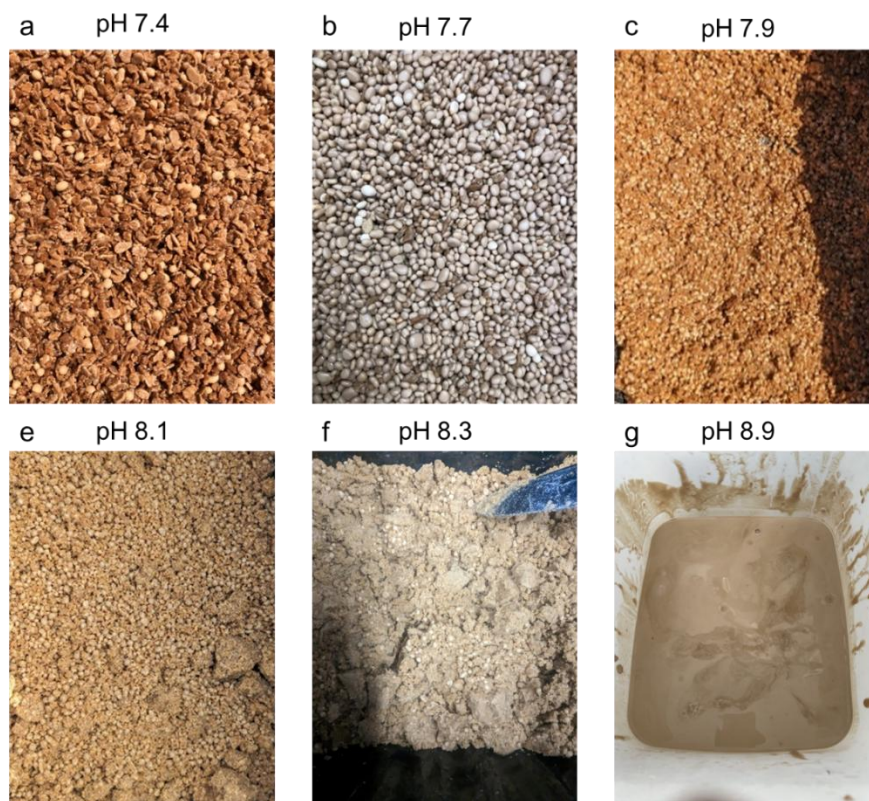


Figure 3-5. A selection of precipitates harvested from the FBR operated at different pH (indicated on top of each image). Each harvest collected particles stratified in the base and core sections.

At lower pH, struvite supersaturation was limited and the nucleated crystals mainly grew into larger agglomerates settling between the base and the middle sections. As the pH rose, so did the SSR and the extent of crystals nucleation and growth, resulting in the observed changes. In such conditions, nucleation rate prevailed over crystal growth and even the FBR top section contained a considerable number of small crystals, which inevitably entered the clarifier. As a consequence in the change in the relative rates of nucleation and growth, the volume of fines received by the clarifier rose when the pH increased, resulting in the need to daily extract a fraction from its base and affected also the size of the harvested precipitates. Operating the reactor at lower pH levels (e.g. 7.4 ± 0.1 –

7.7 ± 0.0) allowed larger pellets to be recovered from the base and core sections (Figure 3-5 a, b), whereas adjusting it to more alkaline conditions yielded an increasingly finer product. To illustrate, from pH 8.9 ± 0.1, the harvest was composed by a sand-like slurry of fine solids (Figure 3-5 g). The formation of large struvite pellets occurred through a combination of crystal growth and particles agglomeration. Initially, a core or seed provided the platform for crystal growth along flat surfaces, forming flake-like structures (Figure 3-6 a-c). During this process, the shear forces within the reactor polished the pellets into smooth spheres, especially the heavier particles stratified in the lower sections and exposed to higher turbulence (Figure 3-6 d). Additionally, some of the largest particles were formed by the agglomeration of smaller, round units, which were cemented together by newly formed crystals (Figure 3-6 e). Further insights on the internal morphology of the pellets are available in the appendix, confirming the described structure (Appendix Figure B-3).

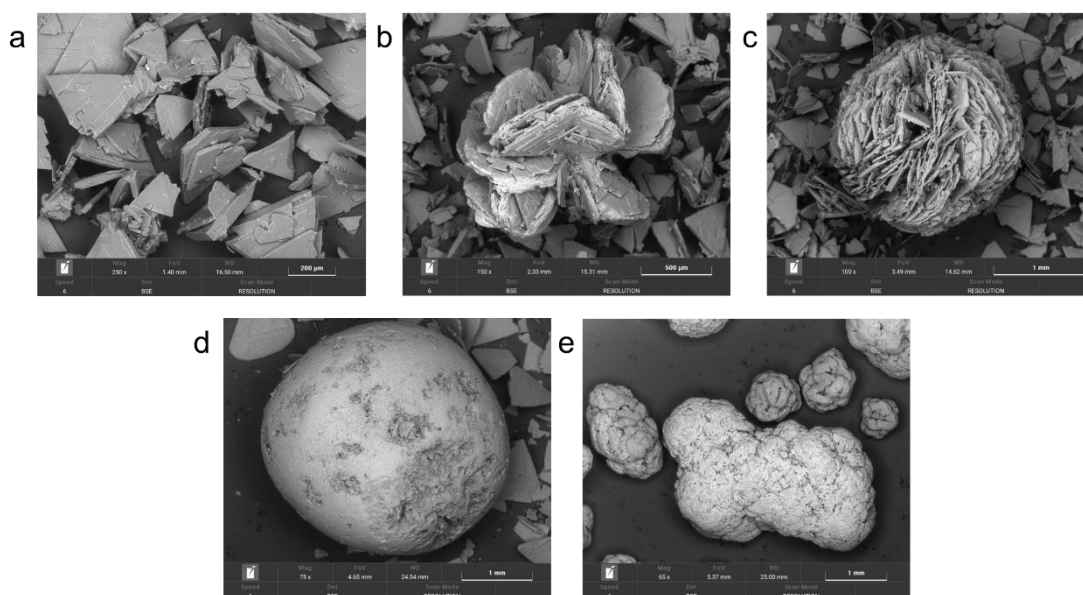


Figure 3-6. Particles harvested in different batches, representing phases of the pellets growth.

The XRD spectra of the harvested material showed alignment with magnesium ammonium phosphate (MAP struvite), with only limited deviations at the higher pH values (spectra available in the Appendix, Figure B-4). Likewise, the fines collected in the clarifier were composed mainly by struvite. The precipitates

composition was assessed also via SEM-EDS analysis of external and cross-sectional surfaces, comparing to the Mg, P, N theoretical content of struvite (Mg 9.9% wt., P 12.6% wt., N 5.7% wt.) (Table 3-2). In most cases the actual N levels matched the theoretical struvite content, yet the amounts of P and Mg often fluctuated and were higher than the expected values, suggesting that potentially other Mg/PO₄ minerals had co-precipitated.

Table 3-2. N, Mg, P content (% wt.) of the precipitates harvested during specific FBR operation pH, and corresponding estimated struvite purity (Eq. 3-4). E= external surface, CS= cross section.

FBR core pH	Surface	N	Mg	P	Purity
7.4 ± 0.1	E	5.6 ± 1.0	15.2 ± 1.4	17.8 ± 0.9	98% ± 17%
7.4 ± 0.1	CS	3.3 ± 0.5	11.1 ± 0.4	13.4 ± 0.8	57% ± 8%
7.9 ± 0.1	E	5.9 ± 1.2	14.9 ± 0.7	17.4 ± 1.6	102% ± 22%
7.9 ± 0.1	CS	5.1 ± 0.7	9.9 ± 1.2	11.6 ± 1.2	90% ± 12%
8.1 ± 0.1	E	4.1 ± 1.4	16.1 ± 0.5	18.0 ± 0.9	72% ± 24%
8.1 ± 0.1	CS	4.7 ± 0.6	10.7 ± 3.5	12.9 ± 4.3	82% ± 11%
8.3 ± 0.2	E	5.2 ± 1.1	15.9 ± 0.9	19.4 ± 2.8	90% ± 20%
8.3 ± 0.2	CS	4.5 ± 1.3	10.9 ± 2.6	12.7 ± 3.1	79% ± 22%
8.9 ± 0.1	E	5.3 ± 0.2	10.3 ± 0.4	11.1 ± 0.3	93% ± 4%
8.9 ± 0.1	Clarifier	3.3 ± 0.7	8.8 ± 0.8	10.4 ± 0.5	58% ± 12%
9.5 ± 0.0	E	4.7 ± 0.4	11.4 ± 1.5	12.8 ± 1.2	83% ± 7%
9.5 ± 0.0	E	4.8 ± 0.7	13.2 ± 1.2	15.1 ± 0.2	85% ± 12%
9.5 ± 0.0	Clarifier	4.2 ± 0.6	11.9 ± 1.3	14.5 ± 0.9	74% ± 11%

Analyses of the dissolved pellets indicated that, except for few limited spots, contamination from Ca, K, Si in the solids was limited or negligible (Table 3-3).

Table 3-3. Metals and COD content (mg/kg) of precipitates harvested after different FBR operation pH, determined after dissolution of the precipitates.

FBR core pH	B	Si	K	Ca	Mn	Fe	Ni	Cu	Zn	Sr	Ba	COD content
7.3 ± 0.1	0.0	3	1873	70	61	5	0.1	0.5	1.1	0.1	0.1	70225
7.4 ± 0.1	0.0	9	2137	61	68	5	0.1	0.7	0.3	0.2	0.0	54959
7.7 ± 0.0	0.0	6	1910	79	57	6	1.4	0.5	1.2	0.1	0.0	55960
7.9 ± 0.1	0.0	8	1530	77	64	3	0.0	0.5	1.2	0.3	0.0	49365
8.1 ± 0.1	0.0	18	1234	90	70	3	0.0	0.5	1.6	0.6	0.0	44320
8.3 ± 0.2	0.0	10	1429	82	69	3	0.0	0.5	0.3	0.3	0.1	29706
8.3 ± 0.2	0.0	0	1375	72	70	10	1.7	0.5	0.7	0.0	0.1	49244
8.9 ± 0.1	0.0	22	2313	116	72	3	0.0	0.3	0.7	0.6	0.0	39550
8.9 ± 0.1 ^a	0.0	11	1782	94	73	3	0.0	0.3	1.2	0.4	0.0	49876
9.5 ± 0.0	0.0	0	1542	73	70	2	0.1	0.3	0.4	0.2	0.0	39940
9.5 ± 0.0	0.0	4	2615	138	80	4	0.5	0.5	1.0	0.6	0.1	34965

^a clarifier precipitates

Similar results were obtained by SEM-EDS analyses of the precipitates, suggesting limited Na content across the testing period ($\leq 2.5\%$ wt. - specific data available in Appendix Table B-5). The presence of organics was limited to $\leq 7\%$ wt. COD (≤ 70225 mg/kg) (Table 3-3), which was potentially associated to the brown colour of the recovered products. Importantly, none of the assessed heavy metals were found in the minerals at critical concentrations (<100 mg/kg) (Table 3-3). An external chemical risk assessment showed negligible risk associated with the application of this struvite on the local fields neighbouring the distillery, considering its content of Cu, Zn, Ni, for both soil and groundwater ³⁶.

Downstream of the FBR, ammonia was recovered as ammonium sulphate, from the batch-operated scrubber. In each batch, the concentration of ammonia increased with operation time, as expected (Figure 3-7), together with a rise in pH until it reached the threshold value determining the end of the batch. The COD level increased as well from less than 25 to 370 mg COD/L within one batch, which was attributed to absorption of volatile organic compounds stripped from the wastewater. The majority of the ammonia partitioned to the air phase was captured in the acidic liquor, with the actual TAN increase over time matching the expected concentration, determined based on the mass of N removed and the scrubber liquor volume (Figure 3-7). Discrepancies arose at the start of the batches, as the acidic solution was prepared by dilution and acidification of a fraction of the previous batch's liquor, resulting in a baseline N load above 0 mg/L.

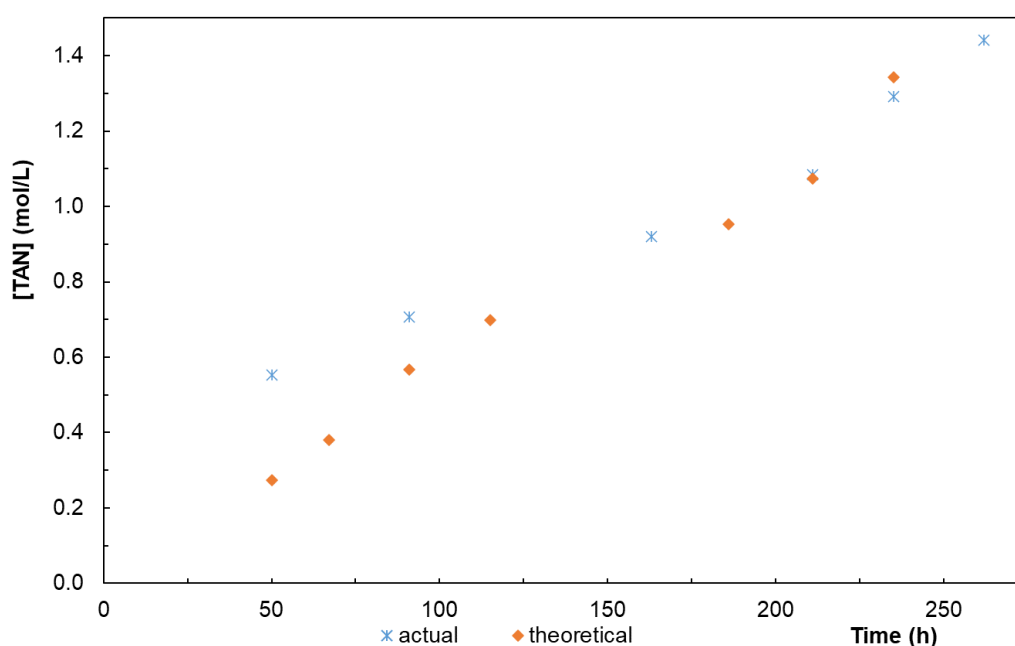


Figure 3-7. Actual and theoretical TAN concentration in the scrubber liquor, as function of time, during one scrubber batch (pH 8.9, 9.5).

The maximum concentration achieved with these settings was 20 g TAN/L (1.4 mol/L), still within the range of values reported in literature: 14 g N/L ³⁷, 30-37 g N/L ³⁸, and 51-61 g N/L ³⁹. The solution was undersaturated compared to the (NH₄)₂SO₄ solubility at 20°C ($\approx$ 750 g (NH₄)₂SO₄ /L ³³). In particular, the N content was affected by dilution of the scrubber liquor due to water carryover from the wastewater to the gas phase and to the scrubber solution, despite the presence of a demister. To illustrate, accounting for such dilution factor for a scrubber liquor with final concentration of 18 g TAN/L (1.3 mol N/L), suggested that, theoretically, a $\approx$ 37 g N/L solution could have been generated (2.6 mol N/L).

3.4 Mass balances of the treatment train

The measured nutrients' removal in the FBR was compared with the simulated (mass balance) and modelled (Visual Minteq) values, pointing to overall a good alignment (Table 3-4).

Table 3-4. Removal (left) and effluent concentrations (right) of PO₄-P, TAN, Mg in mg/L in the FBR (T=34.7°C, pH 9.45) as measured, calculated via a mass balance simulation, and estimated via Visual Minteq (VM).

	TAN	PO ₄ -P	Mg	[TAN]	[PO ₄ -P]	[Mg]
Measured	17 ± 7%	79 ± 2%	81 ± 1%	560 ± 28	53 ± 4	10 ± 1
Simulation	14%	79%	67%	588	53	18
VM	15%	86%	94%	580	35	3

TAN removal was slightly underestimated by both Visual Minteq and mass balance simulations compared to the measured value, due to NH₃ volatilization losses in the FBR. Visual Minteq overestimated P and Mg removal, suggesting that other species in the real water impacted the co-precipitation of these nutrients, possibly calcium and carbonates, but potentially also organic compounds. Meanwhile, mass balance simulations underestimated Mg removal, suggesting it precipitated in forms other than struvite. The precipitation of bobierite (Mg₃(PO₄)₂ · 8 H₂O) and newberyite (MgHPO₄ · 3 H₂O) was excluded, the former having a days-long kinetic and the latter precipitating at pH < 6³⁰. Additional simulations considering co-precipitation of relevant species selected from literature (e.g. CaHPO₄ · 2 H₂O, MgCO₃ · 2 H₂O, Mg(OH)₂³⁰) showed minimal impact on the effluent concentration and struvite formation at pH 9.45, but reduced struvite production by 24% at pH 7.43 due to CaHPO₄ formation. This led to increased P separation but reduced TAN and Mg removal compared to the scenario without co-precipitation. Further details are available in Appendix (Table B-6).

Similarly, the estimated performance of the stripping unit aligned with the actual measurements for a range of selected conditions (Table 3-5). The modelling equations successfully predicted TAN removal for scenarios 1, 2, 3. Overall, the estimated TAN removal efficiency almost entirely depended on the fraction of free ammonia, since, with the current design and operation, the modelled removal efficiencies of specifically NH₃ were always ≥ 88%, even up to 99%. Thus, this suggested that the unit successfully partitioned the TAN present as NH₃ in

solution to the gas phase. The FA fraction was critically affected by the liquid pH and temperature. Operating the reactor at pH 9.47 and 31°C only yielded $33 \pm 4\%$ removal (scenario 4), despite the forecasted 72%, and such discrepancy was potentially ascribed to a drop in the temperature of the liquid within the system, affecting the actual FA, and/or reported issues with the blower, which might have delivered a lower air flow than expected. Solving these operational challenges could help achieve the expected removal. Additionally, the presence of other compounds, in the water might have impacted the availability of TAN, e.g. organic species, although this aspect should be further investigated.

Table 3-5. Measured (M) and estimated (E) values of free ammonia fraction (FA), K_{ova} (1/s), [TAN] concentration (mg/L) in feed (i) and effluent (e), removal efficiency, for 4 scenarios (S).

S	pH	T (°C)	[TAN] _i	FA		K_{ova}	[TAN] _e	Rem. eff.
1	9.79 ± 0.13	20.3 ± 3.2	802 ± 46	71%	M	-	264 ± 145	$69 \pm 16\%$
					E	0.0035	259	68%
2	9.31	30.3 ± 0.3	623	63%	M	-	199	68%
					E	0.0048	236	62%
3	9.38	33.8 ± 1.5	646	72%	M	-	186	71%
					E	0.0054	180	72%
4	9.47 ± 0.03	30.8 ± 1.4	561 ± 22	72%	M	-	406 ± 370	$33 \pm 4\%$
					E	0.0050	19	72%

The highest measured nutrients removal and recovery efficiencies were used to estimate the partitioning capacity of the integrated system and the mass of recovery products generated (Figure 3-8). Confidence in the values can be limited due to errors associated with system stability and grab sampling.

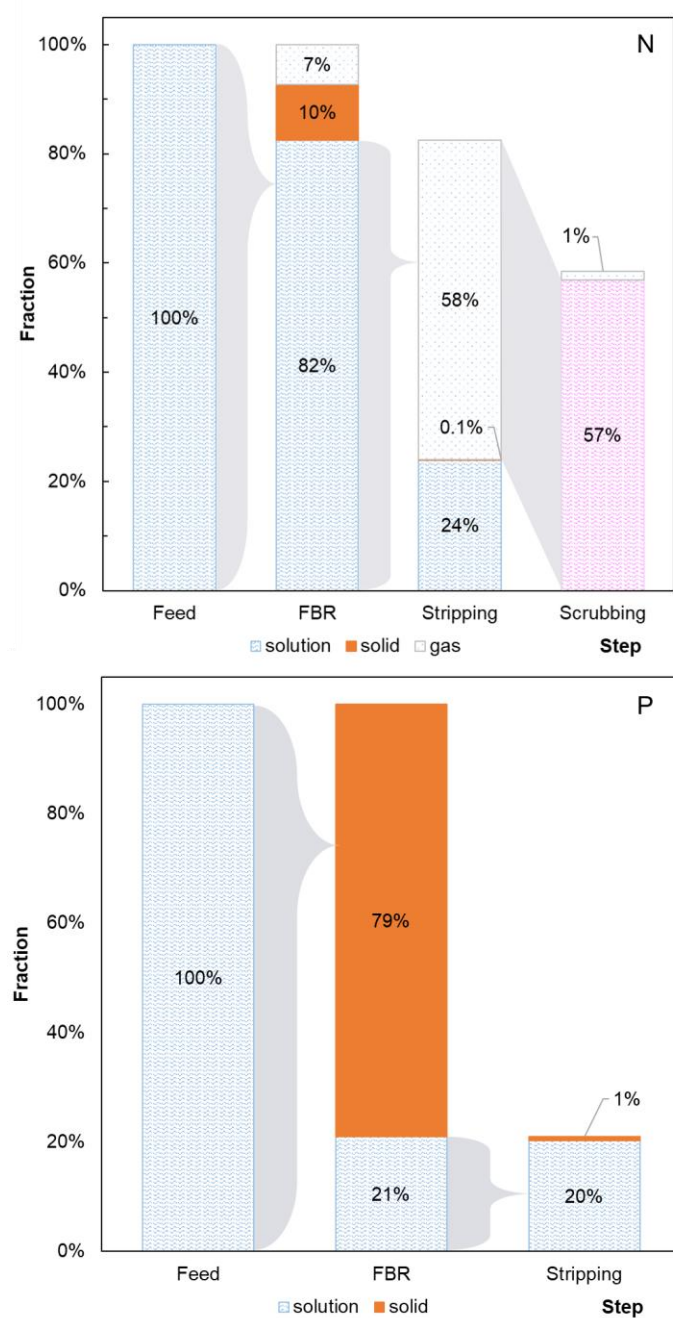


Figure 3-8. Partitioning of TAN (top) and PO₄-P (bottom) into dissolved, solid, gaseous forms, along the treatment train (FBR operation: pH 9.45±0.03, 35±1°C. Stripping operation: pH 9.38, 34±2°C).

The overall treatment train, operating at a pH of 9.4–9.5, successfully separated 76% of the initial TAN load of ca. 24 mol TAN/h, 59% of which occurred across the stripping unit and 18% in the FBR. 88% of such removed TAN was recovered into products (corresponding to 67% of the overall feed load, ca. 16 mol TAN/h),

with the deficits ascribable to lost gaseous ammonia formed in the FBR and in the stripping tower. Out of the initial load of TAN (fully dissolved in solution), in the FBR 10% was partitioned to recoverable, solid struvite particles and 7% was separated as gaseous ammonia and not recovered (Figure 3-8).

Following, in the stripping unit, 59% of the initial load was extracted as NH_3 (71% of the FBR effluent load), which could be recovered with 97% efficiency. Under the same conditions, the overall system achieved an 80% removal rate of P, via precipitation (Figure 3-8). Of this, only 1% was unrecovered, or 'lost,' during the stripping process. This would result in the daily separation of 62 kg of phosphorus from the feed in the fluidized bed reactor (FBR), with virtually all of it recoverable as precipitates from the reactor or the clarifier. It was estimated that in these conditions ammonium struvite composed ca. 77% and 64% (mol/mol) of the solids precipitated in the FBR and in the stripping unit, respectively, based on N/P %wt. ratio measured in the harvested solids. The 77% (mol/mol) purity of precipitates in the reactor approximated the previously estimated 83-85% wt. purity (Table 3-2). Considering a continuous operation, treating $313 \text{ m}^3/\text{d}$ could result in a yearly recovery of ca. 140 t of struvite, equivalent to 8 t of N and 18 t of P, with an additional recovery of 5 t of P as other P-based precipitates. Furthermore, approximately 208 t/y of ammonium sulphate could be harvested in solution, equivalent to 44 t of N per year.

3.4.1 Operational challenges

Several operational challenges were addressed during the testing of the integrated treatment train, expanding the understanding of the critical factors enabling a successful performance. The first challenge was the uncontrolled precipitation of struvite within the pipework feeding into the FBR, upstream and especially downstream of the NaOH and MgCl_2 dosing points. Moreover, initial poor P removal in the FBR was associated with heavy scaling downstream, in the effluent tank and the pipework feeding into the stripping unit. This was mitigated by improving the mixing of chemicals and delivering the pH control at the base of the reactor, rather than upstream, to promote a homogenous distribution of the sodium hydroxide and avoiding reaching localised high SSRs. Moreover, the rate

of pH increase in the FBR across the testing campaign was maintained at a low rate (e.g. 0.2-0.4 pH increase every 4-7 days) to avoid rapidly raising the pH and causing sudden nucleation of fines, clogging the reactor or being washed out. The gradual pH rise allowed particles to form with a range of sizes and at each harvest only the larger and heavier pellets were removed, while the finer particles were retained and constituted the seeds for further crystal growth in the subsequent test at slightly higher pH. Achieving a high P removal in the FBR lowered the scaling potential in the water, thus enabled active pH control in the stripping feed without causing clogging in the pipes or the packed tower. This demonstrated that precipitates removal is necessary as pre-treatment before pH-driven stripping in distillery digestate. pH increase was indeed essential to promote free ammonia formation, considering that the feed temperature was ca. 34°C at maximum. In the tested system the range of accessible temperatures was limited by the buffer tank material tolerance and the additional heating system's efficiency (electric heater within the buffer tank). In a full-scale scenario, these could be ameliorated by using more thermotolerant and isolated materials and heating the feed closer to the stripping tower by means of a heat exchanger, also enabling the exploitation of waste heat. The testing allowed to identify other potential improvements in the stripping unit design and operation to further increase the final product quality. To illustrate, the transport of water in the scrubber solution could be reduced by introducing a longer demister and optimising the gas-to-liquid ratio.

3.5 Discussion

This study demonstrated the technical feasibility of extracting and recovering N and P from digested distillery wastewater, by means of a fluidised bed reactor promoting struvite formation, and chemically/thermally induced stripping coupled to an acid scrubber yielding an ammonium sulphate solution. It was observed that varying pH (7.4-9.5) did not critically affect the high quality of the harvested mineral products. However, it did enable the size of the recovered product to be tuned allowing adjustment to end-user preferences. In addition, the feasibility of running the FBR at higher pH and SSR without clogging was demonstrated,

expanding its operation range compared to previous literature recommendations ($\text{SSR} \leq 5$)⁴⁰. Therefore, the selected operation pH can be a trade-off between P removal, reduction of scaling potential, and product characteristics, depending on the site-specific treatment needs. The removal performance can be further improved by optimising the Mg delivery to achieve higher Mg/P molar ratios^{22,40} and the crystals residence time⁴⁰ and by providing seeds for pellets growth. Recirculating fines settled in the clarifier back into the FBR could allow to increase not only their recovery, but also the overall removal.

While previous research²⁰ showed that struvite-like material could deposit on sludge granules within an upflow anaerobic sludge blanket digester treating digested distillery (58-60% removal at 35-53°C), this study highlighted the advantages of controlling struvite precipitation in a dedicated unit, benefiting its removal efficiency, purity, customisation, and management, decreasing the potential for downstream scaling. Moreover, this research presented P removal performances comparable with literature's benchmarks at lab and bench scale (Table 3-6). Despite operating at lower Mg supply and with a less efficient solids retention system, the design and operation tested in this study yielded final $\text{PO}_4\text{-P}$ levels aligned with previous lab studies (Table 3-6). The results suggested that operating the pilot at higher pH and lower Mg dosing not only enabled the ability to obtain a high P removal with reduced MgCl_2 consumption, but also contributed to the pH increase exploited downstream in the stripping unit. Moreover, the lower effluent [Mg] could further reduce the scaling potential in the water, e.g. reducing the formation of $\text{Mg}(\text{OH})_2$ precipitating at pH 11²².

Table 3-6. Struvite removal from distillery wastewater in different studies. Concentrations are in mg/L. i= influent, e= effluent. n.a. = not available/reported.

Study	21	15	23	6	This study
Reactor	Mixed reactor	Mixed vial	Mixed reactor	Air-bubbled reactor	FBR
Scale	Lab	Lab	Lab	Bench	Pilot
Operation	Batch	Batch	Batch	Continuous	Continuous
Feed	Digested thin stillage	Digested thin stillage	Synthetic digested distillery WW ^b	Digested pot ale	Digested distillery WW
[PO₄-P]_i	493 ± 8	508 ± 5 ^a	489	440	252 ± 14
[TAN]_i	478 ± 11	478 ± 11	800	1260	772 ± 176
[Mg]_i	31 ± 0	0.7 ± 0.0	n.a.	36	54 ± 3
Mg/P	1.4:1	1:1 ± 0.0	1.72:1	1.2:1	0.5-0.9:1
pH	6.9 ± 0.1	6.9	9.0	8.2-8.4	9.5 ± 0.0
Solids separation	Centrifuged (1800 x g for 10 mins)	Filtration (0.45 µm)	Filtration (0.45 µm)	n.a.	Settling
P removal	92%	81%	88-93%	92%	79 ± 2%
N removal	44%	44%	n.a.	23%	17 ± 7%
[PO₄-P]_e	39 ± 2	97 ± 2	59 - 34	35	53 ± 4
[TAN]_e	267 ± 13	267 ± 6	n.a.	970	560 ± 28
[Mg]_e	174 ± 2	113 ± 1	n.a.	n.a.	10 ± 1

^a = TP. ^b= containing phenols (9 g/L) and melanoidins.

In terms of process control and simulation, in this study Visual Minteq estimates seemed to slightly overquantify the P and Mg removal compared to the measured data. This contrasts the work of Kumari et al. who reported a general good agreement between struvite removal performances in synthetic distillery wastewaters and VM simulations, across a range of pH and Mg/P ratios, and accounting for Na, K, SO₄, Cl, phenols influence ²². Likewise, Çelen and colleagues found close alignment between Visual Minteq predictions and P removal from a swine effluent ³⁰. Such difference could be explained by different factors. It is posited that this highlights the need for effective control of fines to maximise recovery and minimise effluent concentrations that are achievable. In addition, it is suggested that the presence of organic compounds, such as

phenols and melanoidins, can play a role in the reduction of struvite formation by sequestering cations, such as Mg^{23,26}, and TAN. The analysis of the precipitates highlighted the co-formation of other Mg and P species was possible. However, the overall analysis demonstrated a predominance of struvite across the tested conditions. Interestingly, calcium seemed to exert a negligible effect on the precipitates composition, despite the Ca/Mg molar ratio was often being observed to be above 1:1, which is generally considered a major limitation to struvite formation⁴¹. Possibly, this could be influenced by Ca sequestration by organic compounds able to complex with cations (e.g. melanoidins, phenols) or interaction with other anions in solutions^{23,42}, slower formation kinetics of some Ca-precipitates such as hydroxyapatite, tricalcium phosphate³⁰, or too low Ca concentration²⁹. Moreover, previous literature reported that struvite formation and morphology were favoured by excess levels of ammonium²⁹, as opposed to amorphous calcium phosphate precipitates³¹.

Previous studies testing ammonia stripping from digested organic waste with packed towers often reported large removals ($\geq 80\%$), at high temperatures (e.g. $\geq 50^\circ\text{C}$)^{43,44}. The results of the current work suggested that the stripping process worked effectively, even at lower temperatures of between 20 and 34°C, generating a maximum removal efficiency of 71%. Extrapolation of the results at pH 9.4 to a temperature of 50°C would result in 90% of TAN as free ammonia, suitable for volatilisation, and in a decrease of FA solubility⁴³, although this should be validated with additional tests. However, increasing temperature, implies the risk of water carryover to the scrubber, potentially shortening batch time and diluting the product. Therefore, it could need to be combined with an improvement of mass transfer selectivity (e.g. application of ideal temperature-pressure combinations³⁵, optimised G/L ratio) and iterative re-acidification of the scrubber liquor to extend its life.

Overall, the study provided evidence suggesting high readiness level of the technologies, at this scale, with real wastewater, being 7 (FBR) and 6 (stripping and scrubbing). The integration of struvite precipitation and ammonia stripping in this pilot test demonstrated effective nutrient removal and recovery, with results

broadly aligned with those observed in comparable scale applications on other wastewaters (Table 3-7). Although nitrogen and phosphorus removals in this study were slightly lower than in previous larger-scale cases, the outcomes provided a basis for further optimization and testing at full scale.

Table 3-7. Selection of studies applying precipitation of P minerals and ammonia stripping to treat wastewater. WW= wastewater. Str= stripping, Pr= precipitation. Str & Pr = in parallel. Concentrations are in mg/L.

Study	45	18	46	47	48	This study
Feed	Vanadium process WW	Urine	Urine	Digested swine WW	Digestate liquor	Digested distillery WW
[TAN]; [P]	23,941; 18 ^a	4500; 309 ^b	4500 ^c ; 311 ^b	298; 115 ^a	≈ 1000 ^c ; n.a.	760; 256 ^b
Scale	Lab	Lab	Pilot - 50 L	Lab	Full	Demo
Removal TAN; P	99.6%; n.a.	85-99%, 99% ^a	91% ^c , 98% ^b	94%, 98% ^a	85-97% ^c , 80-97% ^a	76%; 80% ^b
Sequence	i) Str ii) Pr	i) Str & Pr	i) Pr ii) Str	i) Str & Pr	i) Pr ii) Str	i) Pr ii) Str

^a TP, ^b PO₄-P, ^c TKN.

3.6 Conclusions

This study demonstrated the viability of ammonia recovery via struvite precipitation followed by ammonia stripping and scrubbing from digested distillery wastewater at pilot scale. The results indicated that controlling pH, Mg dosing and temperature enabled high removal TAN (76%) and P (80%), recovered into high quality struvite pellets and ammonium sulphate solution. In particular, pH directly impacted the particle size of the recovered struvite and the stripping of NH₃, thus affecting also the concentration of the ammonium sulphate solution. The location and delivery of the pH adjustment was also shown to be critical to properly integrate the FBR to the stripper unit. Overall, the work demonstrated the viability of the combination of precipitation followed by stripping as an approach to engage in the use of resource recovery-orientated flowsheets for the treatment of distillery wastewater.

Appendix B

Table B-1. Recovery of nutrients from distillery effluents, often after anaerobic digestion. All studies were conducted at lab scale (except for land application field studies and ¹⁵). Default concentrations provided for TAN (total ammoniacal N) and PO₄-P, unless specified. WW= wastewater, TP= total P, RO and FO= reverse and forward osmosis filtration, n.a.= non-available/reported.

