

CRANFIELD UNIVERSITY

SAMUELA GUIDA

AMMONIUM AND PHOSPORUS REMOVAL AND RECOVERY  
FROM WASTEWATER THROUGH THE ION EXCHANGE  
PROCESS

School of Water, Environment and Energy  
Research Degree

PhD

Academic Year: 2017 – 2020

Supervisor: Prof. Ana Soares and Prof. Bruce Jefferson  
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## ABSTRACT

Challenges to implement circular economy principles in the wastewater cycle are connected to the need of reducing nutrients (ammonium as  $\text{NH}_4^+\text{-N}$ , and phosphorus as  $\text{PO}_4\text{-P}$ ) in treated effluent whilst enabling their recovery in an environmentally sustainable way. Conventional biology-based technologies fail to address these challenges by having high greenhouse gases footprint and offering limited possibilities for nutrient recovery. The aim of this work was to underline the mechanisms of removal and recovery of  $\text{NH}_4^+\text{-N}$  and  $\text{PO}_4\text{-P}$  from wastewater through the ion exchange (IEX) process in order to optimise the removal efficiency and maximise the recovery from IEX regenerant brines (sodium hydroxide and potassium chloride), when working at demonstration scale over an extended period of time. The IEX process was tested in a  $10 \text{ m}^3\text{/day}$  demonstration plant for 2.5 years using Zeolite-N and a hybrid anion exchanger (HAIX) for the removal of  $\text{NH}_4^+\text{-N}$  and  $\text{PO}_4\text{-P}$  at empty bed contact times of 10 and 5 min, respectively. The operation at demonstration scale confirmed the resilience and consistency of the IEX process and the possibility to maintain high effluent quality ( $<0.3 \text{ mg PO}_4\text{-P/L}$  and  $<1 \text{ mg NH}_4^+\text{-N/L}$ ) despite changes in influent concentration (i.e.  $<0.006\text{-}26 \text{ mg NH}_4^+\text{-N/L}$ ) and extended operational period (up to 63 consecutive adsorption/regeneration cycles with HAIX). Additionally, the regenerant brines were reused multiple times and nutrients could be recovered as high purity ammonium sulphate and hydroxyapatite using a hollow fibre membrane contactor for ammonium recovery and simple precipitation with calcium hydroxide and filtration for phosphorus recovery. The results obtained from this work additionally highlighted the need of an automated system to start the regeneration when the desired effluent quality is reached, the need of a nearly solids-free influent and high mechanical strength media to avoid media packing and losses. This work significantly moved the IEX process higher in the technology readiness level (from level 5 to level 7) for mainstream wastewater treatment with the advantages of simple operation, consistency, resilience and lower environmental impact (-25% cumulative energy demand, -66% global warming potential, -62% marine eutrophication potential) compared to traditional biological processes.

## **Keywords**

Ammonium, phosphorus, ion exchange, capacity, selectivity, resilience, fertiliser, circular economy.

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*“It is not our part to master all the tides of the world, but to do what is in us for the succour of those years wherein we are set, uprooting the evil in the fields that we know, so that those who live after may have clean earth to till. What weather they shall have is not ours to rule.”*

*Gandalf (J.R.R. Tolkien, The Return of the King)*

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## LIST OF ABBREVIATIONS (alphabetical order)

|                                             |                                                                   |
|---------------------------------------------|-------------------------------------------------------------------|
| [AlO <sub>4</sub> ] <sup>5-</sup>           | Aluminate                                                         |
| [SiO <sub>4</sub> ] <sup>4-</sup>           | Orthosilicate                                                     |
| AEC                                         | Ammonium exchange capacity                                        |
| AEE                                         | Ammonium exchange efficiency                                      |
| Al <sup>3+</sup>                            | Aluminium                                                         |
| anMBR                                       | Anaerobic membrane reactor                                        |
| BV                                          | Bed volume(s)                                                     |
| C                                           | Concentration                                                     |
| Ca(OH) <sub>2</sub>                         | Hydrated lime, calcium hydroxide                                  |
| Ca <sup>2+</sup>                            | Calcium                                                           |
| CaP                                         | Calcium phosphate                                                 |
| CAPEX                                       | Capital expenditure                                               |
| CED                                         | Cumulative energy demand                                          |
| CH <sub>4</sub>                             | Methane                                                           |
| C <sub>in</sub>                             | Influent concentration                                            |
| Cl <sup>-</sup>                             | Chloride                                                          |
| CO <sub>2</sub>                             | Carbon dioxide                                                    |
| COD                                         | Chemical oxygen demand                                            |
| C <sub>t</sub> /C <sub>0</sub>              | Effluent concentration at time t/influent concentration at time t |
| CW                                          | Constructed wetlands                                              |
| CW-BER                                      | Constructed wetlands-biofilm electrode reactor                    |
| EBCT                                        | Empty bed contact time                                            |
| EBPR                                        | Enhanced biological phosphorus removal                            |
| EDX                                         | Energy-dispersive X-ray                                           |
| EU                                          | European Union                                                    |
| FAO                                         | Food and Agriculture Organisation                                 |
| GHG                                         | Greenhouse gas(es)                                                |
| GLO                                         | Global market                                                     |
| GWP                                         | Global warming potential                                          |
| H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> | Hydrogen phosphate                                                |
| HAIX                                        | Hybrid anion exchanger                                            |
| HAP                                         | Hydroxyapatite                                                    |
| HFMC                                        | Hollow fibre membrane contactor                                   |

|                                |                                         |
|--------------------------------|-----------------------------------------|
| HFO-NP                         | Iron hydroxide nanoparticles            |
| $\text{HPO}_4^{2-}$            | Hydrogen phosphate                      |
| IEX                            | Ion exchange                            |
| IEX-D                          | IEX demonstration scale plant           |
| $J_{\text{H}_2\text{O}}$       | Water flux                              |
| $J_{\text{NH}_3 \text{ loss}}$ | Rate of ammonia loss                    |
| $\text{K}^+$                   | Potassium                               |
| KCl                            | Potassium chloride                      |
| $K_{\text{La}}$                | Ammonia mass transfer coefficient       |
| LCA                            | Life cycle assessment                   |
| LOD                            | Lower limit of detection                |
| MEM                            | Membrane stripping                      |
| MEP                            | Marine eutrophication potential         |
| meq                            | Milliequivalent                         |
| $\text{Mg}^+$                  | Magnesium                               |
| MVTS                           | Multicomponent vacuum thermal stripping |
| N                              | Nitrogen                                |
| $\text{N}_2$                   | Gaseous nitrogen                        |
| $\text{Na}^+$                  | Sodium                                  |
| NaCl                           | Sodium chloride                         |
| NaOH                           | Sodium hydroxide                        |
| $\text{NH}_3$                  | Ammonia                                 |
| $\text{NH}_4^+$                | Ammonium                                |
| $\text{NH}_4^+\text{-N}$       | Ammonium as nitrogen                    |
| $\text{NO}_2$                  | Nitrogen dioxide                        |
| $\text{NO}_2^-$                | Nitrite                                 |
| $\text{NO}_3^-$                | Nitrate                                 |
| OPEX                           | Operational expenditure                 |
| P                              | Phosphorus                              |
| P                              | Vacuum pressure                         |
| $\text{P}_2\text{O}_5$         | Phosphoric acid                         |
| PE                             | Population equivalent                   |
| $\text{PO}_4\text{-P}$         | Orthophosphate as phosphorus            |
| Q                              | Ion exchange capacity                   |
| $Q_{\text{reg}}$               | Regeneration capacity                   |

|                               |                                                         |
|-------------------------------|---------------------------------------------------------|
| R <sub>NH3</sub>              | Ammonia recovery efficiency                             |
| RE                            | Regeneration efficiency                                 |
| RoW                           | Rest of the world                                       |
| SEM                           | Scanning electron microscopy                            |
| Si/Al                         | Silicium to aluminium ratio                             |
| SNAD                          | Simultaneous nitrification, anammox and denitrification |
| SO <sub>4</sub> <sup>2-</sup> | Sulphate                                                |
| TN                            | Total nitrogen                                          |
| TP                            | Total phosphorus                                        |
| TS                            | Total solids                                            |
| TSS                           | Total suspended solids                                  |
| UK                            | United Kingdom                                          |
| VAC, VTS                      | Vacuum thermal stripping                                |
| WWTP                          | Wastewater treatment plant                              |
| XRD                           | X-ray powder diffraction                                |

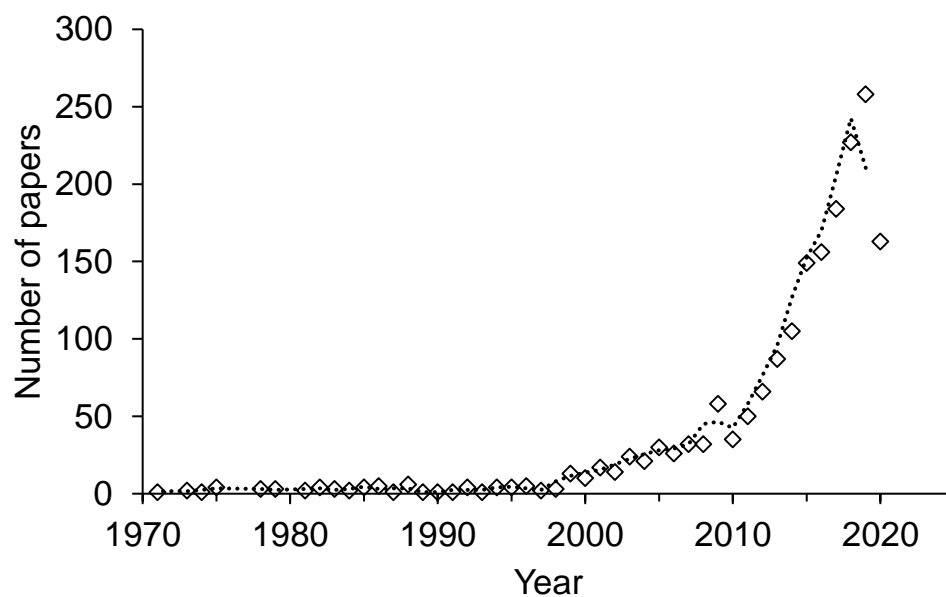




# 1 INTRODUCTION

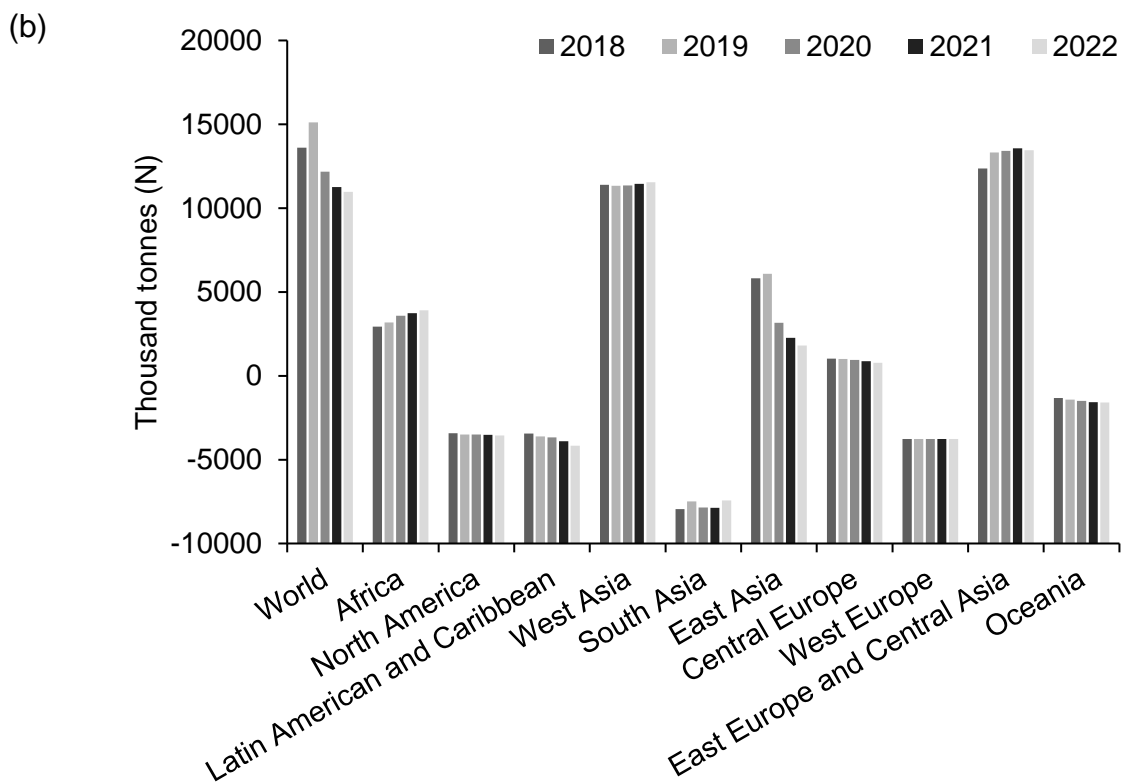
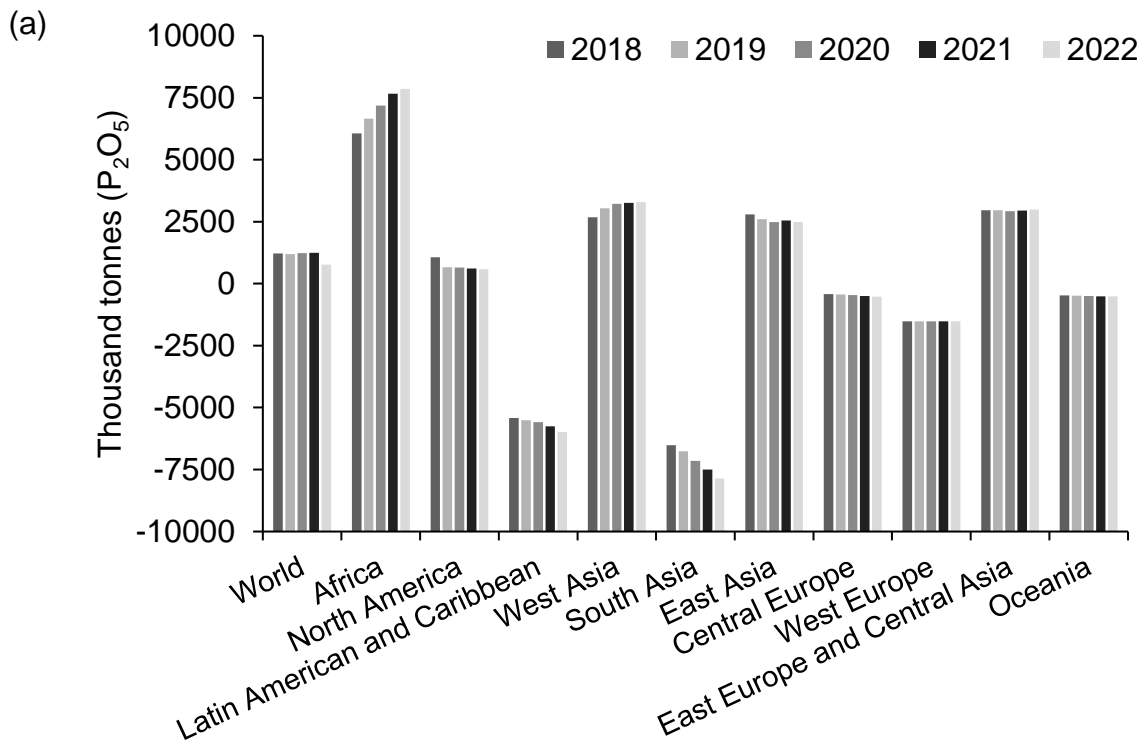
## 1.1. Background

As a result of the increase in world population, there is an unavoidable rise in the demand of food, resources and energy supplies. In particular, phosphorus (P) and nitrogen (N) are essential nutrients for all living organisms and critical for plants growth to sustain agricultural production [1], [2]. In fact, exploitable reserves of phosphorus (mineral rock) are not renewable and, at the same time, the Haber-Bosh process to produce ammonia uses large amount of fossil fuels energy (mainly natural gas) and it is therefore connected to anthropogenic greenhouse emissions [3]. Recycling nutrients through sustainable methods is a suitable option for energy, environmental and economic reasons [4]. Moreover, the combination of nutrients removal and recovery can mitigate the eutrophication of water streams and its serious effect on natural environments [5]. The interest in nutrients recovery from wastewater has undergone accelerate development in the last decade (Figure 1.1). Several studies have investigated the possibility to recover nutrients from domestic and industrial wastewater by upgrading wastewater treatment plants from waste disposal facilities to resource factories focused on nutrient recovery, production of energy, materials and water reuse [6].



**Figure 1.1 Number of scientific publication from 1970 to 2020/ Source: Scopus. Research “recovery”, “nutrients” and “wastewater” in “title-abstract-keywords”.**

According to the Food and Agriculture Organization (FAO) of the United Nations, the world demand for nitrogen and phosphate is forecasted to grow annually on average by 1.2 and 1.7% respectively from 2018 to 2022 [7]. However, the supply/demand ratio for these nutrients has already reached a negative value in 2018 for countries such as Latin American and Caribbean, South Asia, Central Europe *etc.* (Figure 1.2). As evident from Figure 1.2, it is crucial to find new sources for nutrient recovery and to investigate new technologies to ensure an appropriate distribution of nutrients all over the world. It is therefore clear that emerging technologies for wastewater treatment need to focus on the possibility to couple nutrients removal with the resource recovery [4], [8]. Several studies have investigated the recovery of phosphorus as struvite [9] or hydroxyapatite [10]. However, current approaches fail to consider the energy embedded in ammonia which, as high energy molecule, could be used to balance energy demand in wastewater treatment plants both as a fuel and a hydrogen carrier [11]. According to Vecino *et al.* [12], there is still the need to investigate technologies focused on the recovery of ammonia to give it an added value in wastewater treatment plants.



**Figure 1.2 World and regional (a) phosphate (phosphorus and phosphoric acid, expressed as  $P_2O_5$ ) and (b) nitrogen (nitrogen and ammonia, expressed as N) potential**

balance in 2018-2020 (thousand tonnes) considering nutrients capacity, supply capability, fertiliser and non-fertiliser demand, availability for fertiliser (adapted from [7]).

## 1.2. Limitation of biological removal and recovery processes

A wide range of information can be found in the literature about biological N and P removal and recovery. N removal from wastewater is commonly obtained via anaerobic biological processes such as the activated sludge process (ASP) and the trickling filters (TF). Both processes involve the nitrification of ammonium ( $\text{NH}_4^+$ ) to nitrite ( $\text{NO}_2^-$ ) followed by oxidation to nitrate ( $\text{NO}_3^-$ ) and reduction to gaseous nitrogen ( $\text{N}_2$ ) [13], [14] which is then released back into the atmosphere and therefore not recovered [15]. This process is mostly used for low concentrated wastewater with high efficiency; however, with the increase in ammonium concentration, an external carbon source is required with consequent increase in cost and energy requirements [16], [17]. Additionally, the formation of nitrite as intermediate of the nitrification reaction in both ASP and TF rises environmental concerns. In fact, if dissolved oxygen supply is limited, the autotrophic ammonium-oxidising bacteria will reduce  $\text{NO}_2^-$  to nitrous oxide ( $\text{N}_2\text{O}$ ), instead of oxidising it to  $\text{NO}_3^-$  [18]. Nitrous oxide is a greenhouse gas with a crucial role in the destruction of the stratospheric ozone layer [19]. Moreover, it is known that biological nitrogen removal is an energy-intensive process [13] which requires specific conditions (i.e. high aeration to keep dissolved oxygen levels  $>3$  mg/L, a solid retention time and a hydraulic retention time long enough to ensure the growth of the bacteria and the reaction with the ammonium [20]). Additionally, more energy is then required to convert  $\text{N}_2$  to fertiliser [13]. To indicate, Van der Hoek *et al.* [15] reported that the total primary energy requirement for N removal via nitrification-denitrification accounts for about 42.2-45 MJ/kg-N and N-fixation via the Haber-Bosh process can reach up to 37-45 MJ/kg-N [15]. A possibility proposed by Rieger *et al.* [21] is the ammonia controlled aeration in activated sludge systems to obtain an increased effluent quality (below 2 mg/L) as well as a reduction of the total energy consumption. Even though this technology is reported to ensure savings up to 20% for full-scale energy and up to 40% increase of total nitrogen removal, it requires greater knowledge and effort from the operators [21]. Moving forwards towards energy positive wastewater treatment plants and a circular economy concept, it is therefore clear that an alternative to conventional biological removal has to be found. This

alternative has to be more sustainable with respect to energy use and N<sub>2</sub>O emissions and it has to focus on the N recovery rather than its loss [15].

Bacterial-accumulation of phosphorus (P) through enhanced biological removal (EBPR) is widely used in wastewater treatment plants to remove 80-90% of soluble P from the effluent [22]. Depending on the organism, it is possible to obtain different performance and several attempts to use specific microorganisms as accumulating reservoirs were reported, however, their application is challenged by the difficulties of harvesting the bacteria as well as controlling the condition of growth and biochemical pathways [23].

Biological sludge contains high levels of nutrients needed to sustain crops. However, direct land application of sludge is still limited because of pathogens, odour, and contaminants such as heavy metals and industrial waste products [24]. Even though biological removal presents advantages such as the lack of chemical additive costs, the processes and the biochemical pathways are still difficult to control and heavy intellectual and financial investments are needed to improve technologies and to make the sludge a marketable product [25].

Wastewater is also a promising substrate for cost-effective, environmentally friendly and sustainable algae cultivation [4]. Researchers report that algae are able to remove a variety of pollutants including heavy metals and nutrients such as phosphorus. As suggested by Fenton *et al.* [26], the nutrient content of organic fertilisers, runoff and drainage waters can facilitate algal biomass growth. However, nutrient accumulation is dependent on nutrient concentration, algal physiology, light intensity, pH and temperature [22]. Optimal pH growth of algae is in the range of 7.5-8.5 with an optimal temperature between 15-30°C during day and night [27]. Data from pilot algal ponds showed a maximum of 61.4% and 90.6% removal of total nitrogen and total phosphorus, respectively [28]. Microalgae have been identified as an important source of lipids as well as feedstock for biofuel production after conversion of the lipids to fatty acid methyl esters [29] as indicated by the life cycle assessment analysis conducted by Sturm *et al.* [28]. When wastewater is used as substrate for algal and microalgal growth, the growth rate and algae composition change with various wastewater influent characteristic. Nevertheless, algal harvesting is difficult: centrifugation has been considered too energy intensive so other techniques have been considered such

as chemical coagulation of algae, chemical coagulation/flocculation followed by dissolved air flotation (DAF) and dewatering systems (belt filter press, centrifugation, evaporation) [22]. Usually, harvesting requires a solid-liquid separation phase to concentrate the biomass and membrane separation has been suggested [30]. Moreover, the presence of heavy metals, micro-pollutants or pathogens can reduce the possibility of reusing the nutrients [29]. Microalgae have been used to treat pharmaceutical wastewater, dye-containing wastewater, metal-containing wastewater and agro-industrial wastewater by bio-sorption or bio-conversion pathways. Nevertheless, some mechanisms involved in pollutant removal and bio-conversion in microalgae-base wastewater treatment are still not clearly understood and require further investigation [31]. After being harvested, algae need to be converted to liquid biofuel or biogas through a high-efficiency, eco-friendly, and cost-effective pathway [4]. The nutrient-rich biomass can be then processed with nutrient release technologies such as anaerobic digestion or thermochemical methods [22]. As reported by Gao *et al.* [4], novel methods may make it possible to manufacture high-value products from algae, including protein complements and food additives (aquaculture and animal feed), or products used in agriculture (fertilizers, soil conditioners) however these will require a substantial cost investment [32].

Another alternative to decrease nutrient concentration in water streams is the use of wetlands: areas that are inundated or saturated by surface water or groundwater with vegetation adapted for life under those soil conditions. Wetlands are not designed to remove nutrients, however, they can allow nutrient removal because of the plants adsorption and microbial degradation [23]. Constructed wetlands (CW) (engineered wetlands) use rooted water-tolerant plants and gravel or soil media to provide treatment to wastewater without the input of fossil energy. Different types of pollutants can be removed such as N, P, organics, solids, metals and coliforms [33]. Several processes can contribute to N removal in CWs such as  $\text{NH}_3$  volatilization, nitrification, denitrification, nitrogen fixation, mineralization (ammonification), nitrate reduction to ammonium, anaerobic ammonia oxidation (ANAMMOX), as well as plant and microbial uptake, fragmentation, sorption, burial, and leaching [34], [35]. On the other hand, P can be removed via adsorption, precipitation, dissolution, fragmentation, leaching, mineralization, sedimentation, burial as well as plant and microbial uptake [34], [35].

Plants grow accumulating nutrients on the water surface, creating anaerobic conditions in the surrounding water. The anaerobic conditions drive digestion reactions where organic matter is metabolized with the release of soluble nutrients that can be further accumulated by the plants [22]. In the CW, there is a combination of emergent/floating/submergent vegetation and a large variety of microbial communities which are purposely built for water pollution control [23], [33]. Among these, water hyacinths can be used as a substrate for compost or biogas production [28]. The sludge from the biogas process contains almost all of the nutrients of the substrate and can be used as fertiliser [36]. The nutrient accumulation capacity depends on the design of the wetlands (subsurface or surface), the plant species, the waste stream and environmental factors such as pH, temperature, organic carbon availability, salinity level [33], [37]. In temperate climates, the minimum wastewater temperature is usually 7°C with optimum temperature between 25 and 31°C [33] and optimum pH 6.0 and 8.0 [22]. The nature of wetland media is also important to enhance the nutrient absorption. Drizo *et al.* [38] concluded that of seven materials examined (bauxite, shale, burnt oil shale, limestone, zeolite, light expanded clay aggregate and fly ash) shale had the best combination of properties as a substrate for CW systems with a P adsorption capacity of 650-730 mg P/kg [38]. More recently, much work has been done on creating activated carbon adsorbent from industrial by-product to successfully treat wastewater (for example slags, fly ash and iron and aluminium oxides) [39]. As indicated by De-Bashan and Bashan [23], performance of wetlands and CW in removing pollutants can be enhanced by using reactive sorbents (by-product, soils and zeolite) [23]. The performance of adsorption could be enhanced with innovative design [40]: as reported in Wang *et al.* [41], when constructed wetlands are coupled with biofilm-electrode reactor (CW-BER), current, inorganic carbon source and hydrogen generated by the micro-electric field could significantly improve the inorganic nitrogen removal [41]. Microorganisms play a significant role in the N removal processes and, in Li and Tao [40], the integration of simultaneous nitrification, anammox and denitrification (SNAD) pathways into constructed wetlands systems is proposed as emerging alternative to the conventional nitrification-denitrification processes. In Jamieson *et al.* [42], the use of supplemental aeration in constructed wetlands is reported to enhance nitrification activity from 50.5% to 93.3%, due to the addition of dissolved oxygen into the wastewater which would induce a more aerobic environment for this reaction. Microorganisms can also contribute to P removal by forming biofilms

that enhance the P adsorption capacity of the substrate [43]. According to Vymazal [34], soil microorganisms participate in the solubilisation of soil P. Moreover, bacteria have also been shown to regulate the P flux across the sediment–water interface of the wetlands and contribute to P burial through production of refractory organic compounds [34]. Recently, some new types of CWs have been developed to enhance the treatment efficiency, these includes floating treatment wetlands (FTWs), bio-ecological anaerobic-anoxic-aerobic (A2O)-wetland systems and microbial fuel cells (MFCs) [43]. To indicate, in Haq Nawaz et al. [35], a modified bio-ecological A2O wetland system successfully achieved 91%, 85%, 78%, and 92% removal efficiencies for COD, NH<sub>4</sub>-N, TN and TP, respectively [35]. Constructed wetlands could play a strategic role in wastewater reclamation, representing a low cost and environmentally friendly option [6] however, as described above, the process still depends on several environmental parameters as well as on the system design.