Ref	Wastewater	Concentration (g/L)	Method	Recovery of
49	Digested, centrifuged organic matter from wine distillery WW	28.1 (g N/kg), 2.6 (g P/kg)	Land application> biomass growth	Lettuce
50	Digested spent wash	0.68 (TAN), 0.13 (TP)	Land application> biomass growth	Groundnut
51	Digested spent wash	0.68 (TAN), 0.13 (TP)	Land application> biomass growth	Maize
52	Digested spent wash	0.68 (TAN), 0.13 (TP)	Land application> biomass growth	Groundnut
53	Digested distillery WW	≈ 0.5-1.0 (organic N), ≈ 0.05 (TAN), 0.04-0.08 (PO ₄ -P)	Biomass growth	Microalgae
54	Digested sugarcane bioethanol stillage	0.367 (TAN), 45 (PO ₄ -P)	Filtration> biomass growth	Plant biomass
55	Dewatered digestate (fed with stillage, corn maize, bovine slurry)	0.04-0.16 (N)	Biomass growth	Microalgae
56	Digested spent wash	1.923 (TAN), 0.002 (PO ₄ -P)	Biomass growth	Microalgae
57	Filtered, liquid digested sugarcane stillage	0.473 (TAN). 0.032 (PO ₄ -P)	Biomass growth	Microalgae
58	Rice wine distillery WW	0.48-0.95 (TAN). 0.88-1.44 (TP)	Biomass growth	Microalgae
59	Mixed broth bioethanol digested stillage	n.a.	Distillation> biomass growth	Microalgae, NH ₃ solution

Ref	Wastewater	Concentration (g/L)	Method	Recovery of
60	Shochu distillery WW	6.1 (TN). 0.8 (TP)	Biomass growth	Yeast
21	Digested corn bioethanol thin stillage	0.478 (N), ~0.493 (PO ₄ -P)	Precipitation> biomass growth	Struvite; microalgae
23	Synthetic digested distillery WW	0.8 (TAN), 0.5 (PO ₄ -P)	Precipitation	Struvite
20	Digested distillery WW	^a 0.076 (TAN), 0.236 (PO ₄ -P)	Precipitation	Struvite
61	Digested distillery WW	1.26 (TAN), 0.44 (PO ₄ -P)	Precipitation	Struvite
15	Filtered digested thin stillage	0.478 (TAN), 0.508 (TP)	Precipitation	Struvite
62	Digested vinasse	n.a.	Concentration (evaporation, RO, FO)	Nutrient-rich solution
63	Digested pot ale	n.a.	Simulation: stripping	NH ₃ solution

^a pre-digestion

Table B-2. Distillery wastewater (AnMBR feed) composition during two campaigns (n≥23). All concentrations are expressed in mg/L. COD= total COD, TSS= total suspended solids.

	Campaign I	Campaign II
pH	4.61 ± 0.51	4.38 ± 0.72
[TSS]	7700 ± 1381	7641 ± 2208
[COD]	39449 ± 3089	40697 ± 5500
[TAN]	38 ± 7	38 ± 5
[NO ₃ -N]	39 ± 13	52 ± 7
[PO ₄ - P]	361 ± 48	292 ± 37
[SO ₄]	177 ± 20	166 ± 35
[Cl]	312 ± 64	338 ± 31
[Fe]	1.7 ± 0.8	1.5 ± 0.4
[Cu]	2.0 ± 0.5	2.2 ± 0.7
[Mg]	113 ± 9	87 ± 25

Previous analyses showed that TAN constituted about $3.5 \pm 1.7\%$ of the total N concentration in the AnMBR feed.

Table B-3. Acidified AnMBR permeate composition during 2 macro periods of testing. All concentrations are expressed in mg/L (n≥13). Electrical conductivity EC is expressed in mS/cm.

	Campaign I	Campaign II
pH	6.73 ± 0.22	6.62 ± 0.16
EC	7.73 ± 0.31	7.55 ± 0.25
[TSS]	1.47 ± 1.74	1.83 ± 1.09
[COD]	1065 ± 338	885 ± 168
[TAN]	751 ± 113	772 ± 176
[NO ₃ -N]	6.5 ± 0.6	7.8 ± 2.4
[PO ₄ - P]	258 ± 47	252 ± 25
[SO ₄]	1161 ± 565	1268 ± 630
[Cl]	274 ± 36	327 ± 42
[Fe]	1.4 ± 0.3	1.6 ± 0.4
[Cu]	1.5 ± 0.3	1.8 ± 0.5
[Mg]	53 ± 35	57 ± 6
[Na]	-	359 ± 10
[Ca]	-	107 ± 7
[K]	-	704 ± 21

Previous analyses carried out in a different period showed that the AnMBR effluent had high total alkalinity levels (3265 ± 791 mg CaCO₃/L), similar to values reported in literature (3700 ± 300 mg CaCO₃/L) ⁶⁴. Previous analyses showed that the dissolved organic carbon (DOC) in the permeate was 274 mg/L.

Without pH correction, the AnMBR permeate pH was ≥ 7.5 , resulting in a struvite SSR ≥ 9 .

Table B-4. Operation feed pH values and related tests duration (days).

FBR		Stripping	
Duration (d)	pH	Duration (d)	pH
2	7.4±0.2	1	8.7±0.0
2	7.0	2	7.7±0.3
3	7.9±0.2	2	7.8±0.0
4	8.2±0.2	2	7.5±0.1
6	7.3±0.1	8	8.0±0.2
5	7.4±0.1	9	8.3±0.1
4	7.4±0.1	7	8.8±0.2
3	7.7±0.0	6	9.5±0.0
6	7.9±0.1	2	9.8±0.1
8	8.1±0.1	1	9.31
9	8.3±0.2	1	9.38
9	8.9±0.1		
8	9.5±0.0		

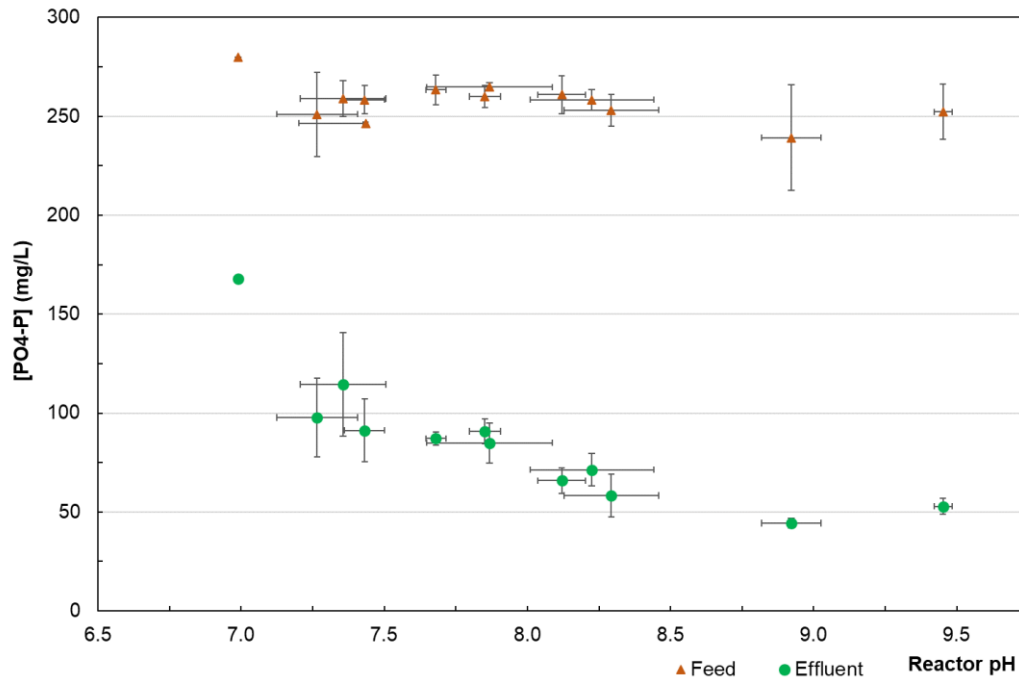


Figure B-1. Feed and effluent PO₄-P concentrations of the FBR, as function of the pH in the reactor's core section.

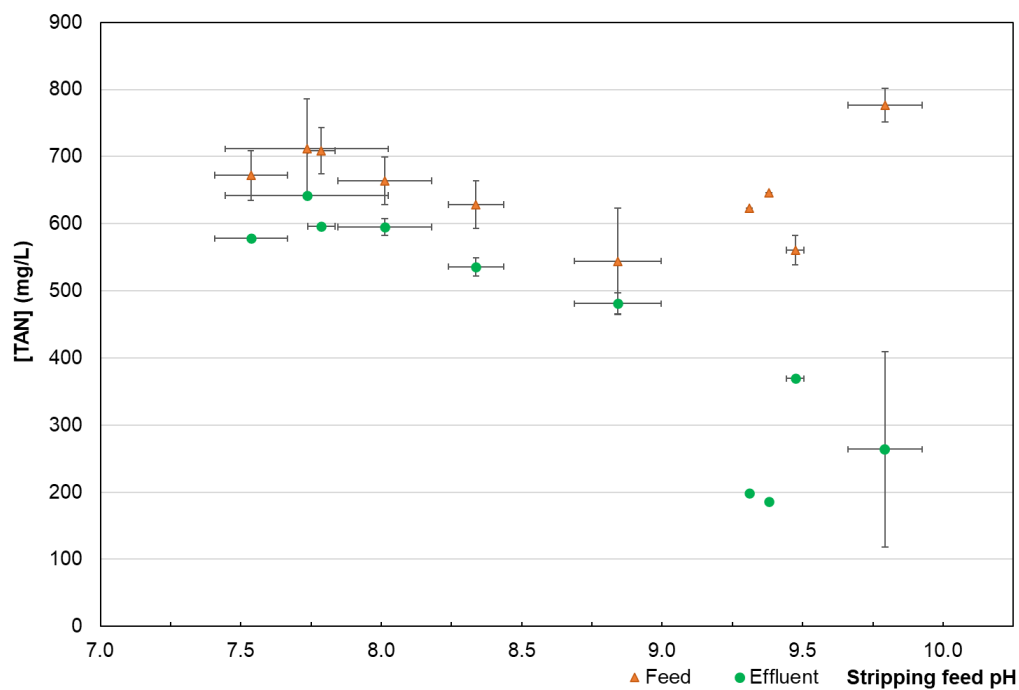


Figure B-2. Feed and effluent TAN concentrations of the stripping tower, as function of the feed pH.

The decrease of the feed TAN concentration observed along the pH increase (Figure B-2) can be ascribed to a change in the AnMBR permeate composition and to a larger removal in the FBR, favoured by the high pH.

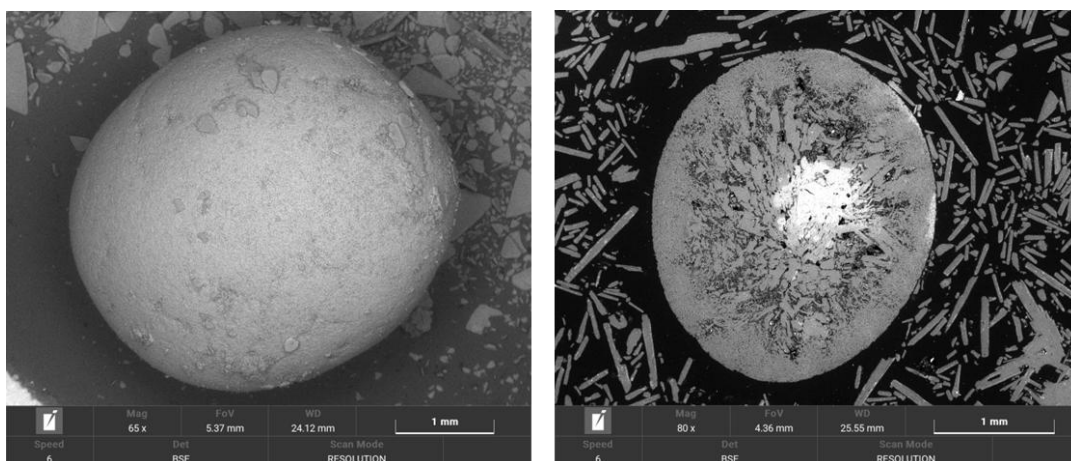


Figure B-3. External and cross-sectional surface of pellets harvested after FBR operation at pH 8.3.

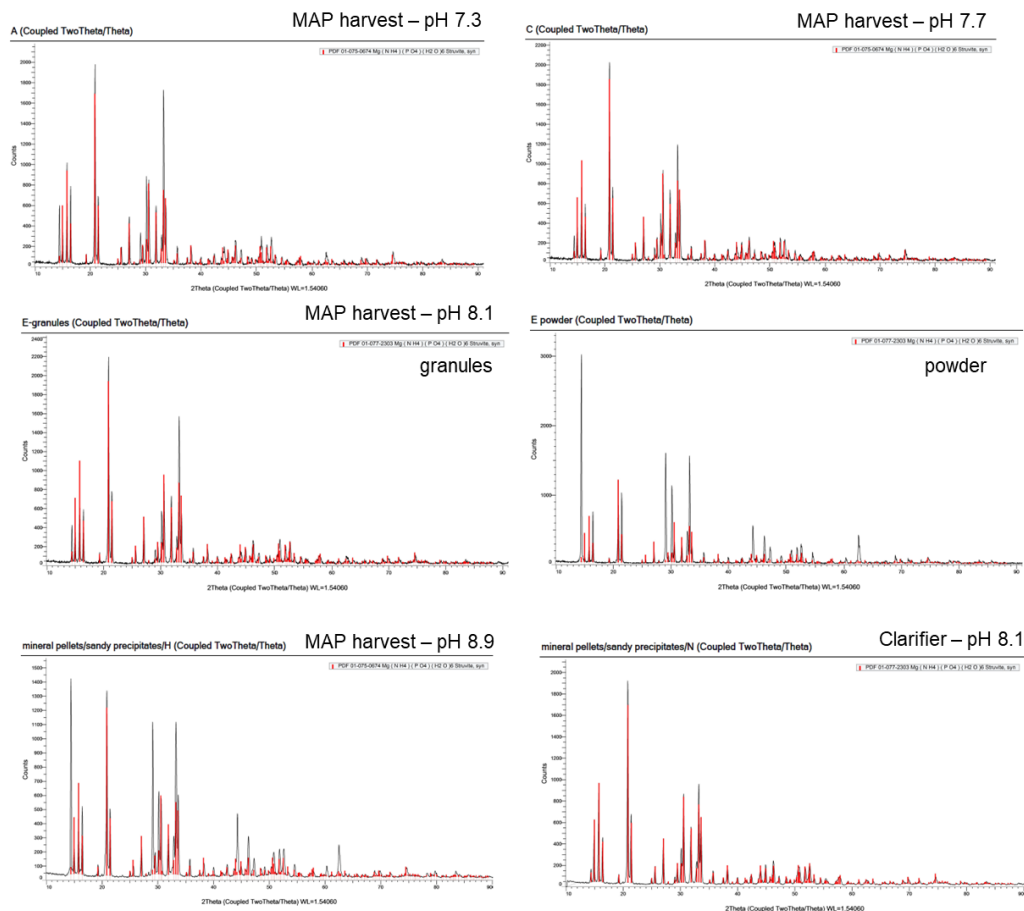


Figure B-4. XRD spectra of precipitates harvested in different batches (pH 7.3, 7.7, 8.1 8.9). The right-bottom spectrum refers to the crystals collected from the clarifier during FBR operation at pH 8.1. The library spectrum of ammonium struvite is shown in red.

Table B-5. Elemental content (% wt.) in precipitates harvested during different FBR operation pH, determined by SEM-EDS analyses. E= external surface, CS= cross section.

FBR core pH	Surface	Na	Al	Si	K	Ca
7.4 ± 0.1	E	0.2 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.7 ± 0.3	0.0 ± 0.0
7.4 ± 0.1	CS	0.0 ± 0.0	0.0 ± 0.0	1.3 ± 0.2	0.2 ± 0.0	0.1 ± 0.0
7.9 ± 0.1	E	0.8 ± 1.4	0.3 ± 0.5	0.0 ± 0.0	0.3 ± 0.1	0.2 ± 0.3
7.9 ± 0.1	CS	0.6 ± 0.4	0.0 ± 0.0	1.2 ± 1.0	0.4 ± 0.4	0.1 ± 0.0
8.1 ± 0.1	E	2.5 ± 2.5	0.0 ± 0.0	0.0 ± 0.0	1.0 ± 1.0	0.1 ± 0.1
8.1 ± 0.1	CS	0.2 ± 0.1	0.0 ± 0.0	2.0 ± 3.2	0.2 ± 0.1	0.1 ± 0.0
8.3 ± 0.2	E	1.1 ± 2.4	0.0 ± 0.0	0.0 ± 0.0	0.5 ± 0.3	0.1 ± 0.1
8.3 ± 0.2	CS	0.6 ± 1.3	0.0 ± 0.0	1.0 ± 0.5	0.3 ± 0.2	0.1 ± 0.1
8.9 ± 0.1	E	0.5 ± 0.2	0.0 ± 0.0	0.0 ± 0.0	0.2 ± 0.0	0.1 ± 0.0
8.9 ± 0.1	Clarifier	0.4 ± 0.2	0.0 ± 0.0	0.0 ± 0.0	0.3 ± 0.1	0.1 ± 0.0
9.5 ± 0.0	E	0.6 ± 0.3	0.0 ± 0.0	0.0 ± 0.0	0.4 ± 0.2	0.1 ± 0.0
9.5 ± 0.0	E	1.0 ± 0.7	0.0 ± 0.0	0.0 ± 0.0	0.4 ± 0.2	0.1 ± 0.0
9.5 ± 0.0	Clarifier	0.2 ± 0.0	0.0 ± 0.0	0.1 ± 0.1	0.3 ± 0.1	0.1 ± 0.0

Table B-6. Removal efficiencies (%) and effluent concentrations (mg/L) of the FBR based on measured data and Visual Minteq simulations (VM). For the simulations, the figures in bold indicate the output from scenarios where other species were allowed to precipitate, in addition to struvite.

	PO ₄ -P	TAN	Mg	[PO ₄ -P]	[TAN]	[Mg]
pH 9.45, 34.7°C						
Measured	79 ± 2%	17 ± 7%	81 ± 1%	53 ± 4	560 ± 28	10 ± 1
VM	86% 86%	15% 15%	94% 94%	35 35	580 580	3 3
pH 7.43, 34.6°C						
Measured	63 ± 8%	8 ± 2%	51%	91 ± 16	712 ± 74	27
VM	70% 76%	11% 10%	52% 42%	76 61	689 693	28 33

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Chapter 4

4 Impact of transition metals and humic acids on ammonia vacuum thermal stripping

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Abstract

Ammonia removal and recovery from wastewater have become critical steps for environmental preservation and circular economy. Separating ammonia from complex matrices, such as industrial effluents, can prove difficult due to interactions of ammonia with other species. This study assessed the impact of selected transition metals (Zn, Ni, Cu) and organic acidic compounds on ammonia removal via vacuum thermal stripping. The tested concentration and N/M molar ratio ranges encompassed values found in real effluents and integrated previous research. All the assessed species showed a detrimental effect on ammonia partitioning to the air phase, with zinc being the most impacting metal. It was proposed that such hindrance was caused by contributing factors, being the formation of metal ammine complexes, adsorption onto solids, mass transfer limitations, electrostatic attraction and chemical fixation. The combined effect of zinc and humic acids (HA) was non-additive, suggesting a limited potential mitigation of the individual impacts. The inhibition of ammonia removal was significant from molar ratios N/Zn $1.1 \pm 0.1:1$, N/Ni $20 \pm 1:1$, N/Cu $4.4 \pm 0.3:1$ and 636 mg HA/L, which restricts the range of effluents where this separation technology will be impaired, especially if applying thermally driven stripping.

Keywords: *ammonia; transition metals; humic acid; stripping; wastewater*

4.1 Introduction

Ammonia (NH_3) removal and recovery from wastewater have gained increasing interest driven by environmental concerns and, more recently, circular economy considerations ¹. Industrial effluents with large NH_3 loads are increasingly considered for potential extraction and valorisation (Chapter 2). Understanding ammonia speciation in liquid matrices is important to predict and control it, and to identify suitable recovery solutions. Ammonia form and partitioning are largely dependent on pH, temperature ^{2,3}, and pressure ^{4,5}. Moreover, the load of other chemical species (controlling the solution ionic strength) can influence its activity coefficient ^{6–8}. Indeed, ammonia can interact with a vast range of organic and inorganic components, including transition metals and complex organic compounds, often found in various amounts in N-rich industrial waters ⁹ (e.g. from metallurgy, mining, agro-industrial, tannery, fermentation sectors, respectively), whose impact on the recovery routes has been limitedly studied. This study focused specifically on effluents containing transition metals and acidic organic compounds.

Industries such as metallurgy, electroplating, printed circuit board (PCB) factories, tannery, explosives, timber production and processing of waste from metal extraction activities generate wastewaters containing significant loads of ammonia and various transition heavy metals such as Cu, Zn, Ni, Pb. Also distillery effluents contain copper, released from the stills, although at lower concentrations. Literature examples of wastewaters containing both ammonia (0.1-3.5 g N/L) and transition metals are illustrated in Appendix Table C-1. Reported total ammonia nitrogen to metal (M) molar ratios (mol:mol) in wastewater can range from 4224:1 (N/Ni in rare-earth material process ¹⁰) to 54:1 (N/Ni, heavy industry ¹¹), 8-23:1 (N/Cu, industrial park and PCB ¹²), and 6-23:1 (N/Zn, zinc plating ¹³).

Transition metals can bind unionised ammonia as a ligand (L) forming ammine complexes ($\text{M}(\text{NH}_3)_n$) by substitution of the water molecules in their hydration shell through stepwise reaction series ¹⁴. These species are reportedly stable in solution ¹², a measure of which is provided by the cumulative formation (K) and

stepwise stability (k) constants (Eq. 4-1 to Eq. 4-3) ¹⁴. The greater the constant is, the higher the stability of the related complex is (Table 4-1, further details in Appendix Table C-2).



$$K_n = \frac{[ML_n]}{[M][L]^n} \quad \text{Eq. 4-2}$$

$$\log k_n = \log K_n - \log K_{n-1} \quad \text{Eq. 4-3}$$

Where, n is the coordination number expressing the number of ligand molecules coordinated by the central metal cation ¹⁴. At increasing pH, more free NH_3 molecules become available as ligands ¹⁵ and n increases ¹². The metal concentration, the N/M ratio and the presence of other chemical species can also influence the equilibrium ^{16,17}.

Table 4-1. Cumulative formation constants of metal ammine complexes (20-25°C, Ionic Strength=0-0.1) ¹⁴.

Metal	Log K_1	Log K_2	Log K_3	Log K_4	Log K_5	Log K_6
Cd	2.65	4.75	6.19	7.12	6.80	5.14
Co (I)	2.11	3.74	4.79	5.55	5.73	5.11
Co (II)	6.7	14.0	20.1	25.7	30.8	35.2
Cu (I)	5.93	10.86	-	-	-	-
Cu (II)	4.31	7.98	11.02	13.32	12.86	-
Fe (II)	1.4	2.2	-	-	-	-
Mn (II)	0.8	1.3	-	-	-	-
Hg (II)	8.8	17.5	18.5	19.28	-	-
Ni	2.80	5.04	6.77	7.96	8.71	8.74
Pt (II)	-	-	-	-	-	35.3
Ag (I)	3.24	7.05	-	-	-	-
Zn	2.37	4.81	7.31	9.46	-	-

The complexation of metals with NH_3 impacts the speciation of both ¹², thus possibly affecting also separation techniques, such as precipitation ¹⁶ and stripping ¹⁸. A preferred method for ammonia separation from concentrated streams is stripping ¹⁹, although reports of its use with metal-ammonia rich

wastewaters are limited in literature. Min *et al.* ¹¹, Mirbagheri and Hosseini ²⁰, Morikubo *et al.* ¹³ applied air stripping to NH₃-rich effluents containing high loads of Ni, Cu, Zn, respectively, and reported limited impairment of the process at the tested conditions (e.g. pH>10.5-11). Yet, further insights on the on the critical N/M ratios and the mechanisms driving a detrimental effect are needed to understand the viability and performance of ammonia stripping from waters containing high levels of transition metals.

Similarly, selected categories of organic compounds can also interfere with ammonia partitioning. Several models describing ammonia speciation in manure and digestate included the impact of generic organic matter ⁸, solids ²¹ and dissolved organic carbon ²². Recalcitrant acidic organics can be found in a range of wastewaters, such as melanoidins in distillery effluents ²³, humic acids in food processing and tannery wastewaters ²⁴, agro-industrial digestates ²⁵, but also leachate ²⁶, with Appendix Table C-3 providing reference figures for concentrations and wastewater types. Humic substances have been used as model compound for DOM²⁷ and have similar chemical behaviour as other recalcitrant species, such as melanoidins ²³. While studies on the ammonia sorption capacity of particulate organics are available ^{4,28}, literature on ammonia interaction with dissolved organic matter (DOM) is sparse ^{6,29}.

Humic compounds can bind total ammonium nitrogen (TAN) via chemical fixation and cation exchange ³⁰, yet the extent of how this can affect stripping has not been explored. Furthermore, they can bind metals as well ³¹, thus the combination of these factors on ammonia volatilisation should be investigated ³². This suggested a gap in knowledge on the interactions between ammonia and humic acids, model compound for dissolved organic matter with acidic behaviour, and how these can impact its availability for recovery via stripping.

In this study, it was hypothesized that transition metals and humic acids, as a proxy for recalcitrant organic acidic compounds, can affect ammonia volatilisation during stripping, above certain ratios and concentrations. The aim is therefore to determine and quantify their effects on the mechanisms driving ammonia partitioning to gas in N-rich effluents. These contributions to knowledge advance

the understanding in research areas sparsely explored, which help to determine the performance of stripping in a range of wastewaters and identify suitable recovery technologies or mitigation measures.

4.2 Materials and Method

4.2.1 Synthetic solutions

The experiments were performed with synthetic solutions to study the impact of individual components. Zinc, nickel, and copper were selected as transition metals (M), given their abundance in industrial effluents, their high formation constants and their different maximum coordination numbers (details available in Appendix Table C-2). A range of nitrogen to metal (N/M) molar ratios (mol:mol) were tested, aiming to encompass ratios reported in literature for industrial effluents (examples in Appendix Table C-1). Likewise, the tested range of humic acids (HA) concentrations was comparable to levels found in different effluents such as industrial wastewaters, but also digestate, leachate (e.g. 40-7000 mg/L, with further examples of comparable compounds in Appendix Table C-3).

Ammonium hydroxide (extra pure, 25% sol. in water) was diluted in ultrapure (UP) water to prepare a control solution of 1 g TAN/L. Copper(II) sulfate pentahydrate (99+%, for analysis), nickel sulfate hexahydrate (99%, for analysis) and zinc sulfate heptahydrate (99.5%, for analysis) were dissolved in UP water to prepare stock solutions (0.25– 30 g M/L). The chemicals were all sourced from Thermo Scientific (UK). Humic acids (Sigma-Aldrich, Dorset, UK) were slowly dissolved in 0.1 M NaOH ³³ as they are more soluble in alkaline conditions ³¹, and then diluted with UP water (overall 0.05 M NaOH), to prepare stock solutions (1-2.5 g HA/L).

Known aliquots of metal stock solutions were diluted with UP water and then spiked with ammonium hydroxide, aiming to obtain specific N/M in 1 and 0.5 L solutions (4,000:1 – 1:1). For Cu, a limited range of molar ratios was tested (70:1 – 1:1), based on preliminary tests (data not reported). Known aliquots of HA stock solution were diluted with UP water and then spiked with ammonium hydroxide, aiming to obtain specific concentrations, in 1 and 0.5 L solutions (ca 25-1000 mg

HA/L). To test the combined effects of HA and a selected transition metal, the stock solutions were dosed to obtain specific [HA] and N/M (at highest and lowest significant levels).

Each prepared solution was used fresh to run a maximum of one or two replicates of the same condition. The metal and TAN concentrations were measured and used to determine the actual molar ratios (details provided in Appendix Table C-4).

Sodium hydroxide (extra pure, 50 wt% in water) (Thermo Scientific, USA) and sulphuric acid (EMSURE®, 98%) (Merck, Darmstadt, Germany) were diluted with UP water to prepare pH correcting solutions (0.02-4 M NaOH; 0.01-3 M H₂SO₄) and HA dissolution media (0.05 M NaOH).

4.2.2 Batch experiments

Vacuum thermal stripping (VTS) was performed in batch with a rotary evaporator (R-100). The set up was completed by a vacuum pump (V-100), a pressure controller with digital interface (I-100), a heating bath with digital display (B-100), 1 L heating flasks (feed), 0.5 L receiving flasks (condensate), a vertical condenser connected to a cooler (SRC4 Stuart) recirculating anti-freeze liquid (T set = 1°C). All these products were sourced from Buchi Ltd (Oldham, UK), except for the cooler (Keison Products, Chelmsford, UK).

Operating conditions were selected based on preliminary tests and literature^{18,34}. The heating bath temperature was set to 67°C (actual feed temperature was ca 65°C) and stabilised for 10 minutes at 220 mbar, at ca. 113 rpm. Subsequently, the pressure was reduced to 203 mbar for 60 minutes. The vacuum pump was operated with 5 mbar hysteresis. pH was adjusted to 10.5 in the feed prior the batch start, by dosing 3 M H₂SO₄ or 4 M NaOH. The feed volume was measured at the start (400 mL) and the end of the run. The temperature and pH of the feed were also measured at the end of each test. The condensate collected in the receiving flask and on the vertical condenser was recovered, its volume and pH were measured. Samples of the feed at the starts (Fs), at the end (Fe) and condensate (C) were taken and processed for analyses.

Tests were performed at least in triplicate (except for one condition). Labware was cleaned in an acid bath (HNO_3 7% v/v in UP water) and rinsed with UP water. For the VTS tests with HA, preliminary tests were carried out to determine the impact of interaction time on ammonia N sequestration by HA (total and filtered fractions, 0.45 μm) in feed at pH 9 and 10.5 (data not shown). Even after 150-270 minutes, the TAN concentration in both fractions was still comparable to the initial content in the fresh solution, with minimum differences. Thus, VTS tests were realised on freshly prepared HA- NH_3 solutions.

Metals and HA precipitates formed in solution were recovered by vacuum filtration with Whatman 0.45 μm retention cellulose nitrate membrane filters (Fisher Scientific, Loughborough, UK). The separated precipitates were air-dried on the filters for at least 24 hours under a fume hood, before being stored in seal tight vials for analyses.

4.2.3 Analytical methods

pH was measured with pH meters 3520 and 3540 (Jenway, Stone, UK). Total concentrations of chemical species were measured, except for selected samples which were also filtered with Millipore 0.45 μm retention membrane (mixed cellulose ester) syringe filters, to determine dissolved concentrations (Fisher Scientific, Loughborough, UK). Samples were stored at 4°C.

TAN concentration was measured with standard ammonium cell tests (VWR International Ltd., Poole, UK) spectrophotometry (Spectroquant Nova 60, Merck-Millipore, Darmstadt, Germany. Spectroquant Pharo 300, Merck-Millipore, Darmstadt, Germany). [TAN] was determined in fresh samples of the feed before and after the run and of condensate, after acidification with concentrated H_2SO_4 (EMSURE®, 98%) (Merck, Darmstadt, Germany) to prevent ammonia losses. For the HA tests, samples were not acidified with H_2SO_4 , to avoid changes in the HA aggregation properties, and were promptly analysed. Samples underwent dilutions prior to analyses if required. With HA solutions, preliminary tests ruled out significant interference from the organic solution colours on the [TAN] determination method.

Cu, Zn, Ni concentrations were determined with PerkinElmer's NexION® 350 Inductively Coupled Plasma Mass spectrometer (ICP-MS), after sample acidification with HNO₃ (Normatom®, 67-69%, for trace metal analysis, VWR International Ltd., Poole, UK) and dilution with UP water. The metals standard solutions were produced by dilution of 1000 ppm stock solutions with ultra-pure water.

HA quantification was realised with UV-vis spectroscopy, using a 6850 UV/Vis Spectrophotometer (Jenway, Stone, UK) equipped with two 1-cm quartz cells. For each sample, an absorbance spectrum (200-900 nm) was recorded and the concentration was determined from the absorbance at 254 nm³⁵. This was based on calibration curves of standard HA solutions, obtained by stock's (1 g/L) serial dilutions with UP water to the range of 5-200 mg/L, where pH was adjusted to 8, 8.5, 10.5 with 0.02-0.1 M H₂SO₄ and 0.02 M NaOH. The following relations were used: for Fs, [HA] = Abs : 0.0316 (calibration at pH 10.5, R²=0.9971); for Fe, [HA] = Abs : 0.0315 (calibration at pH 8-8.5, R²=0.9984). Assuming a simplified formula C₉H₉NO₆ (molecular weight 227 g/mol)³⁶, the equivalent of HA concentration can be estimated as total organic carbon (TOC) and COD concentration based on the conversion factors 0.476 g TOC/g HA (comparable with literature, 0.483³⁵) and 1.06 g COD/g HA, respectively.

The filtered, air-dried precipitates were characterised with scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDS) (Tescan Vega 4, large chamber, Kohoutovice, Czech Republic) to obtain images and their elemental composition. The samples were imaged in Low Vacuum mode using Back Scatter Electrons. A small amount of powder was adhered to a double-sided carbon tab on an SEM stub. For the EDS, an INCA x-act EDS detector and AZtec software were used. X-ray diffraction (XRD) spectra were obtained, using a SIEMENS D5005 diffractometer and Diffrac Eva software to analyse the sample powder (ground and compressed on an aluminium frame) (scan time 1 h, scan angles 10°2θ to 90°2θ).

4.2.4 Evaluation of the impact of selected species on ammonia volatilisation

The ammonia transfer during the VTS process can be described by the Lewis-Whittman model, expressing Fick's law of diffusion in liquid/gas phases (Eq. 4-4)³⁷. The volumetric mass transfer coefficient ($K_{ov}a$) is affected by agitation, gas flow rate (for air stripping), temperature³⁸ and, if these conditions are not changed, it can be assumed to be constant. Hence, the ammonia transfer rate from liquid to gas phase is affected by the fraction of free ammonia (FA). At the tested conditions (pH 10.5, 65°C), 99.7% of TAN is present as NH_3 (details in Appendix Figure C-1, Eq. C-1, Eq. C-4), but it is hypothesized that its interactions with transition metals and humic acids could reduce the FA fraction able to volatilise (Eq. 4-5). The transfer of ammonia is expressed by Eq. 4-4³⁷, assuming the resistance is all on the liquid side³⁹.

$$\frac{dC}{dt} = K_L a \cdot (C - C_s) \quad \text{Eq. 4-4}$$

$$C_{strippable} = C \cdot \theta \quad \text{Eq. 4-5}$$

Where, $\frac{dC}{dt}$ is the rate of ammonia mass transfer (mg/L h), K_{ov} the overall ammonia mass transfer coefficient (m/h), a is the specific interface area (area available for mass transfer per unit volume, 1/m), C_s the ammonia concentration in the feed at air-gas interface in equilibrium with the gas phase (mg/L), C is the bulk free ammonia concentration ([FA]) in the feed at time t (mg/L). θ is the coefficient of strippable ammonia (-), estimated for the VTS tests (further details available in Appendix C). The TAN removal efficiency η (%) and the impact I_i (%) on the removal efficiency at condition i , where calculated with Eq. 4-6 and Eq. 4-7.

$$\eta = \frac{[TAN]_{F_s} V_{F_s} - [TAN]_{F_e} V_{F_e}}{[TAN]_{F_s} V_{F_s}} \times 100\% \quad \text{Eq. 4-6}$$

$$I_i = \eta \text{ change} = \frac{\eta_i - \eta_{control}}{\eta_{control}} \times 100\% \quad \text{Eq. 4-7}$$

Where, η_i and $\eta_{control}$ are the ammonia removal efficiencies (%) at condition i and in the control. $[TAN]_{F_s}$, $[TAN]_{F_e}$ are feed concentration at the run's start and end (mg/L), V_{F_s} , V_{F_e} are the feed volume at the start and end, respectively (L).

4.2.5 Chemical equilibrium software simulation

A chemical equilibria model software, Visual Minteq (version 3.1) was used to estimate the speciation of ammonia and metals in the synthetic solutions. This was done to compare the simulations (valid within limited ionic strengths) with the experimental observations, providing further insights on the reactions taking place. Input data for the software were actual measurements from the tests: temperature, pH, [TAN], [M]. [Na] and [SO₄] were estimated based on the pH adjustment chemicals dosing. Simulations were run for selected N/M ratios conditions: N/Zn 41±1, 3.4±0.0, 1.1±0.1; N/Ni 40±3, 4.5±0.1, 0.8±0.0; N/Cu 41±5, 4.4±0.3, 0.9±0.0.

4.2.6 Statistical analyses

The data is reported as mean values and corresponding standard deviations. The different conditions, i.e. N/M molar ratios and [HA], were considered as groups for analysis of variance with the Levene test. Non-parametric Kruskal Wallis H tests and Post Hoc multi-comparisons tests were used to evaluate significant differences between η medians of the groups. Differences were considered significant with p-value <0.05 (95% confidence). Statistical tests were carried out with Minitab Statistical software (version 21.2 for Windows).

4.3 Results

4.3.1 VTS performance

In all the tested metal-ammonia systems, the ammonia removal efficiency and flux followed a declining trend with an increase in the metal content (decreasing N/M molar ratio) (Figure 4-1 a, b, c). At the higher N/M ratios, the ammonia flux to the gas phase was influenced by the TAN concentration in the feed. In contrast, below a certain threshold ratio, the flux decoupled from the trend of the feed. Specifically, from a ratio of 41:1±1:1 (104±4 mg Zn/L) for Zn, at 87:1±19:1 (48±12

mg Ni/L) and even more intensively at 20:1±1:1 (187±7 mg Ni/L) for Ni, and from 74:1±11:1 (59±7 mg Cu/L) for Cu. Moreover, significant differences with the control removal efficiency were detected from N/Zn = 1.1:1±0.1:1 (p=0.01), N/Ni = 20:1±1:1 (p=0.04), and N/Cu = 4.4:1±0.3:1 (p=0.01). The larger standard deviations were attributed to analytical errors in the TAN concentration quantification.

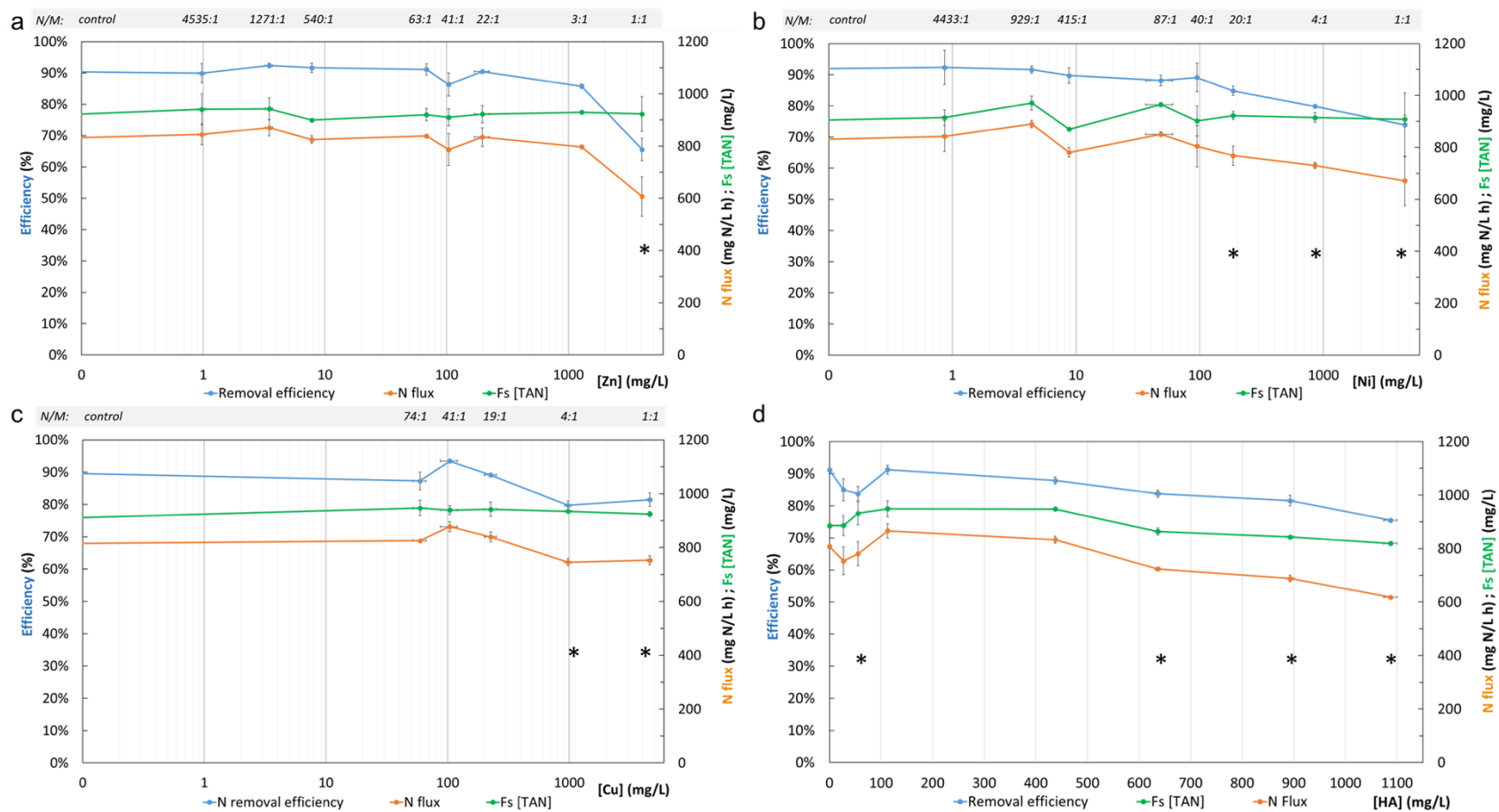


Figure 4-1. Effect of feed TAN and tested component concentrations on TAN removal efficiency and flux (Avg $\pm$ StDev, n=2-4): a) [Zn], b) [Ni], c) [Cu], d) [HA]. Above each metal plot, the actual N/M metal ratios are shown. * indicates a significant difference with the control (p<0.05).

Similar results were observed with humic acid such that a significant impact was observed once the concentration exceeded 636 ± 5 mg HA/L, as the N removal started to deviate from the control's performance, reaching $84 \pm 1\%$ ($p=0.04$) and then $76 \pm 0\%$ at 1087 ± 13 mg HA/L ($p=0.001$). Complementary analyses showed that, along the HA concentration increment, the mass of humic particles larger than $0.45 \mu\text{m}$ in the feed increased (2-7% total HA mass). The critical value corresponded to 303 mg TOC/L and 674 mg COD/L. At humic acids levels below 110 mg/L, the observed fluctuations in removal efficiency and mass flux, compared to the control, were attributed to measurement variability, reflected in the greater standard deviations compared to the other points. These could have originated from slight inconsistencies in TAN quantification before and after stripping, affecting deviations in the calculated removal efficiency and flux. From > 636 mg HA/L, the observed decline was constantly significantly different from the control, suggesting a direct inhibition.

Further analysis was conducted on the potential synergistic or antagonistic impacts of metals and humic acids in combination. Zinc was selected as it had shown the greatest reduction of ammonia volatilisation in the initial trials. Two selected sets of N:Zn and HA concentration were tested: Low with $41:1 \pm 4:1$ and ca 600 mg/L and High with $1.1:1 \pm 0.1:1$ and ca 1000 mg/L. Under the High conditions, the co-presence of humic acid increased the ammonia volatilisation efficiency from $66 \pm 4\%$ to $74 \pm 1\%$, but was still significantly different from the control ($p=0.003$). In the case of the Low condition, no significant difference was observed with the control ($p=0.333$) (Figure 4-2). In both cases, the combined conditions' effects were not significantly different from the individual impacts.

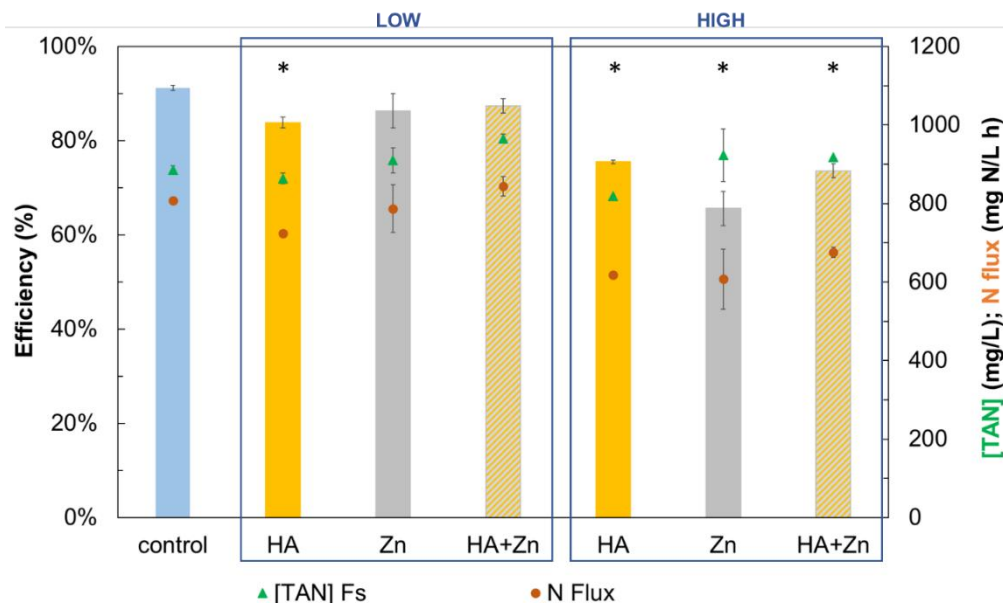


Figure 4-2. TAN removal efficiency (bars), flux and feed TAN concentrations at the different “High” and “Low” conditions (Avg $\pm$ StDev, n=2-3). * indicates a significant difference with the control (p<0.05).

Comparison of the different metals revealed the lowest impact on TAN removal was observed for copper followed by nickel and then zinc (Figure 4-3).

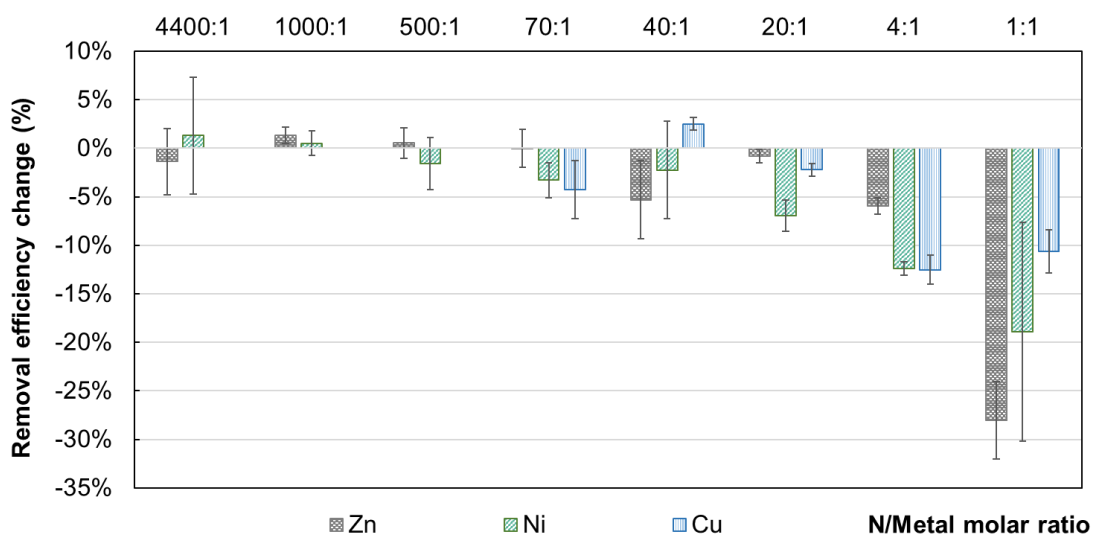


Figure 4-3. Impact of the N/M molar ratios on the TAN removal efficiency (M=Zn, Ni, Cu. Avg $\pm$ StDev, n=2-4). The molar ratios shown are the targeted values and the actual ones are presented in Appendix Table C-4.

To illustrate, at a mole ratio of 1:1 the removal efficiency change from the control was $28 \pm 4\%$, $19 \pm 11\%$ and $11 \pm 2\%$ for Zn, Ni and Cu, respectively. Nickel was expected to exert the largest impact due its high sequestration ability via the formation of complexes holding up to six NH_3 . Changes in the removal efficiency started following a consistent trend with the mole ratio from different threshold values for the three metals. Nickel had a relatively steady decrease from a ratio of 70:1, zinc from 4:1 and copper from 20:1, then stabilising around 4:1. The observed differences are distinguishable also in relation to the coefficients of strippable ammonia (θ) (Figure 4-4).

The estimated coefficient θ indicated that metal could reduce the fraction of available ammonia down to 0.7 at high concentrations. Overall, declines in ammonia volatilisation were recorded from N/M molar ratios of 70:1-20:1 and the metals' impact became significant only at low ratios. This is congruent with previous trials which showed no inhibitory impacts of nickel at a mole ratio of 54:1 when air stripping ammonia at 60°C and pH 11¹¹. In contrast to the current work, Morikubo *et al.* observed no significant impact when air stripping ammonia from a solution with a low mole ratio of 11:1 and a low temperature of 23°C and pH 9¹³. However, they did observe a slight increase in removal at pH 10 and 11, compared to the control, which they attributed to the formation of Zn adsorbing precipitates¹³.

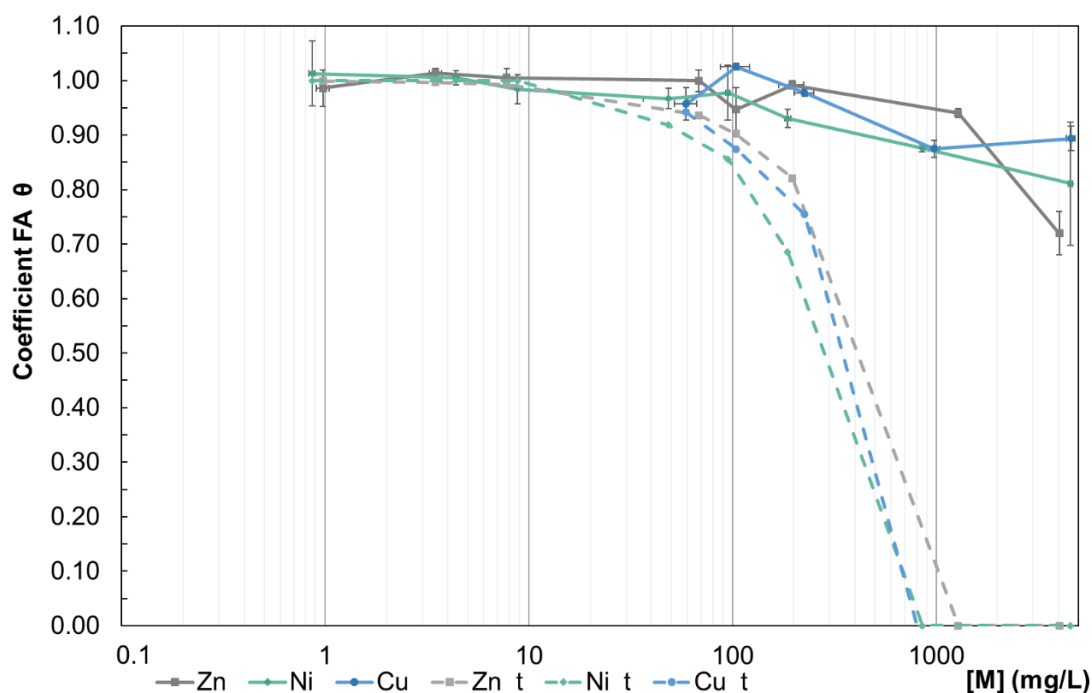


Figure 4-4. Effect of the metal (M) concentration on the coefficient of strippable ammonia, in the metal-ammonia systems, during VTS, solid lines (M=Zn, Ni, Cu. Avg $\pm$ StDev, n=2-4). Dashed lines show hypothetical worst case effect, if all metal atoms were involved in forming ammine complexes.

4.3.2 Precipitates characterisation

Precipitates were observed in solution during the VTS tests, especially at high metal concentrations. Elemental composition (% mass) determined over homogenous areas of the recovered samples was used to estimate their mass ratios of metal to oxygen (Table 4-2). Sulphur content was limited in most samples (max 3%). The observed M:O ratio before and after vacuum thermal stripping can be used to estimate the predominant forms through approximation with likely products. To illustrate for zinc, the Zn:O ratio before stripping was 2.1 ± 0.1 . Comparing this to theoretical values of 4.1:1, 2.0:1 and 1.6:1 for ZnO, Zn(OH)₂, Zn₄(OH)₆SO₄, respectively, can suggest that the majority of the precipitates were in the hydroxide form. After VTS, the ratio became inconsistent (ranging 1.7-3.4) suggesting that a mixture of solids existed including ZnO. Previous literature has reported that ZnO can form by basifying a zinc solution and by hydrothermal treatment of amorphous zinc hydroxide (e.g. 60-170°C)

causing its crystallisation and dehydration to ZnO ^{40,41}. Heating the precipitates suspensions between 60-70°C can yield a mixture of ZnO and ϵ -Zn(OH)₂ ⁴⁰, with other reports suggesting this can occur at even lower temperatures of 40°C ⁴². Morphological analyses of the precipitates after VTS showed a mixture of flower-like particles and disc-shaped and rods-like units (Figure 4-5 a), that could align to a combination of ZnO and Zn(OH)₂ ^{43,44}. XRD analyses detected both ZnO and Zn(OH)₂ in the crystalline phase before and after VTS, with the latter case showing contamination from other crystals and possibly amorphous phase (spectra available in Appendix Figure C-2 a, b).

Table 4-2. Content (%wt) and ratio of transition metal to oxygen in the precipitates formed in solution before and during the VTS tests, at the selected conditions (N/Zn mixed 3:1 - 1:1, N/Ni 1:1, N/Cu 4:1 and 1:1). Average and standard deviations are shown when n=4.

N/M	Before VTS			After VTS		
	Zn	O	Zn/O	Zn	O	Zn/O
3:1 – 1:1	58±2%	27±1%	2.1±0.1	62±11%	27±6%	2.4±0.9
	Ni	O	Ni/O	Ni	O	Ni/O
1:1	43, 29%	51, 64%	1.2, 2.2	54±2%	37±3%	1.5±0.1
	Cu	O	Cu/O	Cu	O	Cu/O
4:1	60±3%	36±2%	1.7±0.2	62±1%	35±1%	1.8±0.1
1:1	56±5%	34±1%	1.7±0.2	54, 54%	35, 36%	1.6, 1.5

In the case of nickel, the reverse happened whereby VTS reduced the level of variation observed in the Ni:O ratio from between 1.2:1-2.2:1 before VTS to 1.3:1-1.6:1 after VTS (Table 4-2). Comparison to theoretical ratios pointed towards species such as Ni(OH)₂, Ni₂O₃ and Ni₄(OH)₆SO₄ which have Ni:O mole ratios of 1.8:1, 1.6:1 and 1.5:1, respectively, compared to 3.7:1 for NiO. This is supported by previous literature reporting that Ni(OH)₂ was obtained by heating alkaline metal solutions to comparable temperatures e.g. 55-90°C ⁴⁵. Morphological analyses of the precipitates revealed assembled flake/platelet-like units, potentially consistent with Ni(OH)₂ ⁴⁶ (Figure 4-5b).

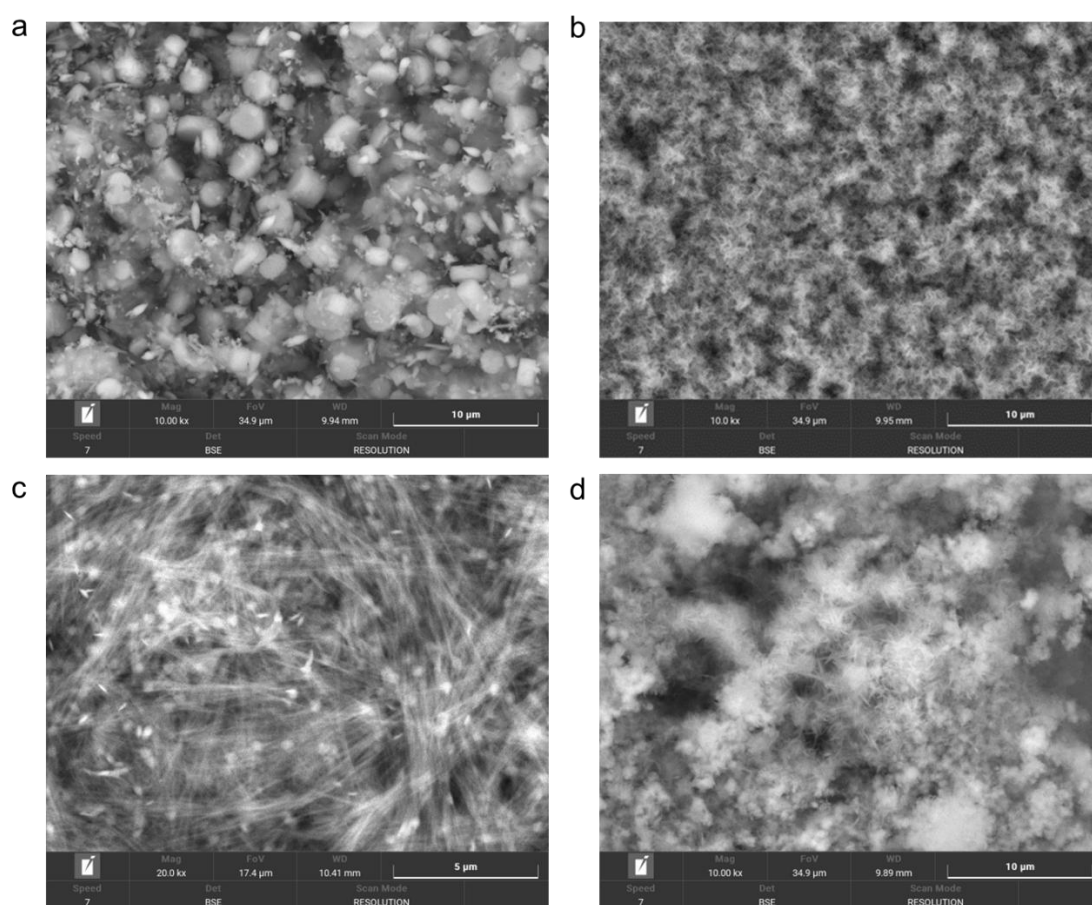


Figure 4-5. SEM images of the precipitates formed in the metal-ammonia synthetic solutions during VTS tests. a= N/Zn 3-1:1, b= N/Ni 1:1, c= N/Cu 4:1, d= N/Cu 1:1.

In the case of copper, the mole ratio remained reasonably stable between 1.6:1 and 1.8:1 in most cases (Table 4-2). This compared well with $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$, $\text{Cu}_3(\text{OH})_4\text{SO}_4$ and $\text{Cu}(\text{OH})_2$, whose theoretical ratios are 1.6:1, 1.5:1, 2.0:1, respectively, whereas CuO has Cu/O ratio 4:1. At N/Cu 4:1, a change in precipitates' colour was observed between samples in fresh solution (blue) and the precipitates after heating (brown-black) (details in Appendix Figure C-3). Conversely, at N/Cu 1:1, the precipitates in the stripped solution were pale blue, which could be associated to $\text{Cu}(\text{OH})_2$ ⁴⁷. XRD analyses showed a predominance of $\text{Cu}(\text{OH})_2$ in the crystalline phase, especially in the precipitates samples before stripping. After VTS, also black-coloured crystals, CuO and Cu_4O_3 (paramelaconite), were detected, together with a noise increase, possibly associated with amorphous phase (spectra available in Appendix Figure C-2, c-

f). Moreover, the precipitates morphology was characterised by wires- and flake-like structures (Figure 4-5 c, d), which can be related to $\text{Cu}(\text{OH})_2$ ⁴⁷.

4.3.3 Visual Minteq simulations

Visual Minteq (VM) simulations were generated for TAN solutions with N/M ratios of 40:1, 3-4:1 and 1:1 for pre and post VTS solutions (Figure 4-6 for zinc, Figure 4-7 for copper and nickel). At higher temperature and lower metal concentrations, the fraction of free ammonia (FA) was higher. To illustrate, at N/M 1:1 and 25°C, the proportion of the TAN as FA were 16% (Ni) < 24% (Cu) < 42% (Zn), whereas at 65°C they became 33% (Ni) < 70% (Zn) < 76% (Cu). The increase in temperature affected the FA (details available in Appendix Eq. C-5), also due to the thermo-sensitivity of the metal ammine complexes ⁴⁸. Consequently, the proportion of the TAN as $\text{Cu}(\text{NH}_3)_4$ dropped from 53% to 16% due to the temperature change (N/M 1:1). In comparison, the proportion of TAN as $\text{Zn}(\text{NH}_3)_4$ only dropped from 42% to 20%. This suggested that copper ammine complexes were more affected by temperature. Once released, the metal became involved in the formation of hydroxide. As expected, the FA fraction declined as the metal concentration increased, due to the formation of more metal ammine complexes. At the same time, the metal fraction associated with FA decreased with increasing metal concentration, as other species progressively formed, e.g. $\text{Cu}_3(\text{OH})_4^{2+}$, $\text{Ni}(\text{OH})_3^-$, $\text{Ni}(\text{OH})_{2(\text{aq})}$, $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_{2(\text{aq})}$.

Interestingly, at 65°C, the most abundant aqueous Zn-containing species was always the hydroxide, with a stable 78-76%. Conversely, along [Cu] increase the fraction of $\text{Cu}(\text{OH})_2$ dropped (down to 16% of total Cu, at N/Cu 1:1), whereas $\text{Cu}_3(\text{OH})_4^{+2}$ was progressively formed (up to 67% in N/Cu 1:1). In the nickel-ammonia system, both $\text{Ni}(\text{OH})_3^-$ and $\text{Ni}(\text{OH})_2$ formations were promoted at growing [Ni], while the fraction of nickel in $\text{Ni}(\text{OH})_2$ was relatively low (19-32%) compared to zinc. Moreover, with rising [Ni], the TAN fraction participating in the high-*n* ligand complexes eventually declined, as progressively more NH_3 molecules became involved in lower *n* complexes, when more Ni atoms were available. The former $\text{Ni}(\text{NH}_3)_n$ species have generally higher stability than the latter (specific data provided in Appendix Table C-2).

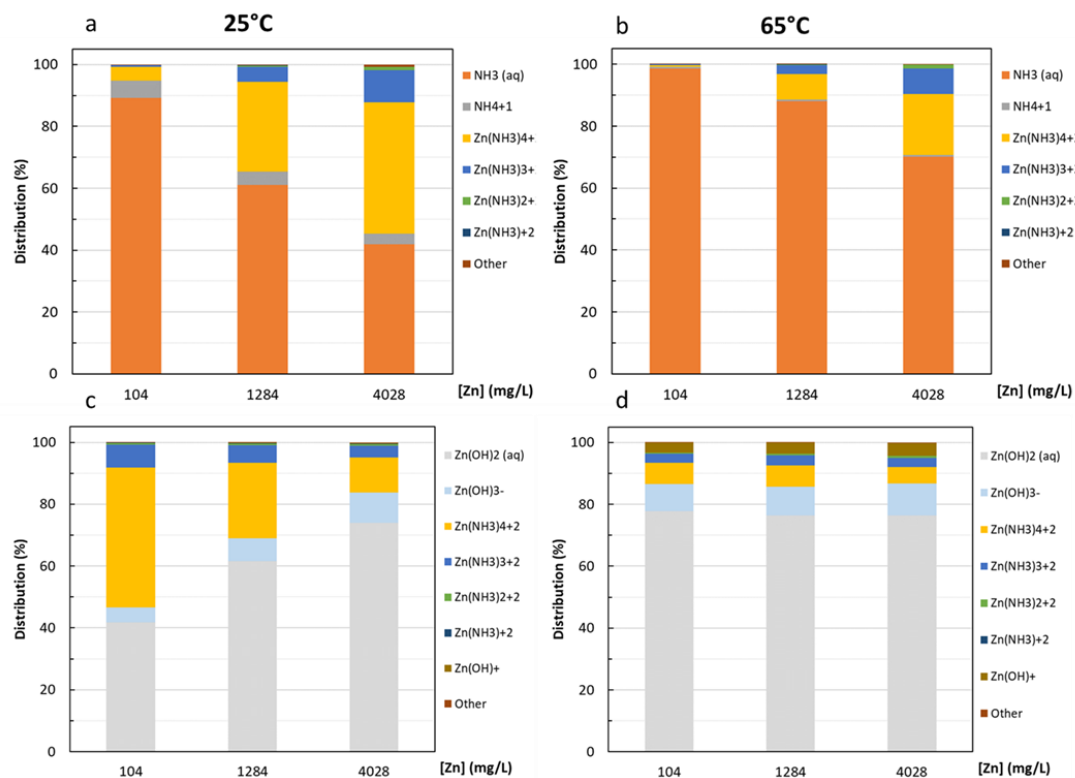


Figure 4-6. Visual Minteq (VM) simulations. Fractions (%) of TAN (top) and total Zn (bottom) involved in different aqueous species formations, as per VM simulation, at N/M ratios 40:1, 3:1 and 1:1 (104, 1284, 4028 mg Zn/L) at 25 and 65°C.

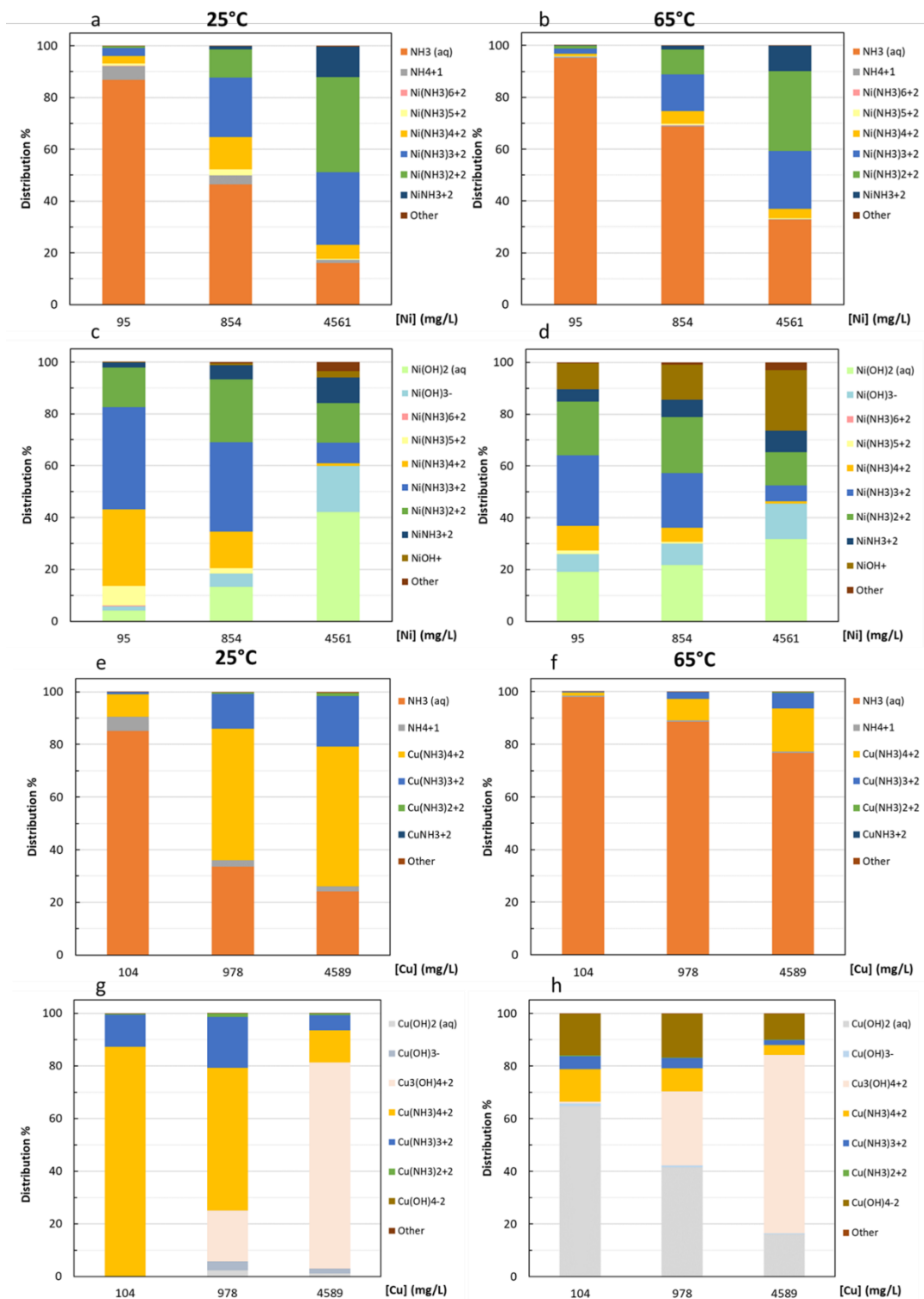


Figure 4-7. VM simulations. a-d: Fractions (%) of TAN (top) and total Ni (bottom) involved in different aqueous species formations, at N/M ratios 40:1, 4:1 and 1:1 (95, 854, 4561 mg Ni/L) at 25 and 65°C. e-h: Fractions (%) of TAN (top) and total Cu (bottom) involved in different species formations, at N/M ratios 40:1, 4:1 and 1:1 (104, 978, 4589 mg Cu/L) at 25 and 65°C.

4.4 Discussion

The results from this study supported the initial hypotheses that the actual free ammonia able to volatilise was lower in solutions containing specific contents of transition metals and humic acids, compared to the control and the estimates based only on the feed TAN concentration, pH, temperature (further details available in Appendix Eq. C-3 to Eq. C-6 (i.e. $\theta < 1$)).