A summary of advantages and disadvantages of biological nutrient removal and recovery is presented in Table 1.1.



**Table 1.1 Advantages and disadvantages of the biological nutrient removal techniques.**

| Method                                                                | Recovered product                                                                                                                                                                  | Advantages                                                                                                                                                                                                                                                                                                           | Disadvantages                                                                                                                                                                                                                                                                                                                                                        | Reference            |
|-----------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|
| Biological ammonium removal through nitrification and denitrification | N <sub>2</sub> lost in atmosphere                                                                                                                                                  | <ul style="list-style-type: none"> <li>• High removal capacities</li> <li>• Well-known process</li> <li>• No chemicals requirements</li> </ul>                                                                                                                                                                       | <ul style="list-style-type: none"> <li>• Environmental concerns due to the production of N<sub>2</sub>O as intermediate</li> <li>• Cost and energy intensive method due to need for aeration and in some cases the supplement of organic carbon</li> <li>• Process does not respond well to ammonium load variations</li> <li>• Nitrogen is not recovered</li> </ul> | [13]-[19]            |
| Biological phosphorus removal                                         | Biological sludge rich in P and other organics such as proteins                                                                                                                    | <ul style="list-style-type: none"> <li>• Sludge volumes are similar to those produced by conventional biological treatment processes</li> <li>• Installation at existing activated sludge plants with limited retrofitting</li> <li>• Resulting sludge rich in P can be used for agricultural application</li> </ul> | <ul style="list-style-type: none"> <li>• Sludge can have poor settling characteristics</li> <li>• Need to control condition of growth of bacteria and biochemical pathways</li> <li>• Sludge land application still limited and heavily regulated</li> </ul>                                                                                                         | [22]-[25]            |
| Algae and microalgae                                                  | <ul style="list-style-type: none"> <li>• Source of lipids</li> <li>• Feedstock for biofuel production (biogas)</li> <li>• High valuable products (proteins complements,</li> </ul> | <ul style="list-style-type: none"> <li>• Wastewater is a good substrate for algae growth</li> <li>• Environmentally friendly and sustainable method</li> <li>• Microalgae can be used as a flexible source of resources</li> </ul>                                                                                   | <ul style="list-style-type: none"> <li>• Algae cultivation depends on nutrient concentration, light intensity, pH and temperature</li> <li>• Need to control condition of growth of bacteria and biochemical pathways</li> </ul>                                                                                                                                     | [4], [22], [26]-[32] |

|                                   |                                                                                                                                                |                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                 |
|-----------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------|
|                                   | food additives, fertilisers)                                                                                                                   |                                                                                                                                                                                                                                                                               | <ul style="list-style-type: none"> <li>• Yields dependant on sunlight hours available and needs shallow reactors (i.e., large foot-prints)</li> <li>• Biomass harvesting requires advanced separation techniques</li> <li>• Biomass can store heavy metals, micro-pollutants and pathogens</li> </ul>                                                                                                                                                                                                           |                                 |
| Wetlands and constructed wetlands | <ul style="list-style-type: none"> <li>• Substrate (plants) for compost and biogas production</li> <li>• Plants used as animal feed</li> </ul> | <ul style="list-style-type: none"> <li>• Different types of pollutants can be removed (i.e. COD, NH<sub>4</sub>-N, TN and TP)</li> <li>• Environmentally friendly and sustainable</li> <li>• After harvesting, plants can be used for compost or biogas production</li> </ul> | <ul style="list-style-type: none"> <li>• The nutrient accumulation capacity depends on several factors (the design of the wetlands, plant species, waste stream and environmental factors)</li> <li>• The nature of the media is important for the performance of the wetland</li> <li>• Need to control condition of growth of plants and pathways of adsorption</li> <li>• Biomass harvesting requires advanced techniques</li> <li>• Influence of pH and costs associating with correcting the pH</li> </ul> | [22], [23], [33],[36] [38]-[41] |

### 1.3. The ion exchange process

The possibility to meet the stringent effluent nutrient discharge limits in wastewater treatment plants (WWTPs) and, at the same time, to produce marketable nutrient-rich products can be accomplished with ion exchange (IEX) technologies [44]. IEX processes require a framework of fixed functional groups on the IEX media, which can be electrically neutralized by mobile counterions (exchanging ions) present in the aqueous phase [45]. The IEX capacity of the media depends on its chemical composition (i.e. its selectivity [46]) and on the concentration of the exchanging ions in the aqueous phase [47]. The chemical adsorption/ion exchange onto selective media can be considered more useful and efficient than other chemical precipitation methods as it allows for the selective removal of phosphorus and ammonium down to very low levels [47], [48]. When compared to traditional biological and physico-chemical technologies, the IEX process shows higher removal efficiency and offers options for recovery from municipal wastewater [49], [50] with competitive sustainability scores [16]. The IEX process, in fact, can operate with relatively low energy demands [51] and it presents high resilience to shock loading and low temperatures [47]. Additionally, the reuse of the regenerant brine solution until saturation ensures both the possibility to restore the initial ion exchange capacity of the resin and to reduce chemical consumption [51]. The saturated brine can successively be used for recovery of the nutrients as high purity products [52], [53].

Other advantages of the IEX process include the ease of operation and control as well as of scale-up. In fact, the IEX is a relatively simple and fast process that does not require any start-up time (“plug and play”) [54]. Regarding the possibility to scale-up the IEX process, Mazur *et al.* [55] highlighted a list of parameters that have to be considered and optimised at laboratory and pilot scale prior implementing the process at full scale. These include the influent wastewater characteristic, the flow rate and cycle length, the desired effluent quality, the regeneration technology, the dimension of the vessel and the type of IEX media [55]. Kavvada *et al.* [56] also investigated the economic and environmental advantages of a decentralised approach from nitrogen recovery from urine: after removal through IEX process at individual building, nitrogen is transported by truck to regeneration and fertiliser production facilities. According to the authors, this decentralized approach resulted in a reduction of cost, unit energy,

and GHG emissions when compared to centralized nitrogen management via nitrification-denitrification if fertilizer production offsets are taken into account [56].

Currently, the most used ion exchange media for ammonium removal is the natural zeolite clinoptilolite, a crystalline aluminosilicate mineral found in nature containing a framework of  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$  tetrahedra linked by their corners through oxygen atoms [57]. Cations present in the wastewater (usually  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ ) can penetrate inside cages and channels within the zeolite matrix and be exchanged with the surroundings [58]. However, due to the relative low ammonium exchange efficiency, clinoptilolite based material are mostly used for small scale applications. To improve the selectivity towards ammonium, chemical modification of clay and other aluminium-bearing minerals has been used to produce synthetic zeolites, such as Zeolite-N (referred as MesoLite in earlier publications [59]), which has an ammonium exchange capacity up to 45-55 g  $\text{NH}_4^+\text{-N/kg}$  media, that is significantly greater than the clinoptilolite (22 g  $\text{NH}_4^+\text{-N/kg}$  media) [49]. The high ammonium exchange capacity makes Zeolite-N a potential media for the selective removal of ammonium from wastewater as it has been investigated in several studies. However, the implementation of the IEX process for ammonium removal at bigger scale is limited by the lack of a supplier for the Zeolite-N. For this reason, there is a need to find a supplier for Zeolite-N or, alternatively, to identify a media which can replicate the high ammonium exchange capacity of the Zeolite-N as well as its mechanical strength. This is in particular connected to the longevity of the media which is affected by high attrition rate and consequent media loss and need to replace it more frequently thus increasing the maintenance and overall costs of the process [60].

On the other hand, one of the most used ion exchangers for phosphorus removal from wastewater is the synthetic hybrid anion exchanger (HAIX) resin: a polymeric base where amorphous iron hydroxide nanoparticles (HFO-NP) have been dispersed [60] with a reported maximum operating capacity of 9.7 g P/kg resin in secondary effluent wastewater [62]. Two processes take place within the HAIX: the exchange of anions between the polymeric base and the liquid phase ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) [63] and the adsorption of phosphorus (as divalent anion  $\text{HPO}_4^{2-}$  and monovalent anion  $\text{H}_2\text{PO}_4^-$  [64]) onto the HFO-NP via Lewis acid (metal oxides) – base (phosphate anion) interactions which increases both the selectivity and the capacity of the resin [63]. HAIX has been used to efficiently remove phosphorus from urine [64], municipal

wastewater [63], surface waters with high concentration concentrations of natural organic matter [65] and urban wastewater treatment plant sludge liquor [52]. Although the results obtained from these studies are very promising, there are bottlenecks that need to be investigated such as demonstrating the technology at large scale and over extended periods of operation as most studies have been conducted at laboratory or small pilot scale, over limited period of time.

Both the Zeolite-N and the HAIX can be regenerated and reused multiple times. High strength ionic brines (sodium chloride or potassium chloride 10% w/v) are commonly used for the regeneration of Zeolite-N [47]. The sodium ( $\text{Na}^+$ ) or potassium ( $\text{K}^+$ ), present in the brine at high concentration, exchange with the ammonium ion ( $\text{NH}_4^+$ ) in the media thus restoring its initial ammonium exchange capacity [66]. On the other hand, the HAIX can be regenerated by passing through the resin bed a high pH solution (usually sodium hydroxide,  $\text{NaOH}$ ) and high strength ionic brine (usually sodium chloride,  $\text{NaCl}$ ). This method allows for both the desorption of the phosphate adsorbed by the HFO-NP and it restores the ion exchange capacity of the polymeric base [67].

The production of waste concentrated regenerant brine has high economic and environmental impact and, therefore, it needs to be managed to ensure both a reduction in chemical use and the nutrients recovery [51]. A number of technologies have been proposed to recover both nutrients and regenerants. These mainly considered the ammonium stripping (as ammonia,  $\text{NH}_3$ ) and distillation for the saturated Zeolite-N regenerant [68], [69] and the precipitation of calcium phosphate products for the saturated HAIX regenerant [50]. However, these technologies have to be investigated at bigger scale and with real regenerant solutions. Additionally, particular attention should be given to potential market opportunities for the recovered products. The phosphorus-based recovered materials can find their applications in agricultural sector as well as be used for industrial purposes [70]. Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) has proven to be a good slow release fertiliser [71], however, its crystallization requires an equimolar ratio of Mg/N/P (1:1:1) and a pH of 9 [72]. Alternatively, hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ), a well-known form of CaP, has been recovered and used as fertiliser, soil conditioner [73] as well as to remediate heavy metal-contaminated-soils [74]. On the other hand, ammonia solution can find application in the chemical sector or in the fertiliser industry as well as be used in the

cleaning sector, in plastics and textile manufacturing [75]. A recently studied application of the ammonia solution includes its use in the microbial protein production to replace conventional animal feed and food supplements [76], [77].

#### 1.4. Aim and objectives

The overall aim of this PhD thesis is to underline the mechanisms of removal and recovery of ammonium ( $\text{NH}_4^+$ ) and phosphorus (as  $\text{PO}_4^{3-}$ ) from wastewater through the ion exchange (IEX) process in order to optimise the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  removal efficiency and maximise their recovery from IEX regenerant brines, when working at demonstration scale over an extended period of time. To deliver against the overall aim, the following objects were set:

- **Objective 1.** To evaluate the ammonium exchange capacity and mechanical strength (resistance to attrition and compression) of synthetic zeolites (Zeolite1-6) and natural (clinoptilolite) zeolites against engineered zeolite, Zeolite-N, used as reference ion exchange media for ammonium removal from wastewater;
- **Objective 2.** To understand the resilience of the Zeolite-N in an ion exchange demonstration scale process meant as its ability to respond to variable ammonium loadings and to compare the environmental benefits of using the ion exchange process for ammonium removal to a reference scenario where COD and nitrogen were removed via nitrification-denitrification through a life cycle assessment (LCA);
- **Objective 3.** To investigate the possibility to obtain high ammonium removal from wastewater with a natural clinoptilolite (Zeoclere30) by using the same operational conditions (demonstration scale plant, 5 min EBCT) used with Zeolite-N and to explore the feasibility of ammonium recovery from the Zeoclere30 by using the same regenerant brine as for Zeolite-N (KCl and NaCl);
- **Objective 4.** To develop a science based understanding of different ammonium (as ammonia,  $\text{NH}_3$ ) recovery techniques from saturated brines regenerant solution by establishing gas/liquid mass transfer coefficients of: (1) thermal vacuum stripping and distillation using a rotary evaporator and (2) a multi-component equipment and (3) liquid-liquid mass transfer technology (hollow fibre membrane contactor);
- **Objective 5.** To investigate the changes in phosphorus (as  $\text{PO}_4\text{-P}$ ) adsorption capacity from wastewater of a hybrid anion exchanger (HAIX) due to its prolonged

use at demonstration scale considering multiple reuse of the regenerant solution and the PO<sub>4</sub>-P recovery from the regenerant;

- **Objective 6.** To understand the influence of mixing time and calcium/phosphate (Ca:P) ratio on the phosphorus recovery from the HAIX regenerant solution (saturated NaOH) by precipitation with hydrated lime, Ca(OH)<sub>2</sub> and to investigate the purity of the recovered product.

## 1.5. Author contribution

All the chapters in this PhD thesis have been written by Samuela Guida, edited by Dr Ana Soared and revised by Prof Bruce Jefferson. The technical chapters (Chapter 2-6) are presented as a series of papers for publication. All experiments were designed, conducted or supervised by Samuela Guida at Cranfield University. The results of the experiments were analysed and combined by Samuela Guida. Additional contributors to the chapters are presented below:

- Chapter 2: Chris Potter (BYK Additives and Instruments, Germany) provided the synthetic zeolites (Zeolite1-6) and contributed with the chemical characterization of the media;
- Chapter 3: the life cycle assessment (LCA) was conducted by Lea Conzelmann (Kompetenzzentrum Wasser Berlin gGmbH) who contributed to the writing of the paper under the supervision of Dr.-Ing Christian Remy (Kompetenzzentrum Wasser Berlin gGmbH). Peter Vale (Sewern Trent Water, UK) provided the data for the biological reference scenario;
- Chapter 4: Eleonora Passioni (Cranfield University) and Dr. Izaro Lizarralde (Universidad de Navarra, Pamplona, Spain) supported the sampling of the demonstration plant and the analysis the ammonium concentration, under the supervision of Samuela Guida;
- Chapter 5: the ammonia (NH<sub>3</sub>) recovery experiments were conducted by Samuela Guida (vacuum thermal stripping), Dr. Andrew McLeod (Cranfield University) (hollow fibre membrane contactor) and Ben Luquami (Cranfield University) (multicomponent vacuum thermal stripping) under the supervision of Prof Ewan J. McAdam;

- Chapter 6: the demonstration plant was run by Samuela Guida with the support of Giorgia Rubertelli (University of Bologna, Italy) under the supervision of Samuela Guida. Giorgia run the demonstration plant for a period of 5 months, collecting and analysing samples and supporting with the experiments on phosphorus recovery.

## **1.6. PhD thesis plan**

A graphical representation of the PhD thesis plan is presented in Figure 1.3.



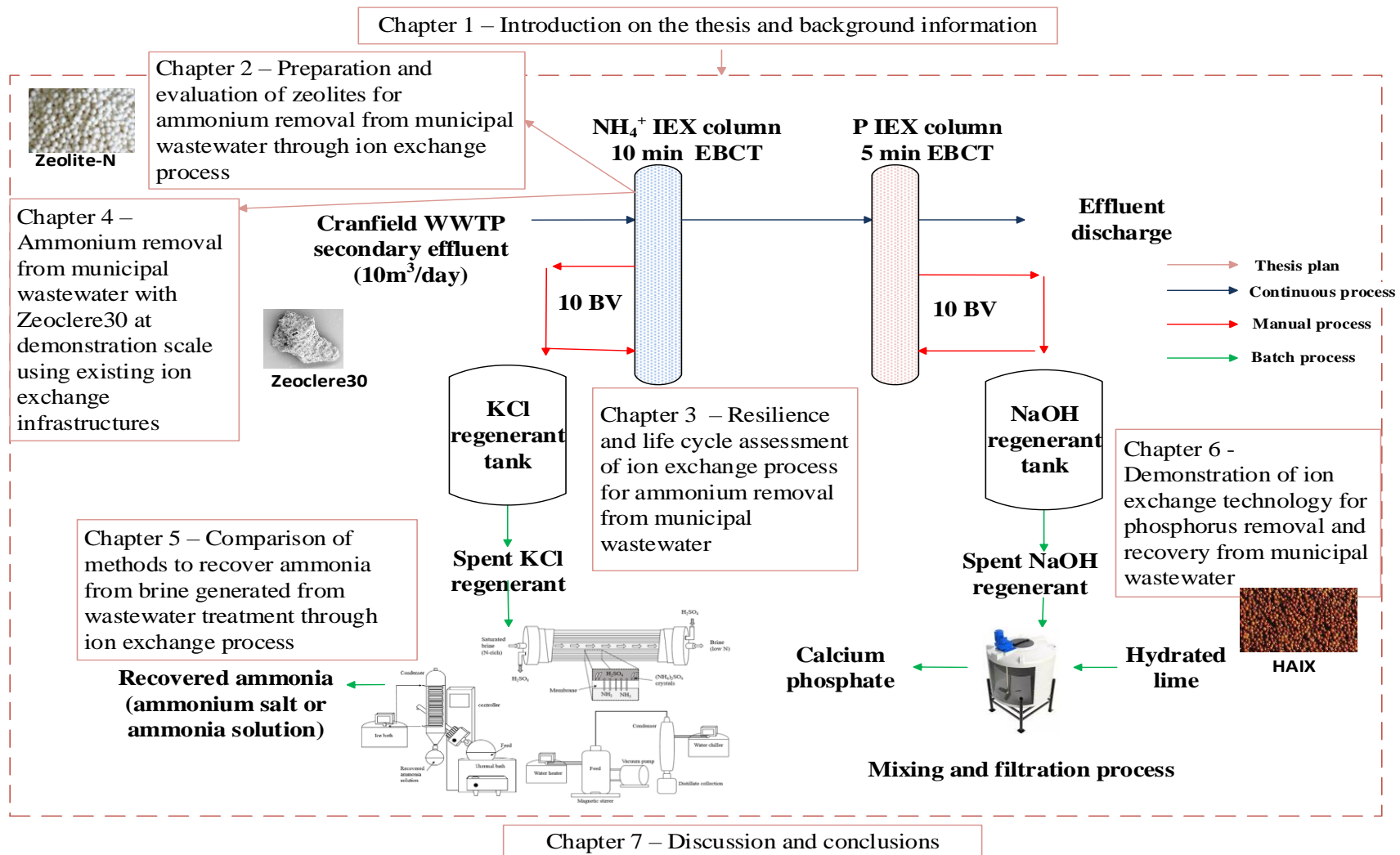


Figure 1.3 Schematic representation of the PhD thesis.

**Chapter 1** presents background information on available biological techniques used to remove and recover ammonium and phosphorus from wastewater and introduces the IEX process as an alternative to these technologies. In particular, the chapter indicates the current gaps in knowledge on the application of IEX process in WWTPs and serve as introduction to the PhD thesis.

To respond to the lack of supplier for the well-known ion exchange media Zeolite-N, **Chapter 2** presents the experimental work performed to compare natural and synthetic zeolites to the Zeolite-N. In particular, the chapter investigates their ability to efficiently remove ammonium ( $\text{NH}_4^+\text{-N}$ ) from municipal wastewater and their durability by investigating their mechanical strength (resistance to attrition and compression). The zeolites taken into consideration were the natural Clinoptilolite (St. Cloud Mining®, New Mexico) and the synthetic Zeolite1-6 (BYK Additives & Instruments Ltd, Germany).

In **Chapter 3**, the resilience of Zeolite-N meant as the capacity to maintain high ammonium exchange efficiency when subjected to variable ammonium concentrations ( $<0.006\text{-}26 \text{ mg NH}_4^+\text{-N/L}$ ) was studied in a demonstration scale plant ( $10 \text{ m}^3/\text{day}$ ). The environmental impacts of the IEX process for ammonium removal and recovery was compared with a reference scenario (COD and nitrogen removed in a trickling filters via nitrification-denitrification) through a life cycle assessment (LCA) focusing on primary energy demand, greenhouse gas (GHG) emissions and eutrophication potential.

**Chapter 4** investigates the possibility of maintaining efficient ammonium removal and recovery by using the same operational conditions (EBCT, regenerant brine) of Zeolite-N, with Zeoclere30, a natural zeolite commercially available and supplied by Mineral Supplies International Ltd (Sussex, UK), mostly used for swimming pool water filtration. Zeoclere30 was chosen as media to be implemented in the demonstration plant ( $10 \text{ m}^3/\text{day}$ ) due to its availability in the market and low cost of production, which makes it a possible candidate to respond to the lack of supplier of Zeolite-N. Particular focus was given to the regeneration method of Zeoclere30 as this represents a limiting step towards the implementation of the media as ion exchanger.

In **Chapter 5**, a combination of synthetic and real brines was treated under conditions previously outlined as optimum for each ammonium (as ammonia,  $\text{NH}_3$ ) recovery technology. The performance of thermal vacuum stripping at the rotary evaporator, thermal vacuum stripping with multi-component equipment and distillation and chemical absorption across a membrane were compared to assess the relative potential of the different options and offer a perspective on future outlook and development. The ammonia recovery efficiency, the ammonia losses and the purity of the recovered product were chosen as indicators of the competence of the technologies.

In **Chapter 6**, the removal and recovery of phosphorus from secondary effluent wastewater using hybrid anion exchanger (HAIX) resin were investigated. To understand the underlying mechanisms of the phosphorus adsorption/desorption as well as the long-term operation applicability of the process, a demonstration plant ( $10 \text{ m}^3/\text{day}$ ) was operated for multiple cycles over a period of two years. The work focused on the optimisation of the bed volumes treated between regenerations to maintain the required effluent quality and the impact of reusing the regenerant solution ( $\text{NaOH}$  2%) until saturation. The spent solution was then used to optimise the recovery process by the addition of  $\text{Ca}(\text{OH})_2$ , mixing and filtration of the calcium phosphate precipitate. An analysis of the purity of the recovered product was also performed to assess the possibility for the calcium phosphate to be used in chemical and fertiliser industry. Additionally, the effect on regeneration capacity of the  $\text{NaOH}$  after the recovery was investigated.

**Chapter 7** presents an overall discussion on the technical applicability of the ion exchange process for the removal and recovery of ammonium and phosphorus from secondary treated wastewater, including future studies. The chapter also presents the overall contribution to scientific knowledge of the PhD thesis.

**Chapter 8** highlights the overall conclusions from the work.

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## 2. PREPARATION AND EVALUATION OF ZEOLITES FOR AMMONIUM REMOVAL FROM MUNICIPAL WASTEWATER THROUGH ION EXCHANGE PROCESS

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### Abstract

The application of ion exchange process for ammonium ( $\text{NH}_4^+\text{-N}$ ) removal from wastewater is limited due to the lack of suppliers of engineered zeolites which present high ammonium exchange capacity (AEC) and mechanical strength. This study focuses on the preparation and evaluation of synthetic zeolites (Zeolite1-6) by measuring AEC and resistance to attrition and compression, against natural (clinoptilolite) and engineered zeolite (reference, Zeolite-N). At high  $\text{NH}_4^+\text{-N}$  concentrations (55.6 meq  $\text{NH}_4^+\text{-N/L}$ ), Zeolite6 and Zeolite2 showed capacities of 4.7 and 4.5 meq  $\text{NH}_4^+\text{-N/g}$  media, respectively. In secondary effluent wastewater (initial  $\text{NH}_4^+\text{-N}$  of 0.7 meq  $\text{NH}_4^+\text{-N/L}$ ), Zeolite1, 2 and 6 showed an AEC of 0.05 meq  $\text{NH}_4^+\text{-N/g}$  media, similar to Zeolite-N (0.06 meq  $\text{NH}_4^+\text{-N/g}$  media). Among the synthetic zeolites, Zeolite3 and 6 showed higher resistance to attrition (disintegration rate=2.7 and 4.1 NTU/h, respectively) when compared with Zeolite-N (disintegration rate=13.2 NTU/h). Zeolite4 and 6 showed higher resistance to compression (11N and 6N, respectively). Due its properties, Zeolite6 was further tested in an ion exchange demonstration scale plant treating secondary effluent from a municipal wastewater treatment plant. However, Zeolite6 disintegrated after 2 months of

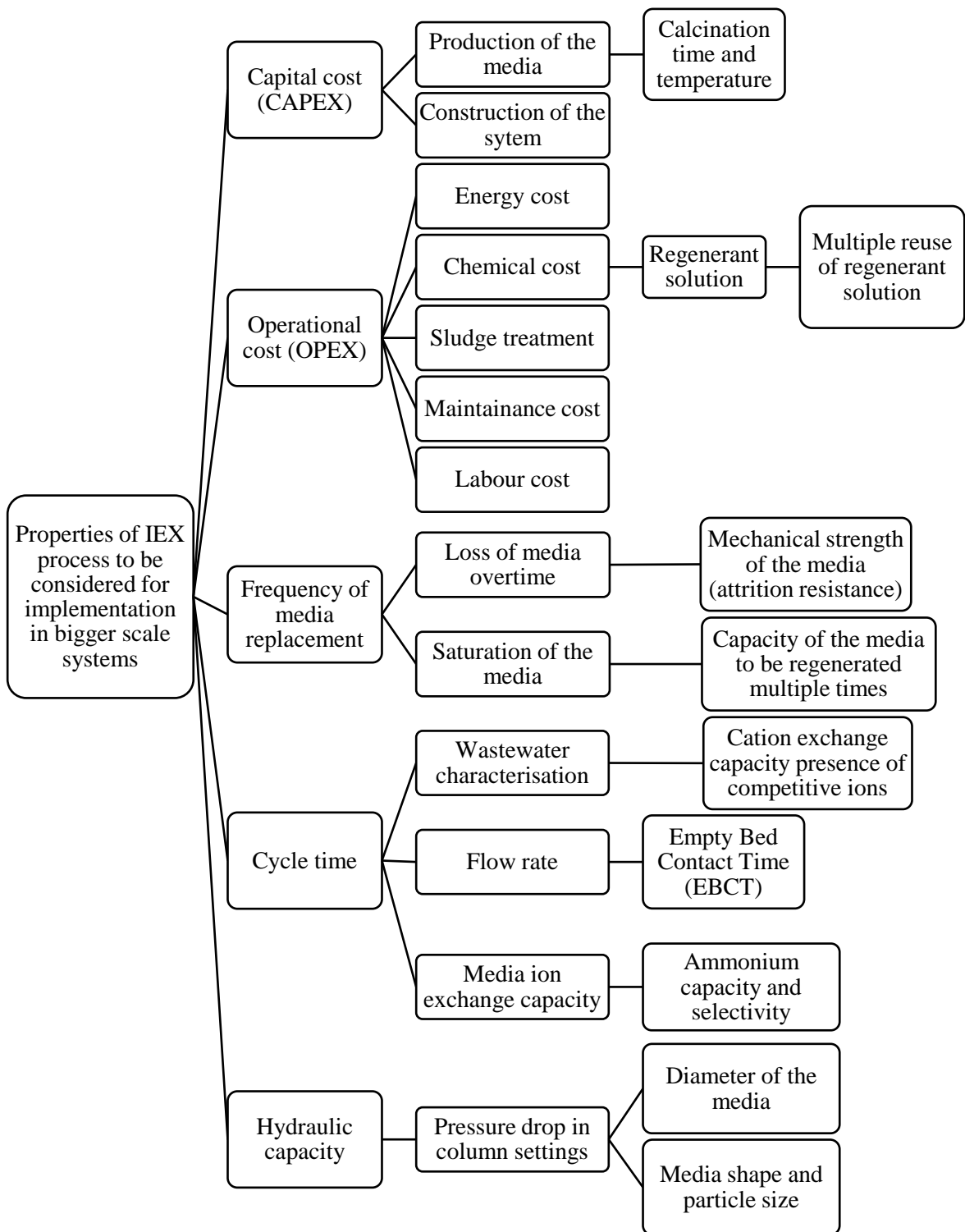
operation, whilst Zeolite-N remained stable for 1.5 year. This highlighted the importance of the zeolite's mechanical strength for successful application. In particular, future work should focus on the optimisation of the zeolite production process (temperature, time and dimension of the kiln during calcination) to obtain an engineered zeolite with a spherical shape thus reducing eventual sharp edges which can affect its mechanical strength.

### **Keywords**

Zeolites; ion exchange; cation exchange capacity; mechanical strength.

## 2.1 Introduction

Nitrogen compounds (such as ammonium, as  $\text{NH}_4^+\text{-N}$ , and nitrate,  $\text{NO}_3^-$ ) can have a detrimental effect on the water quality of rivers and lakes [1]. For this reason, the Water Framework Directive 2000/60/EC and Council Directive 91/271/EEC have established more stringent limits on the discharge of these compounds into water bodies [2], [3]. This new regulation requires for the effluent of wastewater treatment plant to have an ammonium concentration as low as 1 mg  $\text{NH}_4^+\text{-N/L}$  and maximum 30 and 50 mg  $\text{NO}_3^-/\text{L}$  for nitrate discharge in freshwater and seawater, respectively [1]–[3]. Conventional methods to decrease ammonium concentration from wastewater (such as biological nitrification-denitrification [4]) present cost limitation and environmental concern due to the production of greenhouse gases [5]. The use of ion exchange (IEX) systems for the selective removal of ammonium from wastewater is becoming increasingly attractive due to its high removal efficiency, low greenhouse gas emissions, competitive cost, and relative simplicity of operation [6]. The most effective IEX media are characterized by great selectivity for the target pollutant, high specific surface area and ability to be regenerated allowing for its multiple reuse [7]. However, most of the recent studies concerning the IEX process for ammonium removal are limited to laboratory scale analysis [1]. It is crucial to investigate the loss of ion exchange media and its annual replacement as these can increase costs significantly [8]. Other parameters that can impact costs are media capacity in between regenerations (more specifically the empty bed contact time, EBCT) [1] and hydraulic capacity [9]. These properties can be correlated to the production of the IEX media and its physico-chemical characteristics such as the cation exchange capacity [10], the selectivity for ammonium in presence of competitive ions [11], as well as its mechanical strength (Figure 2.1).



**Figure 2.1 Properties of the ion exchange (IEX) process and characteristics of the IEX media needed to be considered for practical implementation of the IEX process at bigger scale.**



Currently, the most used ion exchange media for ammonium removal is the natural zeolite clinoptilolite (in the activated Na-form) which has been showed to have ammonium exchange capacity of up to 19 mg NH<sub>4</sub><sup>+</sup>-N/g media (1.1 meq NH<sub>4</sub><sup>+</sup>-N/g media) when treating domestic wastewater with initial concentration of 27 mg NH<sub>4</sub><sup>+</sup>-N/L (1.5 meq NH<sub>4</sub><sup>+</sup>-N/L) and pH 7.7 [12].

Zeolites are well known crystalline aluminosilicate minerals found in nature containing a framework of [SiO<sub>4</sub>]<sup>4-</sup> and [AlO<sub>4</sub>]<sup>5-</sup> tetrahedra linked by their corners through oxygen atoms. Natural zeolites are characterized by the general formula of M<sub>2/n</sub>OAl<sub>2</sub>O<sub>3</sub>xSiO<sub>2</sub>yH<sub>2</sub>O where *M* is the metal cation which compensates for the excess negative charge of the tetrahedra, *n* is the cation valence, *x* the number of Si tetrahedra (varying from 2 to 10) and *y* is the number of water molecules (varying from 2 to 7) [11], [13]. The chemical bond between oxygen shared by the tetrahedra leads to the formation of cages and channels within the zeolite matrix, which can lodge water molecules as well as cations (usually Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup> and Mg<sup>2+</sup>). These cations can be exchanged with the surroundings, following Equation 2.1.



where,  $z_A^+$  and  $z_B^+$  are the valences of the respective cations and *L* is defined as the portion of the zeolite framework that is negatively charged [13]. In the presence of ammonium rich liquids, NH<sub>4</sub><sup>+</sup>-N is exchanged with the cations present in the framework [14]. The exchange capacity of the zeolite depends on several factors such as the negative charge of its framework structure (due to Si/Al ratio) as well as size, concentration and charge of the exchange ions [13].

To improve the selectivity and the exchange capacity, natural zeolites can be engineered by single or combined treatments that include heating and reaction with chemicals such as acids, bases and inorganic salts [15]. The chemical modification of clay and other aluminium-bearing minerals leads to formation of synthetic zeolites, such as Zeolite-N, which has an ammonium exchange capacity (AEC) up to 45-55 mg NH<sub>4</sub><sup>+</sup>-N/g media (2.5-3.1 meq NH<sub>4</sub><sup>+</sup>-N/g media), that is significantly greater than the natural occurring zeolites [16], [17]. The natural materials present

octahedrally coordinated  $Al^{3+}$  while the synthetic zeolites presents tetrahedrally coordinated  $Al^{3+}$ , which results in increased AEC [18].

The scale-up of the IEX process using engineered zeolites for the removal of ammonium from wastewater is limited by the lack of commercial suppliers. Zeolite-N presented high potential for the wide application of IEX processes [18], but it was commercially available for only a short period of time and no substitute media is currently on the market. Therefore, to maintain the operation and avoid decommissioning of already existing IEX plants and move forward towards implementation of the IEX process at bigger scale, there is a crucial need to find a substitute for the Zeolite-N. However, to the authors' knowledge, no study has been performed to present possible candidates which could replace Zeolite-N. For this reason, the main aim of this work was to evaluate a natural zeolite (clinoptilolite) and six different synthetic zeolites (Zeolite1-6) that could achieve high ammonium exchange capacity and mechanical strength (resistance to attrition and compression) comparable to Zeolite-N. More in details, this work investigated the ammonium exchange capacity of the media as this is required to meet the increasingly stringent regulations in terms of nutrients discharge [19]. Additionally, high mechanical strength was considered an essential characteristic of the tested zeolites as this prevents cracking and disintegration of media in IEX columns which could result in the need to replace the media frequently [20] as well as the need of additional filtering equipment [21].

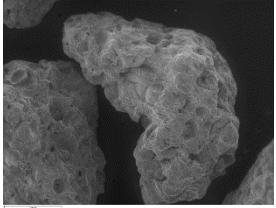

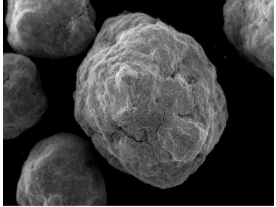
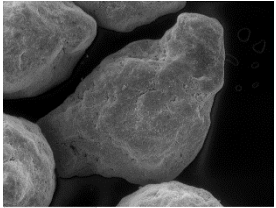
## **2.2 Material and methods**

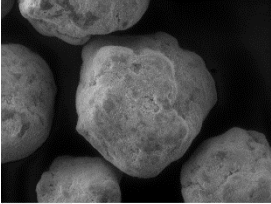
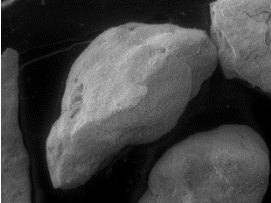
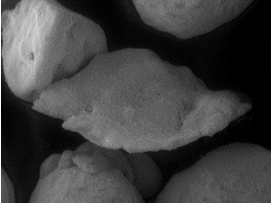
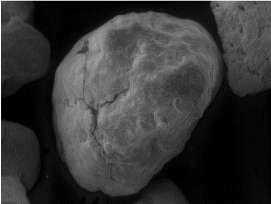
### **2.2.1 Natural and synthetic zeolites**

Zeolite-N (synthetic zeolite, NanoChem Pty Ltd, Australia) was used as reference material and compared to clinoptilolite (natural zeolite, St. Cloud Mining®, New Mexico), and Zeolite1-6 (synthetic zeolites, BYK Additives & Instruments Ltd, Germany). The synthetic zeolites were produced according to Mackinnon, Millar and Stolz [16], granulated according to procedure described in Table 2.1. Clinoptilolite had a  $Si/Al=4.0$  (natural zeolites were reported to have a  $Si/Al=3-5$  [11], [22], [23]) while lower values of  $Si/Al$  (1.5-2.0) were measured for the synthetic zeolites (Table 2.1).

The zeolites were initially washed with deionized water to remove any dust from their surface and sieved to obtain a particle size of 1-2 mm for the synthetic zeolites which is considered as the optimal diameter for applications as IEX media [1]. According to literature, typical media sizes for natural zeolites are between 3 and 9 mm [1], [16], therefore the clinoptilolite was sieved to obtain a particle size of 2.5-3.5.

**Table 2.1 Natural and synthetic zeolites tested in this work.**

| <b>Material</b> | <b>Production process</b>                                                                                                         | <b>Si/Al</b> | <b>SEM images</b>                                                                     |
|-----------------|-----------------------------------------------------------------------------------------------------------------------------------|--------------|---------------------------------------------------------------------------------------|
| Clinoptilolite  | Mined in Inyo County, California and shipped to processing facility in Winston, NM, to be stored, crushed, screened, and packaged | 4.0          |    |
| Zeolite-N       | Recipe in <i>Table 2</i> in [16]; T<100°C, reaction time <20h                                                                     | 1.5          |  |
| Zeolite1        | Calcined in a stepped heat treatment (total of 2h) in a lab scale kiln up to 550°C                                                | 1.8          |  |
| Zeolite2        | Calcined in a lab scale kiln at 550°C for 2h                                                                                      | 1.7          |  |

|          |                                                                    |     |                                                                                      |
|----------|--------------------------------------------------------------------|-----|--------------------------------------------------------------------------------------|
| Zeolite3 | Calcined in an industrial scale kiln at 550°C for 10-12h           | 1.7 |   |
| Zeolite4 | Calcined in an industrial scale kiln at 550°C for 2h               | 1.8 |   |
| Zeolite5 | Calcined in an industrial scale kiln at 500°C for 1h (small batch) | 2.0 |   |
| Zeolite6 | Calcined in an industrial scale kiln at 500°C for 1h (large batch) | 1.8 |  |

### 2.2.2 Municipal wastewater characterization

Municipal wastewater was obtained from Cranfield University wastewater treatment plant in the UK (2,840 population equivalent) after the secondary treatment with trickling filters that removed organic carbon. The wastewater was filtered (filter pore diameter 1.2  $\mu\text{m}$ ) to prevent any residual solids to interfere with the adsorption tests [24]. The composition of the wastewater was: chemical oxygen demand (COD) of  $37.0 \pm 12.3$  mg/L, ammonium ( $\text{NH}_4^+\text{-N}$ ) of  $13.6 \pm 4.6$  mg  $\text{NH}_4^+\text{-N/L}$ , orthophosphate ( $\text{PO}_4\text{-P}$ ) of  $6.0 \pm 0.25$  mg  $\text{PO}_4\text{-P/L}$ , calcium ( $\text{Ca}^{2+}$ ) of  $25.1 \pm 1.2$  mg  $\text{Ca}^{2+}/\text{L}$ , potassium ( $\text{K}^+$ ) of  $25.4 \pm 2.2$  mg  $\text{K}^+/\text{L}$  and the pH was  $7.3 \pm 0.4$ .

### 2.2.3 Ammonium exchange capacity (AEC) of zeolites

The maximum ammonium exchange capacity (AEC) of the zeolites was calculated in mono-component solution with an initial concentration of 1000 mg NH<sub>4</sub><sup>+</sup>-N/L (55.6 meq NH<sub>4</sub><sup>+</sup>-N/L). Successively, the operational AEC in municipal wastewater was calculated starting from an initial concentration of 12.7 mg NH<sub>4</sub><sup>+</sup>-N/L (0.7 meq NH<sub>4</sub><sup>+</sup>-N/L).

The solutions (100 ml) were mixed with 0.5 g of media at 150 rpm for 8 hours using the orbital shaker SSL1 (STUART®, UK), after which, the remaining ammonium was measured. Experiments were conducted in triplicate. The AEC was calculated according to Equation 2.2 [25]:

$$AEC = \frac{[C_i - C_f] * V_{treated}}{M} \quad \text{Equation 2.2}$$

where *AEC* is the ammonium exchange capacity (meq NH<sub>4</sub><sup>+</sup>-N/g media), *C<sub>i</sub>* and *C<sub>f</sub>* are the initial and final ammonium concentration in solutions (meq NH<sub>4</sub><sup>+</sup>-N/L), *V<sub>treated</sub>* is the volume of the solution (L) and *M* is the mass of media (g).

To investigate the reusability of the media over multiple cycles, the zeolites were pre-treated with a fresh solution of potassium chloride (KCl) 10% w/v (the regenerant) for a period of 2 hours to remove any residual ammonium from the fresh media surface. Successively, 100 mL of municipal wastewater were mixed with 1 g of the media (i.e. 10 g/L), in duplicate, mixed by agitation at 150 rpm for a period of 8 hours using the orbital shaker SSL1 (STUART®, UK). The average initial concentration was 12.1±0.3 mg NH<sub>4</sub><sup>+</sup>-N/L (0.7 meq NH<sub>4</sub><sup>+</sup>-N/L). At the end of each cycle, the media were regenerated with a fresh regenerant solution for a period of 2 hours for a total of 10 cycles. The ammonium exchange capacity (AEC) in wastewater was calculated as in Equation 2.2 while the regeneration capacity (*Q<sub>reg</sub>*) was calculated as in Equation 2.3 (adapted from You *et al.* [26]):

$$Q_{reg} = \frac{[C_{r,i} - C_{r,f}] * V_{r.treated}}{M} \quad \text{Equation 2.3}$$

where  $Q_{reg}$  is the capacity of regeneration (meq  $\text{NH}_4^+\text{-N/g}$  media);  $C_{r,i}$  and  $C_{r,f}$  are the concentration of ammonium in the regenerant at the beginning and at the end of each cycle (meq  $\text{NH}_4^+\text{-N/g}$  media);  $V_{r,treated}$  is the volume of regenerant used (L);  $M$  is the same as in Equation 2.2.

#### **2.2.4 Attrition and resistance to compression tests**

For the attrition tests, 3 g of fresh Zeolite were mixed at 200 rpm (in accordance to literature [27], [28]) with 300 mL of deionized water for a period of 24 hours using the orbital shaker SSL1 (STUART®, UK). Samples were taken at regular intervals (each 15 minutes during the first hour of treatment and each 2 hours from 2 to 24 hours of treatment), after 1 minute of settling.

The media resistance to compression was measured using the system Instron 5965 (Instron®, UK). Thirty beads of each zeolite were singularly positioned in between the compressing disks of the system and subjected to an increasing load (measured in Newton, N) until breakage. The force applied at breaking point was registered with an accuracy of 0.5% (according to the supplier specification). Measurements were performed on fresh media.

#### **2.2.5 Ion exchange demonstration scale plant**

Zeolite-N and Zeolite6 were separately tested for ammonium removal in an ion exchange demonstration scale plant (IEX-D) (Table 2.2) treating 10 m<sup>3</sup>/day of municipal wastewater with average ammonium concentrations of 13.6±4.6 mg  $\text{NH}_4^+\text{-N/L}$  (0.8±0.3 meq  $\text{NH}_4^+\text{-N/L}$ ). Firstly, a column with an internal diameter of 307 mm and height of 1566 mm was filled with 69 L (78 kg) of Zeolite-N. The media was first backwashed for 30 minutes to remove any fine particle left over from manufacturing. The wastewater was fed in down-flow operation at an empty bed contact time (EBCT) of 10 minutes. After media saturation, regeneration was completed using 10 bed volumes of potassium chloride (KCl) 10% w/v that were passed through the column in up-flow operation for 2 hours. At the end of the regeneration, the column was drained and the KCl was collected and stored for the next regeneration. The media was backwashed with tap water for 30 minutes (flow rate 500 L/h) at the end of each cycle to remove any residual solids. Successively,

a column with internal diameter of 217 mm and height 1577 mm was filled with 35L (24 kg) of Zeolite6 (Table 2.2). After an initial backwash, the wastewater was fed at an EBCT of 5 minutes. The same operation conditions as for Zeolite-N were used. For both media, the ammonium was measured in the influent and effluent of the columns and in the regenerant. The AEC and  $Q_{reg}$  were obtained as in Equation 2.2 and 2.3, respectively. A sample of both media was analysed at the optical microscope (Optech Microscopes Ltd) for the fresh media and for the media taken from the IEX-D columns after 7 and 3 cycles for Zeolite-N and Zeolite6, respectively and resistance to attrition tests were completed (in triplicate).

**Table 2.2 Ion exchange process – specification of the demonstration scale plant.**

|                                   | Units | Zeolite-N | Zeolite6 |
|-----------------------------------|-------|-----------|----------|
| Operational parameters            |       |           |          |
| Max wastewater flow rate          | L/day | 10000     | 10000    |
| Regenerant                        | w/v   | KCl 10%   | KCl 10%  |
| Flow rate during normal operation | L/h   | 416.7     | 416.7    |
| Flow rate during backwash         | L/h   | 500       | 500      |
| Volume column filled with media   | L     | 69        | 35       |
| Empty bed contact time (EBCT)     | min   | 10        | 5        |
| Bed volumes of regenerant         |       | 10        | 10       |
| Column                            |       |           |          |
| Outer diameter                    | mm    | 315       | 225      |
| Wall thickness                    | mm    | 4         | 4        |

|                           |                 |       |      |
|---------------------------|-----------------|-------|------|
| Inner diameter            | mm              | 307   | 217  |
| Sectional area            | dm <sup>2</sup> | 7.4   | 3.7  |
| Cylindrical column height | mm              | 1566  | 1577 |
| Column volume             | L               | 115.9 | 58.3 |

## 2.2.6 Physico-chemical and statistical analysis

Turbidity was measured using the 2100N Turbidimeter (HACH®, UK) in accordance with the EPA 180.1 method [29]. For the characterization of the wastewater, chemical oxygen demand, calcium and potassium were analysed using Spectroquant® cell tests; ammonium and phosphorus were analysed using the Smartchem200 (AMS Alliance, France). The analysis of the pH was performed using a pH meter (Jenway 3510 pH and conductivity meter, Camlab, UK).

Statistical analyses were performed using the JMP® software (SAS Institute) to identify statistical difference between the ammonium exchange capacity considering the solution treated (municipal wastewater and synthetic solution) and the media (natural and synthetic zeolite). The JMP® tool was also used to detect any statistical difference in the ion exchange capacities of the media comparing the first and tenth cycle of batch test.

## 2.3 Results

### 2.3.1 Maximum ammonium exchange capacity in mono-component solution and operational ammonium exchange capacity in municipal wastewater

When using a mono-component solution containing a high ammonium concentration (55.6 meq NH<sub>4</sub><sup>+</sup>-N/L, 1000 mg NH<sub>4</sub><sup>+</sup>-N/L), the maximum ammonium exchange capacity (AEC) of Zeolite-N was 4.3±0.5 meq NH<sub>4</sub><sup>+</sup>-N/g media (Figure 2.2a). In comparison, Zeolite6 and Zeolite2 presented higher AEC (4.7±0.04 and 4.5±0.4 meq NH<sub>4</sub><sup>+</sup>-N/g media, respectively) while the AEC of the other media

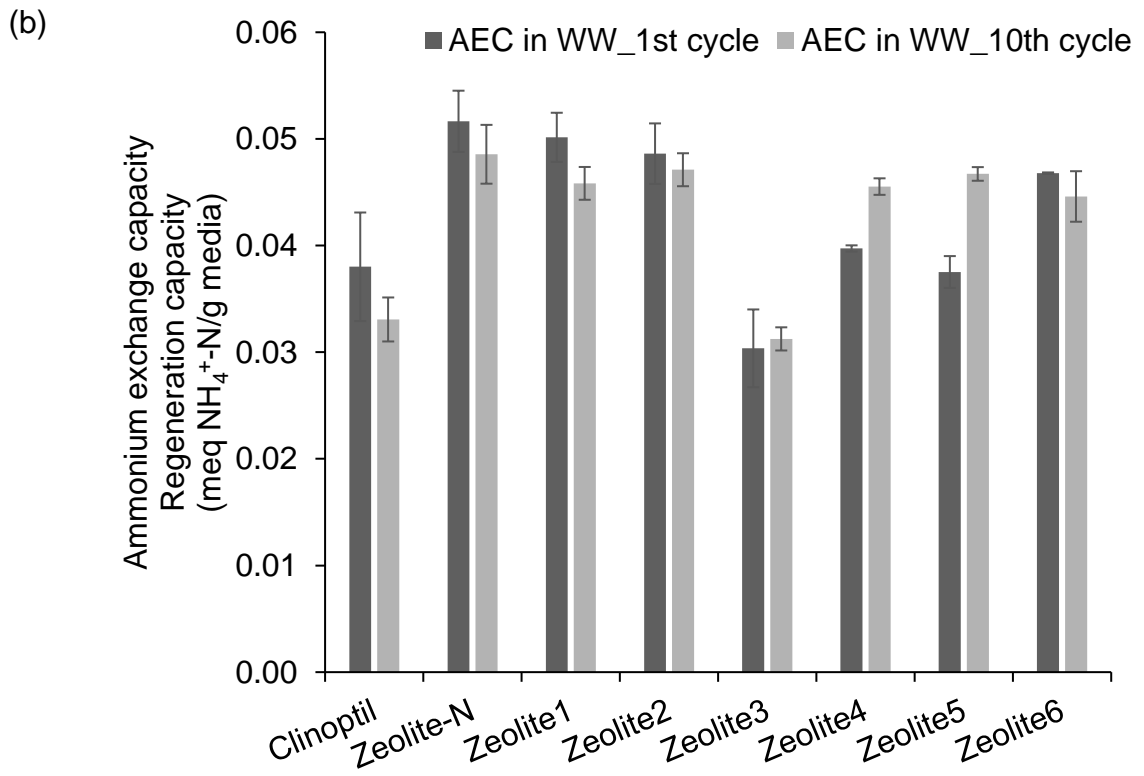
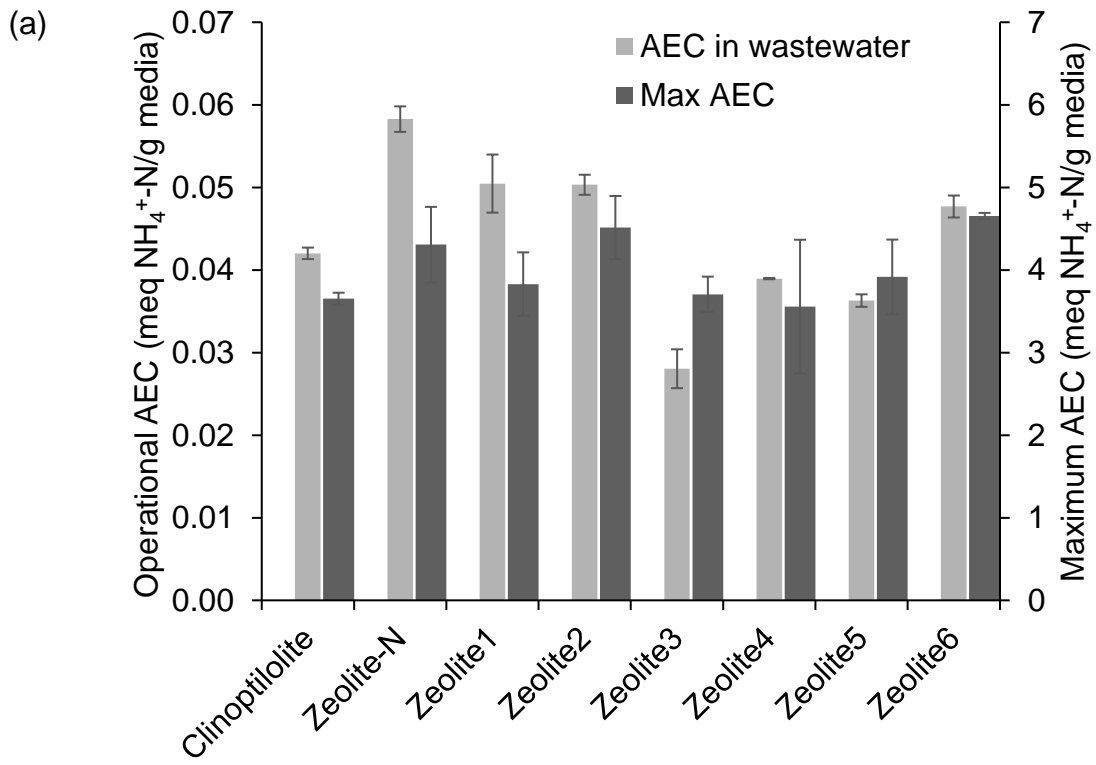