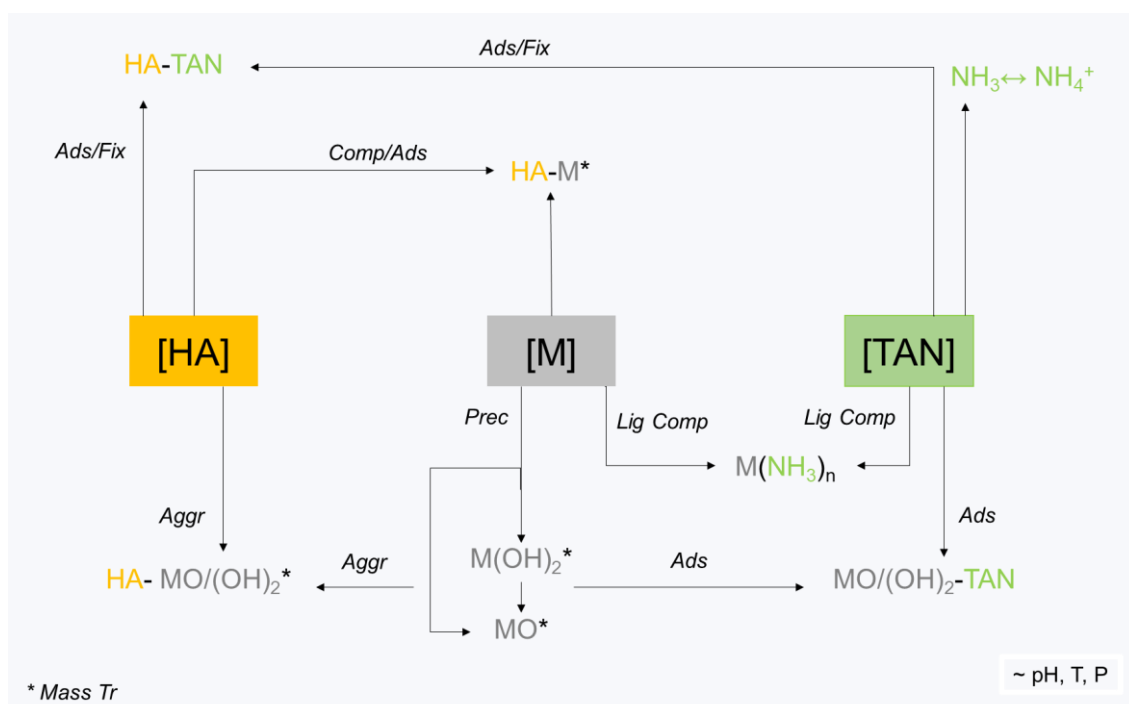


Figure 4-8. Proposed mechanisms affecting TAN partitioning and ammonia volatilisation in VTS, in (co-)presence of humic acids (HA) and/or selected transition metal (M). Ads= adsorption. Fix= fixation. Aggr= aggregation. Prec= precipitation. Lig Comp= ligand complex formation. Mass Tr= mass transfer limitation.

Overall, impairment of ammonia volatilisation was lower than anticipated if expecting all metal atoms in solutions to form ammine complexes. For instance, in a worst-case scenario, considering each metal atom binding the maximum n of NH_3 molecules (Ni 6, Cu 5, Zn 4, Table 4-1), this would result in 100% of the ammonia locked in complexes, at the lowest N/M (Figure 4-4). This did not

happen due to the metals being involved also in the formation of other aqueous and solid species, which impact the process in different ways, and due to the complexes thermosensitivity. Three potential mechanisms affecting ammonia volatilisation in the assessed metal systems were hypothesised (Figure 4-8): metal ammine complexes formation, TAN adsorption to (hydr)oxides, solids-driven hindrance of mass transfer.

Ammonia binding to metal atoms via ligand exchange would be responsible for the sequestration of a fraction of ammonia **(i)**, as highlighted by the VM simulations. The stability constants of the complexes indicate the strength of interactions between their components and ultimately affect the ammonia partitioning. For instance, nickel can bind up to six NH_3 , yet at lower n values it has lower stability constants compared to Cu and Zn ^{14, 49}. On the other hand, despite having high stability constants at room temperature, Cu complexes seemed to be strongly affected by temperature increase. It should be noted that the complexes could be influenced also by combinations of temperature and pressure ⁵⁰, not accounted for by VM.

The formation of metal precipitates could also reduce the ammonia fraction able to volatilise, via adsorption **(ii)**. TAN can adsorb on metal oxides surface, such as ZnO, via different and sometimes simultaneous mechanisms, depending on the level of their hydroxyl coverage ⁵¹. Considering this, metal hydroxides precipitates could also exhibit ammonia binding properties. Previous studies exploited the ammonia adsorption capacity of $\text{Cu}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ ^{52,53} and ZnO ⁵⁴. Moreover, Morikubo and colleagues reported a higher ammonia removal rate, during air stripping, upon increase in zinc concentration (up to N/Zn 11:1) and pH, hypothesising it was due to ZnO formation and its NH_3 adsorptive properties ¹³. Besides forming in different conditions and amounts, these metals precipitates differ also in NH_3 binding capacity. For instance, ammonia gas was reported to bind to ZnO more strongly than NiO ⁵¹. The former binds NH_3 through strong coordination bonds and H-bonds between coordinated NH_3 molecules and surface O/OH^- , whereas the latter mainly via H-bonds. Nonetheless, quantification of the NH_3 adsorptive capacity of these precipitates in water are

sparse and further studies are recommended. Finally, the concentration of suspended solids in solution could have also physically hampered the molecules mass transfer to a limited extent ⁵⁵ (iii).

A combination of these phenomena probably determined the actual ammonia stripping extents measured in these VTS tests. This might explain why, at the tested temperature, at N/M 1:1, the combined impact of Zn-ammine complexes, adsorption to Zn(OH)₂/ZnO and solids formation affected ammonia volatilisation to a greater extent than for the Ni and Cu solutions. It was not possible to differentiate between mechanisms, based on these results, yet additional trials could help identify their respective contributions.

The complexity of the system is further increased by the presence of organics such as humic acids which can further inhibit stripping efficacy. TAN can be bound both by the suspended solids and the dissolved humics fractions. In the current study, the predominant removal pathway was likely through interactions with the acidic groups of the dissolved humic acids, mostly carboxylic and phenolic (Figure 4-8), as the fraction of solids was negligible. NH₃ can bind these and other groups via chemical fixation, promoted by pH above 7 (i) ⁵⁶. Yet, the rate of this reaction is not well defined. In parallel, in soil, these groups can bind available cations as NH₄⁺ via electrostatic attraction (ii) ^{33,57}. Likewise, in solutions, HA become further deprotonated with increasingly alkaline conditions ⁵⁷ and can bind positively charged ions, mainly via electrostatic interaction in a relatively fast reaction ⁵⁸. In solution, the extent of this reaction depends on pH, determining the TAN equilibrium as well as the HA's groups charge and aggregation behaviour ⁵⁸. Similar dynamics take place in co-presence of HA and zinc. Yet, these species can complex with each other, which might have caused a limited mitigation of the factors hampering ammonia volatilisation.

It must be noted that also the impact of the initial TAN concentration in the feed could influence the removal. For instance, higher concentrations would provide a greater driving force (Eq. 4-4). Moreover, testing the identified critical molar ratios or concentrations at greater or lower ammonia levels would consequently be reflected in the metal or HA content. Such concentration changes may shift

equilibrium conditions for the complexes and other forms in which metals and humic acids are involved.

This research was conducted with batch tests. Currently, vacuum thermal stripping has been tested mainly at lab scale, in batch processes^{18,34}, however recent research has explored other configurations, including continuously fed vacuum membrane systems⁵⁹. The results obtained in this study might translate slightly differently in continuous systems. Although the inhibition mechanisms would remain the same, some of the differences could be due to variations in temperature-pressure combinations and profiles, residence time (e.g. lower residence time might influence the stability of the complexes), dilution effect by incoming fresh feed (as opposed to accumulation of interfering species with batch processes, due to water evaporation), pH changes, as well as possible scaling/fouling challenges (which are easier to prevent/control in batch processes). This study's results could then be further integrated by testing continuous setups to understand how these limitations translate in alternative configurations.

4.5 Conclusions

In literature, studies assessing the impact of transition metals and humic acids (recalcitrant organic acidic compounds), found in various effluents, on ammonia stripping are sparse. There is limited reporting of the mechanisms responsible for stripping hampering and of the critical concentrations driving them. This study integrated and expanded previous literature findings by investigating both individual and combined effects of these species, at extended concentration ranges encompassing various wastewaters compositions. Furthermore, evaluating different transition metals in comparable conditions allowed to differentiate their net effect on ammonia volatilisation, caused by specific hampering mechanisms. The results showed that NH_3 vacuum thermal stripping was impaired by high levels of the selected contaminants, with zinc being the most impacting species at the greatest concentration. The limitations to ammonia volatilisation were ascribed to different, contributing mechanisms, mainly metal complex formation, adsorption onto solids, electrostatic interactions, and

chemical fixation. The co-presence of zinc and humic acids showed a non-additive outcome, with the tested settings, suggesting a potential mitigation of the individual impacts and highlighting the importance of studying species interactions within complex matrices. Significant reductions of ammonia removal were caused by the combined impacts of the mentioned mechanisms, particularly relevant at high concentrations of HA and metals, with nitrogen to metal molar ratios close to the theoretical metal ammine complexes one. Nonetheless, at such concentrations, ammonia sequestration likely occurred not only via metal complex formation, but also via sorption to hydroxides and oxides precipitating in alkaline conditions. For the practical implications, this limits the range of effluents where such a separation technology will be impaired, mainly found in the metallurgy, agro-industrial, tannery sectors. Moreover, to mitigate this impairment, the application of thermally driven stripping should be preferred, where possible, to exploit the thermal sensitivity of the metal ammonia complexes and reduce the required pH increase, driving metal precipitation. For stripping of streams containing critical concentrations/ratios, preliminary feasibility studies are recommended to account for hindrances in TAN speciation modelling and costs estimating. On the other hand, future studies on the adsorptive capacity of zinc-based precipitates are recommended, as potentially impacting ammonia separation processes.

Appendix C

Table C-1. N/M molar ratios in various industrial effluents (WW), determined from data available in literature. SW= spent wash, SGS= synthesis gas scrubber WW. The considered waters had $100 \leq [\text{TAN}] \leq 3530$ mg/L. s= simulated, r= real.

Ref	WW Stream	N/Cu	N/Ni	N/Zn	N/Cd	N/Mn	N/Cr	N/V
11	Heavy industry ^a (r)	-	54	-	-		-	
13	Zinc plating (s, r)	-	-	6-23	-		-	
60	Industrial Park (s)	8-23	-	-	-		-	
61	Metal leaching (r)	-	-	-	-	-	-	58
62	Rare-earth process (r)	-	-	84	-	-	1,818	-
62	Rare-earth process (r)	-	-	3	-	-	22	-
63	Metallurgic (s)	9	-	-	-	-	-	-
64	SGS (r)	-	448	-	-	-	-	25
65	Tanning (r)	-	-	-	-	-	1	-
66	Beryllium smelting (r)	546	-	-	17,121	-	-	-
67	Produced water (r)	-	97,378	-	-	2,762	-	-
10	Rare-earth process (r)	3,803	3,988	814	-	6,005	-	-
68	Saponification (r)	8,495	-	2,093	-	8,919	-	-
69	Distillery ^b SW (r)	-	-	10,429	-	3,606	69,182	-
^c	Distillery ^b SW (r)	2,026	-	-	-	-	-	-

^a industries working with hard alloy, catalysts, ceramic capacitors, coated materials, electroplating. ^b digested. ^c analytical results for whiskey distillery.

Table C-2. Critical stability constants reported by ⁴⁹ for selected metals ammine complexes. IS indicates ionic strength. ^a indicates that the empirical values were determined at 25°C and 2.0 IS; ^b indicates that the empirical values were determined at 27°C and 2.0 IS.

Metal	Equilibrium	Log K (25°C, 0 IS)	Log K (25°C, 0.5 IS)	Log K (25°C, 1.0 IS)	ΔH (25°C, 0 IS)	ΔS (25°C, 0 IS)
Ni²⁺	ML/M.L	2.2	2.81±0.04 ^a	-	-4.0±0.0 ^a	-1 ^a
	ML ₂ /M.L ²	4.89	5.08±0.06 ^a	-	-7.8±0.2 ^a	-3 ^a
	ML ₃ /M.L ³	6.55	6.85±0.07 ^a	-	-12.1±0.1 ^a	-9 ^a
	ML ₄ /M.L ⁴	7.67	8.12±0.05 ^a	-	-15.6±0.4 ^a	-15 ^a
	ML ₅ /M.L ⁵	8.34	8.93±0.02 ^a	-	-19±1 ^a	-22 ^a
	ML ₆ /M.L ⁶	8.31	9.08±0.04 ^a	-	-24±1 ^a	-39 ^a
Cu²⁺	ML/M.L	4.04 ± 0.03	4.24±0.03 ^a	4.12±0.03	-5.5±0.1 ^a	1 ^a
	ML ₂ /M.L ²	7.47	7.83±0.04 ^a	7.63±0.02	-11.1±0.1 ^a	-1 ^a
	ML ₃ /M.L ³	10.27	10.80±0.07 ^a	10.51±0.03	-16.6±0.1 ^a	-6 ^a
	ML ₄ /M.L ⁴	11.75	13.00±0.05 ^a	12.60±0.10	-22.0±0.1 ^a	-14 ^a
	ML ₅ /M.L ⁵	-	12.43±0.04 ^a	-	-26±1 ^a	-30 ^a
Zn²⁺	ML/M.L	2.21	2.38±0.03 ^a	2.32	-2.6 ^b	2 ^a
	ML ₂ /M.L ²	4.50	4.88±0.20 ^a	4.81	-5.7 ^b	3 ^a
	ML ₃ /M.L ³	6.86	7.43-0.30 ^a	7.11	-9.6 ^b	2 ^a
	ML ₄ /M.L ⁴	8.89	9.65±0.10 ^a	9.32	-14.8 ^b	-6 ^a

Table C-3. Levels of organic compounds (mg/L), COD (g/L) and N (mg/L) in different effluents. N = TAN, unless specified. TKN= Kjeldahl N, HS=humic substances, HA and FA*= humic and fulvic acids, r= real, s= simulated. “y” indicates that the feed contained significant amount, yet no quantitative data was provided.

WW Type	HS	HA	FA*	Phenols	Melanoidins	COD	N	Source
Tannery (r)	-	y	-	-	-	2	54	70
Industrial (s)	-	40	-	-	-	-	31	27
Distillery digestate (r)	-	-	-	2241	y	73	2798 (TKN)	71
Distillery (r)	-	-	-	-	y	12	430 (TN)	72
Distillery digestate (s)	-	-	-	0-9000	y	-	800	73
Distillery digestate (r)	-	-	-	7202	-	45-52	4284 (TN)	23
Liquid digestate ^a (r)	y	-	-	-	y	0.5-9 ^b	389-2411	25
Sludge digestate (r)	-	4800-6900	-	-	-	-	-	74
Coking (r)	-	-	-	531	-	-	535	75
Coking (r)	y	-	-	566	-	-	266	76
Coking, with humate (r)	3000 ^c	-	-	-	-	-	890	77
Coal gasification (r)	-	-	-	850-950	-	3.8-4.4	230-300	78
Leachate (r)	500-1000 ca.	112-300	474-767	-	-	-	1036-1731 (TKN)	79
Leachate (r)	-	1380	y	-	-	-	2500	80
Leachate (r)	y	-	-	-	-	10-84	193-5210	81
Leachate (r)	y	-	-	-	-	12	3600	82
Leachate (s)	-	50-200	-	-	-	-	600	83
Manure (s)	-	0-500	-	-	-	-	420	84

^a Collection of different feed substrates, including agro-industrial residues. ^b Dissolved organics. ^c as humate.

Table C-4. Aimed and actual N/M molar ratios (mol:mol) used for the stripping tests with Zn, Ni, Cu and ammonia solutions.

Target N/M	Actual N/M		
All	Zn	Ni	Cu
4400 : 1	4535±518 : 1	4433±77 : 1	-
1000 : 1	1271±139 : 1	929±15 : 1	-
500 : 1	540±18 : 1	415±1 : 1	-
70 : 1	63±1 : 1	87±19 : 1	74±11 : 1
40 : 1	41±1 : 1	40±3 : 1	41±5 : 1
20 : 1	22±4 : 1	20±1 : 1	19±2 : 1
4 : 1	3.4±0.0 : 1	4.5±0.1 : 1	4.4±0.3 : 1
1:1	1.1±0.1:1	0.8±0.0:1	0.9±0.0:1



Eq. C-1

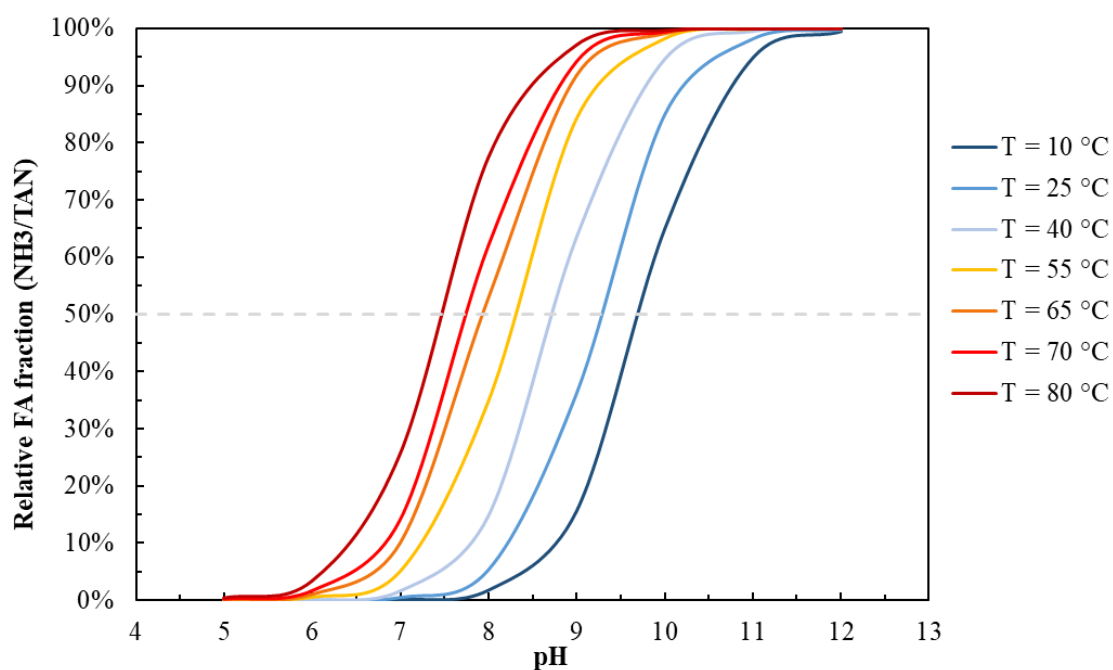


Figure C-1. Relative fraction (%) of free ammonia (FA) over total ammonium nitrogen (TAN) as function of pH and temperature, estimated with pKa calculations from ⁴.

In the tested conditions, it was assumed that the $K_{ov}a$ was constant and the mass transfer resistance was all on the liquid side (Eq. C-2) ^{37, 39}.

$$\frac{dC}{dt} = K_{ov}a \cdot (C - C_s) \quad \text{Eq. C-2}$$

$\frac{dC}{dt}$ is the rate of ammonia mass transfer (mg/L h), $K_{ov}a$ is the volumetric mass transfer coefficient (1/h), C is the ammonia concentration in the feed at time 0= start of the VTS run (mg/L) (C_{est}^0 , Eq. C-6) and C_s is ammonia solution concentration at the interface in equilibrium with the gas phase concentration (mg/L). C_s is described by Henry's law, decreases at increasing temperature and was assumed to be negligible ³⁷. C is a fraction of [TAN] (Eq. C-3) and is affected by pH (Eq. C-4) ³⁷.

$$C_{th} = [TAN] \cdot \alpha_{NH_3} \quad \text{Eq. C-3}$$

$$\alpha_{NH_3} = \frac{1}{1 + 10^{(pK_a^s - pH)}} \quad \text{Eq. C-4}$$

C_{th} is the theoretical free ammonia N concentration (mg/L) calculated based on Eq. C-4, Eq. C-5, α_{NH_3} is the relative fraction of free ammonia N (-), and [TAN] is total ammonia N concentration (accounting for free ammonia and ammonium) (mg/L). pK_a^s is the negative logarithm of the ammonium stoichiometric acid hydrolysis constant and is affected by temperature (Eq. C-5) ³⁷.

$$pK_a^s = pK_{a,298}^s + 0.0324 \cdot (298 - T) \quad \text{Eq. C-5}$$

$pK_{a,298}^s$ and pK_a^s are the hydrolysis constant values at temperature of 298 K and temperature T (K). pK_a^s at 25°C and 1 atm is 9.245 ³⁷. By operating at constant temperature, pH, and pressure, α_{NH_3} should be constant. Yet, it is hypothesised that complex-forming metals and HA can reduce the fraction of free ammonia available to volatilise (Eq. C-6).

$$C_{est}^0 = C_{th}^0 \cdot \theta \quad \text{Eq. C-6}$$

C_{est}^0 and C_{th}^0 are the actual (estimated) and theoretical (from Eq. C-3) free ammonia N concentrations (mg/L), respectively. θ is the coefficient (-) expressing

the impact of the metal/HA content. It was assumed that θ was 1 in the control solution.

In this investigation, pk_a^s , α_{NH_3} , $K_{ov}a$ were determined for the control solution based on experimental data. $K_{ov}a$ is assumed to be constant for all conditions and was estimated based on Eq. C-9: 0.91 ± 0.01 1/h. This was comparable to values obtained with similar set ups and tests, e.g. 0.03-0.094 1/h⁸⁵, 1.96 1/h¹⁸, with differences referable to the mixing, temperature, feed volume and concentration.

$$\frac{dC}{dt} = \frac{\Delta m}{Volume_{FS} \cdot \Delta t} \quad \text{Eq. C-7}$$

$$\Delta m = m^0 - m^t = m_{NH_3-N \text{ volatilised}} \quad \text{Eq. C-8}$$

$$K_{ov}a = \frac{dC}{dt} \cdot \frac{1}{(C_{est}^0 - C_s)} \quad \text{Eq. C-9}$$

Δm is the difference in mass of ammoniacal N (mg N) in solution between the start and end of the stripping run, $Volume_{FS}$ is the volume of the feed at the start of the run (L), Δt is the stripping duration (h). Δm is determined from the actual [TAN] measurements (not C), as it is assumed that the N mass difference corresponds to the free ammonia lost during volatilisation (Eq. C-8). C_s was assumed to be negligible. Based on the estimated $K_{ov}a$, $C_{estimated}^0$ and θ were determined for each condition (Eq. C-6).

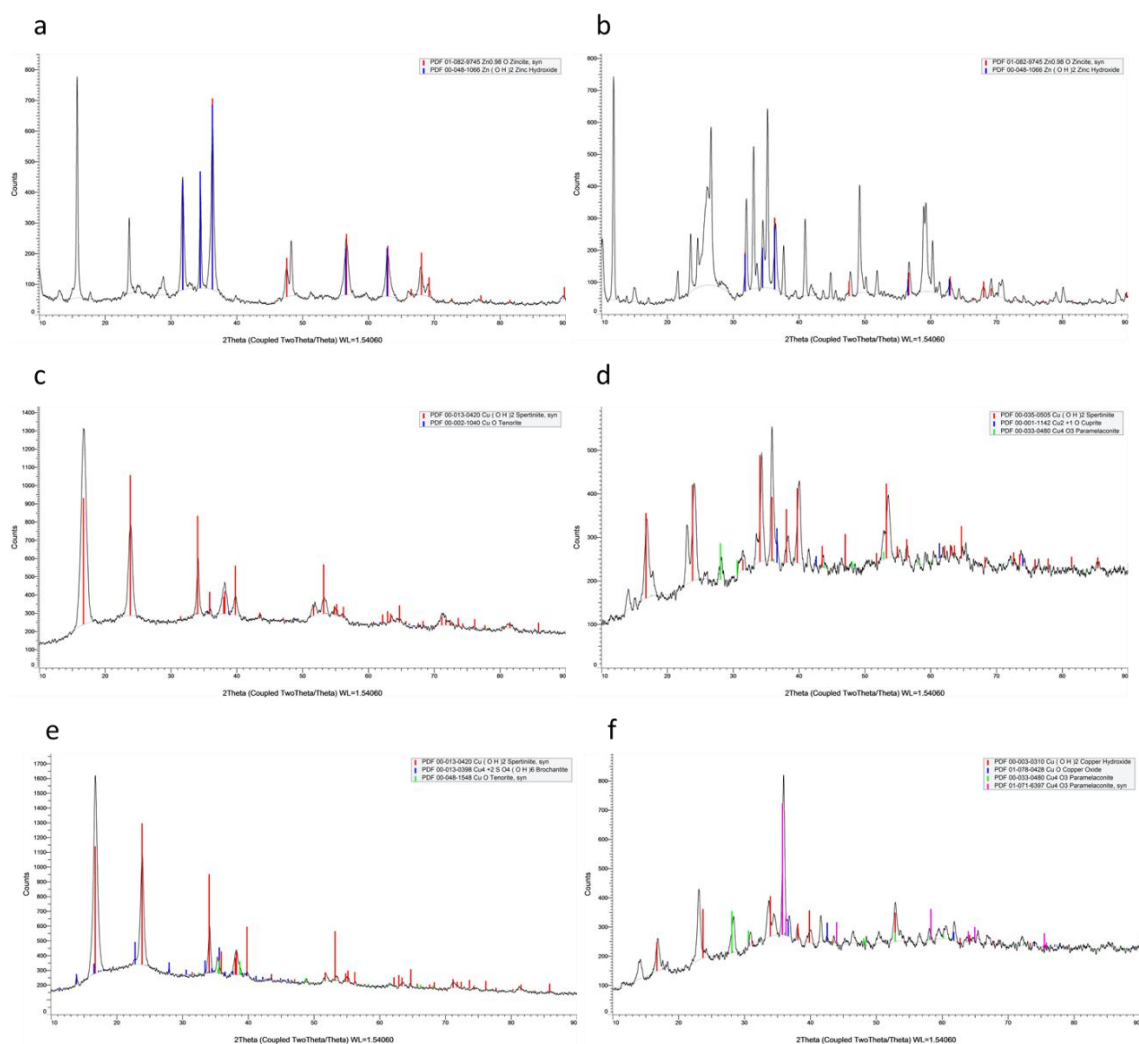


Figure C-2. XRD analyses of the precipitates formed: N/Zn 3:1-1:1 pre (a) and post VTS (b), N/Cu 4:1 pre (c) and post VTS (d), N/Cu 1:1 pre (e) and post VTS (f).

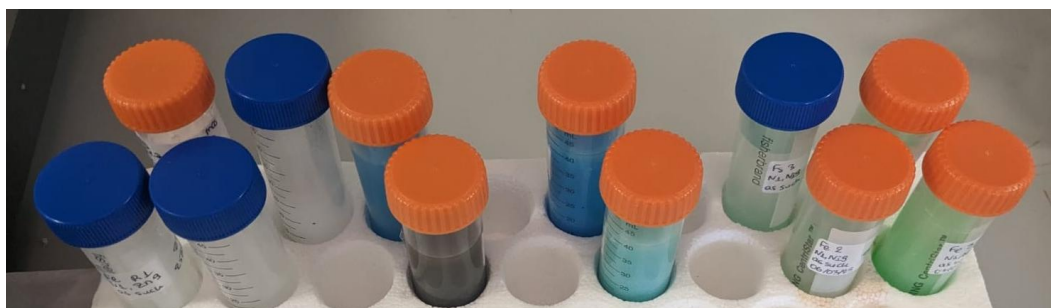


Figure C-3. Precipitates in solution before (top) and after (bottom) VTS. From the left: N/Zn 3:1, 1:1; N/Cu 4:1, 1:1; N/Ni 4:1, 1:1.

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Chapter 5

5 Ammonia removal via ion exchange and molecular adsorption on Zn-hybridised media

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Abstract

Ligand exchange media are gaining increasing popularity due to their potential capacity to selectively separate ammonia from aqueous solutions, exploiting the formation of transition metal ammine complexes (molecular adsorption). In literature, there is a lack of a comparative study assessing the performance of these novel metal-doped media, both in cationic and oxide/hydroxide form, and conventional ion exchange, in synthetic solutions and real wastewaters. Moreover, insights on the operational requirements for the different types of media are limited. This study aimed to cover such gaps, comparing the ammonia removal capacity of zinc-based media and standard cation exchange resin, in solutions of 10-2000 mg N/L, in municipal (9 mg N/L) and industrial effluents (75-704 mg N/L). It was shown that pH and solution buffer capacity determined the viability of ion exchange and ligand exchange, together with the Zn load. The conventional IEX resin achieved high capacity in most conditions (maximum 80 mg N/g), demonstrating it was a viable solution. Zn²⁺-doped media removed ammonia by molecular adsorption and ion exchange, depending on the solution pH, achieving a maximum 75 mg N/g capacity. The benefits of the Zn load on the TAN sorption capacity could be exploited only in limited conditions (pH 9-10), otherwise affected by self-driven acidification or competition between ammonia and hydroxyls. All media showed to be impacted by cations competition in real matrices, although demonstrating good capacities (21-33 mg N/g).

Keywords: *ion-exchange; ligand-exchange; adsorption; ammonia; distillery wastewater; municipal wastewater*

5.1 Introduction

Ion exchange (IEX) processes are considered as a potential technology to enhance ammonia resource recovery by enabling the partitioning of dilute streams into concentrated flows suitable for downstream recovery (e.g. via stripping). IEX is increasingly considered as it is a simple process, can have fast adsorption kinetics and moderate capacity, can concentrate the target species in a high purity product and be applied in modular units ¹. To date, it is predominantly considered for effluents with relatively simple matrices and low total ammonia nitrogen (TAN) loads ², including treated municipal wastewater ¹. To a lesser extent, research has explored IEX applications with higher N load streams, but that are still not sufficiently concentrated to be directly applicable for recovery technologies (Chapter 2). In such cases, the process uptake is restricted by limited cation exchange capacities, quickly saturated with high N loads ³, and sensitivity to complex matrices e.g. containing solids ⁴ or large amounts of competing monovalent and multivalent cations, reducing the actual TAN sorption levels ³.

Ion exchange media work by reversibly exchanging ammonium, NH_4^+ , with other counter-cations held on the negatively-charged functional groups on the media's surface to maintain electroneutrality ⁵. However, NH_4^+ sorption via electrostatic attraction to a negatively charged surface can also occur, without exchanging with a counter-cation, e.g. in biochar, activated carbon and clays ⁶. In addition, ammonia (NH_3) can be removed via a ligand exchange mechanism (LEX) driving molecular adsorption ⁶.

To access a wider range of effluents for TAN recovery, research has focused on developing highly selective media with enhanced capacity, e.g. exploiting the molecular adsorption of NH_3 to metals. Such properties can be obtained by hybridisation of standard cation exchange media with transition metals (e.g. Zn^{2+} , Cu^{2+} , Ni^{2+} , Mn^{2+} , Ag^+ etc.) ⁷⁻⁹. On such media, TAN uptake can occur based on a combination of IEX and LEX depending on the concentration and pH of the system. Nonetheless, the conditions affecting their mechanisms and overall performance have not been fully defined. Transition metals bind ligands, such as

ammonia, in inner-sphere complexes, via Lewis acid-base interactions, with nitrogen acting as donor of the lone electrons pair and the metal acting as Lewis acid, forming a coordinate covalent bond ^{6,7}. This process is selective for NH₃ and less subjected to the competition of other cations present in solution ⁷. Since a metal atom can theoretically hold more than one ligand molecule in its hydration shell, the total ligand exchange capacity can be multiplied compared to the IEX ⁷. Nonetheless, some of the most promising media were reported to adsorb ammonia to metal in a 1:1 molar proportion ^{10,11}. This highlighted a gap in understanding the performance and limitations of these-metal doped media, compared to conventional IEX resins. The doping can be realised by loading an IEX media with transition metal ^{9,10,12,13} or by conditioning such hybridised resin with a base ^{8,14} and locally precipitating metal hydroxide/oxide nanoparticles within the ion exchanger beads structure. The latter form is analogous to hybrid media doped with hydrated metal oxides utilised for phosphate separation from wastewater ¹⁵. Reportedly, these species can bind both NH₃ by forming complexes via molecular adsorption and via H-O bonding, and NH₄⁺ via electrostatic attraction with surface hydroxyls ^{8,16}. Although metal oxides alone, including zinc-based, have been used to adsorb both gaseous and dissolved ammonia ^{17,18}, their effectiveness with liquid matrices is not well defined, with conflicting reports on the role of zinc (hydr)oxide for TAN removal ¹⁹.

Previous research has tested different versions of metal-doped/based media (Table 5-1, with more details available in Appendix Table D-1).

Analysis of the existing literature reveals some knowledge gaps in benchmarking the media performance and understanding the conditions affecting TAN separation mechanisms. Some studies focused on media's selectivity, but only few have compared the capacities of doped and original media in the same settings ^{9,14}, being it synthetic or real effluents. Benchmarking the emergent media performance against the conventional product is important to better understand the relative contribution of mechanisms towards the removal and to determine and compare strengths and weaknesses.

Table 5-1. Summary of tested media doped/based on metal for NH₃ adsorption. CEX= cation exchange resin, AEX= anion exchange resin. Mono= solution containing only ammonia/um, multi= solution containing also competing cations.

Media	Doping metal	Wastewater (WW)	Capacity (mg N/g)	Study
CEX resin	Cu/Zn/Ni	Synthetic (mono/multi) Hydrolysed urine	5-164	8,13
AEX resin	Cu	Synthetic (mono)	13	11
SiO ₂ + primary amines; Zn/Ti hydrous oxide	Cu/ Ni	Synthetic (mono)	13-16	11
CEX resin	Cu/Zn/Ni(OH) ₂	Synthetic (mono/multi) Fishpond WW, lake water, treated WW	1.4-24	14
Graphene oxide	Ni/Sr/Zr oxide	Synthetic (mono) Refinery WW	60-150	16
Zeolite	Fe oxide	Synthetic (multi)	3	20
-	MnO/ ZnO/ Zn(OH) ₂	Synthetic (mono/multi)	0-118	19,21

Moreover, the understanding of the conditions required to ensure the effectiveness for some of these media remains unclear. For instance, Clark and Tarpeh ⁹ reported that the total ammonia concentration in solution determined which TAN removal mechanisms would occur in a fully-loaded metal resin. In particular, they found that concentrations between 3-7 g/L were optimal to drive ligand exchange, minimising aqua-ligand hydrolysis and metal loss via complex formation. Nonetheless, for IEX media partially loaded with transition metal cations or bearing metal (hydr)oxide nanoparticles there is no clear recognition of the factors driving the occurrence of the different ammonia separation mechanisms, being electrostatic interaction (mainly IEX) and molecular adsorption. pH, transition metal and sodium loads are expected to be significant drivers, by controlling the NH₃/NH₄⁺ equilibrium and the sites available for molecular adsorption (LEX) and IEX, respectively. Understanding the impact of

these factors is important for designing media with effective application across different wastewater conditions.

Thus, this study addressed these gaps was by evaluating how selected factors drive the occurrence of ammonia separation mechanisms in synthetic and real wastewaters. This was undertaken for an established cation exchange resin that had undergone hybridisation with transition metal (Zn^{2+}), in cation and (hydr)oxide forms. Among the different transition metals, zinc was selected to dope the IEX media, providing a trade-off between safety and performance, having high cumulative formation constants for ammonia complexes ²² and a pKa compatible with the pH requirement for NH_3 formation ¹⁰. Moreover, previous research reported critical impairment to ammonia stripping, in solution with high Zn content, attributed to sorption onto zinc precipitates and ammine complex formation in solution (Chapter 4). This research contributes new insights into the conditions that allow effective TAN separation using emergent zinc-hybridised sorption media. Moreover, it provides a novel, standardised comparison of the performance of ion exchange media, metal-doped media both in the cationic form and (hydr)oxide form, assessing their performance under different wastewater conditions, including real municipal and industrial effluents. These findings are useful in identifying suitable media for different treatment scenarios and determine areas for improvement of hybridised sorption media.