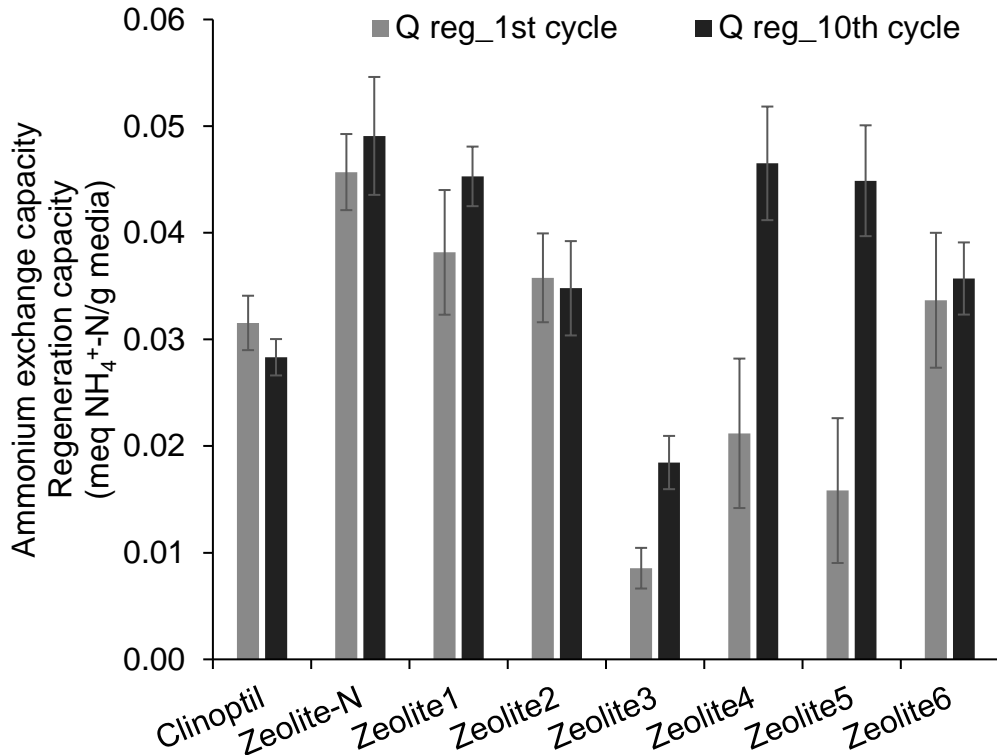
ranged between 3.6-3.9 meq  $\text{NH}_4^+\text{-N/g}$  media with the lowest value registered for Zeolite4 ( $3.6\pm 0.8$  meq  $\text{NH}_4^+\text{-N/g}$  media) (Figure 2.2a).

To investigate the operational AEC of the zeolites, experiments were also performed in municipal wastewater (Figure 2.2a) with initial ammonium concentration of 0.7 meq  $\text{NH}_4^+\text{-N/L}$  (12.7 mg  $\text{NH}_4^+\text{-N/L}$ ). Zeolite-N presented the highest AEC ( $0.06\pm 0.002$  meq  $\text{NH}_4^+\text{-N/g}$  media), followed by Zeolite1, 2 and 6 ( $0.05\pm 0.003$  meq  $\text{NH}_4^+\text{-N/g}$  media). Zeolite3, 5 and Clinoptilolite presented lower AEC (0.03-0.04 meq  $\text{NH}_4^+\text{-N/g}$  media). By using the statistical software JMP®, it was confirmed that AEC depended on the zeolite used ( $p < 0.0001$ ).

The stability of AEC in wastewater and regeneration capacity ( $Q_{\text{reg}}$ ) were assessed over multiple cycles as indicators of the reusability of the media (Figure 2.2b-c). Zeolite-N presented the highest AEC ( $0.052\pm 0.03$  meq  $\text{NH}_4^+\text{-N/g}$  media) with minimum decrease (6%) between the first and tenth cycle (Figure 2.2b). Zeolite-N also presented the highest  $Q_{\text{reg}}$  ( $0.046\pm 0.04$  meq  $\text{NH}_4^+\text{-N/g}$  media) which slightly increased (7%) between the first and the tenth cycles, reaching a regeneration efficiency of 90-100% (Figure 2.2c). For clinoptilolite and Zeolite2, after 10 cycles, the AEC decreased (15% and 3%, respectively) as well as the  $Q_{\text{reg}}$  (11% and 3%, respectively) while no clear pattern in the variation of AEC and  $Q_{\text{reg}}$  was identified for the other zeolites. However, no statistical difference was found when comparing the first and tenth cycles ( $p < 0.986$ ) for the AEC of all the media except Zeolite5 ( $p < 0.008$ ).

Considering all the media and cycles, statistical analysis revealed a significant effect for the ammonium exchange capacity in wastewater and during the regeneration phase depending on the media used ( $p < 0.0001$ ). Additionally,  $Q_{\text{reg}}$  was affected by the number of cycles ( $p < 0.0012$ ) and it depended on the media used ( $p < 0.0219$ ).



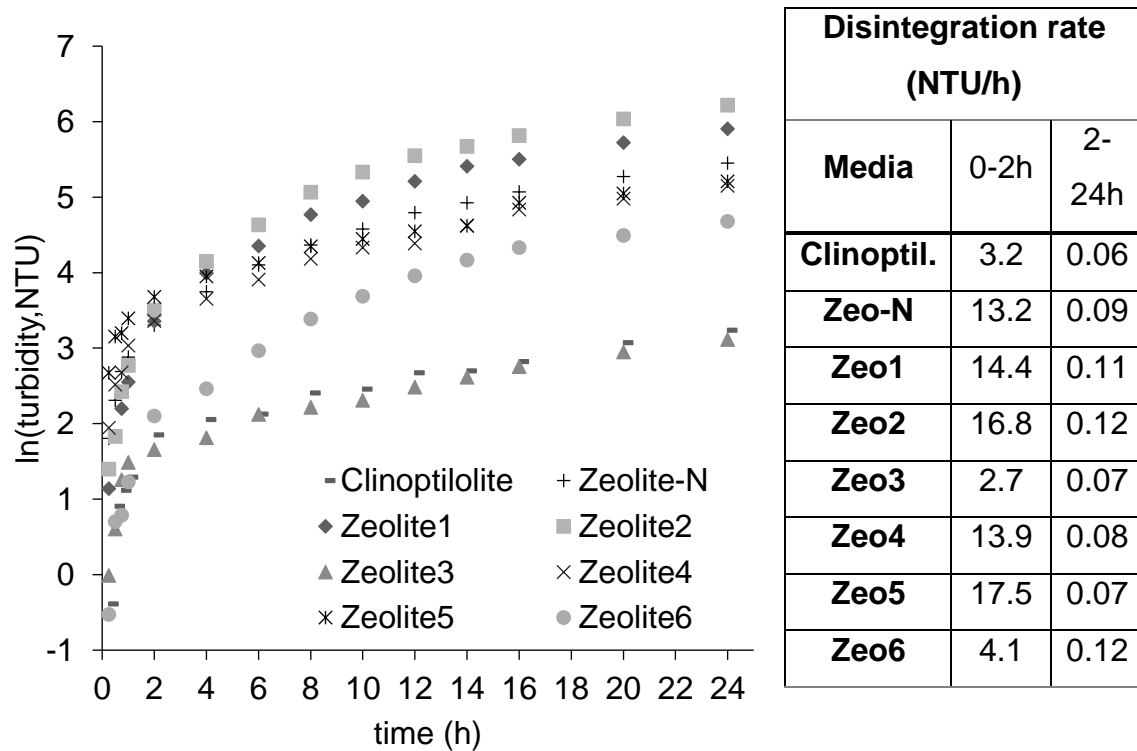


**Figure 2.2 (a) Operational ammonium exchange capacity (AEC) in municipal wastewater ( $C_{\text{initial}}=0.7$  meq  $\text{NH}_4^+\text{-N/L}$ ) and maximum AEC in mono-component solution ( $C_{\text{initial}}=55.6$  meq  $\text{NH}_4^+\text{-N/L}$ ) of natural and synthetic zeolites and (b) comparison of the AEC in wastewater and (c) regeneration capacities ( $Q_{\text{reg}}$ ) of the media at cycle 1 and cycle 10 of batch test in municipal wastewater ( $C_{\text{initial}}=0.7$  meq  $\text{NH}_4^+\text{-N/L}$ ).**

### 2.3.2 Zeolites' mechanical strength

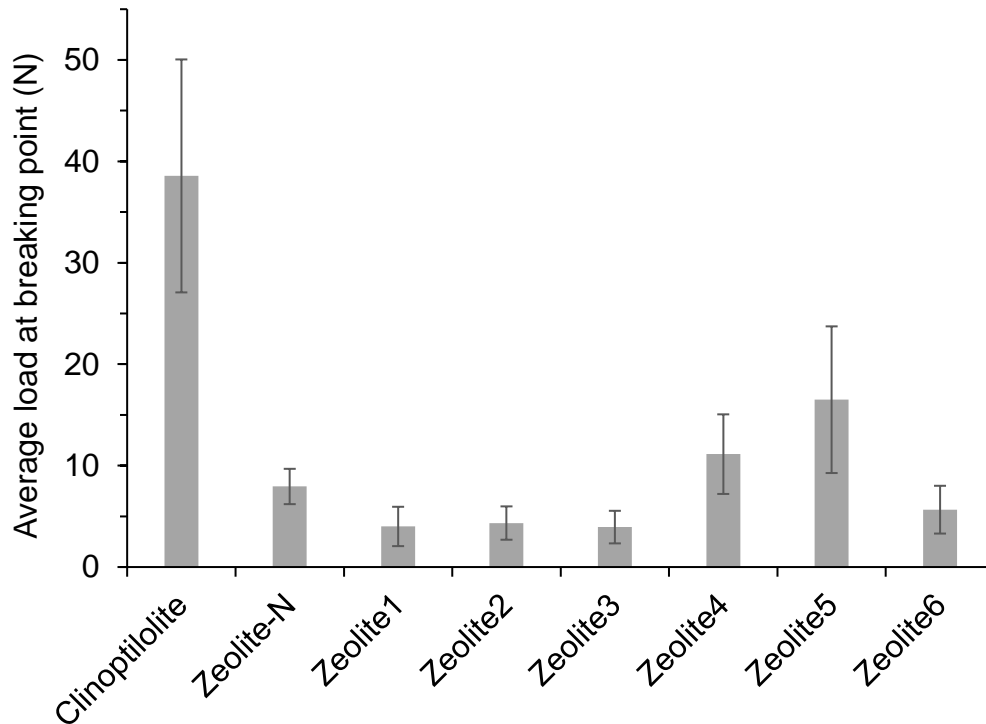
The mechanical strength of the zeolites was defined as the media resistance to attrition and compression. The resistance to attrition was correlated with the turbidity measurements, following the principle that an increase in turbidity was correlated to the media disintegration over time, as an indicator (Figure 2.3). In the first 2 hours of agitation, the disintegration rate of Zeolite-N was 13.2 NTU/h. In comparison, higher values were registered for Zeolite5 and Zeolite2 (17.5 and 16.2 NTU/h, respectively) and Zeolite1 and Zeolite4 (14.4 and 13.9 NTU/h, respectively). On the other hand, Zeolite3, Zeolite6 and Clinoptilolite showed high resistance to attrition with disintegration rates between 2.7 and 4.1 NTU/h. Lower disintegration rates

were registered for all the media in between 2-24 hours of agitation ( $0.09 \pm 0.02 \text{ NTU/h}$ ).



**Figure 2.3.** Turbidity measurements of the ion exchange media over 24h of agitation at 200 rpm ( $t=0-24\text{h}$ ), presented as  $\ln(\text{turbidity, NTU})$  over time; on the right, disintegration rate (NTU/h) of the ion exchange media in the period 0-2h and 2-24h.

For the compression test, each media (30 beads/media) was subjected to increasing loading pressure and the force applied at breaking point was registered (Figure 2.4). Zeolite-N resisted to a pressure up to  $7.9 \pm 1.7 \text{ N}$  before breakage. Clinoptilolite showed the highest compression resistance (loading pressure of  $38.6 \pm 11.5 \text{ N}$  before breakage). Zeolite4 and 5 resisted a load up to  $11.3 \pm 3.9 \text{ N}$  and  $16.5 \pm 3.2 \text{ N}$ , respectively while, for the other media, the average load before breakage was between 3.9-5.7 N (Figure 2.4).

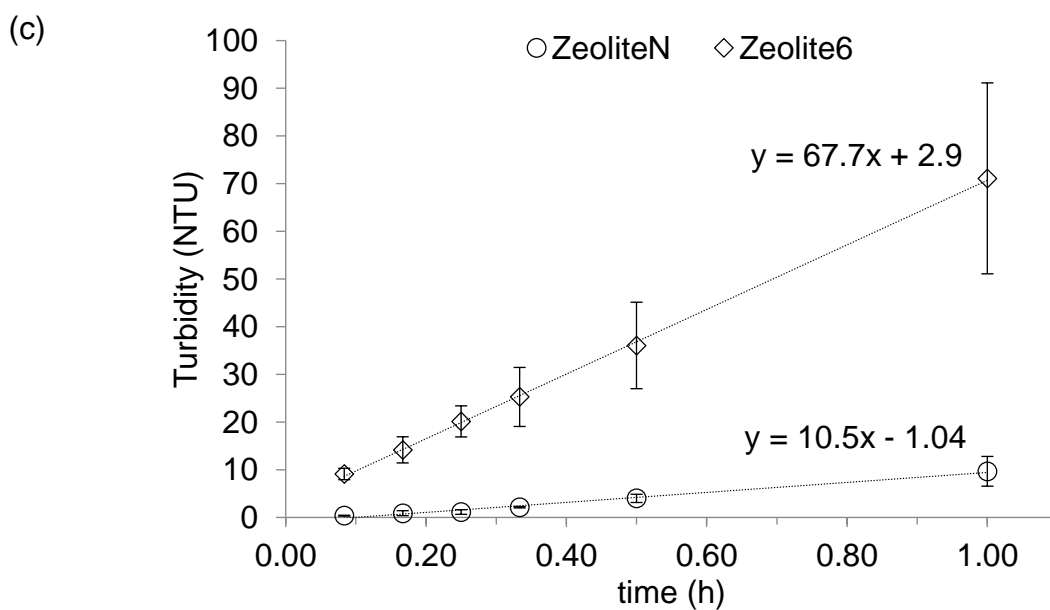
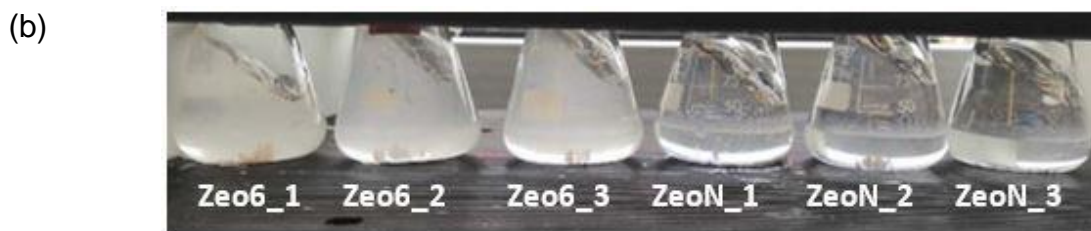
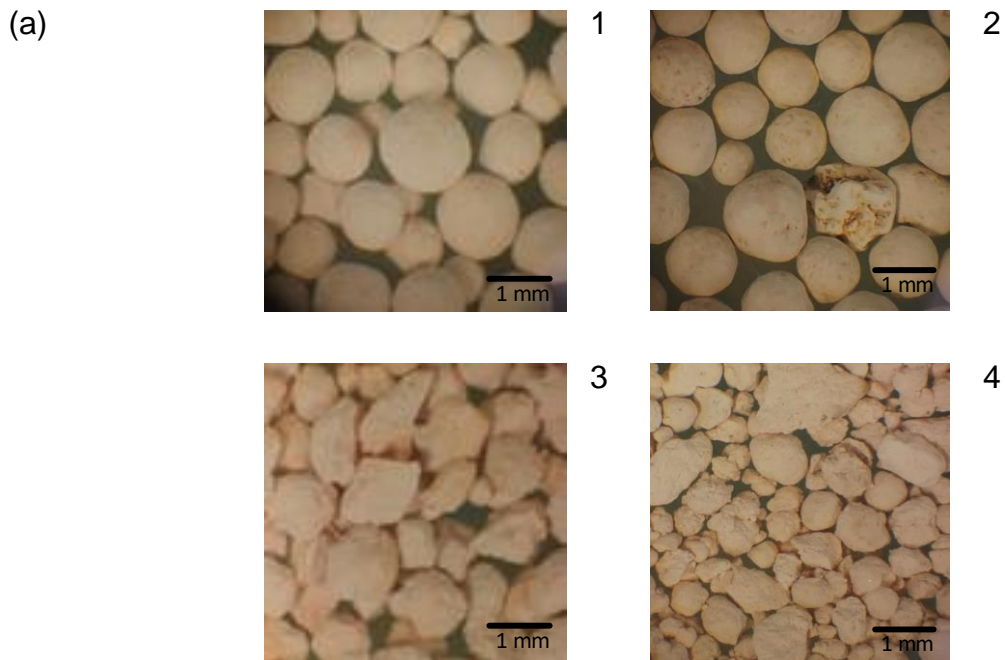


**Figure 2.4. Maximum load at breaking point (N) registered for each media (average of 30 beads/media) when subjected to increasing pressure until breakage; force applied at breaking point was registered with an accuracy of 0.5%. Measurements were performed on fresh media.**

### **2.3.3 Implementation of zeolite at demonstration scale**

Zeolite-N and Zeolite6 were chosen among all the media tested for further tests in a IEX demonstration plant (IEX-D) fed with wastewater with an initial  $\text{NH}_4^+\text{-N}$  of  $0.8 \pm 0.3$  meq  $\text{NH}_4^+\text{-N/L}$  (Table 2.2). In the IEX-D plant, Zeolite-N presented an AEC between 0.13-1.32 meq  $\text{NH}_4^+\text{-N/g}$  media and  $Q_{\text{reg}}$  between 0.05-0.29 meq  $\text{NH}_4^+\text{-N/g}$  media. On the other hand, lower values were registered for Zeolite6 for both AEC (0.01-0.95 meq  $\text{NH}_4^+\text{-N/g}$  media) and  $Q_{\text{reg}}$  (0.14-0.24 meq  $\text{NH}_4^+\text{-N/g}$  media). Zeolite6 was used for a total of 3 cycles due to unexpected intensive breakage of the media which clogged the media bed thus preventing the wastewater and regenerant to flow inside the IEX-D plant. In particular, a media loss of 0.027% per month was estimated for Zeolite-N, while, for Zeolite6, the loss was of 10% per month. After 7 and 3 cycles of operation with Zeolite-N and for Zeolite6, respectively, samples of each media were collected. Analysis at the optical microscope revealed high disintegration (smaller particles) for Zeolite6 when compared to the fresh

material (Figure 2.5a). When completing a strong agitation tests for a period of 1 hour, Zeolite-6 showed higher disintegration rate (67.7 NTU/h) compared to Zeolite-N (10.5 NTU/h) thus indicating the lower mechanical strength (Figure 2.5b-c).



**Figure 2.5 (a) Optical microscope images (Optech Microscopes Ltd, 3X) of Zeolite-N (1;2) and Zeolite6 (3;4) before (1;3) and after (2;4) operation of the IEX demonstration scale plant; (b) Erlenmeyer flask filled with Zeolite6 (Zeo6) and Zeolite-N (ZeoN) after the IEX demonstration plant operation, in agitation for t=20 minutes, experiment in triplicate; (c) Turbidity profile of Zeolite-N and Zeolite6 when subjected to agitation (at 200 rpm).**

## **2.4 Discussion**

Natural and synthetic zeolites were compared to the well-known Zeolite-N for their ability to remove ammonium ( $\text{NH}_4^+\text{-N}$ ) as ion exchanging media from municipal wastewater (Table 2.1). The maximum ammonium exchange capacity (max AEC) in mono-component solution ( $C_{\text{initial}}=55.6 \text{ meq NH}_4^+\text{-N/L}$ ) was considered a primary good indicator for the comparison of the ion exchange media as it defines theoretical amount of ammonium ions that can be accommodated by the ion exchanger [30]. In accordance to literature [16], [17], Zeolite-N presented max AEC of 4.3 meq  $\text{NH}_4^+\text{-N/g}$  media. Similar results were obtained for Zeolite6 and Zeolite2 (4.7 and 4.5 meq  $\text{NH}_4^+\text{-N/g}$  media, respectively). The max AEC of the other media ranged between 3.6 and 3.9 meq  $\text{NH}_4^+\text{-N/g}$  media and, in particular, the max AEC obtained for Clinoptilolite (3.7 meq  $\text{NH}_4^+\text{-N/g}$  media) was in agreement with other studies [17] (Figure 2.2a).

The AEC is dependent on the ammonium concentration in the solution [31] and on the presence of competing ions ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+;3+}$ ) which can affect the selectivity for the ammonium ions [32]. In municipal wastewater ( $C_{\text{initial}}=0.7 \text{ meq NH}_4^+\text{-N/L}$ ), Zeolite-N presented the highest AEC both compared to the other synthetic zeolites and the natural clinoptilolite. The AEC in wastewater can be connected to the lower Si/Al ratio of Zeolite-N (Si/Al=1.5) compared to the clinoptilolite (Si/Al=4) and Zeolite1-6 (Si/Al=1.7-2) (Table 2.1). In fact, an increase in the Si/Al ratio results in a decrease of the cation concentration and ion exchange capacity (proportional to the aluminium content) [33], [34]. Additionally, according to previous studies [1], the variability in AEC when considering different media can be correlated also to the distribution of Al ions within the media framework, the type of neutralising alkaline cations and the zeolites' hydration. These characteristics, in fact, affect the selectivity of the media towards the ammonium in presence of

competitive ions [1]. As for the maximum AEC, also in wastewater, similar results were obtained for Zeolite2 and 6 (Si/Al=1.7 and 1.8, respectively), which indicated that these media could be chosen as potential candidates to replace Zeolite-N (Figure 2.2a).

When subjected to multiple cycles of ammonium uptake and regeneration, Zeolite-N presented similar values for AEC in wastewater and  $Q_{reg}$  thus indicating an efficient ion exchange process (Figure 2.2b). When compared to Zeolite-N, Zeolite1-2 and 6 presented similar AEC which slightly decreased between the first and the last cycle. However, the  $Q_{reg}$  were lower when compared to the one of Zeolite-N indicating that the reusability of these media was not as high as Zeolite-N.

Successively, the media were compared for their mechanical strength. This property was in fact considered necessary for the use of the media in IEX columns where it is subjected to mechanical stress [21]. Operation and maintenance of IEX columns require back-washes and regeneration cycles of media to avoid packing of the media and to maintain the desired effluent quality. The design of the IEX column and the operations can lead to a risk of media erosion and loss. When used for extended period of time, low mechanical strength will result in higher attrition and media loss and, therefore, in the need to substitute the media more frequently, increasing the overall cost of the process. The strength of the media was studied in terms of resistance to attrition and compression (Figure 2.3-2.4). Clinoptilolite presented higher resistance to attrition and compression when compared to Zeolite-N. On the other hand, considering the synthetic zeolites, it was not possible to clearly conclude what media was stronger than Zeolite-N. In fact, Zeolite3 and 6 showed higher resistance to attrition, while Zeolite4 and 5 showed higher resistance to compression. It is important to consider that, as presented in Table 2.1, the media differed for shape and, in the case of the synthetic zeolites, for the production process. In particular, Zeolite1-6 were subjected to different calcination times and temperatures and calcined in different scales of kiln. According to Johnson *et al.* [35] a prolonged calcination process, leaves the material completely porous, thus affecting its resilience or flexibility. In fact, Zeolite3, which was produced with the longest time of calcination when compared to the other media (12 hours, industrial



scale kiln), showed the lowest resistance to compression (3.9 N). Additionally, when compared to Zeolite-N, all the media presented a low sphericity, with sharp edges on their surface which could have had an impact on how the media responded to the mechanical stresses. These results suggested that particular attention needs to be given to the production of the media especially considering its porosity and shape. When producing new media, it is important to obtain an optimal size of the particles. In fact, the AEC of the media is also affected by the particle size with smaller dimension resulting in higher AEC due to an increase in surface area available for the ammonium exchange [6]. Following previous studies [1], all the synthetic zeolites were filtered to obtain a 1-2 mm particle size. On the other hand, the size of the Clinoptilolite particles ranged between 2.5-3.5 mm which could have affected both the AEC capacity tests and the attrition and compression tests.