5.2 Materials and Methods

5.2.1 Cation exchange resin

The Zn-based modifications were performed on Dowex (Amberlite) MAC-3 H^+ (hereafter named “D”), a macroporous weak acid, cation exchange resin, with a polyacrylic matrix functionalised with carboxylic acid groups (Dow Chemical Company, purchased from Sigma Aldrich, Dorset, UK), used also for metals recovery (3.8 eq/L minimum capacity, 1.18 g/mL particle density) ²³. The media had particle size 300-1200 μm (90%), 44-52% moisture retention capacity ²³ and pore size distribution between 10 nm to 100,000 nm approximately, with a predominance of macropores ($\log r > 3$ ²⁴). The choice was based on the effectiveness of carboxylic acids for transition metal loading ^{9,19} and on the resin

macroporosity ²³, which allows for metal (hydr)oxides to precipitate within the pores and still be accessible to the target compound ²⁵. Generally, each zinc can bind two resin's COO⁻ groups via bidentate coordination (inner-sphere chelation) ⁹.

5.2.2 Synthetic solutions and dispersions

The TAN adsorption tests were performed with freshly prepared synthetic NH₄Cl solutions (≥99.5%, ACS reagent) (Sigma-Aldrich, Dorset, UK). Just prior to the tests, pH was adjusted with 1-4 M NaOH (46/51% soln. in water, Analytical reagent grade) (Thermo Fisher Scientific, UK) and 1-3 M H₂SO₄ (EMSURE®, 98%) (Merck, Darmstadt, Germany). Each solution was used fresh to run two replicates of the same condition, for all the media. One media “D-Zn II” (section 5.2.4.1) was tested on a different, yet comparable, set of solutions. 5% w/v NaOH/NaCl solutions were prepared with NaOH and NaCl (>99.0%, ACS reagent) (Sigma-Aldrich, Dorset, UK). An ethanol solution (absolute, 99.8%, analytical reagent grade, Fisher Scientific, Loughborough, UK) was used as a bead rinsing solution. The metal-loading solutions were prepared with ZnCl₂ (98+%, anhydrous) (Fisher Scientific, Loughborough, UK) or ZnSO₄ heptahydrate (99%, ACS reagent) (Sigma-Aldrich, Dorset, UK) dissolved into water and pH-adjusted (based on literature: ≤ 2 ²⁵, < 6.8 ¹⁹) with H₂SO₄ and NaOH solutions. A ZnSO₄ solution was prepared for the precipitation of zinc hydroxide, used in the adsorption tests. A ZnO nanopowder (<100 nm particle size) (Sigma-Aldrich, Dorset, UK) was purchased to produce dispersions assessed in the adsorption tests. All solutions and dispersions were prepared with deionised (DI) water.

5.2.3 Real wastewaters

Three real wastewaters with different ammonia concentrations were tested with the modified resin D media (Table 5-2): pH-corrected permeate from an anaerobic membrane bioreactor (AnMBR) fed with distillery wastewater before (i, “AnMBR”) and after nutrients recovery steps (struvite precipitation, ammonia vacuum thermal stripping) (ii, “PP_Str”), carrying 704 mg TAN/L and 75 mg TAN/L, respectively; effluent from the Cranfield University sewage works, spiked with NH₄Cl to obtain ca. 9 mg TAN/L (iii, “CE”).

Table 5-2. Characterisation of the actual effluents used in this study. Concentrations are expressed in mg/L.

	AnMBR permeate (AnMBR)	Treated AnMBR permeate (PP_Str)	Cranfield Effluent (CE)
pH	7.41	10.33	8.28
[TAN]	704	75	9
[Na]	389	12107	36
[K]	745	2749	7
[Mg]	66	399	4
[Ca]	92	117	73
[Cl]	261	167	50
[NO ₃ -N]	0.2	0.2	9
[PO ₄ -P]	211	3	1
[SO ₄]	1442	302	50
[Zn]	0.08	0.08	0.05

5.2.4 Media preparation

All media were washed with DI water prior to use, dried before and after modifications and stored in sealed containers.

5.2.4.1 Na and Zn-based media modifications

Different versions of resin D were prepared to assess the impact of Na and Zn loading on the TAN removal mechanisms and media performance. The media, originally in H-form (“D-H”), was conditioned with 1 M NaOH (355 mL for 83 g media; ca 5 BV ²⁶) for 3 hours, on a digital orbital shaker KS 501 (IKA-Werke, Staufen, Germany), at 135 rpm, in a 500 mL plastic bottle, to exchange H⁺ with Na⁺. Following, it was rinsed five times with 1 L DI water and then dried at 50°C for 40 hours (adapted from ⁸). The Na-conditioned resin, hereafter referred to as “D-Na⁺”, was used as baseline for the Zn modifications.

Zinc loading on D-Na⁺ was performed with an adapted process reported in literature ^{15,25}. 20 g of resin were conditioned with 567 mL of 1.4 M ZnCl₂ solution (pH 1.80) in a 1 L plastic bottle, horizontally placed on an orbital shaker, at 130

rpm, for 2 hours. The drained media was rinsed with 300 mL DI water for 10 minutes (twice) at 130 rpm, drained and dried at 45°C for 11 hours and at 55°C for 8 hours. The resulting media was referred to as “D-Zn²⁺ I”. Another Zn-media was generated (“D-Zn²⁺ II”), aiming to obtain a higher Zn content compared to D-Zn²⁺ I. 23.6 g of D-Na were conditioned with 755 mL of 2 M ZnSO₄ solution (pH 3.76) in a 1 L plastic bottle, at 120 rpm for one hour. The drained media was then rinsed with 1 L DI water, for 10 minutes (thrice) at 120 rpm, and dried at 55°C for 18 hours.

Zinc oxide/zinc hydroxide loading on D-Na⁺ was performed based on previous literature ^{15,25} (specific details in Appendix Table D-2), aiming to precipitate nanoparticles within the media's pores. 20 g of D-Na⁺ were conditioned as described above for D-Zn²⁺ I with ZnCl₂. The drained Zn-media was exposed to 558 mL of 5% w/v NaOH/NaCl solution, shaken at 130 rpm for 1 h to induce zinc detachment and simultaneous *in situ* hydroxide precipitation. After removing the solvent, the media was rinsed with 215 mL 50% v/v ethanol solution for 30 minutes, and with 240 (twice) + 1000 mL DI water for 10 minutes at 150 rpm. The separated media underwent mild thermal treatment in a beaker with 150 mL DI water at 50°C for 90 minutes, draining and drying at 55°C for 22 hours and then in a desiccator. It was expected that the media contained a mixture of ZnO and Zn(OH)₂ nanoparticles ¹⁴. Hereafter the media is referred to as “D-Zn(OH)₂”.

5.2.4.2 Zn(OH)₂ preparation

Zn(OH)₂ formation was induced in a ZnSO₄ heptahydrate solution (31.6 g/L, 0.11 M) as recommended by previous literature (> 0.05 mM Zn, ¹⁹). The solution pH was adjusted to 12.4 with 1 M NaOH (0.1 mL aliquots) and concentrated H₂SO₄ to precipitate Zn(OH)₂ (10 < pH < 13). The dispersion was left standing, covered, for 15 hours and was then filtered with 0.45 µm retention cellulose nitrate membrane filters (Fisher Scientific, Loughborough, UK). The filtered solids were washed with DI water, then dried at 55°C for 24 hours, and stored in sealed tubes. The harvested precipitates' SEM-EDS analyses yielded a Zn/O molar ratio of 2.3±0.1, compatible with the theoretical value of Zn(OH)₂ (2.0), and a minimum

Na contamination (2.9 ± 2.5 wt%). The XRD spectrum matched ZnO and $\text{Zn}(\text{OH})_2$ (spectra in Appendix Figure D-1).

5.2.5 Experimental tests

5.2.5.1 TAN adsorption isotherms

The sorption capacities of the following media have been assessed in batch tests: D- Na^+ , D- Zn^{2+} I, D- Zn^{2+} II, D- $\text{Zn}(\text{OH})_2$, ZnO nanoparticles, $\text{Zn}(\text{OH})_2$ powder. The adsorption isotherms ($22 \pm 2^\circ\text{C}$) were determined by using synthetic solutions with fixed TAN concentrations, encompassing typical concentrations for a variety of actual effluents: 11 ± 1 , 103 ± 3 , 504 ± 12 , 1015 ± 14 , 2038 ± 22 mg N/L ($n=12$). To assess the impact of pH on the TAN removal mechanisms for each media, three different starting pH have been assessed: 8, 9.5, 10 corresponding to 4%, 59%, 82% fraction of free ammonia (FA) over TAN, at $22 \pm 2^\circ\text{C}$, respectively (details in Appendix Eq. D-1, Eq. D-2). pH was adjusted with 1-4 M NaOH and 1-3 M H_2SO_4 , just prior to the tests. 50 mL centrifuge tubes with sealable cap were used as adsorption reactors (Fisherbrand TM, Fisher Scientific, Loughborough, UK), where a fixed mass of media (0.4 g) was added, followed by 40 mL of fresh, pH-corrected NH_4Cl solution, with a small head space. The ratio of media mass to solution volume (g/mL) was 0.01, within the literature range for these media (0.005^{13} , 0.006^8 to 0.15^{10}). Likewise, the ratio TAN/media (mg/g) was 1-200, within a comparable literature range (10^{12} to 450^{13}). A duplicate control was used (40 mL solution). All the reactors were secured horizontally on the orbital shaker and shaken for 5 hours (based on preliminary studies) at 90 rpm, at room temperature ($22 \pm 2^\circ\text{C}$). All tests for each condition were performed in duplicates, simultaneously. At the end of the tests, the dispersions and the control were vacuum filtered with Whatman 0.45 μm retention cellulose nitrate membrane filters. The filtrate was immediately analysed for pH and TAN concentration determination, then acidified with H_2SO_4 and stored at 4°C . The spent adsorption media was left to dry in a desiccator for at least 42 hours, prior to analyses and storage.

5.2.5.2 TAN adsorption in real effluents

The impact of the effluent matrix and competing cations on the ammonia removal performance was assessed for the sodium and zinc-based modified resins, treating real effluents (Table 5-2). Adsorption tests were performed as described above (section 5.2.5.1), in duplicate. Additional duplicate tests were carried out with synthetic NH_4Cl solutions, reflecting the pH and TAN content of the tested wastewaters: i) pH 7.42, 720 mg TAN/L; ii) pH 10.34, 77 mg TAN/L, iii) pH 8.31, 15 mg TAN/L.

5.2.6 Analytical methods

pH was measured with pH meters 3540 (Jenway, Stone, UK) with DJ113 pH electrode (VWR International Ltd., Poole, UK) and 3510 (Jenway, Stone, UK) with InLab expert Pro sensor (Mettler Toledo, Canada). Concentrations of chemical species were measured in filtered samples. Samples were stored at 4°C. TAN concentration was determined with standard ammonium cell tests (VWR International Ltd., Poole, UK) spectrophotometry (Spectroquant Nova 60, Merck-Millipore, Darmstadt, Germany). TAN concentration was immediately measured in the fresh sample of the feed before and after sorption. Zn concentration was determined with PerkinElmer's NexION® Inductively Coupled Plasma Mass spectrometer (ICP-MS), after sample acidification with HNO_3 (Normatom®, 67-69%, for trace metal analysis, VWR International Ltd., Poole, UK) and dilution with ultra-pure water. Ions' concentrations in the actual effluents were measured by means of ion chromatography (IC): for cations, a Dionex ICS-900 IC and a Dionex IonPac (CS12A) column were employed (Thermo Fisher Scientific, UK), with 0.026 mM Methanesulfonic acid as eluent and 0.98 M Tetrabutylammonium hydroxide regenerant phase; for anions, a Dionex ICS-1600 IC and a AS 9HC column were utilized, with 9 mM Na_2CO_3 mobile phase.

The different beads' versions were characterised with scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDS) (Tescan Vega 4, large chamber, Kohoutovice, Czech Republic) to obtain images and their elemental composition. Both the external and cross section surfaces of the media were analysed, for at least 3 beads/media. The samples were imaged in Low

Vacuum mode using Back Scatter Electrons. A small number of beads was adhered to a double-sided carbon tab on an SEM stub. For the EDS, an INCA x-act EDS detector and AZ-tec software were used. The $\text{Zn}(\text{OH})_2$ powder produced on site was analysed with EDS to validate its elemental composition. Furthermore, its X-ray diffraction (XRD) spectrum was obtained, using a Siemens D5005 diffractometer and Diffrac Eva software to analyse the sample powder (ground and compressed on an aluminium frame) (scan time 1 h, scan angles $10^\circ 2\theta$ to $90^\circ 2\theta$).

5.2.7 Data analyses

TAN adsorption capacity was determined with Eq. 5-1²⁷. The TAN adsorption data was fitted with two commonly adopted adsorption isotherms, in the linearised form: Langmuir (Eq. 5-2, Eq. 5-3) and Freundlich (Eq. 5-4, Eq. 5-5)^{13,15}.

$$q_e = (C_0 - C_e) \cdot \frac{V}{m} \quad \text{Eq. 5-1}$$

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{Eq. 5-2}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \text{Eq. 5-3}$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad \text{Eq. 5-4}$$

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e) \quad \text{Eq. 5-5}$$

Where, $q_e = q_f$ is the TAN equilibrium adsorption capacity (mg/g), C_0 and C_e are the TAN concentrations at the start and equilibrium, respectively (mg/L). V is the solution volume (L) and m is the adsorption media mass (g). q_m is the media maximum capacity (mg TAN sorbed/g of adsorbing media) (estimated). K_L (L/mg) is an equilibrium constant. K_F (mg/g) and n (-) are constants, the former proportional to the solute affinity for the sorption sites, the latter related to the reaction intensity¹⁵.

The media's cations capacities q (eq/g media) were estimated using the mass content results from the SEM EDS analyses (Eq. 5-6).

$$q = \frac{g\ C}{100\ g\ media} \cdot \frac{1}{MM_C} \cdot Z_C \quad \text{Eq. 5-6}$$

MM_C (g/mol) and Z_C are the molar mass and valency of the cation C , respectively. Differences between average specific cation capacities before and after adsorption were used to gain insights on the mechanisms involved in the TAN removal. As standard deviations could not be included, the balances gave high-level indications on such trends.

5.3 Results and Discussion

5.3.1 Media modifications

The elemental composition of the different media was determined prior to the sorption tests (Table 5-3). As expected, the zinc and sodium content differed according to their conditioning methods. The zinc load followed the order D-Zn²⁺ II > D-Zn²⁺ I > D-Zn(OH)₂ > D-Na⁺/D-H⁺, whereas the sodium content had an almost completely reverted sequence: D-Zn(OH)₂ > D-Na⁺ > D-Zn²⁺ I > D-Zn²⁺ II > D-H⁺. The sum of Na and Zn loads suggested capacities greater than the original's resin minimum capacity (3.2 meq/g): 3.6 (D-Na⁺), 3.5 (D-Zn²⁺ I), 3.3 (D-Zn²⁺ II), 6.8 (D-Zn(OH)₂). D-Zn²⁺ II had a greater zinc load and smaller sodium content than D-Zn²⁺ I, as an effect of the loading procedure. The maximum Zn load was in D-Zn²⁺ II with 2.7 ± 1.4 meq/g, corresponding to 88 ± 14 mg Zn/g, on the lower end of the literature values range of similar hybridised systems: 1.6 meq Cu/g on SiO₂ particles and 0.3 meq/g on anion exchange resin ¹¹, 1.7 meq Cu/g to 6.2 meq Cu-Ni/g on iminodiacetic group resin ⁸, 3.9 meq Cu/g on sulphonic group resin ¹³, 7.5 meq Zn/g on carboxylic group resin ¹⁰. A gradient of increasing Zn concentration from the D-Zn²⁺ beads' external surface towards the core was identified (Figure 5-1), but, in both media, the Zn distribution appeared overall reasonably homogeneous on the outer and cross section surfaces (Figure 5-2 a, b).

Table 5-3. Content (wt %) of selected elements in the original (D-H⁺) and modified versions of resin D, before use. Outer and CS refer to the areas analysed being the external and cross section surfaces, respectively. Total refers to their average (n≥6).

Media		Na	Zn	C	O
D-H ⁺	Total	0.1±0.1	0.0±0.0	66±6	33±5
	Outer	0.1±0.1	0.0±0.0	69±8	30±7
	CS	0.1±0.0	0.0±0.0	63±3	35±2
D-Na ⁺	Total	8.2±0.5	0.0±0.0	58±3	34±3
	Outer	8.3±0.7	0.0±0.0	60±3	32±3
	CS	8.0±0.1	0.0±0.0	56±1	36±1
D-Zn ²⁺ I	Total	3.6±0.6	6.1±1.1	58±4	32±3
	Outer	3.2±0.2	5.4±0.8	60±3	31±4
	CS	4.1±0.5	6.8±0.9	55±1	34±2
D-Zn ²⁺ II	Total	1.4±0.2	8.8±1.4	57±3	33±3
	Outer	1.3±0.1	8.1±1.6	60±2	31±4
	CS	1.5±0.3	9.4±0.7	54±1	34±1
D-Zn(OH) ₂	Total	13.5±2.1	2.8±2.0	51±2	30±3
	Outer	13.0±2.0	3.0±1.9	51±2	29±3
	CS	15.1±1.6	2.3±2.9	49±3	34±2

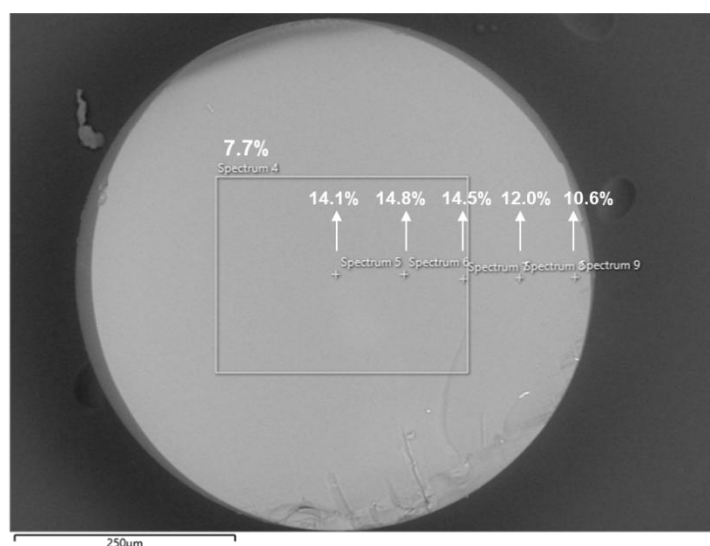


Figure 5-1. Zn content (wt %) in the central area and along a scan line of the cross-section surface of D-Zn²⁺ II media.

D-Zn(OH)₂ had a lower zinc level compared to D-Zn²⁺ I, despite having been conditioned with the same solution. Such reduction occurred during the hydroxide formation process, as it exchanged with the Na introduced with NaOH/NaCl conditioning ²⁵, and diffused out of the pores. Accordingly, D-Zn(OH)₂ had the highest content of sodium (Table 5-3), confirming it sustained a second Na loading, which reached a uniform coverage in the media (Figure 5-2 c). Moreover, Zn accumulated in the beads' surface and subsurface, indicating that the conditioning process led to an heterogenous distribution of the (hydr)oxide (Figure 5-2 c).

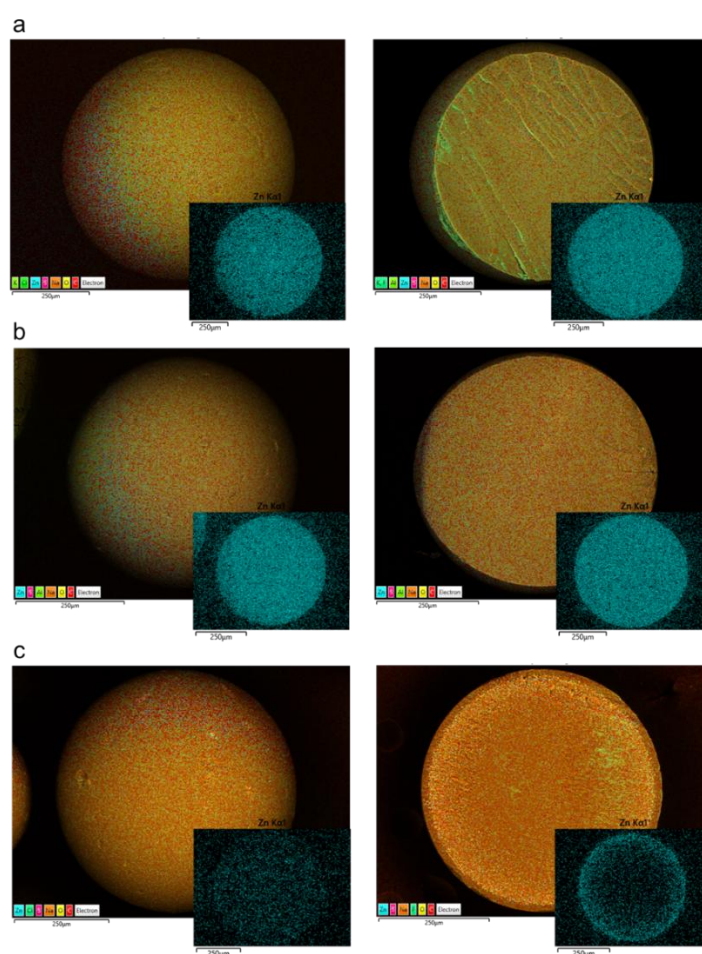
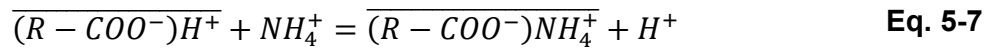


Figure 5-2. Layered mapping of the elemental composition of fresh D-Zn²⁺ I (a), D-Zn²⁺ II (b), and D-Zn(OH)₂ (c), external (left) and cross section (right) surfaces, obtained with SEM-EDS analysis (wt %). Sodium is depicted in orange. The right bottom images show the distribution of zinc alone (in blue).

5.3.2 pH impacting mechanisms

pH directly determines the speciation of TAN and metal, consequently enabling or hindering the removal mechanisms. In turn, pH is affected by several factors, including the removal pathways themselves and the media/water composition.

Ion exchange for TAN separation requires charged ammonium, thus the process is favoured at neutral pH or below, with a lower limit set by the material's resistance and by the competition with protons in solution for the carboxylic sites³. For Dowex MAC-3, such threshold lays at approximately pH 5²³, its pKa value²⁸. NH_4^+ exchanging with residual protons (H^+) on the COO^- groups generates a pH decrease (Eq. 5-7). At the same time, removal of ammonium shifts the equilibrium towards the consumption of H^+ (equimolar proportion) (Eq. 5-8) promoting a pH increase. Accordingly, ion exchange can result in a net drop of pH, in some cases reaching limiting conditions and triggering a self-inhibitory mechanism, especially with low initial pH (pH_{start}).



Molecular adsorption requires the presence of available zinc atoms and ammonia molecules (uncharged), thus alkaline conditions, with an upper limit defined by the competition with hydroxyl ions (OH^-). Generally oxygen is a weaker ligand compared to N⁹, but is in great concentration under high pH conditions and therefore the hydroxyls can outcompete ammonia. Moreover, this mechanism induces a self-limiting effect, since NH_3 removal shifts the equilibrium towards the left and the formation of H^+ (or OH^- consumption) (Eq. 5-8), reducing the pH. With metal oxides, pH influences the overall surface charge²¹, which becomes positive below the pH of point of zero charge, i.e. 8.5-9.1 for ZnO²⁹, limiting NH_4^+ attraction. Above such pH, the negatively charged surface interacts with ammonium via electrostatic forces, and at higher pH the uncharged ammonia form can bind via H-bond or complex formation¹⁶. Likewise, with metal hydroxides, pH affects the speciation and the charge (Appendix Figure D-2).

Increasing pH leads to both higher NH_3 fractions, which can ligand-exchange with aqua and OH^- from the oxide and hydroxide ¹⁵, but also higher OH^- competition.

The zinc content within the beads can contribute to solution acidification through a combination of complexing with NH_3 and reacting with available OH^- /ligand water hydrolysis. At approximately pH 8.5, half of the zinc in solution is already in hydroxylated form (Appendix Figure D-2 ³⁰), configuring the metal as a sink for hydroxyls. This was congruent with the observed pH drops in the test, which were greater with increasing media's Zn load ($\text{D-Zn}^{2+} \text{ II} > \text{D-Zn}^{2+} \text{ I} > \text{D-Na}^+$) (Section 5.3.4). Oppositely, D-Zn(OH)_2 was responsible for basifying the solution, potentially caused by residual NaOH in the media's pores dissolving in water and by release of hydroxyls bound to the zinc. Previous research showed a comparable pH-impacting outcome when using a metal-loaded resin pre-conditioned with NaOH ³¹.

TAN influences the pH by acting as buffer agent ($\text{pKa } 9.25$, $\text{NH}_3 \rightleftharpoons \text{NH}_4^+$ equilibrium), with greater impact at larger concentrations, providing sufficient molecules to neutralise the creation/consumption of protons and hydroxyls.

As a result of all these combined factors, NH_4^+ exchange or attraction and NH_3 molecular adsorption were often co-occurring, triggering or limiting each other in the different media.

5.3.3 Media performance with synthetic solutions

The control experiments showed no critical ammonia removal, indicating that the N concentration reductions observed in the other reactors were due to the sorption mechanisms and not volatilisation (Figure 5-3). Both ZnO and Zn(OH)_2 dispersions showed no or negligible removal, comparable to the control, suggesting that in the tested conditions their active sites were not able to strongly interact with and retain TAN, possibly also due to particles aggregating, reducing the surface active sites. The different media's performances changed depending on the starting pH conditions, with D-Na^+ achieving the highest capacities at initial pH 9.5 (80 mg N/g) and at pH 10 (70 mg N/g), similarly to $\text{D-Zn}^{2+} \text{ I}$ (75 mg N/g), whereas D-Zn(OH)_2 had the greatest capacity at pH 8 (66 mg N/g). Moreover,

although the tests were conducted in duplicate, the similarity of the results suggested consistency, yet further validation with triplicate replicates could provide additional confidence in the values.

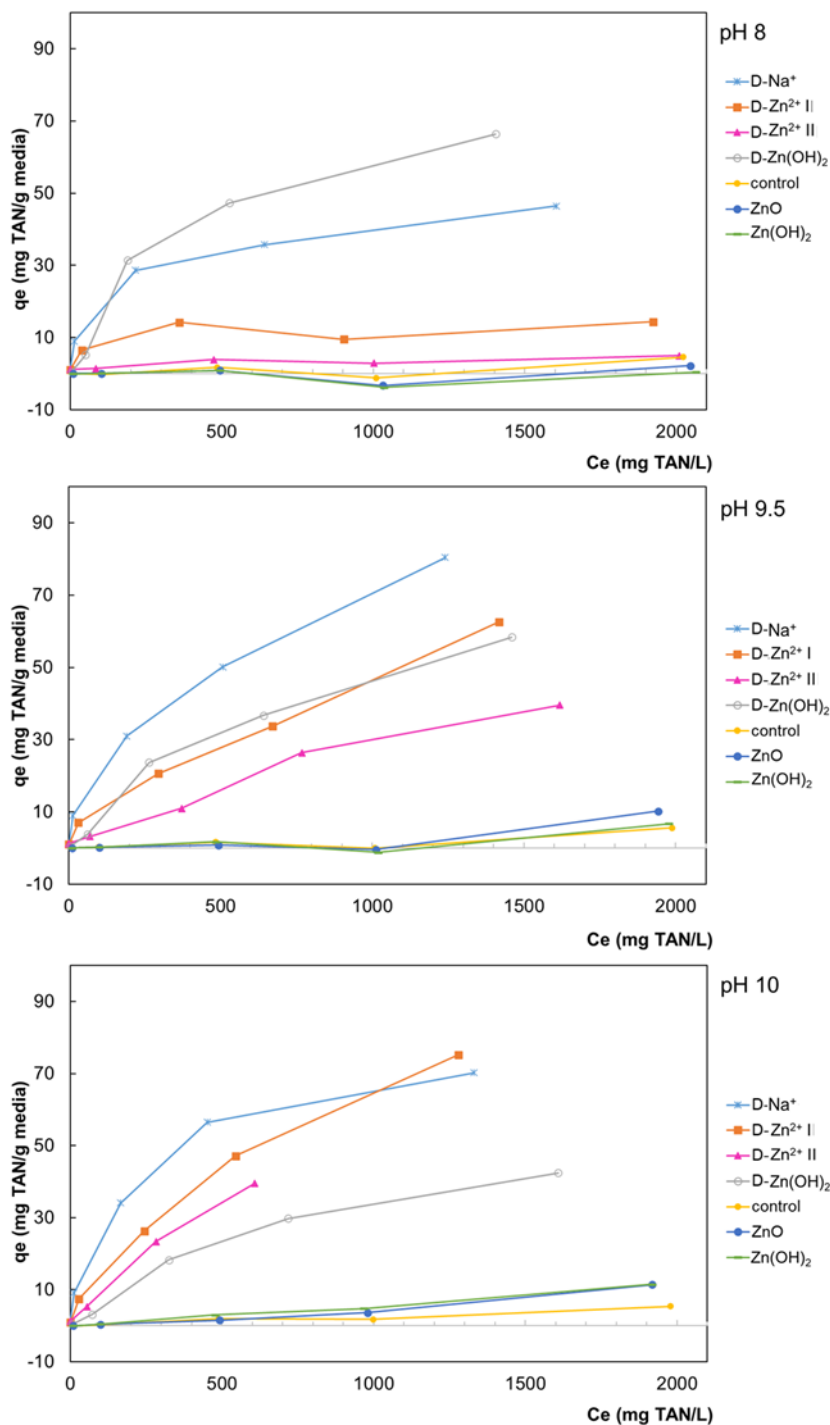


Figure 5-3. Adsorption isotherms of the tested media, with control, at initial pH 8 (top), 9.5 (middle), 10 (bottom). Ce and qe indicate the [TAN] in solution and TAN

adsorption capacity at equilibrium, respectively. Averages of duplicates are shown.

For each media, at the same pH_{start} condition, rising TAN content led to a greater driving force and a capacity increase. The data was fitted to the Langmuir (details provided in Appendix Table D-3) and Freundlich linearised models, with the latter providing the best fit with R² mainly above 0.90 (Table 5-4).

Table 5-4. Parameters obtained by fitting the adsorption data to the Freundlich model.

Media		pH 8.0	pH 9.5	pH 10.0
D-Na ⁺	R ²	1.00	0.99	1.00
	Kf (mg/g)	3.95	4.29	3.55
	1/n	0.34	0.39	0.43
D-Zn ²⁺ I	R ²	0.92	0.99	1.00
	Kf (mg/g)	1.54	1.52	1.37
	1/n	0.31	0.48	0.55
D-Zn ²⁺ II	R ²	0.71	0.81	0.92
	Kf (mg/g)	1.26	2.25	1.94
	1/n	0.14	0.31	0.42
D-Zn(OH) ₂	R ²	0.96	0.99	0.99
	Kf (mg/g)	0.13	0.10	0.09
	1/n	0.93	0.91	0.86

The Freundlich model is associated with a heterogeneous surface and multilayer adsorption ¹². As $\frac{1}{n}$ was always < 1, the adsorption was considered favourable for all media. Previous research found that TAN adsorption on Zn-loaded ¹² and Cu-hybridised media ²⁷ was also favoured, but the Langmuir model better described the reaction (monolayer adsorption). TAN adsorption on CuO-media fitted well both Langmuir and Freundlich equations ¹⁴, similarly to this study. D-Na⁺ had the highest Kf values among all resins, suggesting the greater affinity of TAN for this

media, whereas for the Zn-doped media's Kf ranged between 1.26 – 2.25 mg/g, comparable to values for other metal-doped media (20-25°C) of 0.26 mg/g ¹³, 2.54 mg/g ¹⁴ and 0.73 mg/g ¹². Nonetheless, comparison with other studies can be challenging, as the experimental and modelling values are affected by the operational conditions (e.g. pH, media dosing, temperature) ³.

Based on the results presented in the following sections, it was proposed that ion exchange took place in all the resins, whereas ligand exchange occurred only in the zinc-based versions. Ion exchange could be attributed when there was a cation reduction in the media post adsorption, e.g. sodium, zinc, protons. For Na⁺ and Zn²⁺, this could be directly monitored (Figure 5-5), whereas for H⁺ it could be gauged by pH acidification, caused by the increase of protons in solution (Figure 5-4). Ligand exchange in zinc-based media was suggested by the pH drop, driven also by the NH₃ removal, and by the limited extent of ion exchange, defined by the Na and/or Zn losses from the media, suggesting that TAN was removed as ammonia via molecular adsorption. The zinc (hydr)oxide-doped resin removed TAN via Na⁺-NH₄⁺ exchange, but likely also via electrostatic attraction on the surface of the (hydr)oxide and complexation. Indeed, the sodium losses alone could not balance the amount of sorbed ammonium, indicating that the other viable mechanisms co-occurred.

5.3.4 Changes in pH and media composition

As described above, pH changes can be a key indicator of the mechanisms taking place, thus they were monitored at the end of the adsorption experiments (pH_{end}) (Figure 5-4 for 1000 mg TAN/L, Appendix Figure D-3 for the other tested concentrations).

The pH remained unvaried throughout the adsorption tests in the control and in the dispersions with ZnO and Zn(OH)₂, congruent with the negligible extent of their interactions with ammonia. All the solutions, at any initial TAN concentration, treated with Zn²⁺-hybridised media (I and II) and the sodium-resin had a net pH drop compared to the start conditions, potentially ascribable to exchange with protons (mainly in D-Na⁺) and OH⁻ and NH₃ consumption by zinc. In contrast, D-Zn(OH)₂ adsorption of ammonia was characterised by a rise in the solution pH

compared to the start values, due to the release of hydroxyls resulting from NH_4^+ removal, dissolution of NaOH precipitated on the beads, and OH^- displacement. For all the four resin versions, increasing TAN concentration progressively buffered the magnitude of the pH change, especially when $\text{pH}_{\text{start}} \geq 9.5$ (further details in Appendix Figure D-3). Among the available and relevant literature, only few studies monitored the pH changes ^{10,11,31,32}, although this parameter can provide useful insights to understand the controlling mechanisms. A comparable acidifying trend was observed in other studies ³¹, which was progressively mitigated at increasing TAN concentration buffering such change ³² or by a controlled buffer system ¹⁰.

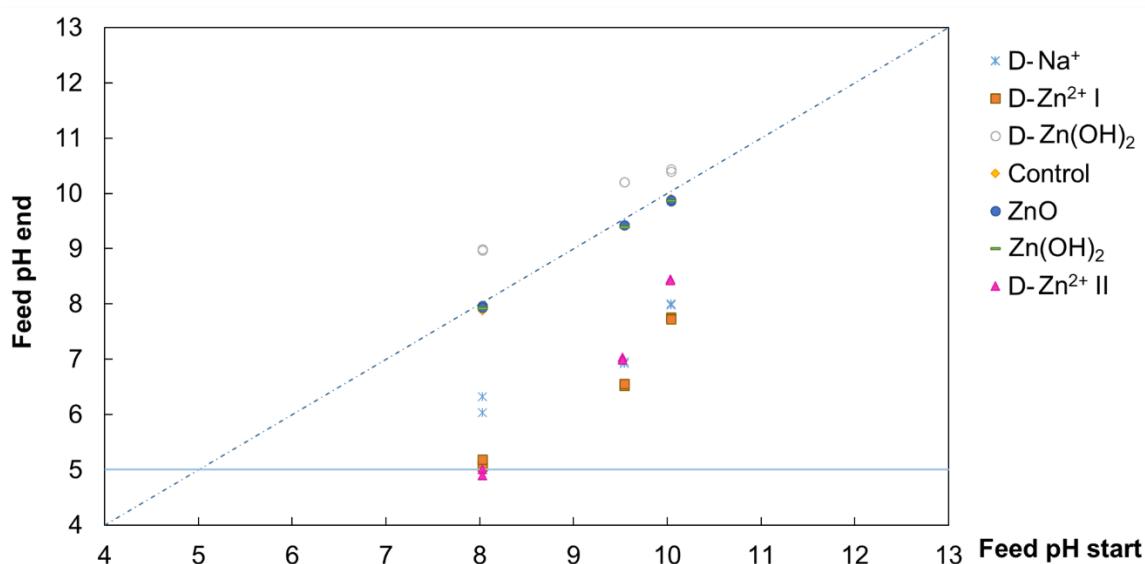


Figure 5-4. Solution pH before (8, 9.5, 10) and after the adsorption tests with different media and control, at initial $[\text{TAN}]_i = 1000 \text{ mg N/L}$. Duplicates are shown.

Given these pH-modifying phenomena, the initial pH conditions exerted a critical effect on the media performance (Figure 5-3). For D-Na⁺ and D-Zn²⁺ I, II, there was a rise in ammonia capacity with increasing pH_{start} . To illustrate, ammonia capacity was 36, 10 and 3 mg N/g for D-Na⁺ and D-Zn²⁺ I, II at a starting pH of 8 compared to capacities of 57, 47, 40 mg N/g at a starting pH of 10 ($\text{TAN} = 1000 \text{ mg N/L}$). LEX in D-Zn²⁺ I and II seemed to be favoured at higher pH, with the abundance of NH_3 , and the induced pH drop likely led to the transition from LEX to IEX mechanisms and ultimately to reaching pH limiting values, at lower pH_{start}

of 8, e.g. pH_{end} of 5 for both D- Zn^{2+} I and II, for TAN of 1000 mg N/L (Figure 5-4). Comparable pH values were reached in solutions with other TAN concentrations and pH_{start} of 8 (Appendix Figure D-3 for more details). Likewise, the acidifying trend might explain why, despite IEX benefits from neutral/acidic environments (NH_4^+ form), D- Na^+ generally performed better at higher initial pH, enabled also by the continuous replenishment of NH_4^+ . For D- $\text{Zn}(\text{OH})_2$, the trend was reverted as the highest performances were always obtained at the lowest pH_{start} and high initial TAN levels, where the net pH would allow both LEX and NH_4^+ sorption/exchange. $\text{pH}_{\text{start}} \geq 9.5$ led to higher final pH conditions (9.5 - 11.6), where LEX of NH_3 could likely be affected by greater competition with hydroxyls and removal based on electrostatic attraction was potentially limited by the scarcity of NH_4^+ .

To gain further insights on the mechanisms involved in the TAN removal and understand the impact of the Na/Zn loads, the tested media were analysed with SEM-EDS after sorption in solution with 2000 mg TAN/L, to determine any composition changes (Figure 5-5). Comparable trends were observed also after treatment of solutions containing 10 and 1000 mg TAN/L (details in Appendix Table D-4). Losses in sodium were attributed to ion exchange with NH_4^+ , which was particularly evident in D- Na^+ , especially at pH 8 with a 2.8 Na mmol vs 3.3 mmol TAN balance, and in D- $\text{Zn}(\text{OH})_2$. At pH 9.5 and 10, the Na loss was smaller in D- Na^+ , while in D- Zn^{2+} I and II there was even a limited uptake, explained by the greater concentration of sodium, introduced with NaOH. The difference in moles of Na^+ vs NH_4^+ in D- Na^+ could be explained by the exchange of protons, likely still held on the media.

The zinc load appeared relatively constant in D- Zn^{2+} I and II in all the tested conditions. In these media, NH_4^+ exchange with Na^+ seemed to have only a small contribution towards TAN removal, and mainly at lower pH, as suggested by the SEM-EDS results. With increasing pH_{start} , the TAN removal was ascribed to NH_3 ligand coordination with the available zinc. Previous research reported stoichiometric ratios for removal of 1 to 1 N:Zn (experimental) and 2:1 (theoretical) with bidentate carboxylic-zinc complex ¹⁰. Even accounting for the

best case scenario (2:1), the available Zn could not explain the moles of TAN removed (actual N:Zn up to 5.7), suggesting that some TAN was also exchanged with protons as NH_4^+ , when suitable pH conditions were met, or that zinc was not bound in a bidentate chelation and had more capacity for NH_3 complexation. The metal load in D-Zn(OH)_2 was slightly reduced, at all pH conditions, suggesting it was not sufficiently stable on the media.

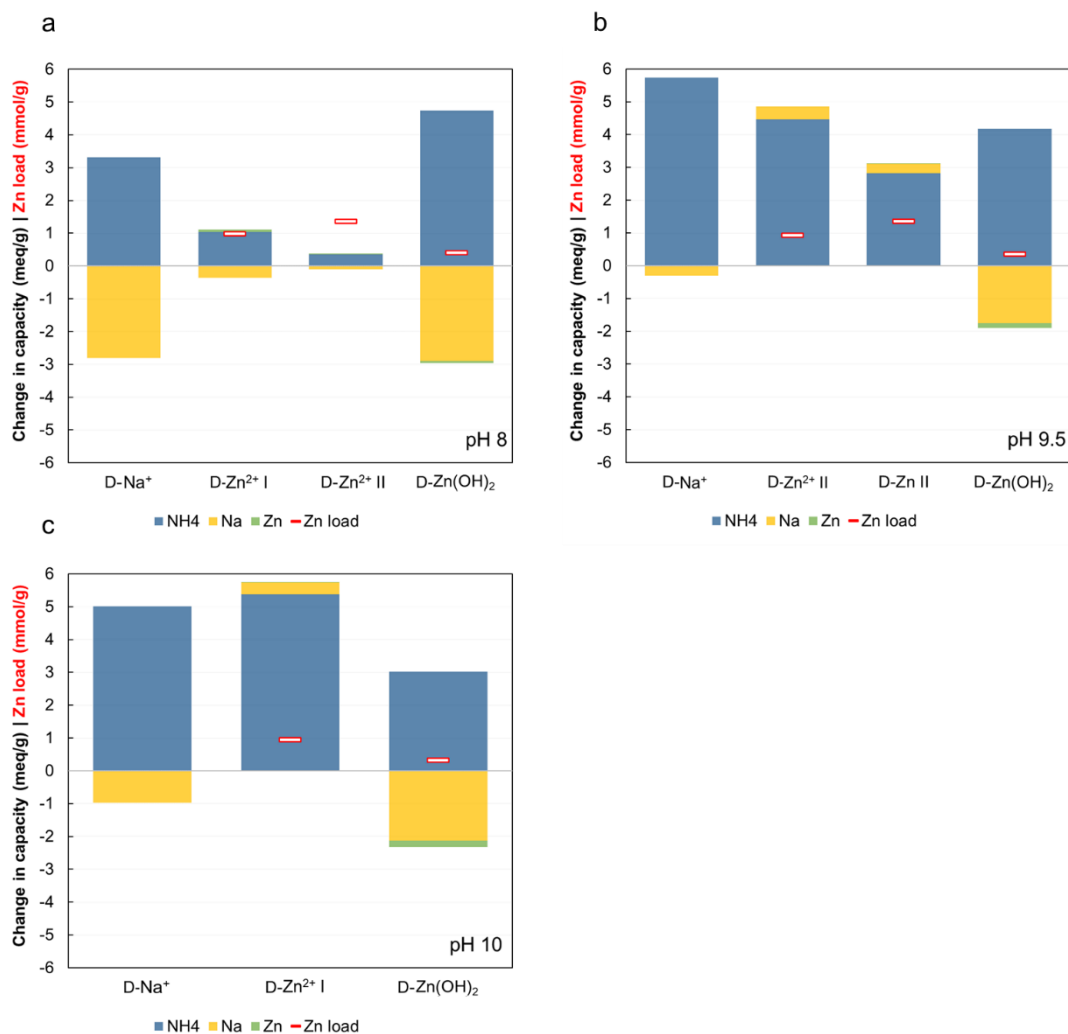


Figure 5-5. Changes in the media's composition (meq/g), compared to the baseline (Table 5-3), after adsorption with solution of $[\text{TAN}] = 2000 \text{ mg/L}$, at initial pH 8 (a), 9.5 (b), 10 (c). Negative values show losses, whereas positive values show sorption. TAN capacity was calculated from differences in concentrations. The Zn load remaining after the adsorption tests is shown in red (mmol/g).

5.3.5 Adsorption in real wastewaters

When assessed with real effluents, the resins led to different performances, as expected (Figure 5-6). Losses in the controls were negligible (< 8%, Appendix Table D-5). The changes in the media composition, compared to the baseline, suggested insights on the TAN removal mechanisms in the water matrices with different degrees of complexity to be elucidated (Figure 5-7).

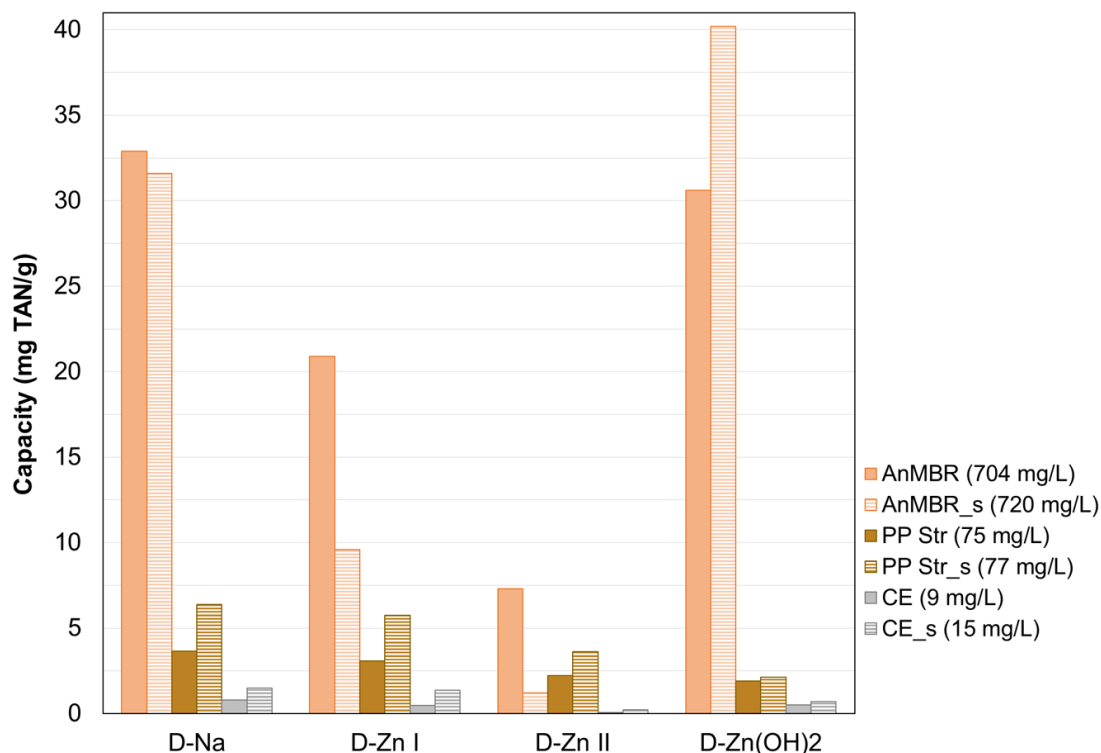


Figure 5-6. TAN adsorption capacities (mg/g) of the tested media treating actual (solid) and synthetic (“_s”, ruled) effluents: effluent of the anaerobic digester before (“AnMBR”) and after nutrients recovery (“PP_Str”), municipal sewage works effluent (“CE”). The TAN concentration (mg/L) is shown in brackets.

As observed with most of the adsorption isotherm tests, the Na-rich resins performed well with all real waters, demonstrating that IEX removal of TAN was efficient even in more complex matrices and led to the highest capacities for D-Na⁺: 0.8 mg/g in the Cranfield effluent (“CE”), 3.7 mg/g in the treated AnMBR effluent (“PP_Str”) and 33 mg/g in the raw digester permeate (“AnMBR”), which was comparable to the capacity achieved by D-Zn(OH)₂ (31 mg/g). D-Zn(OH)₂ worked best in the AnMBR effluent, which had the lowest pH compared to the

other streams (Table 5-2), enabling electrostatic attraction of ammonium, including via IEX with sodium. The same acidifying (D-Na^+ , D-Zn^{2+}) and basifying effects (D-Zn(OH)_2) that emerged in the isotherms tests were observed in the real effluents (details available in Appendix Table D-5).

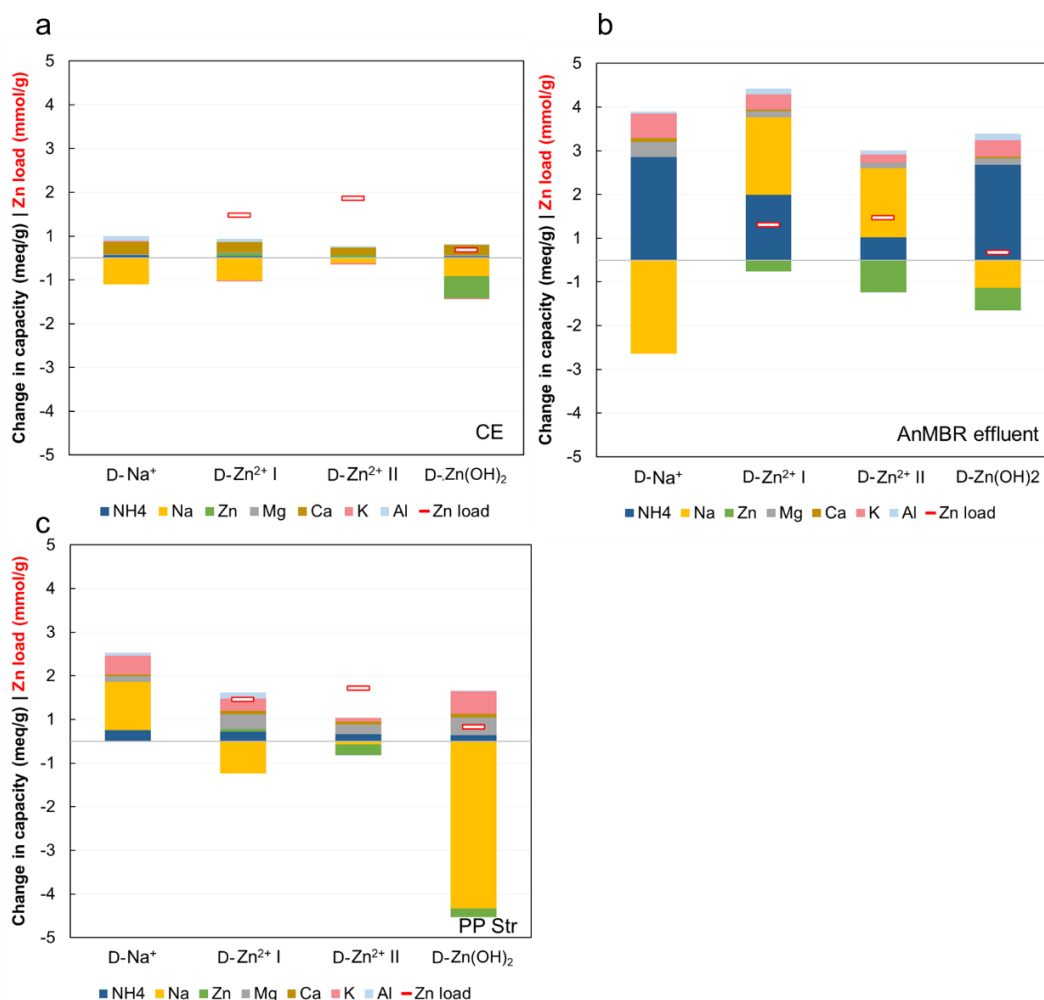


Figure 5-7. Change in cations capacity (meq/g) of the tested media after treatment of the real effluents, compared to the baseline: a) Cranfield sewage works effluent (CE), b) AnMBR permeate, c) AnMBR permeate after nutrients removal (PP_Str). TAN capacity was calculated from differences in concentrations. The Zn load remaining after the adsorption tests is shown in red (mmol/g).

Ion exchange occurred in all the media. In D-Na^+ , ammonium was exchanged with sodium and protons, as highlighted by the Na release (Figure 5-7 a, b) and pH drop to 7.4-8.7 (details in Appendix Table D-5). D-Zn^{2+} I's better performance of 0.5 – 20.9 mg N/g, compared to that of D-Zn^{2+} II at 0.1 – 7.3 mg N/g, could be

ascribed to a greater exchange of Na^+ with NH_4^+ , in the municipal effluent and the treated digestate. This suggested that IEX was favoured over LEX, with D- Zn^{2+} I benefitting not only from a greater initial Na load, but also from a smaller Zn-driven acidification. In “PP_Str” the high pH_{start} 10.33 potentially caused significant competition for NH_3 adsorption in D- Zn^{2+} II, and the amount of removed NH_3 was below its potential, based on the zinc load. This highlighted the likely sensitivity of the Zn-based media, requiring a narrow and stable range of operational pH.

In the raw AnMBR permeate both Zn^{2+} -media lost some zinc, by exchange with cations, including sodium and ammonium present in high concentrations in the solution. D- Zn^{2+} I appeared less prone to zinc loss, releasing up to 14% of its original content in “AnMBR”, compared to 28% for D- Zn^{2+} II. Such difference could be explained by a greater amount of Na^+ and H^+ in D- Zn^{2+} I, that could be preferentially exchanged compared to the divalent zinc, having high affinity for COO^- ³³.

The uptake extent of “foreign” cations changed depending on their abundance in each wastewater (Figure 5-7). Ca^{2+} was the most exchanged competing ion in “CE” (Figure 5-7 a), whereas K^+ , Mg^{2+} and Al^{3+} represented the largest fraction of sorbed cations from the AnMBR permeate before and after the nutrients removal treatment (Figure 5-7 b,c). To illustrate, in the municipal effluent, all media sorbed between 0.18-0.23 meq Ca/g, a higher load compared to the other sorbed cations, including NH_4^+ (≤ 0.06 meq TAN/g), as calcium was present in higher concentration (73 mg/L, Table 5-2). In the treated AnMBR permeate, the high magnesium and potassium content (Table 5-2) promoted their sorption in all media by 0.13-0.41 meq Mg/g and 0.09-0.51 meq K/g, over calcium (0.06-0.09 meq Ca/g). The uptake and release of cations from the beads were reflected in some of the general trends of the wastewaters composition adjustments (details in Appendix Figure D-4). Although a selectivity factor could not be determined, due to the non-equimolar concentrations of cations in solution, series of preferential uptake were estimated for the AnMBR permeate before and after sorption (Table 5-5). These were based on the meq/g increase of each cation

compared to the baseline, and Na and Zn were excluded as already present on the media pre-sorption. In the untreated AnMBR effluent, all media appeared to preferentially sorb ammonia/um nitrogen, due to its high content, followed by potassium and magnesium/aluminium.

Table 5-5. Estimated series of preferential uptake by the tested media in the AnMBR permeate before and after nutrients separation (“Treated”).

AnMBR permeate	
D-Na ⁺	TAN > K > Mg > Ca > Al
D-Zn ²⁺ I	TAN > K > Mg > Al > Ca
D-Zn ²⁺ II	TAN > K > Mg > Al > Ca
D-Zn(OH) ₂	TAN > K > Al > Mg > Ca
Treated AnMBR permeate	
D-Na ⁺	K > TAN > Mg > Al > Ca
D-Zn ²⁺ I	Mg > K > TAN > Al > Ca
D-Zn ²⁺ II	Mg > TAN > K > Ca > Al
D-Zn(OH) ₂	K > Mg > TAN > Ca > Al

In the AnMBR effluent post nutrients removal, the TAN concentration was significantly lower and, consequently, TAN positioned third/second in the sorption series. In this case, for the Na-rich resins, potassium could have been preferentially sorbed via monovalent cation exchange, whereas in the Zn²⁺-rich media, the high levels of divalent magnesium drove the uptake, also exchanging divalent zinc in D-Zn²⁺ II. The large uptake of Mg might have limited the expected NH₃ selectivity in D-Zn²⁺ II, which was likely reduced also by the non-optimal pH conditions (10.33) causing competition with hydroxyls. These results suggested that the levels of alternative cations in each wastewater determined the driving force for competing ion exchange, affecting the TAN removal and zinc-retaining capacities of the media. The benefit of selective ammonia adsorption can be attenuated in complex wastewater, with the metal itself being subjected to potential displacement by ion exchange. Comparable results were obtained in previous research with metal-doped resins, reporting Zn and Cu elution by Mg and Ca in a fully-loaded media ⁹ and reduced capacity as an effect of competition between ammonium and other cations exchange in partially-doped resins ^{13,27,31}.

Besides the competition from other cations, other factors impacted the overall sorption ability of the media. Among the real effluents, the highest TAN capacities were measured in the AnMBR effluent, which had the lowest initial pH (7.41, Table 5-2) and the greatest TAN load. The high ammonia content not only resulted in a larger gradient promoting sorption, but also mitigated pH alterations, contributing to the buffer capacity together with the phosphates and carbonates equilibria. Indeed, D-Na⁺ and to a greater extent D-Zn²⁺ I and II performed better in the real digestate than in the synthetic one (Figure 5-6), with the latter always having lower pH_{end} than the actual AnMBR effluent (more details available in Appendix Table D-5). In the other cases, the synthetic solutions had better TAN sorption capacities than the real wastewaters (Figure 5-6), as expected. Also anions such as NO₃, Cl, SO₄ might have negatively impacted the removal, as previously reported with Cu-doped media ¹³. Moreover, all the media exposed to the “AnMBR” and “PP_Str” effluents developed a brown colour, due to the uptake of coloured organic compounds present in digestate ³⁴. Comparable substances like humic acid or natural organic matter can affect ion exchange by binding cations and can complex with metals ^{35,36}. Additionally, in “CE”, the better performance in the synthetic water was also explained by a higher initial TAN concentration.

5.3.6 Overall capacities comparison

D-Na⁺ reached its greatest capacity of 80 mg N/g in the synthetic solution ([TAN]_{start} 2044 mg/L, pH_{start} 9.5) and 33 mg N/g in the AnMBR effluent ([TAN]_{start} 704 mg/L, pH_{start} 7.4), comparing well with Dowex MAC-3's capacity of ca. 45 mg N/g and previous research reporting ca. 59 mg N/g (ca. 4 mmol TAN/g) treating undiluted urine (3.8 g TAN/L, pH 9) ²⁸. D-Zn²⁺ I's highest capacities were 70 mg N/g in synthetic solution ([TAN]_{start} 2032 mg/L, pH_{start} 10.1) and 21 mg N/g in the AnMBR permeate, whereas D-Zn²⁺ II had a lower performance, reaching 40 mg N/g in synthetic solution ([TAN]_{start} 1002 mg/L, pH_{start} 10.0) and 7 mg N/g in the AnMBR effluent. These values were comparable with what observed in previous studies with metal-doped resins (Table 5-1, with specific examples in Appendix Table A-1). In more concentrated matrices (4-7 g TAN/L, pH 9.5), for instance,

Clark and colleagues measured capacities of 41-112 mg N/g with fully loaded Zn-resins ⁹, while Chen et al. ¹² reported 32 mg N/g for partially loaded Zn-resin treating a synthetic solution of 3290 mg N/L (pH_{start} 9.5) ¹². Also D-Zn(OH)₂ yielded results in agreement with previous literature. 66 mg N/g in synthetic solution ([TAN]_{start} 2068 mg/L, pH_{start} 8.1) and 31 mg N/g in the digester permeate compared well with the results from resins loaded with Cu, Ni, Zn and conditioned with NaOH: ≈8 mg N/g ⁸, 15 mg N/g ³¹, 23 mg N/g ¹⁴.

5.3.7 Conditions for TAN removal mechanisms in Zn-doped media

Based on the experimental results for the zinc-hybridised resins, the beads composition, the pH and the buffer capacity were identified as critical factors enabling or hindering the removal mechanisms.

The Zn²⁺ doping seemed to be beneficial in limited conditions i.e. with high initial TAN concentrations, mitigating acidification, and with relatively stable suitable pH. With 2000 mg TAN/L and pH_{start} 10, the final pH was 9.1, allowing sufficient NH₃ molecules for adsorption throughout the test duration. In these conditions, LEX was favoured over IEX: with the same initial setting (2000 mg TAN/L, pH_{start} 10), D-Na⁺ yielded 70 mg N/g by solely relying on IEX (pH_{end} 9.5), whereas D-Zn²⁺ I achieved 75 mg N/g with the combined contribution of mainly molecular adsorption supplemented with IEX. Beyond this case, it was proposed that either the self-driven pH limitation occurred or hydroxyls were outcompeting NH₃, hindering further adsorption. In most cases, IEX was more favoured and resins with higher Na and protons loads (and therefore lower Zn load) performed better, as they were more easily exchangeable with ammonium.

The TAN concentration appeared critical in determining the onset and continuation of the removal mechanisms. To maintain LEX-suitable pH conditions, a sufficient level of ammonia, was required to buffer the pH drop caused by hydroxyls reaction with zinc and ammonia effect as weak base ^{9,37}. Higher N/metal molar ratios allow such mitigation and thus NH₃ complexing of the metal ³⁷. The N/Zn molar ratios in this study were ≤ 0.6 (D-Zn²⁺ I) and ≤ 0.4 (D-Zn²⁺ II), suggesting that the available TAN concentration would have been insufficient to compensate for a hypothetical complete hydroxyls consumption.

With a fully loaded Zn-resin, Clark and colleagues identified an ideal range of TAN concentration (220-500 meq/L) for ligand exchange at pH_{start} 9.5⁹. Based on the data available in their study, such values translated to N/Zn of 11-25, with pH_{start} 9.5, adequate for zinc neutralisation and ammonia complexation³⁷. Using solutions with lower pH_{start} (e.g. 8) and higher pH_{start} (e.g. 10) would increase and decrease, respectively, the required N/Zn ratios to buffer the pH drop. To illustrate, with D-Zn²⁺ I, in the 2000 mg TAN/L solution the pH_{start} 9.5 decreased to 7.3, whereas a similar pH_{end} (7.7) was reached by the less concentrated solution of 1000 mg TAN/L treated at pH_{start} 10 (N/Zn 0.3). Previous literature reported that for Cu-resin^{27,31,38} and Zn-resin¹² increasing pH_{start} improved the TAN removal via LEX until optimum at 9.3-9.5, in unbuffered solutions. Above such threshold, the removal rapidly declined, attributed to the increased OH⁻ competition, leading to the metal hydroxide formation. Nonetheless, most metal-doped resins tested in literature were likely acting via both IEX and molecular adsorption^{13,27,31}, leaving it unclear which of the two mechanisms dictated the upper pH limit. Clark and colleagues¹⁰ applied a resin-based pH buffering strategy with a fully loaded zinc-resin and confirmed that pH 9-10 led to an optimal TAN removal via ligand exchange. This was consistent with the best performance of D-Zn²⁺ I at pH_{start} 10 (pH_{end} 9.1), confirming that buffering at ca. pH 9.5 would further favour molecular adsorption in D-Zn²⁺ II. The onset of a specific mechanism could also be affected by the relative coverage of Na and Zn. The greater abundance of sites for IEX or LEX could have contributed to the predominance of a mechanism over the other. To illustrate, in D-Zn²⁺ I, the Na and Zn loads were 1.6 ± 0.3 mmol/g and 0.9 ± 0.2 mmol/g, respectively. In D-Zn²⁺ II, these values almost reverted: 0.6 ± 0.1 mmol Na/g and 1.3 ± 0.2 mmol Zn/g. Additionally, also the residual protons on the resin would contribute to the number of IEX sites.

The metal (hydr)oxide version performed better at lower pH, favouring IEX with Na⁺ and hydroxyl–ammonium interaction on the Zn (hydr)oxide surface (above pH 8.5-9.1), both limited by the availability of NH₄⁺ at higher pH. Given the basifying effect of the media, also LEX was likely more favoured at lower pH_{start} , with less competition from OH⁻. Previous studies reported that metal oxide-

bearing media separated TAN by forming inner-sphere metal ammonia complexes and via electrostatic attraction of ammonium by $\text{Cu}(\text{OH})_3^-$ at pH 7¹⁴, and pH 11⁸. Nonetheless, in this study, large releases of sodium were observed at any pH, suggesting that IEX was an important contributor to TAN removal.

Media carrying both Na and Zn proved to be versatile, being able to remove TAN over a large range of pH and in diverse matrices, likely by exploiting mechanisms effective in complementary conditions. Given these characteristics, such adsorbent could be effective when used for a polishing step for effluents with high variability in pH, in non-buffered conditions. Nonetheless, its capacity is limited due to the nature of the loading: at lower pH, mainly -Na sites are easily exchangeable with ammonium, especially if the metal-resin bond is sufficiently strong, whereas at more alkaline pH only -Zn sites could adsorb molecular ammonia. Adjustments to improve the capacity of this media include: i) using a Na-form resin with high affinity for zinc (instead of an H-form resin, implying potential protons carryover), ii) fully load the media with zinc, iii) necessarily apply a buffer system to counteract the acidification driven by the consumption of OH^- and NH_3 by high zinc load.

Based on the observed results, both IEX and LEX media can achieve discrete capacity if operated in their suitable pH range (7-9 and 9-10, respectively) and with a buffer system, making them suitable for diluted and concentrated effluents. For ammonia removal from complex matrices (high ammonia and competing ions concentrations), such as some industrial effluents like digested distillery wastewater, conventional IEX still offer significant capacity, despite limitations, whereas LEX could be preferred due to selective removal if the resin-metal bond is sufficiently strong to counteract competing cations.

Batch experiments provide useful insights over the mechanisms driving ammonia sorption over time, under controlled conditions allowing to reach equilibrium. However, these studies must be complemented by continuous operation testing, such as fixed bed column processes, which are most commonly adopted for sorption applications. With continuous processes, the constant renewal of feed maintains a high driving force for sorption, potentially until saturation³⁹. On the

other hand, the flow rate and water residence time can critically influence the removal efficiency. pH changes observed in batch tests were attributed to both IEX and LEX mechanisms and to the cations loading of the media. These variations would occur also with continuous processes ³¹, however, the continuous replenishment of fresh feed would prevent reaching extreme self-inhibiting values recorded in batch tests, due to a dilution effect. Given a shorter contact time, sorption kinetics differences between IEX and LEX might determine whether a mechanism occurs first, e.g. in a fixed bed column, temporarily altering the local pH in that transfer zone and the ones below. The use of buffer would still be recommended for mitigation, also to ensure meeting acceptable pH levels in the effluent. This study's results should then be validated in dedicated studies testing continuous processes e.g. with fixed or fluidised bed columns, to determine how they could translate for real-application scenarios.

5.4 Conclusions

Sorption media functionalised with zinc offers potential to enhance selective partitioning of ammonia from a range of source waters from wastewater final effluent to industrial wastewater. This increases the potential to extend the audit of ammonia that can be recovered and hence reduce the need for de novo ammonia production. Nonetheless, the media sorption capacity must be considered and benchmarked against conventional IEX media.

The results indicated that the initial pH and solution buffer capacity were critical parameters to drive the onset and sustain the conditions for ion exchange and molecular adsorption, influencing the sorption capacity. The buffer capacity was related to the N/Zn molar ratio, determined by the available TAN concentration in solution and the transition metal load. The Zn²⁺-hybridised resins removed TAN over a range of conditions (TAN concentration, pH, competing cations) by switching between molecular adsorption and ion exchange. Nonetheless, the zinc doping boosted the TAN sorption capacity only in limited settings, as it was shown to be bound by a self-inhibiting acidifying effect and competition with hydroxyls at high pH. Most conditions yielded a net pH promoting ion exchange and thus greater sodium and protons coverages were often beneficial. The resin loaded

with metal (hydr)oxide likely separated TAN with both mechanisms, yet the high sodium content promoted ion exchange and overshadowed the contribution of the (hydr)oxide particles. Furthermore, this media was responsible for a net solution basification, up to levels hampering both ion exchange and molecular adsorption. Cations in real wastewaters impacted the operation of all media by competing with ammonium for IEX and exchanging with Zn, needed for LEX. This suggested that stronger metal-resin bonds are necessary to improve LEX operation in complex matrices. Nonetheless, most resins performed discretely even with such effluents, reaching capacities of 21-33 mg N/g.

The conventional IEX resin proved to be an effective media, yielding high capacity in all the tested conditions (maximum 80 mg N/g). The sorption capacity in the Zn²⁺-hybridised media (75 mg N/g) can be further improved by ensuring a full metal loading and an effective buffer system to control the pH in the narrow range of suitability. Future research should also focus on testing new methodologies to embed the resin with zinc (hydr)oxide nanoparticles, limiting the NaOH requirements and the alkalinising effect.

Appendix D

Table D-1. Studies testing transition metal-based media for ammonia separation from liquid and gaseous mixtures. WA= weak acid, WB= weak base, SA= strong acid, MaP= Macroporous, MiP= microporous, S-DVB= Styrene-divinylbenzene, IDA= iminodiacetic acid; L, T, E = determined with Langmuir isotherm, Thomas model, experimentally, respectively. Values reported in ammonia (NH₃) or ammonium (NH₄) were converted to N. Concentrations are in mg N/L and capacities in mg N/g, except ¹⁹.

Source	Metal	Media	Media size & porosity	Methodology	[N] _{feed}	WW type	Capacity (q)
40	Cu	Chitosan (polymeric polyamine)	n.a.	Batch, stirred, 1 g/20 mL of TAN solution+100 mL Di water, pH 8.9-9.0	1400	Synthetic (mono)	28 mg/g
38	Cu	S-DVB resin + IDA (WA)	MaP 0.4-1.25 mm, pore 451 nm, MiP 4.3 m ² /g, pore V=10.3 cm ³ /g	Batch, flasks shaken at 200 rpm, 1 g/100 mL, pH 9.5, 15-25°C, 24 h	8-3300	Synthetic (mono)	qm=35-34 mg/g (L, 15-25°C)
27	Cu	S-DVB resin + IDA (WA)	MaP, size 0.4-1.25 mm >95%	Batch, flasks shaken at 200 rpm, 100 mL/1 g media, pH 9.5, 25°C, 300 mins	1600-3300	Synthetic (multi)	qm=38 mg/g (L)
11	Cu	SiO ₂ + 1ary amino groups	440 nm	Batch, stirring, 0.04 g/20 mL, pH 5.9-8, < 1 min	116	Synthetic (mono)	qe=13-16 mg/g (E), 17 mg/g (L)
11	Cu	Amberlite IRA 96F: S-DVB + 2ary amino groups (WB)	Porous	Batch, stirring, 0.1 g/15 mL, pH 7.4-9.5, 20-60 mins	116 (i); 250 (ii)	Synthetic (mono)	qe= 13 mg/g (pH 9.5) (E) (i) qe= 11 mg/g (pH 7.4-7.9) (pseudo 2nd order) (ii)
13	Cu	Amberlite IRC-120: S-DVB + sulfonate (SA)	0.6-8.0 mm	Batch, 0.1 g resin R-Cu/20 mL, 1 h	872	Synthetic (multi)	n.a.
13	Cu	Amberlite IRC-120: S-DVB + sulfonate (SA)	0.6-8.0 mm	Batch, 120 rpm, 0.1 g resin R-Cu/20 mL, 30°C, 1 h	26	Synthetic (multi)	n.a.