Finally, the possibility to replace Zeolite-N with one of the other media in a demonstration scale system was investigated (Table 2.2). In particular, Zeolite6 was chosen as, from the experiments conducted at laboratory scale, Zeolite6 and Zeolite-N presented similar ammonium exchange capacities in wastewater (0.06 and 0.05 meq  $\text{NH}_4^+\text{-N/g}$  media, respectively). Regarding the mechanical strength, the laboratory scale experiments showed that the Zeolite-N had slightly higher resistance to compression but lower resistance to attrition, when compared to Zeolite6. Following the results from previous studies [1], [36], at demonstration scale, Zeolite-N was used to remove ammonium from secondary effluent wastewater at an empty bed contact time of 10 minutes while 10 bed volumes of regenerant were used for restoring the initial capacity of the media. In these conditions, Zeolite-N presented AEC of 0.13-1.32 meq  $\text{NH}_4^+\text{-N/g}$  media and  $Q_{\text{reg}}$  of 0.05-0.29 meq  $\text{NH}_4^+\text{-N/g}$  media. When Zeolite-N was substituted with Zeolite6, a lower EBCT (5 minutes) was used to test the ammonium exchange capacity of the media in wastewater. Compared to Zeolite-N, Zeolite6 presented lower values for both AEC in wastewater (0.01-0.95 meq  $\text{NH}_4^+\text{-N/g}$  media) and during regeneration (0.14-0.24 meq  $\text{NH}_4^+\text{-N/g}$  media). The AEC capacity at higher EBCT could not be tested due to the intensive breakage of Zeolite6 forced the stopping of the column (10% media loss/month). The high disintegration of Zeolite6 was correlated to the low sphericity of the media when compared to Zeolite-N.

The ion exchange process is efficient at selectively removing ammonium from wastewater. The work completed demonstrates the potential benefits of using Zeolite-N and outlines the key challenges that any new zeolites must meet to be able to be used within the water sector. The implementation of the IEX process at bigger scale is limited by the lack of a supplier for Zeolite-N which, as confirmed in this study, is the most efficient IEX media for ammonium removal. Even though the high ammonium exchange capacity is a crucial property of ion exchange media, this work highlighted the necessity to investigate a more efficient production method, which can ensure high mechanical strength and, therefore, a longer lifespan of the media thus reducing the costs connected to a frequent media replacement.

## 2.5 Conclusions

This study focused on the preparation and evaluation of synthetic zeolites (Zeolite1-6) by measuring AEC and resistance to attrition and compression, against natural (clinoptilolite) and engineered zeolite (reference, Zeolite-N). Finding an ion exchange media, which could substitute Zeolite-N, that is no longer available commercially, is important to ensure implementation of the process in wastewater treatment plants. The following conclusion were made:

- Zeolite6 and Zeolite2 showed increased maximum AEC (4.7 and 4.5 meq NH<sub>4</sub><sup>+</sup>-N/g media, respectively) when compared to Zeolite-N (4.3 meq NH<sub>4</sub><sup>+</sup>-N/g media).
- In secondary effluent wastewater ( $C_{initial}=0.7$  meq NH<sub>4</sub><sup>+</sup>-N/L), Zeolite1, 2 and 6 showed AEC of 0.05 meq NH<sub>4</sub><sup>+</sup>-N/g media, similar to Zeolite-N (0.06 meq NH<sub>4</sub><sup>+</sup>-N/g media). The slight increase of AEC in Zeolite-N can be due to the lower Si/Al ratio (1.5) compared Zeolite1-6 (Si/Al=1.7-2).
- All the media showed lower reusability during the 10 cycles of batch test when compared to Zeolite-N.
- When compared to Zeolite-N, the natural clinoptilolite showed higher mechanical strength, Zeolite3 and 6 showed higher resistance to attrition while Zeolite4 and 6 showed higher resistance to compression. The variability of the mechanical strength of the synthetic zeolites was attributed to the difference in the production process (temperature, time and dimension of the kiln during calcination).
- This study highlighted the importance of producing synthetic zeolites with high mechanical strength to reduce media loss during operations (10% loss/month with Zeolite6 in the demonstration scale plant). In particular, a media with more spherical shape would reduce eventual sharp edges which could have an impact on both the resistance to attrition and compression.

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### 3. RESILIENCE AND LIFE CYCLE ASSESSMENT OF ION EXCHANGE PROCESS FOR AMMONIUM REMOVAL FROM MUNICIPAL WASTEWATER

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#### Abstract

A demonstration scale (10 m<sup>3</sup>/day) ion exchange process was used to remove ammonium (NH<sub>4</sub><sup>+</sup>-N) from municipal wastewater as tertiary treatment and investigate its resilience, i.e., capacity to adapt to variable influent NH<sub>4</sub><sup>+</sup>-N concentrations. The synthetic Zeolite-N was used as ion exchange media and regeneration was completed with potassium chloride (KCl) 10%. The ammonium (NH<sub>4</sub><sup>+</sup>-N) variability in the influent concentration (<0.006-26 mg NH<sub>4</sub><sup>+</sup>-N/L) affected the NH<sub>4</sub><sup>+</sup>-N exchange capacity which ranged from 0.9 mg NH<sub>4</sub><sup>+</sup>-N/g media to 17.7 mg NH<sub>4</sub><sup>+</sup>-N/g media. When the influent concentration dropped below 2.5 mg NH<sub>4</sub><sup>+</sup>-N/L, the Zeolite-N released NH<sub>4</sub><sup>+</sup>-N (up to 12%) due to ion exchange equilibria. However, the NH<sub>4</sub><sup>+</sup>-N exchange efficiency of the media successively increased again up to 62% with increased ammonium influent concentration (4.4 mg NH<sub>4</sub><sup>+</sup>-N/L) confirming the resilience of the media. At the same time, the NH<sub>4</sub><sup>+</sup>-N on the media also affected the efficiency of regeneration. A 94% regeneration efficiency was obtained with fresh regenerant after the first cycle, however, with the increase of the mass of NH<sub>4</sub><sup>+</sup>-N on the media, the regeneration efficiency decreased to 18%. To further explore the benefits on the IEX technology, a life cycle analysis (LCA) was conducted in a wastewater treatment plant with 10,000



population equivalent and this was compared to a reference scenario with traditional nitrification-denitrification process. The LCA revealed that the use of the IEX process with membrane stripping process as the  $\text{NH}_4^+$ -N recovery technology and NaCl used as regenerant brine resulted in savings of 25% cumulative energy demand, a reduction of 66% of the global warming potential and of 62% of the marine eutrophication potential, when compared to traditional process. This work demonstrated that the IEX process is an efficient and environmentally friendly technology able to adapt to variable  $\text{NH}_4^+$ -N wastewater quality.

## **Keywords**

Resilience, ion exchange process, life cycle assessment, variability, synthetic zeolite

### 3.1 Introduction

Municipal wastewater quality is affected by many factors such as the number of inhabitants connected to the wastewater treatment plant (WWTP), size of the catchment, seasonal and diurnal water usage patterns, infiltration, industrial discharges, soil type, environmental factors including rainfall patterns [1] and temperature [2], [3]. These factors influence the concentration of pollutants such as chemical and biological oxygen demand (COD and BOD), total nitrogen (TN), total phosphorus (TP) and solids content [2] in the wastewater. In particular, the ammonium ( $\text{NH}_4^+\text{-N}$ ) concentration can range between 20 to 50 mg  $\text{NH}_4^+\text{-N/L}$  [4], [11] in the influent of a WWTP (Table 3.1). This variability is also observed through the different treatment stages of WWTP, including in the influent to secondary treatment process where the  $\text{NH}_4^+\text{-N}$  concentration has been reported to range between 0.1 and 25 mg  $\text{NH}_4^+\text{-N/L}$  [11], [12], [15] (Table 3.1). Conventionally, nitrification and denitrification are used to remove  $\text{NH}_4^+\text{-N}$  from wastewater by oxidising  $\text{NH}_4^+\text{-N}$  to nitrate ( $\text{NO}_3^-$ ) and reducing it to nitrogen gas ( $\text{N}_2$ ) [5], [6]. However, the high variability in the influent concentration is a major issue that limits the removal efficiency [6]. It has been reported that an increase in total  $\text{NH}_4^+\text{-N}$  concentration by up to 80% reduced the rate of nitrification in a trickling filter by 60% [7]. Effluent from secondary treatment processes are also affected: Zarate [8] reported a variation from 1.9 to 15.4 mg  $\text{NH}_4^+\text{-N/L}$  after treatment in the trickling filters of a 5500 pe WWTP due to the impact of seasonal temperature variation on nitrification (Table 3.1). Besides temperature, Raboni *et al.* [9] reported a daily variation in the denitrification efficiency from 40% to 78% depending on C:N ratio. Additionally, Yamashita and Yamamoto-Ikemoto [10] measured a variation from <0.5 to 20 mg  $\text{NH}_4^+\text{-N/L}$  at the effluent of trickling filter packed with foam ceramics for nitrification (Table 3.1). Hence, secondary effluent wastewater quality is not constant, and it suffers from great variability in ammonium concentrations (Table 3.1).

**Table 3.1 Variability of ammonium ( $\text{NH}_4^+\text{-N}$ ) concentration in different stages of wastewater treatment.**

| Type of wastewater | Average | Min | Max | Notes | Ref |
|--------------------|---------|-----|-----|-------|-----|
|                    |         |     |     |       |     |

|                                                        | mg NH <sub>4</sub> <sup>+</sup> -<br>N/L | mg NH <sub>4</sub> <sup>+</sup> -<br>N/L | mg NH <sub>4</sub> <sup>+</sup> -<br>N/L |                                                                                                                                                                 |      |
|--------------------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Influent/raw<br>wastewater                             | 37.7                                     | 30                                       | 50                                       | Full-scale<br>modelling<br>study                                                                                                                                | [4]  |
| Settled<br>sewage                                      | 38                                       | 20                                       | 50                                       | Full-scale<br>nitrifying<br>activated<br>sludge<br>treatment<br>plant                                                                                           | [11] |
| Influent to<br>aeration<br>zones                       | 15.3                                     | 8                                        | 20                                       |                                                                                                                                                                 |      |
| Influent of<br>nitrifying<br>trickling filter<br>(NTF) | 1.1                                      | 0.1                                      | 17.4                                     | Pilot scale<br>study                                                                                                                                            | [12] |
| Effluent of<br>secondary<br>treatment<br>process       | 7.4                                      | 1.9                                      | 15.4                                     | Secondary<br>process with<br>trickling filters<br>in a 5500 p.e.<br>WWTP                                                                                        | [8]  |
| Influent<br>secondary<br>treatment<br>process          | N/A                                      | 1-2                                      | 25                                       | Secondary<br>process with<br>anoxic<br>bioreactor<br>packed with<br>wood and iron<br>+ trickling filter<br>packed with<br>foam<br>ceramics for<br>nitrification | [10] |
| Effluent<br>secondary<br>treatment<br>process          | N/A                                      | <0.5                                     | 20                                       |                                                                                                                                                                 |      |

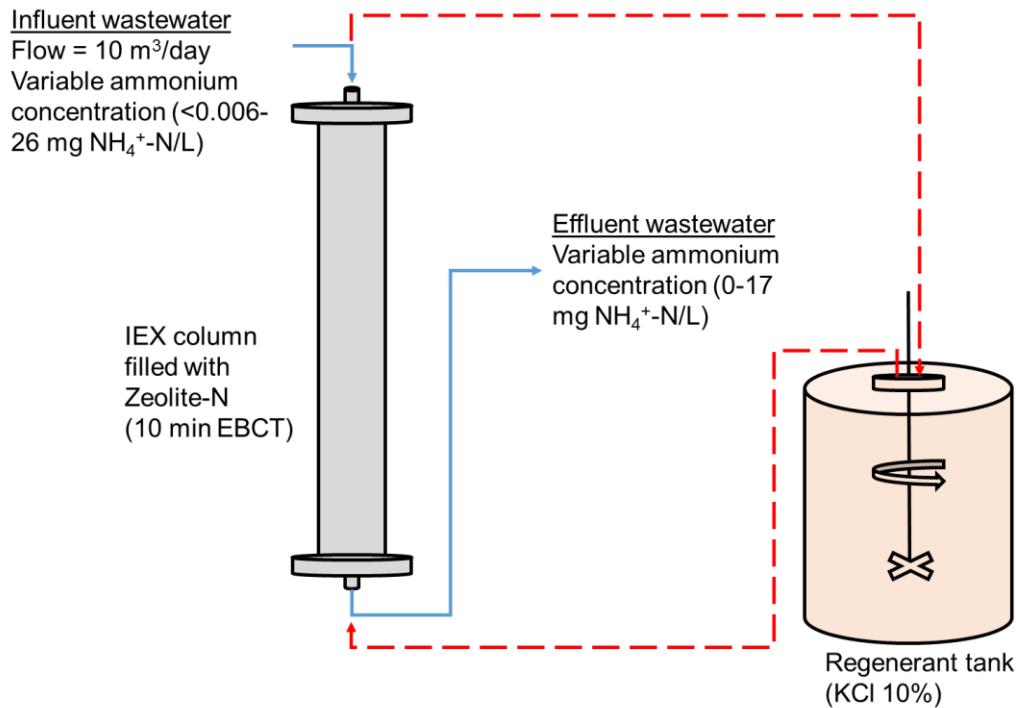
For this reason, to ensure high effluent quality in the discharged wastewater, there is a need for a flexible and resilient technology which can adapt to the variability in the influent while ensuring efficient  $\text{NH}_4^+\text{-N}$  removal. At the same time, conventional biological removal processes pose an environmental concern due to the production of  $\text{N}_2\text{O}$  (a greenhouse gas) as an intermediate of aerobic  $\text{NH}_4^+\text{-N}$  oxidation [13]. As such, technologies that can remove ammonium with variable concentrations and have low GHG emissions are highly desirable. Recently, the wastewater treatment industry is starting to consider the use of the ion exchange (IEX) as tertiary treatment process [14]. One of the most efficient IEX media for  $\text{NH}_4^+\text{-N}$  removal is the synthetic zeolites, Zeolite-N (chemical formula  $\text{K}_{12}\text{Al}_{10}\text{Si}_{10}\text{O}_{40}\text{Cl}_2\cdot 8\text{H}_2\text{O}$  [15]), which has shown  $\text{NH}_4^+\text{-N}$  removal efficiency >95% [16], [17] when treating sludge dewatering liquors at laboratory scale [18]. After exhaustion of the  $\text{NH}_4^+\text{-N}$  exchange capacity, the media is regenerated, commonly by using high strength ionic brines such as sodium chloride (NaCl) or potassium chloride (KCl) [19], [6]. In particular, previous studies confirmed KCl as a more effective regenerant solution than NaCl when regenerating Zeolite-N with regeneration efficiency between 72-94% and 64–68%, respectively [6], [20]. The brine can be used multiple times until saturation [6], however, once saturated, its disposal as a hazardous waste can constitute a cost limitation for the implementation of the IEX process at full scale [20]. For this reason, the possibility to recover ammonia ( $\text{NH}_3$ ) from the saturated brine has been recently investigated to increase the overall environmental and economical sustainability of the IEX process [21], [22]. In particular, vacuum thermal stripping [23] and membrane stripping [24] represent potential processes for the brine management and for the recovery of the  $\text{NH}_4^+\text{-N}$  as valuable resource. In the vacuum thermal stripping process, the vacuum-induced boiling of saturated brine increases the transfer of the ammonia gas ( $\text{NH}_{3(g)}$ ) to vapour bubbles [25] which are then condensed in an overall distillation process where  $\text{NH}_{3(g)}$  is recovered as aqueous ammonia ( $\text{NH}_{3(aq)}$ ), a valuable chemical [26]. On the other hand, in the membrane stripping process, the use of microporous and hydrophobic hollow fibres allows for the transfer of  $\text{NH}_{3(g)}$  from shell-side of the membrane to the lumen-side where a strong acid solution promotes the precipitation of  $\text{NH}_4^+\text{-N}$  salts with application in the fertiliser industry (i.e. ammonium sulphate) [27].

The possibility to reuse the same regenerant brine multiple times and recover the  $\text{NH}_4^+\text{-N}$  as a valuable product aligns the IEX process to the concept of the circular economy. However, the ability of the Zeolite-N to maintain high removal capacity in variable  $\text{NH}_4^+\text{-N}$  concentration and an analysis of the environmental impact connected to the use of Zeolite-N for  $\text{NH}_4^+\text{-N}$  removal and recovery have not been reported in literature to date. Therefore, the aim of this work was to investigate the resilience of the IEX process when subjected to variable  $\text{NH}_4^+\text{-N}$  concentrations and to compare the environmental impact of the IEX process with a reference scenario where COD and nitrogen were removed in trickling filters via nitrification-denitrification. The reference scenario was chosen considering that 49% of the secondary treatment used in wastewater treatment plants in England and Wales make use of biological filters (BF), mainly trickling filters and rotating biological contactors [28]. The data obtained from a demonstration scale plant ( $10 \text{ m}^3/\text{day}$ ) were used for a life cycle assessment (LCA) focusing on primary energy demand, greenhouse gas (GHG) emissions and eutrophication potential of the IEX process and the reference scenario.

## **3.2 Materials and methods**

### **3.2.1 Demonstration plant and operation**

Municipal wastewater, obtained from Cranfield University's wastewater treatment plant (WWTP), was fed to the ion exchange (IEX) demonstration plant after secondary treatment in trickling filters. The demonstration plant consisted of a drum filter (SIBO Fluidra, Netherlands) for solids removal; compressed air diaphragm pump with float flow for measurement; two manometers to measure pressure loss; storage tank with mixer for the regenerant brine and column for the IEX media mounted on a steel rack. The column was provided with a nozzle in each of the end plates (0.2-2 mm) at the bottom to drain the liquid (wastewater or regenerant brine) and combined with an air vent on the top plate to remove air/gases. The plant design allowed for downflow and upflow operation and it was operated manually (Figure 3.1).



**Figure 3.1 Schematic representation of the ion exchange demonstration plant.**

The column (internal diameter of 307 mm, height of 1566 mm) was filled with 69L of Zeolite-N (78 kg) (Nanochem Pty Ltd, Australia). The media was first washed with tap water in upflow operation until the effluent run clear. The wastewater was fed at a flow of 10 m<sup>3</sup>/day in downflow operation and empty bed contact time (EBCT) of 10 minutes [20]. The EBCT was calculated considering the bed volume,  $V_R$  (L) and the flow rate in the bed,  $F$  (L/min) according to Equation 3.1 [29]:

$$EBCT = V_R/F \quad \text{Equation 3.1}$$

The influent and effluent quality was monitored daily. Once the effluent concentration had increased to beyond the target level, the flow of wastewater was interrupted to initiate the regeneration sequence. The column was drained and the regeneration was completed using 10 bed volumes (BV) of potassium chloride 10% (KCl 10% w/v, Easy Chemicals Ltd, Denbigh, UK) [6] that were passed through the column in upflow operation for 2 hours. At the end of the regeneration, the column was drained and the KCl was collected and stored for the next regeneration (Figure 3.1). A total of 9 cycles of regeneration were performed. Two batches of regenerant brine were prepared: the same KCl was reused from cycle 1 to 6 and from cycle 7 to 9. The

media was backwashed in upflow operation with tap water for 30 minutes (flow rate 500 L/h) at the end of each cycle to remove any solids. The  $\text{NH}_4^+\text{-N}$  exchange capacity (AEC, mg  $\text{NH}_4^+\text{-N/g}$  media) after  $n$  samples was calculated according to Equation 3.2 [17]:

$$\text{AEC} = \frac{\int_{V=0}^{V^{\text{fin}}} (C_{\text{in}} - C_{\text{out}}) dV}{M} = \frac{\sum_0^n [(C_0 - C_n) * (V_n - V_{n-1})]}{M} \quad \text{Equation 3.2}$$

where  $C_{\text{in}}$  and  $C_{\text{out}}$  are the influent and effluent  $\text{NH}_4^+\text{-N}$  concentration (mg  $\text{NH}_4^+\text{-N/L}$ );  $V$  is the volume of wastewater treated (L) and  $M$  is the mass of Zeolite-N (g). The regeneration capacity  $Q_{\text{reg}}$  (mg  $\text{NH}_4^+\text{-N/g}$  media) was calculated according to Equation 3.3 (adapted from You *et al.* [30]):

$$Q_{\text{reg}} = \frac{[C_{r,i} - C_{r,f}] * V_{r,\text{treated}}}{M} \quad \text{Equation 3.3}$$

where  $C_{r,i}$  and  $C_{r,f}$  are the  $\text{NH}_4^+\text{-N}$  concentration in the regenerant at the beginning and at the end of each regeneration cycle (mg  $\text{NH}_4^+\text{-N/L}$ );  $V_{r,\text{treated}}$  is the volume of regenerant used (L) and  $M$  is the same as in Equation 3.2.

### 3.3 Chemical analysis

Samples were taken from the demonstration plant daily. Chemical oxygen demand (COD), potassium ( $\text{K}^+$ ) and calcium ( $\text{Ca}^{2+}$ ) were analysed using Spectroquant® cell tests; ammonium ( $\text{NH}_4^+\text{-N}$ ) was analysed using the Smartchem200 (AMS Alliance, France) (lower limit of detection (LOD) of 0.006 mg  $\text{NH}_4^+\text{-N/L}$ ). The analysis of the pH and temperature was performed using a pH meter (Jenway 3510 pH and conductivity meter, Camlab, UK) and a temperature meter (portable Jenway 470 conductivity, salinity and temperature meter, Camlab, UK), respectively. Total suspended solids (TSS) were analysed following the Standard Methods 2540 [31].

### 3.4 Life cycle assessment

#### 3.4.1 Scenarios

The life cycle assessment (LCA) is a widely used methodology to quantify environmental impacts of a technology [32]. In this study, the IEX process was

compared to a selected reference scenario, which used a conventional nutrient removal technology, to show the benefits of the IEX against the current state. For this comparison, two different targets for the IEX scenarios were defined: a) polishing of effluent to very low ammonium limits and b) maximum ammonium recovery with the IEX process. The first approach required high ammonium removal already in the biological stage with the conventional technology and the downstream IEX was only removing the residual nutrients to reach very low effluent limits. For the second approach, the upstream biological treatment removed only a limited amount of ammonium, so that the following IEX stage could remove and recover the maximum amount of ammonium. The LCA was carried out in accordance with ISO 14040/44 [33] considering a WWTP with 10,000 population equivalent (pe). Five different scenarios were taken into consideration (Table 3.2): in the reference scenario, COD and nitrogen (N) were removed in the trickling filter (nitrification) while the IEX process was used for the removal of  $\text{NH}_4^+\text{-N}$  in the scenarios 1 to 4. The data for the reference scenario (influent and effluent characterization, return load concentration, energy and chemical demand and emissions) were assumed considering the information provided in Severn Trent Water (UK) Design Manual (P. Vale, Severn Trent Water, 2018, personal email communication, 18 October). The LCA for scenarios 1-4 was based on up-scaling of the data obtained from the demonstration plant to reflect full-scale mainstream IEX including brine regeneration and product recovery. As possible regenerants, potassium chloride (KCl) and sodium chloride (NaCl) were compared [6] while vacuum thermal stripping (VAC) and membrane stripping (MEM) were compared as recovery processes [23], [24].

**Table 3.2 LCA scenarios for ammonium ( $\text{NH}_4^+\text{-N}$ ) removal and recovery in WWTP (10,000 pe): reference scenario and IEX scenarios (1-4) considering two different regeneration brines (KCl and NaCl) and two different recovery processes (vacuum stripping, VAC, and membrane stripping, MEM).**

| Scenario  | COD elimination  | $\text{NH}_4^+\text{-N}$ removal and recovery            |
|-----------|------------------|----------------------------------------------------------|
| Reference | Trickling filter | Trickling filter<br>(with denitrification/nitrification) |



|   |                  |              |
|---|------------------|--------------|
| 1 | Trickling filter | IEX-KCl-VAC  |
| 2 |                  | IEX-NaCl-VAC |
| 3 |                  | IEX-KCl-MEM  |
| 4 |                  | IEX-NaCl-MEM |

### 3.4.2 Function and functional unit of the LCA

The function of the different scenarios was related to the treatment of municipal wastewater for compliance with defined limit values for  $\text{NH}_4^+\text{-N}$  in the discharged effluent [34]. The treatment of sewage sludge resulting from wastewater treatment was also taken into account including dewatering units, biogas production and sludge disposal in agriculture. Consequently, the functional unit of the LCA was defined as “*the impact of a wastewater treatment process per population equivalent (pe) annually [impacts/pexa]*”. The LCA was conducted by using the LCA software *Umberto* referring to the Ecoinvent database [35].

### 3.4.3 Environmental indicators

The environmental indicators considered were: cumulative energy demand (CED), global warming potential (GWP) and marine eutrophication potential (MEP). The CED (MJ/pexa) considered the total non-renewable (fossil and nuclear) energy [32], [36]. The GWP considered of all greenhouse gases (namely  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$ ) expressed as  $\text{CO}_2$  equivalent (kg  $\text{CO}_2$  eq/pexa) [31], [36] and was estimated for a time horizon of 100 years. Finally, MEP (kg N eq/pexa) was determined considering the effluent quality, following the approach in ReCiPe2016 [37].

### 3.4.4 System boundaries

The boundaries of the LCA included all processes of the WWTP, sludge treatment and disposal [39]. In particular, the following boundaries were considered: a defined effluent quality; sludge thickening, digestion, dewatering, transport and disposal in agriculture; biogas valorisation in a combined heat and power (CHP) plant; processes

required for production of electricity, chemicals, and fuels and additional infrastructure for the IEX system. Additionally, the nutrients delivered to soil/agriculture via sludge application or via products recovered from IEX were credited considering avoided mineral fertiliser production (“avoided burden” approach).

### **3.4.5 Inventory (input data)**

Table 3.3 shows the input data for the LCA of the reference and IEX scenarios. For the effluent quality, removal rates >95% for total solids (TS), >92 % for chemical oxygen demand (COD), >92% and >95% for ammonium (as  $\text{NH}_4^+\text{-N}$ ) in reference scenario and IEX scenarios, respectively, were assumed. The high removal rates of COD and TS were considered due to the post-treatment with sand filter and micro screen for reference and IEX scenarios, respectively. The effluent was assumed to be directly discharged into surface water. The thickened sludge and dewatering liquor were assumed to be treated in a centralised WWTP. Therefore, the return load treated on-site consisted of supernatant from gravity thickening and, for the reference scenario, included also the sand filter backwash water (4% v/v of sand filter influent).

The specific energy consumption for the primary treatment (0.05 kWh/m<sup>3</sup>), trickling filter (0.19 kWh/m<sup>3</sup>), and sludge treatment (thickening, digestion and dewatering) was assumed to be equal for all scenarios (Table 3.3). Regarding the chemical consumption in the reference scenario, polymer for sludge treatment (3 kg/t dry solids mass) was considered. In the IEX scenarios, the chemical consumption considered the media, chemicals for the regenerant and for product recovery. The saturated Zeolite-N, enriched with  $\text{NH}_4^+\text{-N}$ , can theoretically be used as fertiliser [40], therefore, disposal expenditure for the media was neglected. However, nutrient credits for its use as fertiliser were not given because this application for Zeolite-N is still not confirmed. The amount of sodium chloride (2 kg NaCl/kg N removed) and potassium chloride (3.4 kg KCl/kg N removed) required for the regeneration was calculated by molar ion balancing considering that each  $\text{NH}_4^+$  ion would replace one  $\text{K}^+$  or  $\text{Na}^+$  ion [6] which has to be replaced with fresh salt solution. In addition, 2% losses of the regeneration solution were estimated per year considering the results obtained with the demonstration scale plant (Table 3.3).

The input data for the LCA also considered the direct emissions of greenhouse gases [31], [35] (Table 3.3). For the reference scenario, direct N<sub>2</sub>O emissions were estimated to be 1% of TN influent concentration of the biological stage, based on a linear correlation between TN removal and N<sub>2</sub>O emission factors [40]. The LCA also considered direct NH<sub>3(g)</sub> emissions during the biological treatment (assumed 0.6% of NH<sub>4</sub><sup>+</sup>-N at the influent [42]). For the IEX scenarios, no N<sub>2</sub>O emissions of the biological stage were assumed.

For the sludge treatment, trickling filters removed mainly COD and nutrients by biomass growth only (assumed -5% for TN into the sludge). Due to the lower sludge age, an increase of 10% in organic sludge yield was assumed for the trickling filter in IEX scenarios. The transport of the thickened sludge in a centralised WWTP at 15 km distance was considered. For the treatment of liquor from sludge dewatering, electricity factors were defined according to German Association for Water, Wastewater and Waste [43]. Elimination efficiencies for the centralised dewatering liquor treatment were estimated at 90% for COD, 99% for NH<sub>4</sub><sup>+</sup>-N, 80% TN via denitrification [43].

For the sludge and product application in agriculture, the dewatered sludge was considered suitable for agricultural application [44]. For the crediting of nitrogen in the sewage sludge, the substitution potential of nutrients in sludge and products in relation to mineral fertiliser were calculated according to the chamber of Agriculture Lower Saxony [45] [42]. For nitrogen, an accounting rate of 25% for sewage sludge and 100% for ammonium sulphate or ammonia solution was considered [45].

The direct emissions into groundwater and air due to product and sludge application in agriculture were estimated for the non-utilised fraction [38]. Direct emissions of NH<sub>3(g)</sub> connected to nutrient application were assumed to be 10.7% and 6.2% of TN in sludge and conventional fertiliser, respectively [46], [47]. Direct emissions of N<sub>2</sub>O and NO<sub>2</sub> were assumed to be 1.0% and 1.2% of the TN, respectively [46],[47]. Emissions of nitrogen to groundwater were calculated at 7.9% of TN [35].

**Table 3.3 Input data for water quality, energy and chemical demand for reference and IEX scenarios.**

| Wastewater line                                               | Unit               | Reference scenario            | IEX scenarios 1-4             | Comment/reference                                                                                                                                                                                                |
|---------------------------------------------------------------|--------------------|-------------------------------|-------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Water quality (influent WWTP - effluent of biological stage)  |                    |                               |                               |                                                                                                                                                                                                                  |
| TSS                                                           | mg/L               | Influent: 260<br>Effluent: 20 | Influent: 260<br>Effluent: 10 | Severn Trent Water (UK) Design Manual (P. Vale, Severn Trent Water, 2018, personal email communication, 18 October).<br>Data for the IEX scenarios based on the operation from demonstration plant in this study |
| COD                                                           | mg/L               | Influent: 480<br>Effluent: 44 | Influent: 480<br>Effluent: 40 |                                                                                                                                                                                                                  |
| NH <sub>4</sub> <sup>+</sup> -N                               | mg/L               | Influent: 30<br>Effluent: 3   | Influent: 30<br>Effluent: 30  |                                                                                                                                                                                                                  |
| Total N                                                       | mg/L               | Influent: 40<br>Effluent: 20  | Influent: 40<br>Effluent:38   |                                                                                                                                                                                                                  |
| Water quality (effluent of biological stage - final effluent) |                    |                               |                               |                                                                                                                                                                                                                  |
| TSS                                                           | mg/L               | Influent: 20<br>Effluent: 10  | Influent: 10<br>Effluent: 1   | Severn Trent Water (UK) Design Manual (P. Vale, Severn Trent Water, 2018, personal email communication, 18 October).<br>Data for the IEX scenarios based on the operation from demonstration plant in this study |
| COD                                                           | mg/L               | Influent: 44<br>Effluent: 35  | Influent: 40<br>Effluent: 25  |                                                                                                                                                                                                                  |
| NH <sub>4</sub> <sup>+</sup> -N                               | mg/L               | Influent: 3<br>Effluent: 2    | Influent: 30<br>Effluent: 3   |                                                                                                                                                                                                                  |
| Total N                                                       | mg/L               | Influent: 20<br>Effluent: 20  | Influent: 38<br>Effluent:8    |                                                                                                                                                                                                                  |
| Energy consumption                                            |                    |                               |                               |                                                                                                                                                                                                                  |
| Primary treatment                                             |                    |                               |                               |                                                                                                                                                                                                                  |
| Electricity rake                                              | kWh/m <sup>3</sup> | 0.05                          | 0.05                          | Severn Trent Water (UK) Design Manual (P. Vale, Severn Trent Water, 2018, personal email communication, 18 October).                                                                                             |
| Electricity primary treatment                                 | kWh/m <sup>3</sup> | 0.05                          | 0.05                          |                                                                                                                                                                                                                  |
| Secondary treatment (Trickling filter)                        |                    |                               |                               |                                                                                                                                                                                                                  |
| Electricity                                                   | kWh/m <sup>3</sup> | 0.19                          | 0.19                          | Severn Trent Water (UK) Design Manual (P. Vale, Severn Trent Water, 2018, personal email                                                                                                                         |

|                                              |                                |       |               |                                                                                                                                                                          |
|----------------------------------------------|--------------------------------|-------|---------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                              |                                |       |               | communication, 18 October).                                                                                                                                              |
| Tertiary treatment (Sand filter/IEX columns) |                                |       |               |                                                                                                                                                                          |
| Electricity sand filter                      | kWh/ m <sup>3</sup>            | 0.08  | -             | Severn Trent Water (UK) Design Manual (P. Vale, Severn Trent Water, 2018, personal email communication, 18 October).                                                     |
| Electricity micro screen                     | kWh/m <sup>3</sup>             | -     | 0.01          | [48]                                                                                                                                                                     |
| Electricity IEX                              | kWh/m <sup>3</sup>             | -     | 0.01          | Estimated electricity to pump water in the column considering height of the column of 2 m                                                                                |
| Nutrient recovery                            |                                |       |               |                                                                                                                                                                          |
| Electricity                                  | kWh/ m <sup>3</sup> regenerant | -     | N: 0.25 (VAC) | Estimated electricity needed to heat up regenerant from 14 to 40°C                                                                                                       |
| Heat                                         | MJ/m <sup>3</sup> regenerant   | -     | 44.76 (VAC)   |                                                                                                                                                                          |
| Electricity                                  | kWh/m <sup>3</sup> regenerant  | -     | 0.53 (MEM)    | 0.74 kWh/kg NH <sub>4</sub> recovered for recirculation pumps in stripper [47]. The membrane stripper is assumed to be operated at room temperature (no heat necessary). |
| Thickening                                   |                                |       |               |                                                                                                                                                                          |
| Electricity                                  | kWh/ m <sup>3</sup> sludge     | 0.06  | 0.06          | Severn Trent Water (UK) Design Manual (P. Vale, Severn Trent Water, 2018, personal email communication, 18 October).                                                     |
| Digestion                                    |                                |       |               |                                                                                                                                                                          |
| Electricity demand                           | kWh/ m <sup>3</sup> sludge     | 16.64 | 16.64         | Severn Trent Water (UK) Design Manual                                                                                                                                    |

|                                                                        |                                        |       |             |                                                                                                                                                                                                                                                                                                                                                                           |
|------------------------------------------------------------------------|----------------------------------------|-------|-------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Methane yield                                                          | N m <sup>3</sup> / t<br>COD<br>removed | 350   | 350         | (P. Vale, Severn<br>Trent Water, 2018,<br>personal email<br>communication, 18<br>October).                                                                                                                                                                                                                                                                                |
| COD<br>degradation<br>ratio                                            | %                                      | 48    | 48          |                                                                                                                                                                                                                                                                                                                                                                           |
| Electrical<br>efficiency of<br>CHP                                     | %                                      | 41.70 | 41.70       |                                                                                                                                                                                                                                                                                                                                                                           |
| Dewatering                                                             |                                        |       |             |                                                                                                                                                                                                                                                                                                                                                                           |
| Electricity                                                            | kWh/ m <sup>3</sup><br>sludge          | 2.00  | 2.00        | Severn Trent Water<br>(UK) Design Manual<br>(P. Vale, Severn<br>Trent Water, 2018,<br>personal email<br>communication, 18<br>October).                                                                                                                                                                                                                                    |
| Chemical consumption                                                   |                                        |       |             |                                                                                                                                                                                                                                                                                                                                                                           |
| Tertiary treatment (IEX columns)                                       |                                        |       |             |                                                                                                                                                                                                                                                                                                                                                                           |
| Potassium<br>chloride<br>(100%)<br>(Sodium<br>chloride) <sup>(1)</sup> | kg KCl<br>(NaCl) / kg<br>N removed     | -     | 3.42 (2.02) | Estimation (including<br>2% losses)<br>considering that each<br>NH <sub>4</sub> <sup>+</sup> ion replaces<br>one K <sup>+</sup> or Na <sup>+</sup> ion <sup>(1-2)</sup> :<br>KCl (100%): 5.4 kg/kg<br>N removed<br>NaCl (100%) = 4.3<br>kg/kg N removed<br><br>Assumption: Nutrient<br>recovery from<br>regeneration solution<br>takes place if 800 mg<br>N/ L is reached |
| IEX media                                                              | t/ a                                   | -     | 1.23        | Estimation from IEX-<br>D: Life time 5 years, 4<br>% abrasion per year                                                                                                                                                                                                                                                                                                    |
| Nutrient recovery                                                      |                                        |       |             |                                                                                                                                                                                                                                                                                                                                                                           |
| Sulphuric acid<br>(98%) for N<br>recovery                              | kg/ kg N in<br>product                 | -     | 3.57        | Estimation from<br>laboratory<br>experiments – data<br>not published;<br>Sulphuric acid is used<br>to produce<br>ammonium sulphate<br>(21% N). The amount                                                                                                                                                                                                                 |

|                                        |          |                  |                                      |                                                                                                                                                                                                                  |
|----------------------------------------|----------|------------------|--------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                        |          |                  |                                      | needed is calculated stoichiometrically.                                                                                                                                                                         |
| <b>Thickening</b>                      |          |                  |                                      |                                                                                                                                                                                                                  |
| Polymer (100% active substance)        | kg/ t DS | 3.00             | 3.00                                 | Severn Trent Water (UK) Design Manual (P. Vale, Severn Trent Water, 2018, personal email communication, 18 October).                                                                                             |
| <b>Credit for nutrients in product</b> |          |                  |                                      |                                                                                                                                                                                                                  |
| Recovered N (100% N)                   | t/ a     | N in sludge: 6.1 | N in sludge: 1.1<br>N in product: 25 | Severn Trent Water (UK) Design Manual (P. Vale, Severn Trent Water, 2018, personal email communication, 18 October).<br>Data for the IEX scenarios based on the operation from demonstration plant in this study |

$$^1 1 \text{ kg NH}_4 - \text{N} = 1.3 \text{ kg NH}_4^+$$

$$^2 1 \text{ kg KCl (NaCl)} = \left[ \frac{1.3 \text{ kg NH}_4^+ \times \text{MM}_{\text{K(Na)}^+} \left( \frac{\text{g}}{\text{mol}} \right)}{\text{MM}_{\text{NH}_4^+} \left( \frac{\text{g}}{\text{mol}} \right)} \times \text{MM}_{\text{KCl (NaCl)}} \left( \frac{\text{g}}{\text{mol}} \right) \right] / \text{MM}_{\text{K(Na)}^+} \left( \frac{\text{g}}{\text{mol}} \right)$$

MM = molar mass

## 3.5 Results

### 3.5.1 Wastewater characterization

The municipal wastewater fed to the ion exchange demonstration plant presented variable  $\text{NH}_4^+\text{-N}$  concentration with minimum and maximum values of  $<0.006 \text{ mg NH}_4^+\text{-N/L}$  (lower limit of detection) and  $26 \text{ mg NH}_4^+\text{-N/L}$ , respectively (Table 3.4). The pH was constant at around 7.1 while the average total suspended solids (TSS) concentration was  $35 \pm 8 \text{ mg TSS/L}$  during the entire period of operation. The main competing ions in wastewater that could interfere with the  $\text{NH}_4^+\text{-N}$  exchange, namely potassium, calcium, magnesium and sodium [6] were measured at concentrations of  $16.9 \pm 0.1 \text{ mg K}^+\text{/L}$ ,  $69 \pm 14 \text{ mg Ca}^{2+}\text{/L}$ ,  $7 \pm 0.7 \text{ mg Mg}^{2+}\text{/L}$  and  $60.2 \pm 14.6 \text{ mg Na}^+\text{/L}$ , respectively (Table 3.4).

**Table 3.4 Chemical characterization of wastewater fed to the ion exchange demonstration plant.**

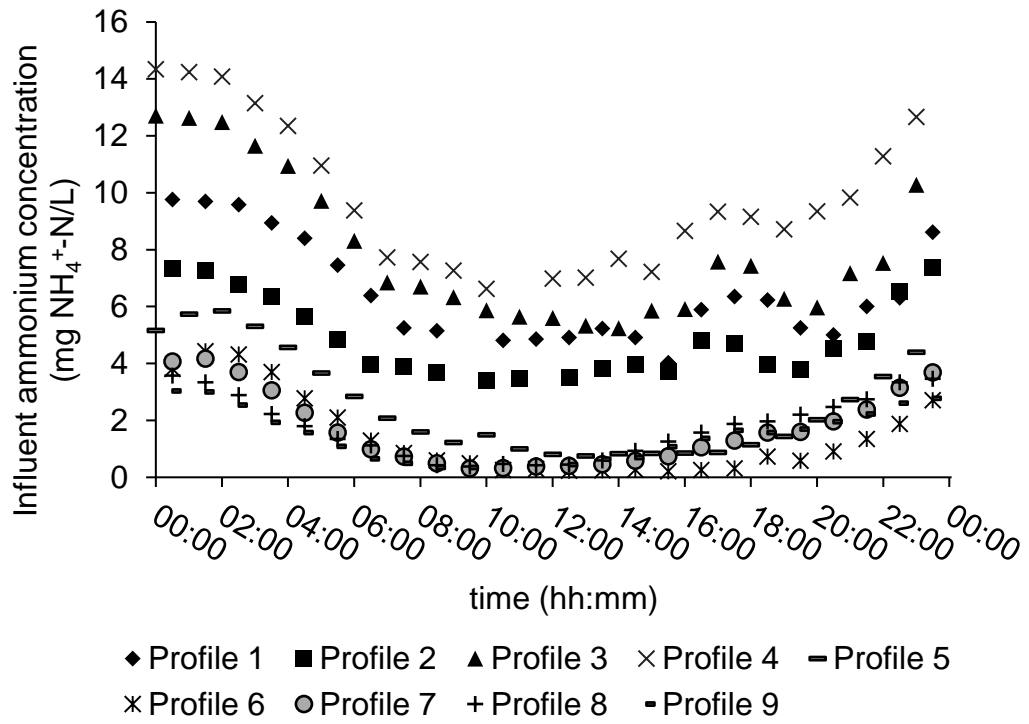
| <b>Pollutant</b>            | COD          | NH <sub>4</sub> -N | Ca <sup>2+</sup> | Mg <sup>2+</sup> | K <sup>+</sup> | Na <sup>+</sup> | Cl <sup>-</sup> | PO <sub>4</sub> -P | SO <sub>4</sub> <sup>2-</sup> |
|-----------------------------|--------------|--------------------|------------------|------------------|----------------|-----------------|-----------------|--------------------|-------------------------------|
| <b>Average conc. (mg/L)</b> | 54.0<br>±5.7 | Min:<LOD<br>Max:26 | 69.0<br>±14      | 7.0<br>±0.7      | 16.9<br>±0.1   | 60.2<br>±14.6   | 75.6<br>±9.6    | 5.9<br>±0.1        | 75.4<br>±6.2                  |

### 3.5.2 Ammonium diurnal and seasonal variability

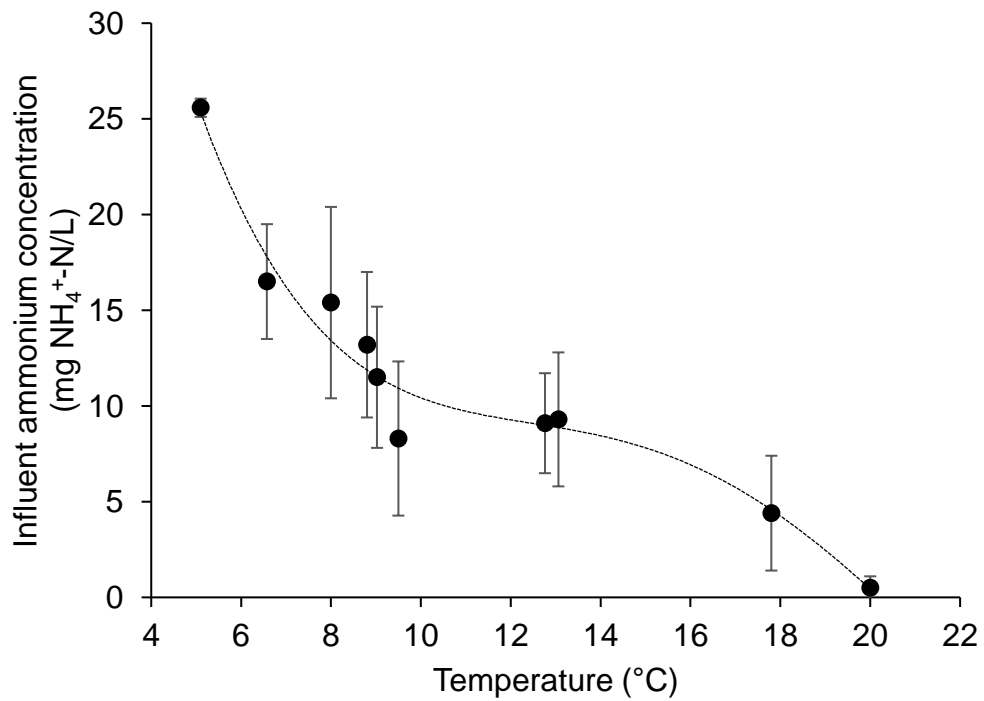
The NH<sub>4</sub><sup>+</sup>-N concentration at the influent of the IEX demonstration plant was influenced by diurnal and seasonal variations. Figure 3.2a shows the diurnal NH<sub>4</sub><sup>+</sup>-N concentration in the influent wastewater for nine different daily profiles. Overall, the NH<sub>4</sub><sup>+</sup>-N concentration was higher during the night (from 22:00 to 4:00) and lower during the day with a minimum usually registered at around 12:00 (Figure 3.2a). Additionally, the profiles also presented different ranges of NH<sub>4</sub><sup>+</sup>-N variation with some cycles presenting higher values at around 14 mg NH<sub>4</sub><sup>+</sup>-N/L and other presenting maximum values of 3 mg NH<sub>4</sub><sup>+</sup>-N/L. The seasonal variability was mainly related to temperature, which affected nitrification taking place in the secondary process composed of trickling filters, before the IEX tertiary treatment (Figure 3.2b). During winter, lower temperatures of 5-8°C, impacted nitrification [48] and the wastewater entering the IEX demonstration plant contained up to 26 mg NH<sub>4</sub><sup>+</sup>-N/L. During summer, the wastewater temperature increased up to 20°C, full nitrification was observed in the trickling filters and the NH<sub>4</sub><sup>+</sup>-N concentration reaching the IEX demonstration plant was 0.5-1 mg NH<sub>4</sub><sup>+</sup>-N/L or lower (Figure 3.2b). Figure 3.2c shows the NH<sub>4</sub><sup>+</sup>-N concentration and average temperature in the influent wastewater of the IEX demonstration plant over the entire period of operation, represented as bed volumes of wastewater fed. A drop in the NH<sub>4</sub><sup>+</sup>-N influent concentration ( $C_{\text{influent}} < 3 \text{ mg NH}_4^+\text{-N/L}$ ) was observed between 6000 BV and 16000 BV, corresponding to the summer period. On the other hand, increased concentration was obtained in the autumn-winter period with highly variable loading peaks (Figure 3.2c).



(a)



(b)



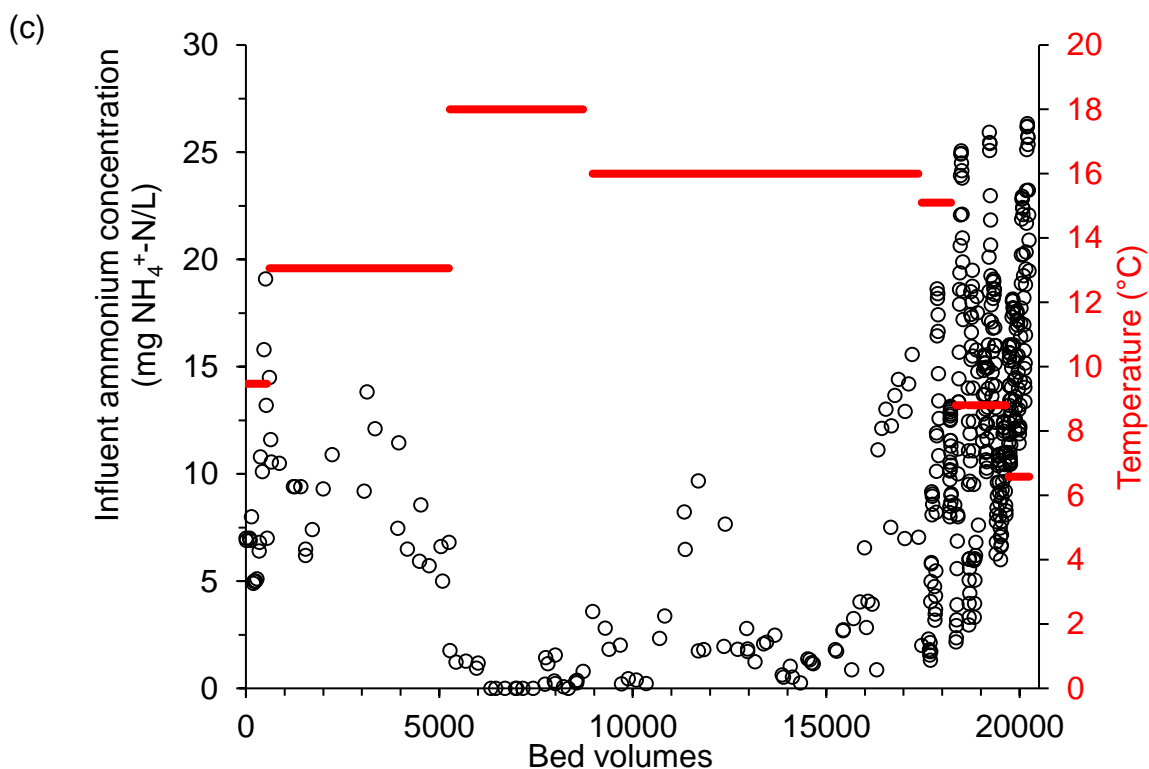


Figure 3.2 Diurnal (a) and seasonal (b) variability in the ammonium (NH<sub>4</sub><sup>+</sup>-N) concentration in the secondary effluent wastewater, fed to the ion exchange (IEX) demonstration plant and (c) influent profile and temperature variation during operation of the IEX demonstration plant.