Source	Metal	Media	Media size & porosity	Methodology	[N] _{feed}	WW type	Capacity (q)
12	Zn	S-DVB resin + IDA (WA)	Resin pore size: 513 nm	Batch, in 120 mL reactors, shaken 200 rpm, 1 g/100 mL, pH 9.54, 25°C, 10 h	50-4000	Synthetic (mono)	Qm N=39 mg/g (L)
19	Zn	DoweXTM 50WX8-400 (tested) (S-DVB + sulfonate);	MiP; 200-400 mesh size	Batch, mixing, 3 mL media/99-116 mL solution, pH 8, 15 mins	≈ 67-179	Synthetic (mono)	qm=5.2 g/L resin (L)
10	Zn	WACG: acrylate + DVB + carboxylate (WA)	400-1200 µm	Column, 800 mg Zn-WACG (= 1 mL) + 1600 mg IRA67 in a 35 mL column, flow 1 mL/min for 125 min (125 BV)	3520-7030	Synthetic (multi)	n.a.
10	Zn	WACG: acrylate + DVB + carboxylate	400-1200 µm	Batch, mixing, 1 mL TAN solution in 1.5 mL tube + 225 mg/mL Zn-WACG + 550 mg/L IRA67 (pH buffering resin) in 1.5 mL tube, pH 9.5, 12 h	14007 (tested up to 20000)	Synthetic (multi)	qm=55 mg/g (E)
10	Zn	WACG: acrylate + DVB + carboxylate (WA)	400-1200 µm	Batch, mixing, 125 mg/mL Zn-WACG + 250 mg/L IRA67 (pH buffering resin), pH 9.3, 12 h	4230	Hydrolysed urine	n.a.
32	Cu, Ni, Zn	Amberlite IRC-50: methacrylic acid-DVB + carboxylate (WA)	0.3-1.8 mm	Batch, 0.1 g/30 mL, 17°C, 24 h	7007	Synthetic (mono)	q= 672 mg/g (Zn at 17°C), 490 mg/g (Ni, 25°C), 420 mg/g (Cu, 25°C)
7	Cu, Ni, Ag, Zn, Co, Fe	Amberlite IRC-50: methacrylic acid-DVB + carboxylate (WA)	0.3-1.8 mm	Batch, shaken occasionally, 1 g/100-500 mL, 30°C, 2-4 h	1410-140000	Synthetic (multi)	/
13	Cu, Ni, Co	Amberlite IRC-120: S-DVB + sulfonate (SA)	0.6-8.0 mm	Batch in 100 mL flasks shaken at 120 rpm, 0.1 g/20 mL, pH 8.6, 30°C, 30-60 mins	872	Synthetic (mono)	qe N=164 mg/g (Cu, E), 131 mg/g (Ni, E), 118 mg/g (Co, E)

Source	Metal	Media	Media size & porosity	Methodology	[N] _{feed}	WW type	Capacity (q)
41	Cu, Ni	DoweX A-1, Dowex 50W-X8, Chelex, Duolite CC-3 Duolite ES-63, IRC-50	n.a.	pH 9-12	n.a.	n.a.	n.a.
9	Zn, Cu (Ni, Co)	WACG: acrylate + DVB + carboxylate (WA)	Gel, 16-50 screen size distr.	Batch, mixing, 15 mg resin/1.5 mL solution in 1.5 mL tubes, pH 9.5, 24 h	7030	Synthetic (multi)	Cu-WACG: qm= 112 mg/g (E); Zn-WACG qm= ca 84 mg/g (E)
9	Zn, Cu (Ni, Co)	SIR: S-DVB + IDA (WA)	MaP, 16-50 screen size distr.	Batch, mixing, 15 mg resin/1.5 mL solution in 1.5 mL tubes, pH 9.5, 24 h	7030	Synthetic (multi)	Cu-SIR: qm= ca 53 mg/g (E) ; Zn-SIR qm= ca 41 mg/g (E)
9	Zn, Cu (Ni, Co)	WACG: acrylate + DVB + carboxylate (WA) / SIR: S-DVB + IDA (WA)	As above	Batch, mixing, 15 mg resin/1.5 mL solution in 1.5 mL tubes, pH 9.2, 24 h	4000	synthetic urine	qm=45 mg/g (SIR-Zn, E), qm= 96 mg/g (Cu-WACG, E)
8	Cu, Zn, Ni	D751: S+DVB + IDA (WA)	MaP, 0.-1.2 mm size. Pore V=0.012-0.020 cm ³ /g; pore d=4.3-4.5 nm	Batch, 250 mL reactors shaken at 120 rpm, 0.6 g/100 mL, pH 11, 25°C, 1.5 h	100	Synthetic (mono)	q=5.4 mg/g (Cu, E), 5.8 mg/g (Cu+Ni, E), 5.7 mg/g (Cu+Zn, E)
8	Cu, Zn, Ni	Cu/Zn/Ni(OH) ₂ + D751: S+DVB + IDA (WA)	MaP, 0.-1.2 mm. Pore V=0.013-0.016 m ³ /g, pore d= 4.3-4.4 nm	Batch, 250 mL reactors shaken at 120 rpm, 0.6 g/100 mL, pH 11, 25°C, 1.5 h	100	Synthetic (mono)	q=5.8 mg/g (Cu, E), 8.3 mg/g (Cu+Ni, E), 7.9 mg/g (Cu+Zn, E)
31	Cu	Cu(OH) ₂ + S-DVB resin with IDA (WA)	MaP, size 0.4-1.25 mm >95%	Column (d 15.6 mm, 700 mm h), 1 mL/min pH 7.8	806	Synthetic (mono)	q=15 mg/g
31	Cu	Cu(OH) ₂ + S-DVB resin with IDA (WA)	MaP, size 0.4-1.25 mm >95%	Column (d 15.6 mm, 700 mm h), 1 mL/min pH 7.8	806	Synthetic (multi)	q=9.48 mg/g (with Na), 7 mg/g (with Ca)
14	Cu	Cu(OH) ₂ + D61: S-DVB + sulfonate (SA)	100-500 nm macropores	Batch, mixing in 50 mL tubes, 0.1 g/50 mL, pH 7, 22°C	2-200	Synthetic (mono)	qm=24 mg N/g (L)
14	Cu	Cu(OH) ₂ + D61: S-DVB + sulfonate (SA)	100-500 nm macropores	Column, 5 mL media in column (d 9 mm), 100 mL	1-10	Synthetic (multi)	qe=1.4 mg/g (T); qe= ca 0.9 mg/g (with cations) (E)

Source	Metal	Media	Media size & porosity	Methodology	[N] _{feed}	WW type	Capacity (q)
				solution, pH 7, EBCT 2.5 mins			
14	Cu	Cu(OH) ₂ + D61: S-DVB sulfonate (SA)	100-500 nm macropores	Column, 5 mL media in column (d 9 mm), 100 mL solution, pH 7, EBCT 2.5 mins	0.95-5.04	Fishpond, Lake water, treated WW	n.a.
41	Cu, Ni	Hydrous oxide of Zr/Ti	n.a.	pH 9-12	n.a.	n.a.	n.a.
16	Ni/Sr/Zr oxides	Graphene oxide	n.a.	Batch, shaking, 50 mg/30 mL, pH 5-8, RT, 15 mins	4-148	Synthetic (mono)	qm=150 mg/g (L), qe=140 mg/g (E))
16	Ni/Sr/Zr oxides	Graphene oxide	n.a.	Batch, shaking, 50 mg/30 mL, pH 5-8, RT, 1 h	414	Refinery WW	qe=60 mg/g (E)
16	Ni/Sr/Zr oxides	Graphene oxide	n.a.	Batch, shaking, 50 mg/30 mL, 30 mins	414	Refinery WW (modified)	n.a.
20	Fe oxide	Zeolite	Fe oxide was 60 nm	Batch, in 50 mL tube shaken at 250 rpm, 25 mL + media (1 g/L), pH 7, 20°C, 2000 mins	16	Synthetic (multi)	qe=3 mg/g (pseudo 2nd order)
19	Zn	ZnO	n.a.	Batch, stirring, 0.22 g/100 mL, pH 8, 20 mins	≈ 123	Synthetic (mono)	no adsorption
19	Zn	Zn(OH) ₂	n.a.	Batch, stirring, NH ₃ sol. + 4 mL ZnCl ₂ (200 g/L) (total V 12-103 mL), pH 9.5, 30 mins	≈ 35-669	Synthetic (mono)	qm= 118 mg/g Zn(OH) ₂ (L)
21	Mn	MnO	n.a.	Batch, stirring, 0.1 g/25 mL 25°C, pH 7 (i); 55°C /ii), 24 h	20 (i); 10-250 (ii)	Synthetic (mono)	qe=4 mg/g (pseudo 2nd order) (i) qm= 29 mg/g (L) (ii)
21	Mn	MnO	n.a.	Batch, stirring, 0.1 g/25 mL, 25°C, pH 7, 2 h	20	Synthetic (multi)	qm= 4.2 mg/g (only NH ₃), 2.8 (with Na), 1.0 (with K), 2.5 (with Mg), 0.9 (with Ca)

Table D-2. Metal (hydr)oxide loading methodologies. P= Purolite, HFO= hydrated ferric oxide, NP= nanoparticles, LR= loading ratio (mol metal in solution/mass resin in solution), [R]= resin concentration (mass resin/volume loading solution), EtOH= ethanol, 2x=twice. ^a Integrated with personal communication.

	15a	25	42	43	44	14	8	This study
Resin type	IRA-400 (AEX)	P. C-145 (CEX)	P. A-400 and IRA-900 (AEX), P. C-100 (CEX)	P. A502P (AEX)	P. C100 and C145 (CEX), PAD610, P. S930+, GAC	Resin D61 (CEX)	D751 (CEX) in Na form	Dowex MAC-H
Loading	Hydrated Fe(III), Cu (III), Zr (IV) oxide	HFO	Hydrated Fe(III) oxide	Fe(OH) ₃ , MnO ₂ NP	HFO	Hydrated CuO	Cu(OH) _x , Ni(OH) _x , Zn(OH) _x	ZnO / Zn(OH) ₂
Resin mass (g)	21.15	n.a.	n.a.	96	20	n.a.	1	20
Method	Column	Column	Column	Flask	Flask, shaker (150 rpm), 3 h	n.a.	Flask, stirring	Flask, shaker (130 rpm), 2 h
Metal solution	1 M FeCl ₃ + 1 M HCl 600 mL, 1 h (10 mL/min, 1 h)	0.25 M FeCl ₃ (4%w/v), pH 2	0.25 M FeCl ₃ (4%w/v), pH ≤ 2	5% w/v FeCl ₃ , MnSO ₄ in 50% v/v H ₂ O&EtOH.	160 mL 5% w/v FeCl ₃	0.30 M CuCl ₂ (4%w/v), pH 2	0.05 M Cu/Zn/Ni, 200 mL, 1.5-3 h, 120 rpm.	1.39 M ZnCl ₂ , 567 mL
LR (mol/g)	0.03	n.a.	n.a.	n.a.	n.a.	n.a.	0.01	0.04
[R] (g/L)	35.25	n.a.	n.a.	n.a.	n.a.	n.a.	5.00	35.27
Alkaline solution	1 M NaOH, 1 M NaCl. 600 mL, 1 h (10 mL/min, 1 h)	1.25 M NaOH, 0.86 M NaCl (2x)	1.25 M NaOH, 0.86 M NaCl	1.25 M NaOH, 1 h	1.25 M NaOH 160 mL, 1 h (2x)	1.25 M NaOH, 0.86 M NaCl (2x)	0.005-0.2 M NaOH 100 mL, 45 mins, 120 rpm	1.25 M NaOH, 0.86 M NaCl 558 mL, 1 h, 130 rpm

	15a	25	42	43	44	14	8	This study
EtOH/H₂O rinse	10/90% v/v 225 mL (7.5 mL/min for 30 mins)	50%/50% v/v	50%/50% v/v	n.a.	n.a.	50%/50% v/v	n.a.	50%/50% v/v, 242 mL for 30 mins, 130 rpm)
DI water rinse	255 mL (8.5 mL/min for 30 mins)	n.a.	n.a.	✓	✓	-	✓	242 mL, 10 mins, 150 rpm (2x)
Thermal treatment	In 200 mL DI water, 55°C, 3 h, 60 rpm	50-60°C, 1 h	50-60°C, 1-12 hours	Air drying, 24 h	n.a.	50°C, 3 hours	Drying 300 mins 50°C	In 150 mL DI water, 50°C, 1.5 h. Drying 55°C, 22 h

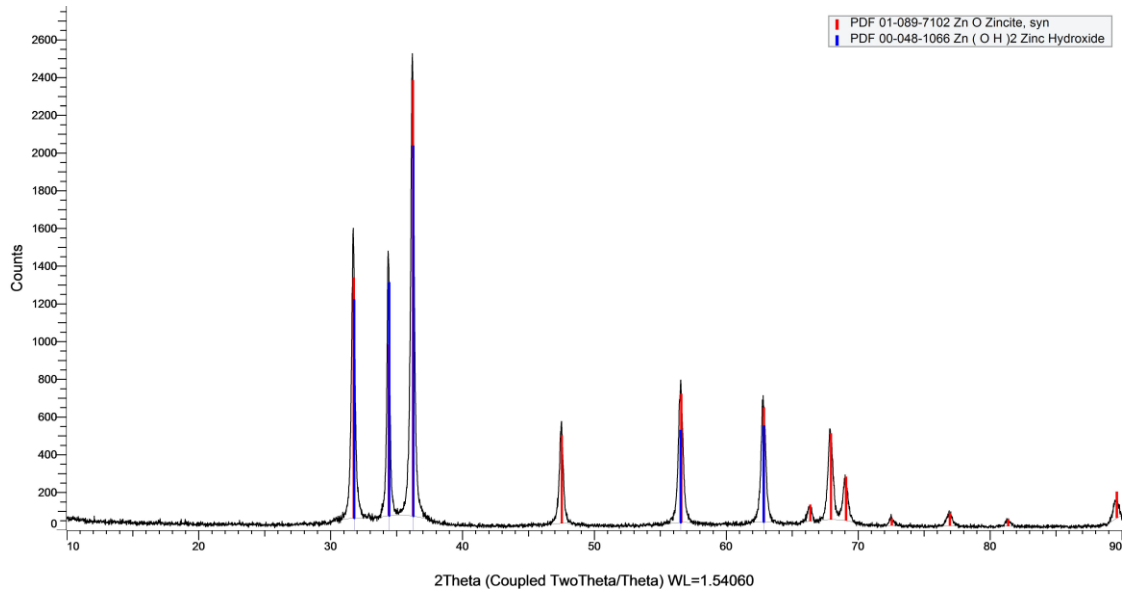


Figure D-1. XRD spectra of the precipitated zinc powder used for the preparation of dispersions, showing alignment with zinc hydroxide (blue) and oxide (red).

$$FA = \frac{1}{1 + 10^{pK_a^S - pH}} \quad \text{Eq. D-1}$$

$$pK_{a,T}^S = pK_{a,298}^S + 0.0324 \cdot (298 - T) \quad \text{Eq. D-2}$$

Where FA is the fraction of free ammonia (NH_3) over the total ammonia concentration (-). $pK_{a,T}^S$ is the acid dissociation constant of $\text{NH}_3/\text{NH}_4^+$ (-) at temperature T (K) ⁴⁵.

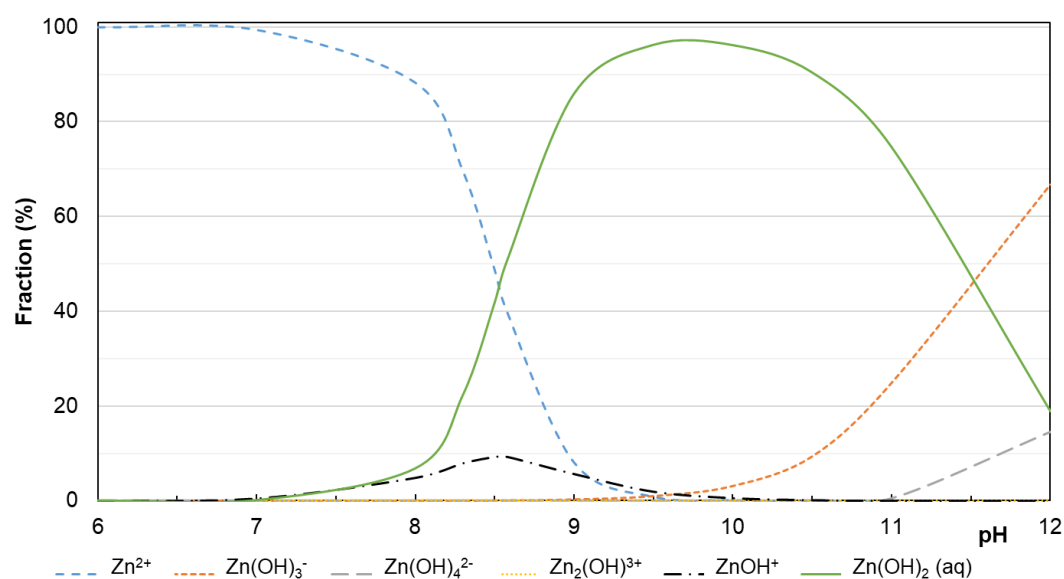


Figure D-2. Zn speciation across pH change, obtained with Visual Minteq software (Zn 0.009 M corresponding to 0.4 g D-Zn I in 40 mL solution, 22°C).

Table D-3. Parameters obtained from the linearised Langmuir adsorption isotherm model fitted to the experimental data.

Media		pH 8	pH 9.5	pH 10
D-Na ⁺	R ²	0.98	0.91	0.98
	KI (L/mg)	0.011	0.006	0.010
	qmax (mg/g)	47	85	74
D-Zn ²⁺ I	R ²	0.94	0.78	0.87
	KI (L/mg)	0.012	0.003	0.003
	qmax (mg/g)	14	69	87
D-Zn ²⁺ II	R ²	0.89	0.58	0.64
	KI (L/mg)	0.005	0.001	0.004
	qmax (mg/g)	5	55	52
D-Zn(OH) ₂	R ²	0.75	0.82	0.85
	KI (L/mg)	0.001	0.001	0.001
	qmax (mg/g)	119	121	78

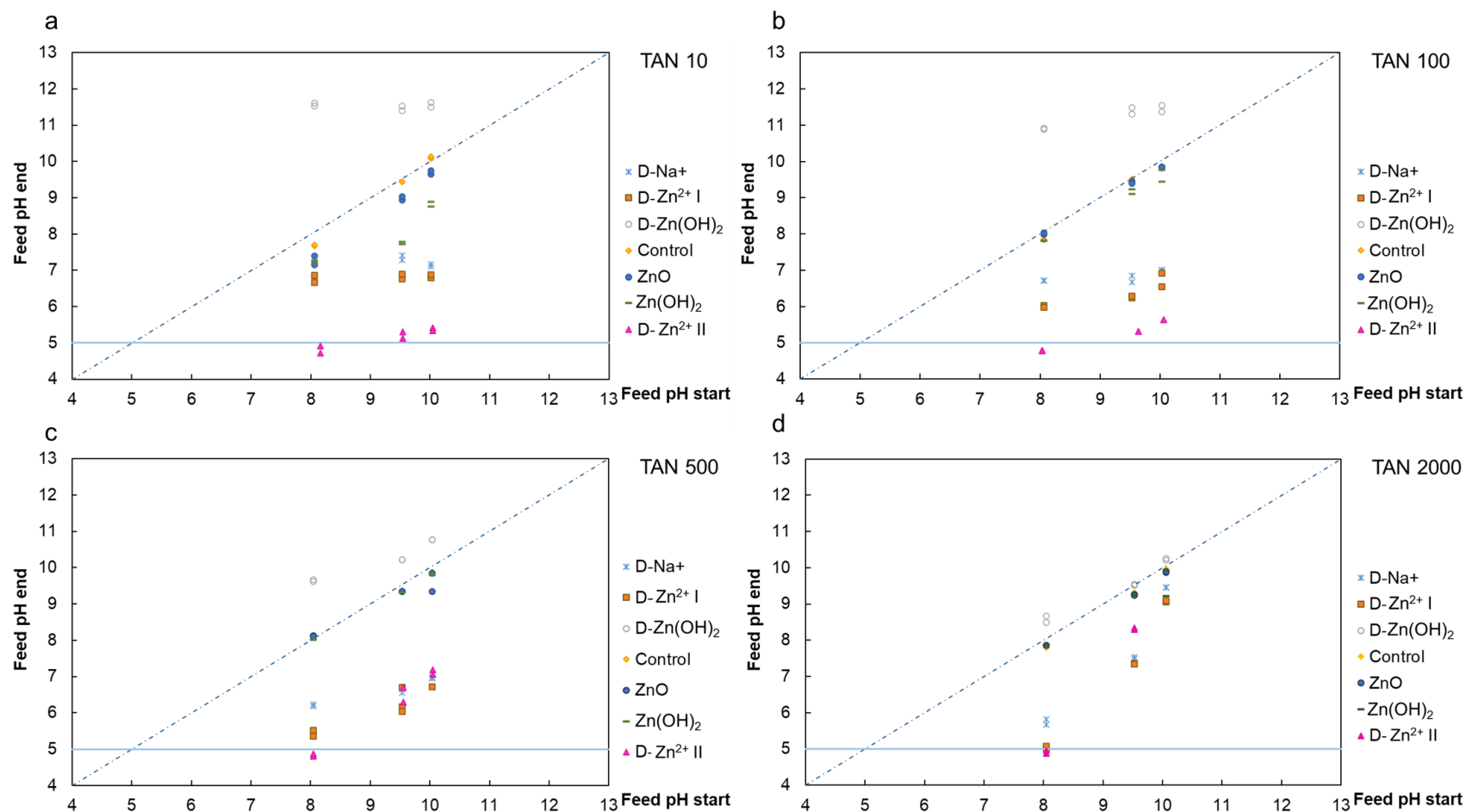


Figure D-3. Solution pH before (8, 9.5, 10) and after the adsorption tests with different media and control, at initial TAN concentration = 10 (a), 100 (b), 500 (c), 2000 (d) mg N/L. Duplicates are shown.

Table D-4. Beads composition (wt %) after adsorption at 10, 1000, 2000 mg TAN/L.

			Na	Zn	C	O
[TAN] = 10 mg/L	pH 8	D-Na ⁺	7.5±0.4	0.0±0.0	55±2	36±2
		D-Zn ²⁺ I	3.2±0.2	6.0±0.9	51±1	35±1
		D-Zn ²⁺ II	0.6±0.7	8.4±0.4	56±1	32±1
		D-Zn(OH) ₂	14.0±0.7	1.4±0.2	49±3	34±2
	pH 9.5	D-Na ⁺	7.9±0.3	0.0±0.0	54±2	37±1
		D-Zn ²⁺ I	3.2±0.1	6.3±0.3	54±1	32±1
		D-Zn ²⁺ II	0.4±0.6	8.8±0.6	56±3	32±3
		D-Zn(OH) ₂	14.3±0.6	1.7±1.1	47±3	36±3
	pH 10	D-Na ⁺	6.6±0.2	0.0±0.0	55±1	36±1
		D-Zn ²⁺ I	3.2±0.2	6.4±1.3	54±2	32±2
		D-Zn ²⁺ II	0.5±0.7	8.6±1.5	56±1	32±2
		D-Zn(OH) ₂	13.0±0.3	2.2±0.4	47±1	36±2
[TAN] = 1000 mg/L	pH 8	D-Na ⁺	-	-	-	-
		D-Zn ²⁺ I	1.7±0.3	7.4±0.6	59±3	28±4
		D-Zn ²⁺ II	1.2±0.1	8.4±0.4	55±2	33±2
		D-Zn(OH) ₂	7.1±1.1	2.6±0.4	57±3	32±3
	pH 9.5	D- Na ⁺	6.2±0.3	0.0±0.0	61±2	32±2
		D-Zn ²⁺ I	3.2±0.3	7.4±0.9	58±2	28±2
		D-Zn ²⁺ II	2.0±0.1	8.7±1.0	54±2	32±2
		D-Zn(OH) ₂	10.1±0.6	2.5±0.3	55±2	32±2
	pH 10	D-Na ⁺	6.7±2.0	0.0±0.0	61±8	32±6
		D-Zn ²⁺ I	5.0±0.6	6.9±1.0	59±3	29±4
		D-Zn ²⁺ II	-	-	-	-
		D-Zn(OH) ₂	-	-	-	-
[TAN] = 2000 mg/L	pH 8	D-Na ⁺	1.7±0.1	0.0±0.0	59±1	32±2
		D-Zn ²⁺ I	2.8±0.1	6.4±0.9	55±2	30±2
		D-Zn ²⁺ II	1.2±0.1	8.9±0.8	55±1	32±2
		D-Zn(OH) ₂	6.8±0.3	2.6±0.2	53±2	34±2
	pH 9.5	D-Na ⁺	7.5±0.2	0.0±0.0	55±2	35±2
		D-Zn ²⁺ I	4.5±0.2	6.1±0.7	54±1	31±1
		D-Zn ²⁺ II	2.1±0.2	8.8±1.2	54±2	31±3
		D-Zn(OH) ₂	9.4±0.3	2.4±0.2	52±1	34±1
	pH 10	D-Na ⁺	5.9±0.4	0.0±0.0	54±3	35±2
		D-Zn ²⁺ I	4.5±0.3	6.2±0.7	54±2	31±2
		D-Zn ²⁺ II	-	-	-	-
		D-Zn(OH) ₂	8.6±0.5	2.2±0.3	52±2	33±2

Table D-5. TAN adsorption in real and synthetic effluents. CE= Cranfield sewage works effluent. PP_Str= treated AnMBR effluent. Synth.= synthetic. qf= adsorption capacity (mg/g). Ads = TAN adsorption (%). TAN concentration ([TAN]) is expressed as mg/L. Averages of duplicates are shown.

		CE	AnMBR effluent	PP_Str	CE synth.	AnMBR synth.	PP_Str synth.
Feed start	[TAN]	9.1	704	75	15.3	720	77
	pH	8.28	7.41	10.33	8.31	7.42	10.34
D-Na	pH _{end}	7.78	7.37	8.72	8.26	6.49	7.24
	[TAN] _{end}	1.1	375	39	0.2	404	13
	qf	0.8	32.9	3.7	1.5	31.6	6.4
	Ads%	88%	47%	49%	99%	44%	83%
D-Zn²⁺ I	pH _{end}	6.97	7.29	8.97	8.11	5.38	6.80
	[TAN] _{end}	4.4	495	44	1.6	624	20
	qf	0.5	20.9	3.1	1.4	9.6	5.7
	Ads%	52%	30%	41%	90%	13%	74%
D-Zn²⁺ II	pH _{end}	5.69	7.41	9.60	6.09	4.84	6.48
	[TAN] _{end}	8.5	631	53	13.2	708	41
	qf	0.1	7.3	2.2	0.2	1.2	3.6
	Ads%	7%	10%	30%	14%	2%	47%
D-Zn(OH)₂	pH _{end}	10.76	8.37	10.40	11.43	9.06	11.50
	[TAN] _{end}	4.1	398	56	8.2	318	56
	qf	0.5	30.6	1.9	0.7	40.2	2.1
	Ads%	55%	43%	25%	46%	56%	28%
Control	pH	8.52	7.75	10.36	8.05	7.35	10.30
	[TAN]	9.3	671	69	15.9	742	78
	Rem %	-2%	5%	8%	-3%	-3%	-1%

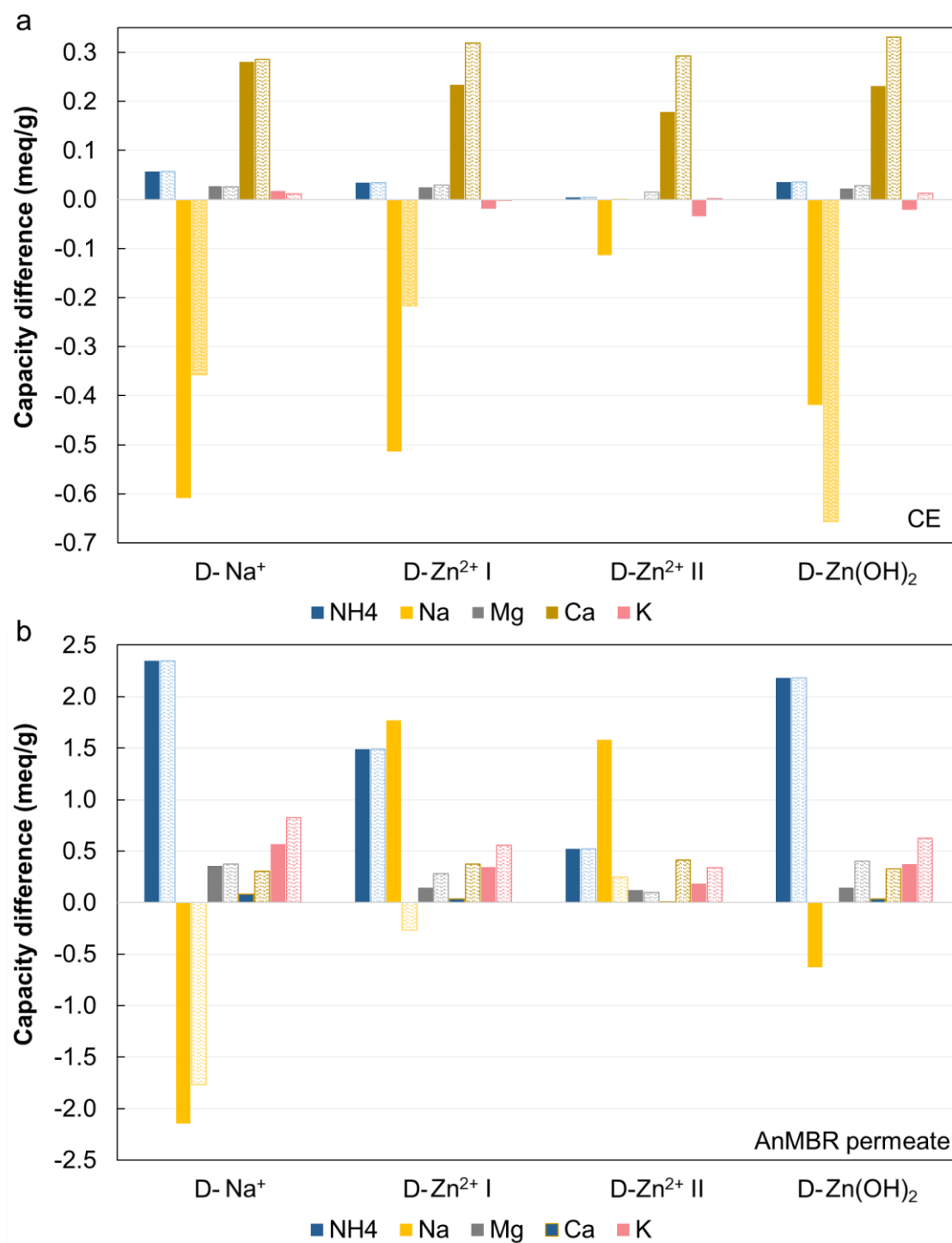


Figure D-4. Changes in cations composition (meq/g) of the media treating the sewage works effluent (a) and the AnMBR permeate (b), as estimated via beads' SEM-EDS analyses (solid) and via IC analyses of the treated waters (waves).

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Chapter 6

6 Implications of the work

The overall aim of this thesis was to understand and critically evaluate the impact of the water matrix on the mechanisms controlling ammonia partitioning in complex fluids and to establish optimum transfer routes into gas, liquid, solid phases from industrial effluents.

Ammonia removal from wastewater is a necessity ¹, widely recognised and regulated by legislations worldwide. Conventional ammonia removal (i.e. via biological processes) can often lead to high capital and operational expenses (e.g. associated with aeration, 3.1 kWh/kg N)² and to significant greenhouse gas N₂O emissions ^{3,4}. Industries have to comply with effluents discharge regulations and are subjected to an increasing pressure to reduce emissions and waste streams. Ammonia recovery has attracted growing interest in the water sector, as it has potential to pursue environmental protection and provide economic benefits ⁵, including the sale of recovered products (e.g. 521 USD/ton ammonium sulphate solution 21% ⁶) and savings on maintenance needs (e.g. struvite removal to prevent equipment and pipework clogging). Ammonia harvesting from industrial effluents can contribute to a resource management based on the circular economy ⁷, potentially fostering water industrial symbioses ⁸. Industrial effluents have physico-chemical characteristics with wide ranges of compounds and concentrations, including ammonia and industry-specific compounds ⁷. Despite the potential role of ammonia recovery, no recommendations currently exist for selecting and operating appropriate technologies to recover ammonia from industrial effluents. Contributions to knowledge in this thesis advanced the understanding of factors driving the performance of processes partitioning ammonia to solid, gas and liquid phases, thus facilitating more informed technology selection and operation.

In particular, key factors impacting technology selection and operation were established and used to determine an ideal flowsheet to recover ammonia from distillery wastewater, used as case study. The technical viability of such a flowsheet, comprising struvite precipitation and ammonia stripping and

scrubbing, was proved in a pilot scale study, which demonstrated the critical role of pH for the processes' performance. The feasibility of stripping ammonia from effluents containing transition metals and acidic organic compounds (e.g. humic acids) was investigated, revealing a significant hindrance only at high concentrations, found in niche wastewaters. Lastly, the use of ion- and ligand-exchange media with real municipal and industrial effluents was investigated, also as potential integration in a treatment train. The results showed a discrete performance, despite the high concentration of competing cations, and informed on the ideal conditions to promote nitrogen removal.

Although a part of this study focused on distillery wastewater, the findings and process selection criteria apply more broadly to other industrial effluents as well, providing a framework for informed decision-making, particularly for sectors considering ammonia recovery as alternative or upgrade to nitrogen removal. Industrial stakeholders often target cost-effective compliance with discharge limits, therefore recovery approaches should be competitive with conventional removal technologies. Prior to assessing the financial competitiveness of the recovery options, it is essential to better understand their processes operation to establish the conditions for comparison to the removal options. The technical viability of these technologies and flowsheet has been assessed in this study, nonetheless also economic and environmental analyses of advantages and disadvantages need to be conducted, based on the specific case. The environmental benefits of ammonia recovery are various and recognised ^{9,10}, however their quantification and potential translation in economic benefits is needed for a more comprehensive comparison with conventional removal pathways. Moreover, distinct recovery technologies have different costs associated both with capital and operational expenses, which largely depend on the specific site (e.g. availability of land and excess energy/heat to recover, cost of required materials) and the wastewater characteristics (e.g. buffer capacity, concentrations of competing cations and other interfering species etc.).