### 3.5.3 Effect of ammonium influent variation on Zeolite-N ammonium exchange capacity at demonstration scale

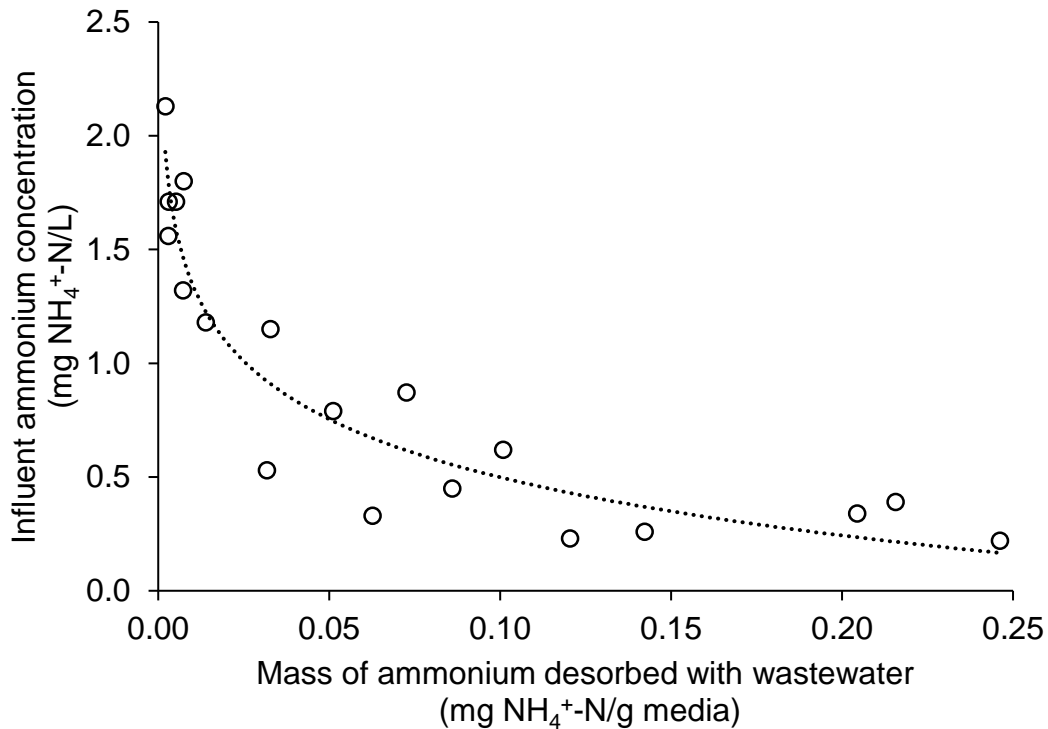
In total, 9 cycles of NH<sub>4</sub><sup>+</sup>-N uptake and regeneration were performed with different influent concentration of the wastewater (<0.006-26 mg NH<sub>4</sub><sup>+</sup>-N/L) (Figure 3.2c) fed to the demonstration plant and consequently different NH<sub>4</sub><sup>+</sup>-N exchange capacities (AEC) were measured (Table 3.5). During the first cycle, the influent concentration was 8.3±4.0 mg NH<sub>4</sub><sup>+</sup>-N/L (mass loads of 320 g NH<sub>4</sub><sup>+</sup>-N) and an AEC of 3.9 mg NH<sub>4</sub><sup>+</sup>-N/g media (0.2 meq NH<sub>4</sub><sup>+</sup>-N/g media) was measured with an NH<sub>4</sub><sup>+</sup>-N exchange efficiency of 96%. During the second cycle, the influent concentration was 9.0±2.6 mg NH<sub>4</sub><sup>+</sup>-N/L, however, due to an increase in the volume of wastewater treated (mass load of 2339.4 g NH<sub>4</sub><sup>+</sup>-N), an AEC of 15.3 mg NH<sub>4</sub><sup>+</sup>-N/g media (0.85 meq NH<sub>4</sub><sup>+</sup>-N/g media) was registered (ammonium exchange efficiency of 51%) (Table 3.5).

Successively, the influent concentration decreased to  $0.5\pm 0.6$  mg  $\text{NH}_4^+\text{-N/L}$  and the AEC dropped to  $-2.5$  mg  $\text{NH}_4^+\text{-N/g}$  media ( $0.14$  meq  $\text{NH}_4^+\text{-N/g}$  media) indicating a release of the  $\text{NH}_4^+\text{-N}$  into the wastewater (Table 3.5). However, in the following cycle, the average influent concentration increased again to  $4.4\pm 4.4$  mg  $\text{NH}_4^+\text{-N/L}$  and the measured AEC was  $17.1$  mg  $\text{NH}_4^+\text{-N/g}$  media ( $0.95$  meq  $\text{NH}_4^+\text{-N/g}$  media) with an  $\text{NH}_4^+\text{-N}$  exchange efficiency of 62% (Table 3.5). Overall, a good correlation ( $R_2 = 0.95$ ) between influent mass load and ammonium exchange efficiency was detected (Figure A1a, in appendix).

Importantly, a decrease of the  $C_{\text{influent}}$  to  $<2.5$  mg  $\text{NH}_4^+\text{-N/L}$  resulted in a release of the  $\text{NH}_4^+\text{-N}$  from the Zeolite-N to the wastewater (cycle 3 in Table 3.5 and Figure 3.3). The highest release ( $0.25$  mg  $\text{NH}_4^+\text{-N/g}$  media,  $0.014$  meq  $\text{NH}_4^+\text{-N/g}$  media) was registered when  $C_{\text{influent}}$  was  $0.22$  mg  $\text{NH}_4^+\text{-N/L}$  (Figure 3.3).

**Table 3.5 Cycles performed at demonstration scale with Zeolite-N for ammonium removal from different ammonium influent loads and effect on the ammonium exchange capacity of the media.**

| Cycle | Total volume treated | Average influent $\text{NH}_4^+\text{-N}$ concentration | Influent mass load         | $\text{NH}_4^+\text{-N}$ exchange capacity | $\text{NH}_4^+\text{-N}$ exchange efficiency |
|-------|----------------------|---------------------------------------------------------|----------------------------|--------------------------------------------|----------------------------------------------|
|       | $\text{m}^3$         | mg $\text{NH}_4^+\text{-N/L}$                           | g $\text{NH}_4^+\text{-N}$ | mg $\text{NH}_4^+\text{-N/g}$ media        | %                                            |
| 1     | 37.4                 | $8.3\pm 4.0$                                            | 319.9                      | 3.9                                        | 96%                                          |
| 2     | 249.8                | $9.0\pm 2.6$                                            | 2339.4                     | 15.3                                       | 51%                                          |
| 3     | 237.7                | $0.5\pm 0.6$                                            | 105.4                      | -2.5                                       | -                                            |
| 4     | 580.9                | $4.4\pm 4.4$                                            | 2165.8                     | 17.1                                       | 62%                                          |
| 5     | 58.8                 | $9.3\pm 4.7$                                            | 452.9                      | 1.6                                        | 28%                                          |
| 6     | 12.8                 | $15.3\pm 7.8$                                           | 198.7                      | 0.9                                        | 34%                                          |
| 7     | 41.8                 | $13.2\pm 5.5$                                           | 537.9                      | 4.3                                        | 62%                                          |
| 8     | 25.5                 | $11.5\pm 3.7$                                           | 291.6                      | 1.4                                        | 39%                                          |
| 9     | 36.4                 | $16.5\pm 4.2$                                           | 624.1                      | 4.3                                        | 54%                                          |



**Figure 3.3 NH<sub>4</sub><sup>+</sup>-N desorption (mg NH<sub>4</sub><sup>+</sup>-N/g media) with wastewater when C<sub>influent</sub> < 2.5 mg NH<sub>4</sub><sup>+</sup>-N/L.**

For the first 800 bed volumes of wastewater treated (average C<sub>influent</sub> = 8.3±4 mg NH<sub>4</sub><sup>+</sup>-N/L, Table 3.5), the effluent concentration was kept below 2 mg NH<sub>4</sub><sup>+</sup>-N/L (Figure 3.4a). After 1300 bed volumes, the effluent profile reached a plateau and it stabilized at a concentration of 5 mg NH<sub>4</sub><sup>+</sup>-N/L (Figure 3.4a). For the following cycles, the NH<sub>4</sub><sup>+</sup>-N effluent profiles mirrored the NH<sub>4</sub><sup>+</sup>-N influent concentration. As an example, Figure 3.4b shows the profiles in cycles 8-9. During cycle 8, three influent NH<sub>4</sub><sup>+</sup>-N loading peaks were registered at 19, 11 and 13 mg NH<sub>4</sub><sup>+</sup>-N/L, the corresponding maximum effluent concentration was 7.3, 6.1 and 8.2 mg NH<sub>4</sub><sup>+</sup>-N/L. During cycle 9, the high variability in NH<sub>4</sub><sup>+</sup>-N at the influent concentration (16.5±4.2 mg NH<sub>4</sub><sup>+</sup>-N/L) caused an effluent quality between 4.6 and 12.6 mg NH<sub>4</sub><sup>+</sup>-N/L (Figure 3.4b).

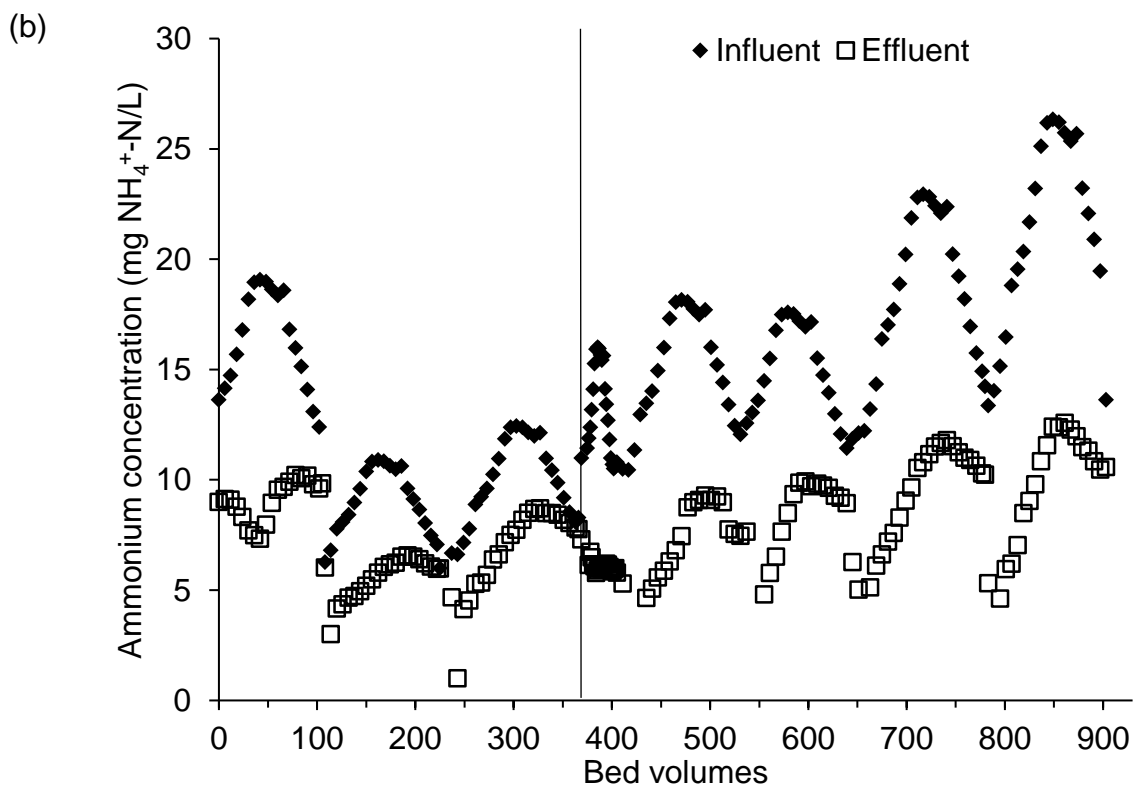
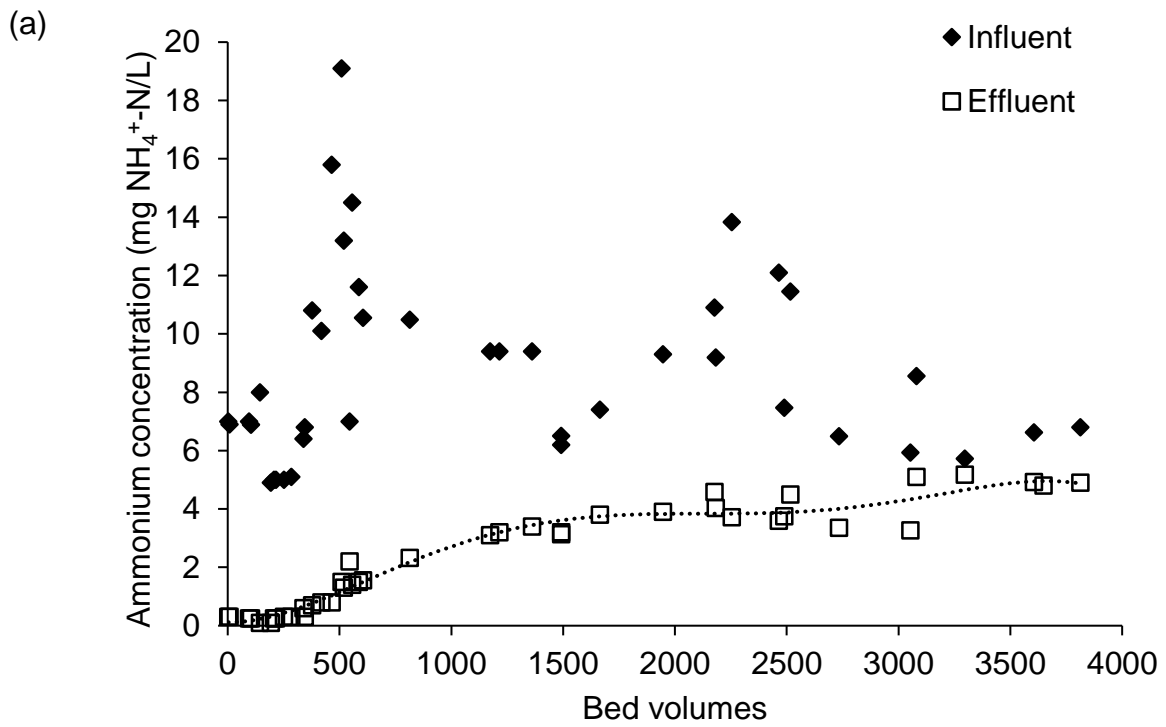


Figure 3.4 (a) Breakthrough curve obtained during the first cycle with Zeolite-N at demonstration scale; (b) correlation between ammonium influent concentration and effluent profiles in cycles 8 and 9 (vertical line represents the regeneration).

In the first cycle at demonstration scale, 94% of the total amount of  $\text{NH}_4^+\text{-N}$  in the media was recovered in the regeneration phase (Table 3.6). For the following cycles (cycle 2-cycle 9), the regeneration efficiencies depended on the mass of  $\text{NH}_4^+\text{-N}$  in the media, which was a result of the mass of  $\text{NH}_4^+\text{-N}$  removed from wastewater and the mass recovered in the previous regeneration cycles (Table 3.6). During cycles 1-6, the mass remaining in the media after the regeneration increased up to 1282.3 g  $\text{NH}_4^+\text{-N}$  and as a result, the efficiency of regeneration decreased to 22%. The  $\text{NH}_4^+\text{-N}$  concentration of the KCl 10% regenerant brine increased from 140 mg  $\text{NH}_4^+\text{-N/L}$  to 520 mg  $\text{NH}_4^+\text{-N/L}$  from the cycle 1 to 6 while from cycle 6 to 9, the concentration in the brine reached 700 mg  $\text{NH}_4^+\text{-N/L}$ .

Interestingly, even though in cycle 7 the regeneration was performed with a fresh brine, the resulting regeneration efficiency was 28%, similar to the 22% of cycle 6, obtained after reusing the same regenerant brine for six times. In particular, the mass of ammonium in the media before regeneration in cycle 6 and 7 was 1562 and 1616 g  $\text{NH}_4^+\text{-N}$ , respectively (Table 3.6).

**Table 3.6 Zeolite-N regeneration cycles performed at demonstration scale with potassium chloride (KCl) 10%.**

| <b>Cycle</b> | <b>Mass removed</b>        | <b>Mass recovered</b>      | <b>Mass in media after regen.</b> | <b>Regen. efficiency (1<sup>st</sup> batch of regen.)</b> | <b>Regen. efficiency (2<sup>nd</sup> batch of regen.)</b> | <b><math>\text{NH}_4^+\text{-N}</math> released</b> |
|--------------|----------------------------|----------------------------|-----------------------------------|-----------------------------------------------------------|-----------------------------------------------------------|-----------------------------------------------------|
|              | g $\text{NH}_4^+\text{-N}$ | g $\text{NH}_4^+\text{-N}$ | g $\text{NH}_4^+\text{-N}$        | %                                                         | %                                                         | %                                                   |
| 1            | 306.6                      | 287.0                      | 19.6                              | 94%                                                       | -                                                         | -                                                   |
| 2            | 1193.4                     | 225.0                      | 988.0                             | 30%                                                       | -                                                         | -                                                   |
| 3            | -195.5                     | 224.1                      | 568.4                             | 39%                                                       | -                                                         | 12%                                                 |
| 4            | 1332.3                     | 261.9                      | 1638.7                            | 16%                                                       | -                                                         | 2%                                                  |
| 5            | 127.5                      | 269.9                      | 1496.3                            | 18%                                                       | -                                                         | 1%                                                  |

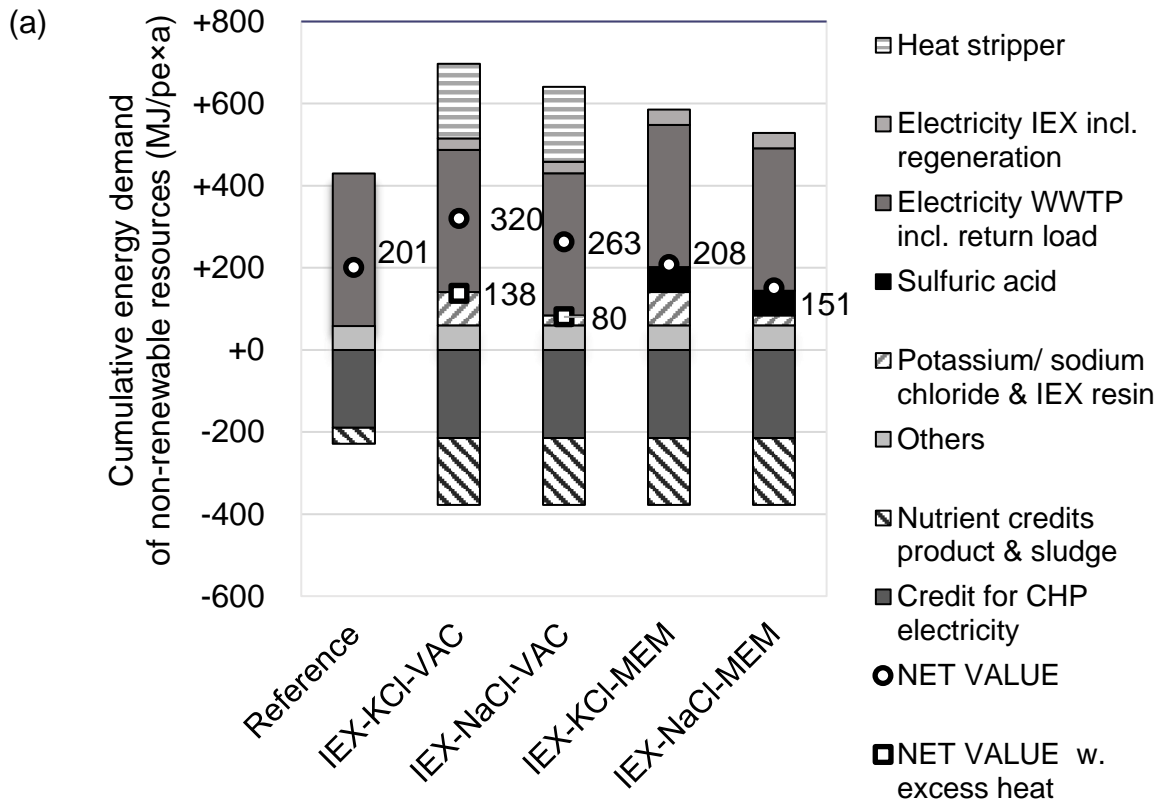
|   |       |       |        |     |     |   |
|---|-------|-------|--------|-----|-----|---|
| 6 | 66.8  | 280.8 | 1282.3 | 22% | -   | - |
| 7 | 334.3 | 350.5 | 1266.1 | -   | 28% | - |
| 8 | 112.8 | 372.2 | 1006.7 | -   | 37% | - |
| 9 | 334.1 | 378.0 | 962.9  | -   | 39% | - |

### 3.5.4 Results of life cycle assessment

Figure 3.5 presents the net (a) cumulative energy demand (CED), (b) global warming potential (GWP) and (c) marine eutrophication potential (MEP) of the reference scenario and of the IEX scenarios. The CED, GWP and MEP of the reference scenario resulted in 201 MJ/pe $\times$ a, 33 kg CO<sub>2</sub> eq/pe $\times$ a and 2.1 kg N eq/pe $\times$ a, respectively. Compared to the reference scenario, the implementation of the IEX process with vacuum thermal stripping (VAC) for ammonia recovery process increased the net CED, if no excess heat was available on site (Figure 3.5a). This accounted for 320 MJ/pe $\times$ a and 263 MJ/pe $\times$ a for the IEX scenarios with KCl-VAC and NaCl-VAC, respectively. On the other hand, if excess heat was considered available [49], the net CED for the IEX-KCl-VAC and IEX-NaCl-VAC was 138 and 80 MJ/pe $\times$ a, respectively, which corresponded to a decrease in the CED of 31% and 60% compared to the reference scenario. The implementation of the membrane stripping as recovery process from the saturated KCl or NaCl resulted in a CED of 208 and 151 MJ/pe $\times$ a, respectively which corresponded to a 3% increase and a 25% decrease of CED, respectively, compared to the reference scenario. The lower CED of the NaCl resulted from the lower quantity of NaCl needed to remove 1 kg of NH<sub>4</sub><sup>+</sup> from the saturate brine compared to the amount of KCl (Table 3.3)

Regarding the GWP, the IEX process scenarios presented a net improvement when compared to the reference scenario (Figure 3.5b). In particular, the IEX-KCl-VAC and IEX-NaCl-VAC scenarios with excess heat available on site resulted in a reduction of 60% and 72% of the GWP, respectively, compared to the reference scenario with a net GWP of 12 and 9 kg CO<sub>2</sub> eq/pe $\times$ a. If no excess heat was available, the GWP of these scenarios slightly increased up to 23 and 20 kg CO<sub>2</sub> eq/pe $\times$ a, respectively. In

comparison, the implementation of the membrane stripping for the  $\text{NH}_4^+\text{-N}$  recovery resulted in a GWP of 14 and 11  $\text{kg CO}_2 \text{ eq/pe}\times\text{a}$  for the IEX-KCl-MEM and IEX-NaCl-MEM, respectively, which corresponded to a 58% and 66% reduction of the GWP compared to the reference scenario. Finally, all the IEX process scenario presented the same MEP of 0.8  $\text{kg N eq/pe}\times\text{a}$  which corresponded to a 62% reduction compared to the MEP of the reference scenario (2.1  $\text{kg N eq/pe}\times\text{a}$ ) (Figure 3.5c).





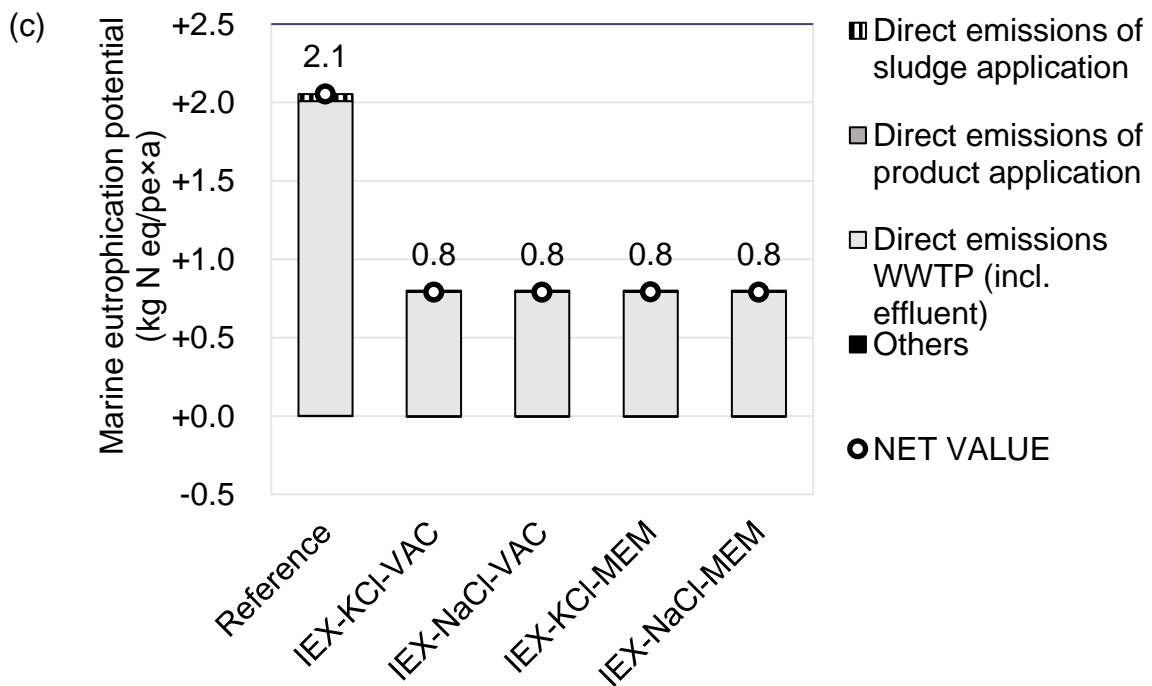
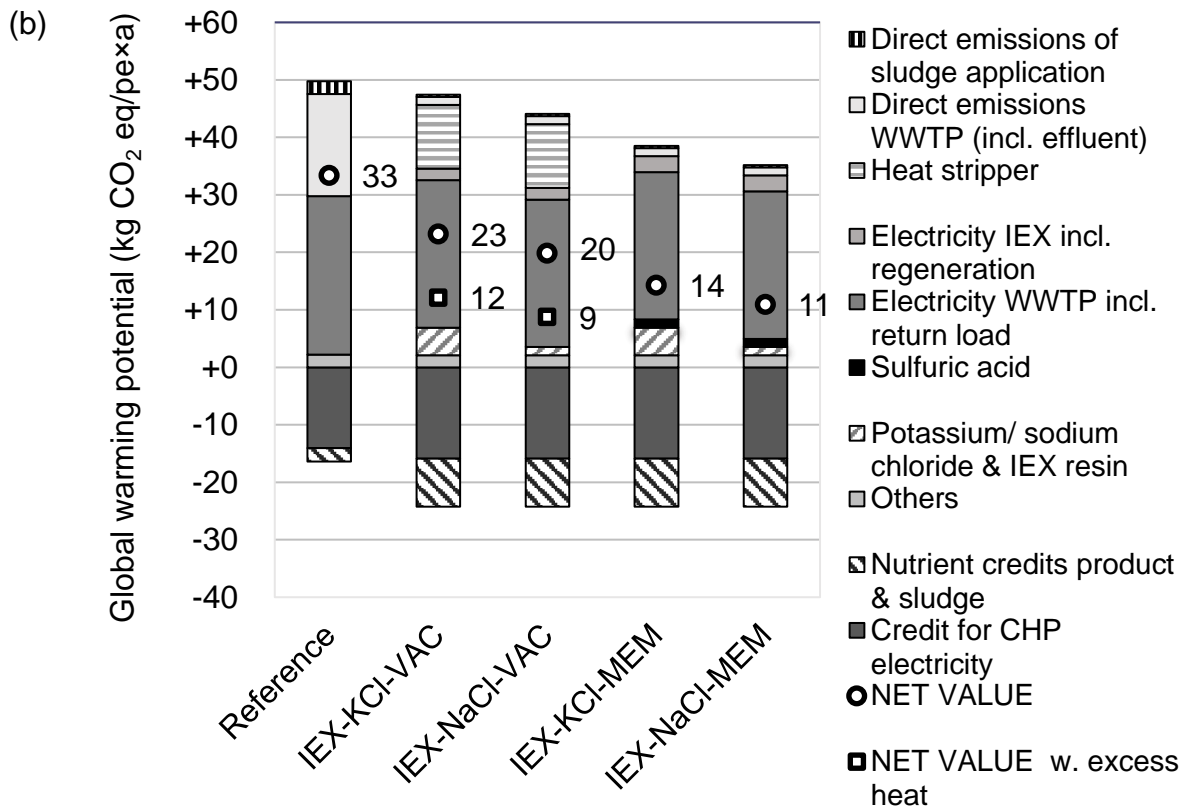


Figure 3.5. (a) Cumulative non-renewable energy demand, (b) global warming potential and (c) marine eutrophication potential of reference scenario (biological ammonium removal) and IEX exchange process scenarios (ammonium removal and recovery).