To illustrate, this study highlighted that pH control is a critical factor influencing the efficiency of all the investigated technologies, as directly impacting the

proportions of NH_3 and NH_4^+ . Maintaining alkaline conditions for processes like stripping and struvite precipitation can inflate operational costs, due to chemical dosing requirements largely affected by the water buffer capacity. For instance, NH_3 stripping using thermally driven volatilisation and/or CO_2 stripping ¹¹ could lower the chemicals footprint of the process, although a case-by-case assessment is needed. Moreover, elevated concentrations of transition metals and organic, acidic compounds in niche effluents can reduce stripping efficiency, potentially creating the need for mitigation pre-treatment (e.g. metals or organics removal) or post-treatment with other technologies to achieve the target effluent levels, increasing capital and operational expenses. Likewise, NH_4^+ recovery, e.g. via conventional ion exchange and precipitation, requires maintaining suitable pH conditions, and it can be subjected to cations competitions, as documented in this study, affecting the required chemicals/material inputs. Overall, these technologies operation should consider trade-offs between removal efficiency and the capital and operational expenses required to achieve it.

The implications for the sector generated by this thesis' outcomes are presented as answers to the following relevant questions.

6.1 What drives the selection and operation of an ammonia partitioning technologies to be applied to industrial effluents?

The most established ammonia partitioning processes are precipitation, mainly as struvite, stripping and sorption ¹². This thesis provided evidence of the impacts of different physico-chemical parameters on the performance of ammonia recovery technologies, based on literature and experimental results (Table 6-1). Building on this knowledge, the following recommendations for selection and for operation were developed, considering the quality of the end-product and the removal capacity.

The preliminary indication is to favour, where possible, technologies yielding a high-value recovery product. Indeed, the quality and the versatility of the end-product increasingly become a central criterion in recovered ammonia

management ¹³. Stripping and selective sorption can generate N-rich aqueous solutions with various applications, thus offering more market opportunities as compared to struvite (and other ammonium-based precipitates), mainly used as a fertiliser. Such advantage can shift the common practice from implementation of struvite to the application of stripping and sorption, as standalone or integrated units. Naturally, the local demand for a particular product should also be explored, to further guide the selection e.g. the reuse of sorption media regeneration brine in situ or at nearby facilities, creating circular economy symbioses. Such product-oriented approach needs alignment with the wastewater profile, to assess the process viability.

Precipitation, particularly of struvite, can be sensitive to the presence of competing ions, reducing its precipitation potential and thus removal, and to the co-precipitation of other solids, affecting the end-product purity. Although calcium is a major competitor for phosphate, the pilot study demonstrated that even with molar ratios Ca:P 0.3:1 and Ca:Mg $\leq$ 1:1 good quality struvite was recovered from distillery effluent (Ch. 3). Nonetheless, greater Ca content can contribute to a reduced removal performance. Furthermore, the operational costs to dose chemicals to optimise the components molar ratios might offset the overall advantages of the technology. Therefore, struvite precipitation is advised if the Mg and P molar contents are close to or higher than the N load and/or if the supersaturation (SSR) exceeds 1. In the latter case, this choice addresses both N recovery, even if partial, and protection of downstream treatment steps from uncontrolled scaling (Ch. 3). The content of dissolved organics might decrease struvite precipitation efficiency to a limited extent (Ch. 3), so preliminary studies on this effect are warranted. For the operation, suitable conditions for precipitation include moderate temperatures (around 25-35°C), a limited content of suspended solids to act as nucleation seeds, and optimised molar ratios of Mg:N:P. To increase the product purity, nitrogen should be more abundant than magnesium and phosphorus, whereas for maximum nitrogen removal via struvite, an excess of magnesium and phosphorus is necessary. For low TAN content effluents (< 0.5-1 g N/L), precipitation can provide a solution when high-capacity and selective

sorption media are not available, even in cases of unbalanced components molar ratios, which can be adjusted with limited operational expenses.

Overall, stripping processes are particularly suited for conditions involving high total ammonia nitrogen (TAN) concentrations in the feed ($> 0.5\text{--}1\text{ g N/L}$) to promote economic feasibility. Furthermore, the following conditions are beneficial: high water temperatures or access to waste heat, elevated carbonate alkalinity which can be exploited for pH increase, and a low scaling potential for precipitates such as struvite. Furthermore, these processes are generally robust in treating effluents containing large concentrations of ions. This highlights the advantages of volatilisation as a mean to partition ammonia from such complex streams, as opposed to ammonium precipitation and sorption processes which are more sensitive to product contamination and competition. Stripping proved to be a successful TAN separation method also in wastewaters containing moderate levels of transition metals and acidic organic compounds (e.g. humic acids, HA), despite the fact that these species can sequester TAN. In solutions with up to N:M 20-1:1 molar ratios and $\approx 600\text{ mg HA/L}$, thermal stripping (65°C) could effectively partition ammonia, indicating it as a viable strategy (Ch. 4). Nonetheless, for more concentrated streams, mitigation options must be explored, which can involve treatment at higher temperatures and/or inducing a selective precipitation of the metal or solvent extraction ¹⁴, as a pre-treatment. These high ratios/content are less common even in industrial effluents, yet some niche wastewaters can be found in the metallurgy sector, including the cases where ammonia solutions are used specifically as a leaching agent, or tannery effluents, carrying high loads of both ammonia and the transition metal chromium ¹⁵. Although the critical HA levels can be rare in industrial effluents, substances with similar chemical behaviour are found at comparable concentrations (Ch. 4). These results can be relevant when applying stripping on the liquid fraction of agro-fermentation effluents, before and after anaerobic digestion, yielding high loads of ammonia and recalcitrant, dissolved organic matter such as fulvic-, humic-like compounds and melanoidins ^{16,17}. Accordingly, the pilot study testing showed that the levels of dissolved organic carbon compounds contained in

digested distillery wastewater (ca. 275 mg DOC/L, equivalent to ca. 575 mg HA/L) did not critically affect ammonia stripping at the tested conditions (Ch. 3).

When TAN concentration is below 0.5-1 g/L, sorption processes can be used, as these are most effective for more diluted effluents to remain economically viable. NH_4^+ -based sorption is sensitive to competing cations, including metals, which can either inhibit the process or generate a contaminated brine. Furthermore, some recalcitrant organic compounds can sorb on sorption media (Ch. 5), potentially affecting their binding capacity, or sequester a fraction of the ammonium. For complex matrices cases, the use of high-capacity, selective media is recommended, e.g. involving NH_3 -based adsorption. Transition metal-hybridised media are noted for NH_3 selectivity, however their optimal operation for high capacity strictly depends on a narrow, buffered pH range (9-10) and on a strong media-metal bond (Ch. 5). The major benefit of sorption processes is the recovery of a N-rich brine with less complex matrix than the original feed, which can be used as such or further processes for stripping or precipitation.

Table 6-1. Validation/contribution on the impact of critical parameters on the selection and operation of the recovery processes.

Literature Review		Contribution/Validation
1) Critical factors for selection		
Product value	Ammonia/um solution, obtained via stripping or sorption, can have more applications than precipitated struvite	-
[TAN] _{feed}	<p>→ High [TAN] (≥ 0.5-1 g N/L) favours stripping viability</p> <p>→ Low [TAN] (< 0.8-1 g N/L) preferable for sorption processes</p> <p>→ Any [TAN] suitable for struvite precipitation, if competition of other ions and/or co-precipitation is limited and molar ratios are suitable</p>	<p>→ Stripping proved to be suitable to treat concentrated effluents with [TAN] ≥ 0.7 g N/L, removing 70-90% load (Ch. 3)</p> <p>→ Sorption processes are suited for low [TAN] effluents (e.g. from sewage works), but could handle greater loads (e.g. ~ 0.7-0.07 g N/L), when sufficient media is provided (Ch. 5)</p>
Competing cations e.g. Na/K/Ca/Mg (X)	<p>→ Stripping can handle wastewaters with low N:X</p> <p>→ IEX sorption is inhibited by low N:X and the product quality is reduced. Alternative: media with high capacity and selectivity (e.g. LEX)</p> <p>→ Struvite precipitation is inhibited by low N:X, specifically with high levels of Na, K, Ca (Ca:Mg and Ca:P should be $< 1:1$), but can be mitigated by Mg:N:P optimisation</p>	<p>→ Stripping NH₃ from cations-rich distillery wastewater was not impacted (Ch. 3)</p> <p>→ Although both LEX and IEX media's capacities were reduced by impact of competing cations, TAN was removed from distillery WW. With LEX, stronger metal-resin bond is required (Ch. 5)</p> <p>→ Molar ratios of Ca/P = 0.3:1 and Ca/Mg $\leq 1:1$ allowed struvite precipitation, over calcium precipitates (Ch. 3). Molar ratios of N/P 7:1 and N/Mg 24:1 yielded good purity struvite products (Ch. 3)</p>
Struvite SSR	<p>→ If > 1, struvite could precipitate and thus should be exploited/controlled via precipitation for recovery, especially prior recovery via stripping/sorption</p> <p>→ Between 1 and 3-6 favours struvite pellets growth</p>	<p>→ Scaling agents (.e.g. struvite) removal is necessary prior stripping, when SSR is > 1 (Ch. 3)</p> <p>→ With SSR 3.5 (> 2.5), particles of up to 5 mm size were reached. Increasing SSR led to smaller particles formation. Even with high SSR (e.g. 7.6-16.8), high removal efficiencies were achieved ($\approx 80\%$) without clogging (Ch. 3)</p>
2) Interfering factors impacting operation		
pH	<p>→ pH > 9.2 (25°C), more than 50% of TAN is present as NH₃, favouring stripping</p> <p>→ pH 5-7 suitable for NH₄⁺ sorption</p>	<p>→ Increasing pH improved N removal, reaching 70%, pH 9.4 (Ch. 3)</p> <p>→ IEX media effectively sorbed NH₄ from solution with initial pH 8-10 and was negatively affected by pH < 6 and > 9.5. Zn²⁺-hybridised</p>

	Literature Review	Contribution/Validation
	→ pH > 8.0-9.5 favours struvite formation	media best operated at pH 9-10, by NH ₃ sorption (LEX). pH buffer system is necessary for optimised performance (Ch. 5) → pH ≥ 7.9 enabled ≥ 70% removal, up to 80% (pH 8.9 -9.4) via struvite precipitation. pH determined the struvite particle size (Ch. 3)
Temperature	→ Higher temperature favours NH ₃ form and desorption (e.g. ≥ 50°C). Optimum pH-temperature combination should be found → T ≤ 30-35°C favours struvite precipitation → T = 25-30°C suitable for sorption processes	→ 70% N removal was achieved at 34°C (pH 9.4) (Ch. 3) → Struvite crystallisation was viable between 24-38°C (Ch. 3)
TSS	→ > 0.6 g/L and 1.5 g/L are detrimental for stripping and sorption processes, respectively → < 1 g/L is recommended for struvite precipitation	-
Anions	→ Anions can affect surface tension and reduce sorption performance → SO ₄ , F, CO ₃ can sequester struvite-forming ions and co-precipitate (critical threshold N:SO ₄ /F ≤ 0.2:1). Mitigation includes optimising Mg:N:P dosing, CO ₂ stripping	-
Heavy metals	→ Transition metals potentially affecting stripping processes, by complexing NH ₃ → Metals can compete with NH ₄ ⁺ for sorption. Transition metal can sequester NH ₃ → Metals can impair struvite precipitation and contaminate product, but can be mitigated by Mg:N:P optimisation	→ At molar ratios N/Zn 1:1, N/Cu 4:1, N/Ni 20:1, ammonia stripping was significantly hindered, via complex formation and sorption on metal oxide/hydroxide. These mechanisms can be exploited for NH ₃ partitioning (Ch. 4)
Organic compounds	→ Potentially affecting stripping processes, by binding TAN. Volatile organic compounds (VOCs) can contaminate stripping recovery product → Specific effect on sorption media to be assessed (conflicting results in literature) → Some organic compounds can impair struvite precipitation, binding NH ₄ and Mg, and contaminate product	→ With ≥ 636 mg HA/L, NH ₃ vacuum thermal stripping (1 g N/L) was significantly hindered (Ch. 4). The type and concentration of DOC (275 mg/L) in distillery WW did not critically impact NH ₃ air stripping (Ch. 3) → COD content in (NH ₄) ₂ SO ₄ scrubber liquor increased, likely due to VOCs from distillery wastewater (Ch. 3)

Literature Review		Contribution/Validation
		→ Organic compounds sorbed on sorption media, suggesting that their impact on TAN sorption should be further assessed (Ch. 5) → Organic species found in digested distillery effluent minimally contaminated struvite pellets, yet might have slightly impacted the removal (Ch. 3)
3) Conveniency factors		
Heat	→ High feed temperature and/or available waste heat favours stripping viability ($T \geq 50^{\circ}\text{C}$)	-
pH	→ Critical in determining TAN form, should be optimised for each process. Yet, initial high pH can be exploited for stripping ($\geq 9.5-10$) / struvite (8.5-9.5)	-
Alkalinity	→ If $\text{NH}_4:\text{HCO}_3 \leq 1$, carbonates can be stripped to increase the pH	-

6.1.1 Examples

To illustrate the selection process, three different industrial wastewaters were considered: digested abattoir, pharmaceutical & cosmetic, and digested whiskey distillery effluents. The latter case is explained in detail in section 6.2.

For AnMBR-treated abattoir wastewater, the composition profile was obtained from literature ¹⁸: 52-86 mg TAN/L, 65-238 mg PO₄/L, 4-16 mg Mg/L, 5-631 mg Ca/L, 44-230 mg K/L, 132-270 mg Na/L, 767-959 mg COD/L. In this case, the low ammonia content excludes stripping, due to economic viability. The N:P molar ratios range between 2.5 and 5.4. Given the high concentrations of competing cations (Na, Ca, K), the performance of conventional sorption media would likely be negatively affected. If a high-capacity and selective sorption media is available, its use is recommended to overcome this hindrance and recover a high purity brine. Alternatively, struvite precipitation would be recommended. Although competing cations may reduce struvite removal efficiency, adjustments to the molar ratios by dosing magnesium and phosphate can mitigate such effect and also improve the purity of the precipitates.

The characterisation of the pharmaceutical & cosmetic industry effluent was sourced from ¹⁹: 220 mg TAN/L, 17 mg PO₄/L, 384 mg NO₂/L, 4.2 mg Cl/L, 894 mg SO₄/L, 1753 mg COD/L, BOD₅/COD (biodegradability) 0.11, pH 7.3. The low ammonium and phosphate content and the absence of competing cations justify the selection of sorption as partitioning pathway. This process would allow the concentration of ammonium into a brine to then be treated with stripping. Nonetheless, preliminary tests are advised to evaluate the potential impact of elevated anions and organic compounds on the process.

6.2 What is a suitable flowsheet to maximise N recovery and product value from distillery wastewater?

The N recovery strategy depends on the criteria expressed in section 6.1. Distillery wastewater was considered as a case study to determine a suitable flowsheet for ammonia removal and recovery (Figure 6-1). Anaerobic biological

treatment is commonly applied to remove organic carbon and harvest biogas²⁰ and is responsible for the mineralisation of nutrients in organic matter into ammonia and phosphate²¹. Membrane ultrafiltration enables the retention of most particles in the anaerobic reactor, delivering a solids-free permeate, suitable for treatment with all TAN partitioning processes.

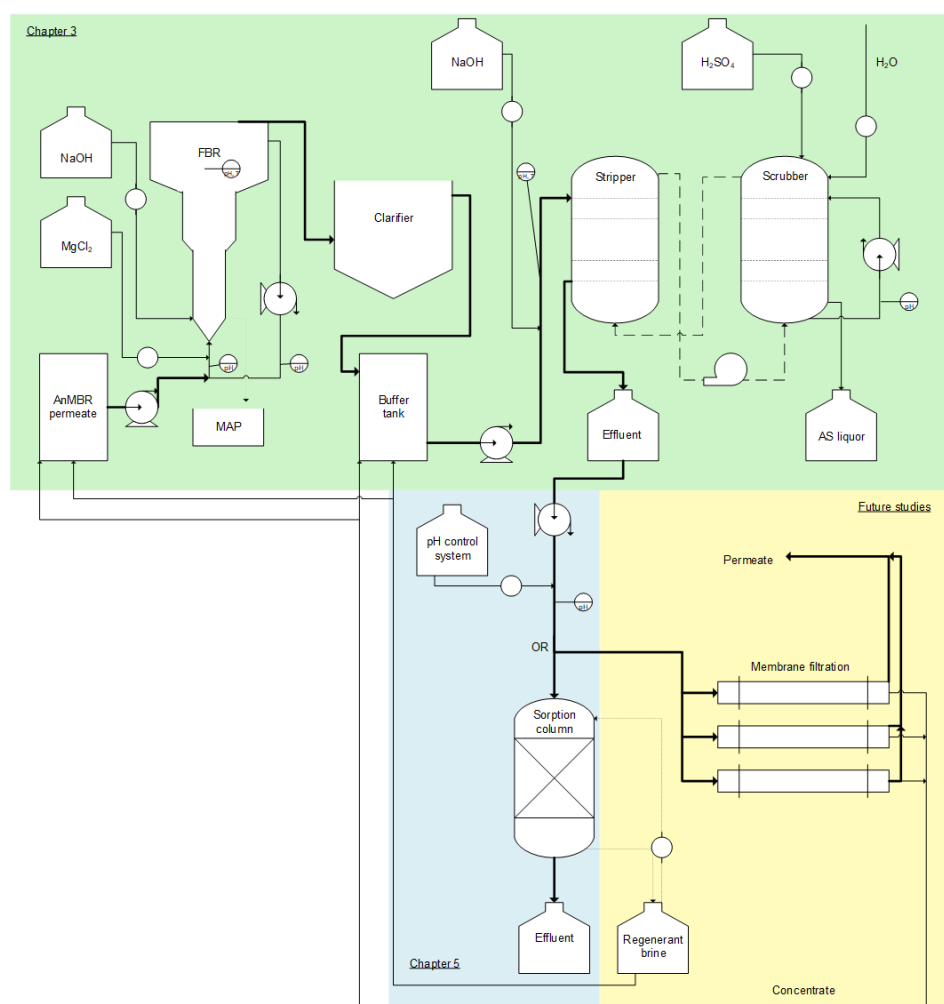


Figure 6-1. Integrated treatment train for digested distillery wastewater and other effluents in comparable settings.

Due to the presence of magnesium and high nutrients levels (≈ 55 mg Mg/L, 760 mg TAN/L, 256 mg $\text{PO}_4\text{-P/L}$) (Ch. 3), the effluent has significant potential for struvite precipitation (SSR 9) and therefore it must be controlled. This can be obtained with a fluidised bed reactor (FBR) with recirculation, self-seeding, and continuous operation (Ch. 3) (Figure 6-1). By controlling the pH via NaOH dosing,

the Mg:P via MgCl_2 supply and the dilution via effluent recirculation, the FBR can achieve i) high P removal (70-80%), limited TAN removal (up to 18%), ii) protection of the downstream units by minimising the scaling potential, iii) recovery of a high-quality struvite product with tuneable morphology. In particular, increasing pH from 7.7 to 9.5 achieved an increase in P removal from 67 to 79% and reduce struvite particles size from up to 5 mm pellets to fine crystals. Although lower pH conditions (e.g. 7.4) had a smaller removal, this could be ameliorated by dosing more Mg and increasing the struvite SSR. The residual ammonia load is then volatilised in a stripping packed tower, exploiting the already high pH and water temperature, and recovered into an ammonium sulphate solution in an acid scrubber (Ch. 3) (Figure 6-1). Preliminary lab tests and pilot demonstrations indicated removal of 90 and 71%, respectively, validating that pH and temperature greatly promoted the process performance. With pH 9.4 and 34°C , a 71% NH_3 removal was achieved, and further exploitation of waste heat is advised to thermally drive stripping, increasing removal, and also lowering the solubility of potential residual P-based precipitates. To increase the ammonium sulphate concentration in solution, it is advised to minimise the water dilution via design (e.g. efficient demister) and operation (e.g. temperature/pressure/air combination) adjustments, and also by iterative acidification of the scrubber liquors. Ammonium sulphate is often used as fertiliser, supplying both N and S, with the latter being increasingly deficient in some British soils ^{22,23}. It can also be used as chemical reagent ⁷ or be further extracted via distillation and condensed in ammonia water ²⁴. The pilot study gathered evidence showing that the FBR and stripping-scrubbing units reached technology readiness levels of 7 and 6, respectively, (Ch. 3) in a scale from 1 to 9, which is the maximum achievable at pilot scale (7) ^{25,26}.

As shown in Ch. 3, the overall system removed 76% of TAN, close to the regulatory minimum load reduction (70-80%) in the UK ²⁷. Nonetheless, the residual ammonia content in the stripping effluent (186 mg TAN/L in the pilot study – Ch. 3, 75 mg TAN/L in the lab-scale study – Ch. 5) was above the concentration limit for discharge in the UK, generally 10 mg TN/L ²⁷, but even 3

mg TAN/L in some cases ²⁸. The removal can be increased by integrating the system with a sorption process, separating the residual TAN and concentrating it in a brine to be reintroduced in the system or used. Both conventional IEX and Zn-doped media removed TAN from the pre-treated AnMBR permeate with capacities of 2.2 to 3.7 mg N/g (Ch. 5). Applying the necessary dose of media would enable compliant discharge. Alternatively, membrane filtration can be considered to meet the regulatory requirements for discharge and potentially reuse. Future studies could evaluate the practical and the economic viability of such integrated treatment train (Figure 6-1).

The distillery site in this case study was granted a license by the Scottish environmental protection agency to discharge the AnMBR permeate in the estuary where it is located. Nonetheless, many distilleries are located inland, in rural areas, and need to comply with the standard limits for discharge, often having to tanker their effluents to centralised treatment facilities. The Scottish government has promoted the investigation of circular approaches since 2016, aiming to contribute to a sustainable economic growth ²⁹. Accordingly, the industrial partner in this project is exploring the possibility to replicate and further develop the treatment system at other sites, to tackle removal and enable recovery. Importantly, a local demand for the end-products supports the economic viability of the system. Alternatively, the reuse of the recovery products can be placed in a broader market, at national level. Industrial symbioses can create the conditions for exchange of resources, such as waste heat, reclaimed water, nutrients and raw materials. To illustrate, the generated struvite could be integrated in the already existing practice of applying the digestate solid fraction on the local fields used for growing cereals for the fermentation process. The high-quality struvite harvested across the operation campaign had limited organics content and no contamination from the tested heavy metals, posing negligible risks for its use on the local fields as fertiliser. The chemical composition was partially compatible with the European Commission legislation for fertiliser precipitated phosphate salts (P content, impurities content) ³⁰, but

further analyses would be required (e.g. other heavy metals contents) to assess full compliance.

6.3 What is the role of metal-ammonia interactions in ammonia partitioning technologies and how can that be harnessed?

Transition metals can form complexes with ammonia, via coordinative bonds ³¹. The strength of the bonds depend on the complex formation constants, with zinc showing high values and being able to bind up to four ligand molecules ³². Such interaction can affect ammonia partitioning technologies. It was demonstrated that low N:M molar ratios can lead to ammonia sequestration and reduce its volatilisation via vacuum thermal stripping (Ch. 4). The results showed that zinc caused the greatest reduction of TAN removal, at the highest tested concentration (N:M 1:1), compared to copper and nickel. This was attributed to the adsorption of NH_3 onto metal (hydr)oxides and to dissolved metal ion. Such properties were explored and exploited for selective ammonia separation from the liquid phase via Zn-doped media (Ch. 5). The tested resin with Zn in ion form showed ammonia removal capacity, but was limited by the self-inhibiting pH changes it induced and was still affected by the presence of competing cations (including NH_4^+), displacing zinc. Overall, zinc-ammonia interactions can be harnessed to separate ammonia from solution and further research is needed to demonstrate that its capacity and selectivity can be superior to conventional IEX media. Results from this study showed that, in the same type of wastewater, with conventional IEX resin NH_4^+ was subjected to greater competition from potassium, whereas with Zn-loaded media TAN sorption was outcompeted by magnesium. This suggested that, in the latter media, divalent exchange between dissolved Mg and sorbed Zn contributed to a loss of TAN capacity and highlighted the need to improve the metal-resin bond to minimise metal loss. This could unlock a critical space for ammonia recovery technologies for streams less suitable to other technologies such as stripping.

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Chapter 7

7 Conclusion and future work

This thesis advanced the understanding of the impact of water physico-chemical characteristics on the mechanisms driving ammonia partitioning, aiming to establish optimum transfer routes into gas, liquid and solid phases from industrial wastewaters.

The following contributions were generated. The current state of implementation of ammonia partitioning technologies in industrial effluents was elucidated, outlining the drivers behind selection and operation and the opportunities for recovery. These criteria encompassed the type of recovery product preference, ammonia concentration, levels of competing cations, and precipitation potential of struvite in the feed. Accordingly, guidelines for technology selection and operation were developed, aiming to maximise ammonia removal and recovered product quality. These were also based on the impact of competing cations, anions, solids, organic compounds and transition metals. Such recommendations were summarised in a decision tree and were used to define an ammonia recovery strategy from distillery effluent. The successful performance of this integrated system was demonstrated at pilot scale using real distillery wastewater for the first time, addressing operational challenges and enhancing technology readiness for real-world applications. Gaps regarding the impact of selected species, particularly transition metals and recalcitrant, acidic organic compounds, on ammonia separation processes were highlighted. Consequently, the detrimental impact of transition metals and recalcitrant organic acids on ammonia partitioning through stripping in synthetic solutions was assessed and quantified, proposing mechanisms and conditions for removal. In addition, the exploitation of such metal-ammonia bond for NH_3 adsorption was explored in emergent zinc-hybridized media, using both real and synthetic effluents, and compared to conventional IEX media. pH, buffer capacity and Na/Zn loads were identified as drivers behind the partitioning mechanisms. The overall conclusions are presented hereafter, along with the objective they addressed.

Objective 1: To review the drivers for ammonia partitioning technologies' use in industrial wastewaters and develop preliminary guidelines for their selection and operation based on the impact of water physicochemical properties.

- Ammonia recovery from industrial effluents has received interest across different industry sectors, with coke processing and fertiliser manufacturing being the most represented (15% and 14% of the studies, respectively).
- Struvite precipitation was the most applied technology (49% of the studies), often driven by convenience (e.g. co-presence of N and P, spontaneous formation).
- Sorption processes adoption was limited to 18% of the studies analysed, positioning them as complementary technology, suitable with low TAN concentrations effluents ($< 0.5\text{--}1\text{ g N/L}$). Improving the media capacity and selectivity will expand the range of application of these processes.
- Maximising the removal efficiency and the recovery product quality and value is expected to shift the ammonia partitioning technology selection towards stripping and selective, high-capacity sorption processes.
- Such selection is driven by the recovery product type (i.e. TAN solutions more versatile than struvite), TAN content, the levels of competing cations and the spontaneous precipitation of struvite and/or other scaling agents. The recommendations for the technologies operation are based on the impact of suspended solids, anions and cations levels, including transition metals, and organic compounds concentrations.
- Further understanding of the impact of transition metals, organic acidic compounds and foreign ions on the three technologies is required to validate the technology selection and operation guidelines.

Objective 2: To assess the viability and determine the performance of ammonia partitioning in real complex industrial wastewater treated with an integrate system comprising chemical precipitation and air stripping, at

demonstration scale. To determine and mitigate bottlenecks in real application, aiming to advance the technologies readiness levels (TRL).

- Ammonia recovery via struvite precipitation and stripping and scrubbing from distillery wastewater was assessed and demonstrated at pilot scale, reaching high overall TAN removal efficiencies, up to 76% at conditions: FBR pH 8.1, Mg/P $\approx$ 0.7, SSR. Stripping pH 9.4, 34°C. Simultaneously, 80% of phosphate was recovered via precipitation.
- High quality N-products were recovered from distillery wastewater. These were i) heavy metals-free struvite pellets, posing negligible risk for application on soil, and whose size can be tuned with pH control (up to 5 mm), ii) ammonium sulphate solution with up to 20 g N/L, whose concentration can be increased upon adjustment in unit design and operation.
- The system performance was improved by solving operational challenges, such as chemical mixing, uncontrolled precipitation, pH control, ultimately demonstrating technologies readiness levels of 6-7, which represent the highest possible ratings achievable at this testing scale, within the 1-9 range.
- The observed system performance slightly deviated from the theoretical prediction due to operational challenges with temperature and air supply control, but potentially also due to recalcitrant, acidic organic compounds sequestering cations.

Objective 3: To elucidate the mechanisms of ammonia partitioning in water matrices containing selected transition metals and organic compounds, assessing and quantifying their impact on ammonia volatilisation during vacuum thermal stripping.

- The tested transition metals significantly hampered ammonia volatilisation starting from molar ratios: N/Zn 1:1, N/Cu 4:1, N/Ni 20:1. Overall, the lowest estimated fraction of ammonia available for volatilization (0.7) was observed at N:Zn 1:1.

- The impact of transition metals on the ammonia partitioning to the gas phase was attributed mainly to metal-ammine complex formation in solution and sorption to metal oxide/hydroxide.
- Humic acids significantly hindered ammonia stripping (1 g TAN/L) from 636 mg HA/L. Such impact was attributed to TAN electrostatic attraction and chemical fixation.
- The combination of zinc and humic acid did not show an additive negative effect.
- The results showed that ammonia vacuum thermal stripping would not be significantly impacted for the majority of effluents containing transition metals and organic acidic compounds. Nonetheless, for niche wastewaters rich in transition metals and these organic species, this hindrance should be factored during operation and design of ammonia partitioning processes.

Objective 4: To determine the factors driving ammonia partitioning mechanisms in metal-hybridised sorption media. To compare their capacity and performance in real wastewaters with conventional IEX media.

- Both ion exchange (IEX) and ligand exchange (LEX) occurred on partially loaded zinc-doped media.
- A combination of factors including the initial pH, solution buffer capacity, load of zinc and sodium on the media were found to impact the conditions enabling these ammonia partitioning mechanisms. All tested media were affected by self-driven and self-limiting pH changes, highlighting the need for a pH buffer system.
- All tested media were sensitive to foreign cations, causing competition for ammonium sorption via IEX and/or zinc displacement.
- Partially Zn-loaded media displayed limited capacity in most cases with synthetic solutions, compared to conventional IEX media, due to unsuitable pH conditions. The former requires a stable narrow pH range ($\approx$ 9-10) to exploit its Zn-based potential, reaching high capacity (75 meq

N/g). Nonetheless, such media with double Na/Zn loading showed versatility to operate in a wide range of pH, switching between LEX and IEX (favoured in mildly acidic-neutral conditions).

- Both conventional IEX and LEX media removed TAN from real domestic and industrial effluents, with the former showing, overall, a higher capacity: 0.8-33 mg N/g vs 0.1-21 mg N/g for Zn-doped media vs 0.5-31 mg N/g for Zn (hydr)oxide media.

7.1 Future work

The work conducted in this thesis highlighted further opportunities for research, whose addressing can advance the theoretical and practical knowledge to apply ammonia partitioning technologies to industrial effluents:

1. The mechanisms of TAN binding by organic acid compounds should be further clarified, by assessing different species with varying loads of carboxylic and phenolic groups (e.g. fulvic acids), thus changing the proportion of charged acidic groups of the molecules, and determining the type of bonds with TAN via Fourier Transform Infrared Spectroscopy. Furthermore, the TAN binding capacity of the species should be determined, directly depending on the number of available functional sites. In this regard, the impact of pH and temperature on the TAN binding capacity should be also investigated, providing insights on mitigating measures. For the sorption media, the impact of model dissolved organic compounds on the TAN sorption capacity of the media should be clarified. This should be achieved via testing sorption with synthetic solutions containing the model compounds at different concentrations, with and without ammonia, over a range of pH, to determine the media's sorption capacity for the organics and for ammonia/um in the different scenarios.
2. Future work should test whether applying the identified molar ratios at different concentrations would yield comparable results during VTS, determining whether also the concentration has an impact on the observed hindrances. Furthermore, different pressure/temperature combinations

should be tested to assess their effect on the stability of the metal-ammonia bonds, indicating how strongly metals bind to ammonia under different environmental conditions. This could expand the understanding of conditions favouring ammonia retention or volatilisation and potential energy barriers associated with it.

3. Future work should focus on measures to further increase the Zn-doped media capacity. Although zinc provides a convenient trade-off between safety, availability and ligand capacity, other transition metals able to bind more ligand molecules could be tested and benchmarked against zinc (e.g. Co^{2+} binding up to 6 ligands). Future studies can also evaluate resins with different functional groups to determine the one(s) able to establish and maintain the strongest bonds with the transition metal, avoiding displacement by competing cations/ligands and maintaining the capacity. Moreover, to maximise the media capacity, the resin should be fully loaded with the selected metal and the application of a buffer should be ensured to maintain the pH in the suitable range. The performance of the Zn (hydr)oxide media can also be further improved, by testing new media preparation methodologies, aiming to minimize the release of sodium and hydroxyls during the use, as observed in this thesis. A possible route to be tested could be the use of an electrochemically generated hydroxyls solution to precipitate the zinc in the media, avoiding Na/K bases.
4. Besides the capacity improvement in the Zn-doped sorption media, future research should focus on testing continuous process and on developing an efficient methodology for their regeneration and demonstrate the quality of the generated brine (i.e. content of TAN, metal and competing cations). Previous studies tested acid regeneration which implied a trade-off between TAN recovery and metal elution. Another route to be assessed could be thermal desorption, coupled to mild acid regeneration, investigating the metal-ammonia bond's sensitivity to temperature and pH changes.

5. Research opportunities identified in thesis include i) assessing the impact of volatile organic compounds on the recovered product purity from ammonia stripping, along with potential mitigation measures, ii) determining the critical ratios of TAN to competing cations (e.g. Na, K, Ca etc.) on the viability and product quality of ammonium precipitation (solids) and sorption (brines). These can be studied in preliminary tests with controlled synthetic solutions, changing the concentrations of such species, individually and in combination, and monitoring their impact on the process performance.
6. The presented recommendations for technology selections can be complemented by considering these criteria: i) the energy efficiency and the environmental impact of the technologies and ii) the cost-effectiveness of the treatment train, which depend on case-specific conditions. The former assessment can be realised with a life cycle assessment, with different scenarios assuming a comprehensive range of inputs (e.g. source of electricity, source of chemicals used). The costing assessment should include capital and operational expenditures, but also potential revenues, considering a trade-off between removal efficiency and quality/value of the end-product and benchmarking the options against treatment alone, without recovery. Such analysis could be carried out also for this specific case study (distillery wastewater) and the proposed treatment train, to further assess its viability at larger scale.
7. The performance of the processes in the proposed treatment train can be further improved. The temperature control and scrubber operation should be optimised to selectively favour ammonia transfer and increase the end product value. Furthermore, vacuum thermal stripping can be considered as alternative to air stripping, aiming to obtain such selectivity, by manipulation of temperature and vacuum, as reported in literature ¹. After these optimisations, the system should be scaled up, assessing its long term robustness and further demonstrating the level of readiness.

Moreover, the system readiness level should be established, considering the integration of the different technologies.

7.2 References

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8 November 2024

Dear Ms Gritti ,

Reference: CURES/23901/2024

Project ID: 13372

Title: Ammonia partitioning and recovery from industrial wastewater: exploring precipitation, stripping, and sorption technologies

Thank you for your application to the Cranfield University Research Ethics System (CURES).

We are pleased to inform you your project title change request, reference CURES/23901/2024 has been approved.

If you have any queries, please contact CURES Support.

Regards,

CURES Team