**“Others” refers to polymer for dewatering, additional infrastructure for the IEX system and sludge transportation. Functional unit: 10,000 population equivalent (pe).**

In Table 3.7, a detailed analysis of the factors influencing the net values for CED, GWP and MEP of the reference and IEX scenarios is presented. For the reference scenario, the CED and GWP were mainly a result of the electricity of the WWTP (371.8 MJ/pe×a and 27.5 kg CO<sub>2</sub> eq/pe×a, respectively) and the sludge dewatering and transportation (58 MJ/pe×a and 2.2 kg CO<sub>2</sub> eq/pe×a, respectively). Additionally, the GWP of the reference scenario was impacted by the direct greenhouse gas emissions of the effluent (17.8 kg CO<sub>2</sub> eq/pe×a) and sludge application (2.2 kg CO<sub>2</sub> eq/pe×a). These were also responsible for the MEP of the reference scenario (2.01 and 0.05 kg N eq/pe×a, respectively). Biogas production and sludge applications resulted in saving of -189.6 MJ/pe×a and -39.6 MJ/pe×a respectively and reduced the GWP of -14 and -2.4 kg CO<sub>2</sub> eq/pe×a, respectively. For the IEX scenarios, the main difference in the CED was due to the energy needed to heat the regenerant solution during the recovery via vacuum thermal stripping (182 MJ/pe×a). Similarly, when using potassium chloride, the CED resulted in 81.5 MJ/pe×a while the use of sodium chloride lowered the CED to 24.4 MJ/pe×a. Compared to the reference scenario, the CED of IEX scenarios presented higher credits for the biogas valorisation (-214 MJ/pe×a) and products application (-163 MJ/pe×a). For the GWP, the main differences between the IEX scenarios was again connected to the use of potassium or sodium chloride as regenerant solution (4.8 and 1.4 kg CO<sub>2</sub> eq/pe×a), the heat for the VAC process (11.1 kg CO<sub>2</sub> eq/pe×a) and the sulfuric acid production for the MEM process (1.4 kg CO<sub>2</sub> eq/pe×a). Importantly, the use of IEX process reduced the MEP connected to the direct emission of the effluent and sludge application to 0.79 and 0.01 kg N eq/pe×a, respectively.

**Table 3.7 Cumulative energy demand (CED), global warming potential (GWP) and marine eutrophication potential (MEP) of the reference scenario and of the IEX scenarios (1: KCl-VAC; 2: NaCl-VAC; 3: KCl-MEM, 4: NaCl-MEM). Functional unit: 10,000 population equivalent (pe).**

| Scenario                               | Cumulative non-renewable energy demand (MJ/pe×a) |       |       |       |       | Global warming potential (kg CO <sub>2</sub> eq/pe×a) |      |      |      |      | Marine eutrophication potential (kg N eq/pe×a) |   |   |   |   |
|----------------------------------------|--------------------------------------------------|-------|-------|-------|-------|-------------------------------------------------------|------|------|------|------|------------------------------------------------|---|---|---|---|
|                                        | Refer.                                           | 1     | 2     | 3     | 4     | Refer.                                                | 1    | 2    | 3    | 4    | Refer.                                         | 1 | 2 | 3 | 4 |
| Potassium/sodium chloride & IEX media  | 0.0                                              | 81.5  | 24.4  | 81.5  | 24.4  | 0.0                                                   | 4.8  | 1.4  | 4.8  | 1.4  | -                                              | - | - | - | - |
| Sulfuric acid production               | 0.0                                              | 0.0   | 0.0   | 60.5  | 60.3  | 0.0                                                   | 0.0  | 0.0  | 1.4  | 1.4  | -                                              | - | - | - | - |
| Electricity WWTP including return load | 371.8                                            | 346.3 | 346.5 | 346.3 | 346.5 | 27.5                                                  | 25.6 | 25.7 | 25.6 | 25.7 | -                                              | - | - | - | - |

|                                        |      |       |       |      |      |      |      |      |     |     |      |      |      |      |      |
|----------------------------------------|------|-------|-------|------|------|------|------|------|-----|-----|------|------|------|------|------|
| Electricity IEX including regeneration | 0.0  | 27.5  | 27.5  | 37.4 | 37.4 | 0.0  | 2.0  | 2.0  | 2.8 | 2.8 | -    | -    | -    | -    | -    |
| Heat stripper                          | 0.0  | 182.3 | 182.4 | 0.0  | 0.0  | 0.0  | 11.1 | 11.1 | 0.0 | 0.0 | -    | -    | -    | -    | -    |
| Direct emission of sludge application  | 0.0  | 0.0   | 0.0   | 0.0  | 0.0  | 2.2  | 0.4  | 0.4  | 0.4 | 0.4 | 0.05 | 0.01 | 0.01 | 0.01 | 0.01 |
| Direct emission of product application | 0.0  | 0.0   | 0.0   | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0 | 0.0 | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  |
| Direct emission effluent               | 0.0  | 0.0   | 0.0   | 0.0  | 0.0  | 17.8 | 1.4  | 1.4  | 1.4 | 1.4 | 2.01 | 0.79 | 0.79 | 0.79 | 0.79 |
| Others <sup>a</sup>                    | 58.0 | 59.7  | 59.7  | 59.7 | 59.7 | 2.2  | 2.1  | 2.1  | 2.1 | 21  | -    | -    | -    | -    | -    |

|                                                                 |            |            |            |            |            |           |           |           |           |           |            |             |             |             |             |
|-----------------------------------------------------------------|------------|------------|------------|------------|------------|-----------|-----------|-----------|-----------|-----------|------------|-------------|-------------|-------------|-------------|
| Credit for biogas valorisation in combined heat and power (CHP) | -189.6     | -214.5     | -214.6     | -214.5     | -214.6     | -14.0     | -15.9     | -15.9     | -15.9     | -15.9     | -          | -           | -           | -           | -           |
| Nutrient credits for sludge and product                         | -39.6      | -163.0     | -163.0     | -163.0     | -163.0     | -2.4      | -8.4      | -8.4      | -8.4      | -8.4      | -          | -           | -           | -           | -           |
| <b>NET VALUE</b>                                                | <b>201</b> | <b>320</b> | <b>263</b> | <b>208</b> | <b>151</b> | <b>33</b> | <b>23</b> | <b>20</b> | <b>14</b> | <b>11</b> | <b>2.1</b> | <b>0.80</b> | <b>0.80</b> | <b>0.80</b> | <b>0.80</b> |
| <b>NET VALUE with excess heat</b>                               |            | <b>138</b> | <b>80</b>  |            |            |           | <b>12</b> | <b>9</b>  |           |           |            | <b>0.80</b> | <b>0.80</b> |             |             |

<sup>a</sup> “Others” refers to polymer for dewatering, additional infrastructure for the IEX system and sludge transportation.

### 3.6 Discussion

The secondary treated wastewater presented an ammonium ( $\text{NH}_4^+\text{-N}$ ) concentration ranging from  $<0.006$  (lower detection limit) to  $26 \text{ mg NH}_4^+\text{-N/L}$  (Table 3.4). The diurnal and seasonal variability was related with the temperature, which affected the efficiency of nitrification in the trickling filters used for secondary treatment (Figure 3.2). In this work, the resilience of the IEX process, used as tertiary treatment, was considered as the ability of the Zeolite-N to adapt to the variability of the influent  $\text{NH}_4^+\text{-N}$  concentration by maintaining high removal capacities. Zeolite-N maintained an effluent concentration below  $2 \text{ mg NH}_4^+\text{-N/L}$  (Figure 3.4b) for the first 800 bed volumes of wastewater treated. However, the AEC in the following cycles was strongly affected ( $R^2=0.95$ ) by the variability in the influent mass load ( $105.4\text{-}2339.4 \text{ g NH}_4^+\text{-N}$ ) which was a result of the variable influent concentrations and the volumes of wastewater treated (Table 3.5). The classical ion exchange reaction on the surface of the media (R) between two ions with equal charges ( $\text{A}^+$  and  $\text{B}^+$ ) is expressed by equation 3.4 [51]:



At equilibrium, the electrochemical potential of  $\text{A}^+$  and  $\text{B}^+$  is equal for both the ion in the exchanger and in the aqueous phase [51]. Higher  $\text{NH}_4^+\text{-N}$  concentrations in the aqueous phase ( $\text{A}^+$ ) increase the driving force so that the  $\text{NH}_4^+\text{-N}$  ions can be exchanged with cations ( $\text{B}^+$ ) on the surface of the media [52], [53]. As a result, AEC of  $15.7\text{-}17.1 \text{ mg NH}_4^+\text{-N/g media}$  ( $0.87\text{-}0.95 \text{ meq NH}_4^+\text{-N/g media}$ ) were measured when the influent mass load was  $2166\text{-}2339 \text{ g NH}_4^+\text{-N}$ . On the other hand, the AEC was  $0.9\text{-}1.4 \text{ mg NH}_4^+\text{-N/g media}$  ( $0.05\text{-}0.08 \text{ meq NH}_4^+\text{-N/g media}$ ) when the amount of ammonium fed to the demonstration plant decreased ( $199\text{-}292 \text{ g NH}_4^+\text{-N}$ ) (Table 3.5). The capacities measured in this work are in accordance to the values presented in previous studies where the AEC of the Zeolite-N ranged between  $0.37$  to  $49 \text{ mg NH}_4^+\text{-N/g media}$  ( $0.02\text{-}2.7 \text{ meq NH}_4^+\text{-N/g media}$ ) with influent concentration increasing from  $2$  to  $1000 \text{ mg NH}_4^+\text{-N/L}$  [17]. More in particular, a comparison to literature revealed that the AEC of the Zeolite-N can be increased up to  $55 \text{ mg NH}_4^+\text{-N/g media}$  ( $3.1 \text{ meq}$

NH<sub>4</sub><sup>+</sup>-N/g media) when treating wastewater with ammonium concentrations up to 1500 mg NH<sub>4</sub><sup>+</sup>-N/L [54].

Interestingly, when the influent concentration decreased below 2.5 mg NH<sub>4</sub><sup>+</sup>-N/L, the ammonium on the Zeolite-N was desorbed with the wastewater (Figure 3.3) due to the equilibrium presented in Equation 3.4. In particular, the selectivity of Zeolites towards different cations is K<sup>+</sup>>NH<sub>4</sub><sup>+</sup>>Na<sup>+</sup>>Ca<sup>2+</sup>>Fe<sup>3+</sup>>Al<sup>3+</sup>>Mg<sup>2+</sup> [55]. Therefore, with low NH<sub>4</sub><sup>+</sup>-N concentration, due to the shift in the ion exchange equilibria [56], it is expected for the Zeolite-N to release NH<sub>4</sub><sup>+</sup>-N and uptake other cations present in wastewater at higher concentrations (such as 17 mg K<sup>+</sup>/L, 69 mg Ca<sup>2+</sup>/L, 7 mg Mg<sup>2+</sup>/L and 60 mg Na<sup>+</sup>/L, Table 3.4). The release of NH<sub>4</sub><sup>+</sup>-N caused by a drop in the influent concentration was previously detected by Hankins *et al.*, [57] while using clinoptilolite for the NH<sub>4</sub><sup>+</sup>-N removal from synthetic solution. It is important to notice that a constant monitor of the influent concentration could ensure better control of the effluent quality. In fact, if the influent quality is in compliance with the regulation on ammonium discharge, an automated system could stop the operation of the IEX plant thus avoiding the release of ammonium from the media into the wastewater and the decrease of the effluent quality. This was not possible in this work as the plant was operated manually and, as a result, the variation in the influent concentration (Figure 3.4b) were reflected in the effluent profile. Importantly, the ammonium release could limit the technology suitability to meet tighter effluent permits (<1 mg NH<sub>4</sub><sup>+</sup>-N/L [33]) and therefore it needs to be studied more in details. An automated system could start the regeneration of the media when the desired effluent quality has been reached thus ensuring a more appropriate control of the operations. The possibility of being regenerated to restore the media initial ion exchange capacity is a crucial property of the ion exchange process as it ensures the presence of ammonium exchange sites on the media, which would limit the ammonium release.

In this work, it was evident that the efficiency of regeneration was strongly affected by the amount of NH<sub>4</sub><sup>+</sup>-N in the media resulting from the NH<sub>4</sub><sup>+</sup>-N influent concentration and load and the NH<sub>4</sub><sup>+</sup>-N accumulated from previous cycles (R<sup>2</sup>=0.93, Figure A1b, in appendix) (Table 3.6). The maximum amount of NH<sub>4</sub><sup>+</sup>-N that was recovered in the regenerant brine was 378 g NH<sub>4</sub><sup>+</sup>-N (cycle 9, Table 3.6) which corresponded to 39%

of regeneration efficiency. It is important to notice that the decrease in the regeneration efficiency could be correlated to the reuse of the regenerant brine which would result in the loss of  $K^+$  in the brine and in fewer  $K^+$  ions available for the next regeneration [6]. In fact, at the end of the first cycle, when the mass of  $NH_4^+-N$  on the media was 306 g  $NH_4^+-N$  (cycle 1), 94% regeneration efficiency was obtained with fresh regenerant (Table 3.6). However, for cycle 7, with mass of  $NH_4^+-N$  on the media before regeneration of 1616 g  $NH_4^+-N$ , a regeneration efficiency of 28% was obtained with fresh brine. This was similar to the regeneration efficiency of cycle 6 (22%) when the  $NH_4^+-N$  on the media before regeneration was 1562 g  $NH_4^+-N$ . This an important finding as it shows that the mass of ammonium present in the media, and consequently the ammonium concentration in the influent, is the key factor influencing the IEX process efficiency while the reuse of the regenerant is a secondary factor. In this work, 10 BV of brine were used as regenerant solution [6] and passed through the media for 2 hours. However, to increase the regeneration efficiency an increased volume of brine or contact time between the media bed and the brine should be investigated. Moreover, it is suggested a top-up of the regenerant brine with new KCl after each cycle to provide the ionic balance needed to maintain an high  $NH_4^+-N$  exchange capacity of the brine [58].

As a consequence of the need for regeneration, the application of the ion exchange process often entails a significant chemical consumption [59], costs and environmental impact connected to the disposal of the saturated brine as hazardous waste [20], hence regenerant reuse must be optimised. In particular, the possibility to recover the  $NH_4^+-N$  from the regeneration solution as a valuable product has been investigated in previous studies [23] to ensure the economic feasibility of the process by allowing for the reusability of the brine [20]. For this reason, the LCA was conducted looking at the impact of KCl or NaCl as regenerants and included  $NH_4^+-N$  recovery via vacuum thermal stripping (VAC) and membrane stripping (MEM) which were used in previous studies to recover up to 99% of the  $NH_4^+-N$  from saturated solutions [21], [23]. According to the LCA, compared to the reference scenario, the implementation of the IEX process for the removal and recovery of  $NH_4^+-N$  as tertiary treatment process reduced the cumulative energy demand (CED) if NaCl was used as regenerant brine and the membrane stripping was used for the recovery process (Table 3.8).



**Table 3.8 Net cumulative energy demand (CED), global warming potential (GWP) and marine eutrophication potential (MEP) for reference and IEX process scenarios (percentages for the IEX process scenarios are in comparison with the reference scenario).**

| Indicator |                                        | Scenario |                |                  |                |                  |               |               |
|-----------|----------------------------------------|----------|----------------|------------------|----------------|------------------|---------------|---------------|
|           |                                        | Ref.     | IEX-KCl-VAC    |                  | IEX-NaCl-VAC   |                  | IEX-KCl-MEM   | IEX-NaCl-MEM  |
|           |                                        |          | No excess heat | With excess heat | No excess heat | With excess heat |               |               |
| CED       | MJ/pe <sub>xa</sub>                    | 201      | 320<br>(+59%)  | 138<br>(-31%)    | 263<br>(+30%)  | 80<br>(-60%)     | 208<br>(+3%)  | 151<br>(-25%) |
| GWP       | kg CO <sub>2</sub> eq/pe <sub>xa</sub> | 33       | 23<br>(-30)    | 12<br>(-60%)     | 20<br>(-39%)   | 9<br>(-72%)      | 14<br>(-58%)  | 11<br>(-66%)  |
| MEP       | kg N eq/pe <sub>xa</sub>               | 2.1      | 0.8<br>(-62%)  |                  | 0.8<br>(-62%)  |                  | 0.8<br>(-62%) | 0.8<br>(-62%) |

In this case, the net CED was 151 MJ/pe<sub>xa</sub> compared to 201 MJ/pe<sub>xa</sub> obtained from the reference scenario. This reduction was due to the possibility to recover the NH<sub>4</sub><sup>+</sup>-N as ammonium sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) which can be used in the fertiliser industry [60]. The difference in CED between the IEX-KCl-MEM and IEX-NaCl-MEM scenarios (208 and 151 MJ/pe<sub>xa</sub>, respectively) was due to the higher energy required for the production of KCl compared to NaCl [35]. Considering that one ion of NH<sub>4</sub><sup>+</sup> in the media is substitute with one K<sup>+</sup> or one Na<sup>+</sup> in the regenerant, the required quantity of KCl (5.3 kg KCl/kg NH<sub>4</sub><sup>+</sup>) was higher than the quantity of NaCl (4.2 kg KCl/kg NH<sub>4</sub><sup>+</sup>) (Table 3.3); therefore, the production of KCl will demand more energy. However, it is important to consider that, even though the LCA showed the NaCl as a more sustainable option compared to KCl (Table 3.3), this has been identified as a more

efficient regenerant for Zeolite-N [6] which needs to be taken into consideration when selecting the optimal regenerant brine. This difference also affected the net CED for the IEX-KCl-VAC and IEX-NaCl-VAC scenarios (320 and 263 MJ/pe×a) (Table 3.6). In this case, however, the net CED was mainly a result of the energy required for the vacuum thermal stripping which requires additional heat for the boiling of the saturated brine and energy for the vacuum pump [23]. Importantly, the need for additional heat could be reduced by applying the recovery process to an anaerobic digester recirculation line [61]. In fact, if excess heat (recovered from heat pumps and exchangers and the use of digester gas in CHP systems [49]) was considered to be available on site, the CED of the IEX-KCl-VAC and IEX-NaCl-VAC scenarios was reduced to 138 and 80 MJ/(pe×a), respectively, thus making this energy-intensive process more profitable [23] compared to the reference and the IEX-KCl-MEM and IEX-NaCl-MEM scenarios.

The conventional biological removal in reference scenario was responsible for greenhouse gas emissions (namely CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> [20]) and lack of resource recovery [39] which resulted in a global warming potential of 33 kg CO<sub>2</sub> eq/pe×a. In comparison, the IEX scenarios accounted for 9-23 kg CO<sub>2</sub> eq/pe×a (Table 3.6). According to Huang *et al.* [20], coupling IEX process with AnMBR reduced direct greenhouse emissions of 82% compared to the biological nutrient removal process. At the same time, Lin *et al.* [39], confirmed that the IEX process had the lowest GWP when compared to Anammox process and conventional nitrification and denitrification [39].

The IEX scenarios allowed for a reduction of 62% of the marine eutrophication potential (MEP), compared to the reference scenario. This was mainly due to the reduced TN discharges limits (8 mg TN/L) of the IEX process compared to the nitrification-denitrification (20 mg TN/L). Even though high NH<sub>4</sub><sup>+</sup>-N loads can cause eutrophication of the waterways, Lin *et al.* noticed that the environmental footprint of the IEX process for NH<sub>4</sub><sup>+</sup>-N removal is mainly due to the phosphorus emission [39]. For this reason, the coupling of nitrogen and phosphorus removal can allow for a more effective reduction of the MEP of the IEX process and it should be considered in future studies.

Moreover, it is important to consider that, even though the LCA allowed for a comparison between the reference and the IEX scenarios, this approach presents some limitations because it relies on estimations and it is limited to the comparison to a particular reference scenario. To indicate, Table 3.9 presents the data quality for LCA. Therefore, to increase the reliability of the LCA, it is necessary to perform additional studies or expand the data source thus limiting the estimations and including additional technologies for the comparison with the IEX process.

**Table 3.9 Data quality for the LCA of nutrient removal and recovery.**

| <b>Process</b>                                                                                | <b>Data source</b>                                        | <b>Responsible partner</b> | <b>Data quality</b> |
|-----------------------------------------------------------------------------------------------|-----------------------------------------------------------|----------------------------|---------------------|
| Small and large WWTP reference system: influent, effluent, sludge, energy and chemical demand | Full-scale data of operator                               | Severn Trent Water         | High                |
| Operational data of upstream WWTP in IEX scenarios                                            | Estimations                                               | Severn Trent Water         | Medium to high      |
| IEX for ammonium removal layout and operation, including regenerant management                | Demonstration scale plant                                 | Cranfield University       | Medium to high      |
| Ammonium recovery from regeneration solution (vacuum degasser and membrane stripper)          | Estimations (laboratory experiments – data not published) | Cranfield University       | Low to medium       |

### 3.7 Conclusions

- The variability in the influent of secondary treatment as well as seasonal and diurnal temperature variation affected the efficiency of nitrification. This resulted in loading peaks in secondary effluents. The ammonium ( $\text{NH}_4^+\text{-N}$ ) variability (<0.006 and 26 mg  $\text{NH}_4^+\text{-N/L}$ ) affected the  $\text{NH}_4^+\text{-N}$  exchange capacity which ranged from 17.7 mg  $\text{NH}_4^+\text{-N/g}$  media, down to 0.9 mg  $\text{NH}_4^+\text{-N/g}$  media.
- Due to ammonium exchange equilibrium between the media and the wastewater, with influent concentration below 2.5 mg  $\text{NH}_4^+\text{-N/L}$ , the Zeolite-N released the ammonium up taken in previous cycles into the wastewater causing an increase of the ammonium effluent concentration. The use of an automated system is suggested to better control the effluent quality.
- The ammonium present in the media affected the efficiencies of regeneration. After the first cycle (94% regeneration efficiency), due to the accumulation of ammonium on the media, the maximum efficiency of regeneration was 39%. An optimisation of the volume of brine and the contact time between the brine and the media is suggested.
- The LCA revealed that the optimal scenario in terms of CED, GWP and MEP was the IEX-NaCl-MEM scenario. This presented -25% CED (mainly connected to the savings in electricity demand of the biological treatment stage), -66% GWP (due to the reduction in the production of greenhouse gases), -62% MEP (due to the different defined TN values in the effluent) compared to the reference scenario.
- The CED of the IEX-KCl-VAC and IEX-NaCl-VAC was mainly related to heat needed to bring the saturated brine to boiling point which can be minimized by using available excess heat in WWTPs (CED from 320 to 138 MJ/pe $\times$ a for IEX-KCl-VAC; from 263 to 80 MJ/pe $\times$ a for IEX-NaCl-VAC).
- Switching from potassium chloride (KCl) to sodium chloride (NaCl) for the regeneration process resulted in a substantially lower CED and lower GWP in all the scenarios.

### 3.8 References

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## **4. AMMONIUM REMOVAL FROM MUNICIPAL WASTEWATER WITH ZEOCLERE30 AT DEMONSTRATION SCALE USING EXISTING ION EXCHANGE INFRASTRUCTURES**

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### **Abstract**

Zeoclere30 is an ion exchange media commercialised to remove ammonium from swimming pool waters. The suitability of Zeoclere30 to replace Zeolite-N, that is no longer available in the market, was investigated in an ion exchange (IEX) demonstration plant with a capacity to treat 10 m<sup>3</sup>/day of secondary effluent wastewater. Zeoclere30 was tested under the existing IEX plant design specifications, i.e., an empty bed contact time (EBCT) of 5 min and sodium chloride (NaCl) or potassium chloride (KCl) as regenerants. Zeoclere30 presented maximum ammonium exchange capacity of 3.7 mg NH<sub>4</sub><sup>+</sup>-N/g media (0.21 meq NH<sub>4</sub><sup>+</sup>-N/g media) during the first cycle (ammonium exchange efficiency of 88%) but the capacity progressively decreased due to poor regeneration efficiency and hence this was further investigated. For the first 3 cycles, the regeneration took place with 2 bed volumes (BV) of KCl 10% w/v recirculated for 24h. For the following 9 cycles, NaCl 10% w/v was used as a regenerant in three different conditions: recirculation of 2 BV of NaCl 10% at pH 7 for 24h, recirculation of 2 BV of NaCl 10% at pH 10 for 24h and recirculation of 2 BV of NaCl 10% at pH 10 for 5 days. The regeneration efficiencies were low for both KCl (13%-29%) and NaCl (3-6%). The low ammonium exchange capacity was attributed to the short EBCT while the low regeneration efficiency was attributed to the unsuitable regenerant solution. This study demonstrated that Zeoclere30 cannot substitute

Zeolite-N in existing IEX infrastructure. Additionally, this study proved that when changing one ion exchange media with another one in existing IEX infrastructure the media properties need to be carefully considered.

## **Keywords**

Ammonium; Zeolite-N, Zeoclere30, wastewater, ion exchange; regeneration.

## 4.1 Introduction

The level of ammonium ion (as  $\text{NH}_4^+\text{-N}$ ) in treated effluents of wastewater treatment plants (WWTPs) is regulated to concentrations as low as 1 mg  $\text{NH}_4^+\text{-N/L}$  [1] in order to avoid eutrophication in receiving water bodies and reduction of environmental water quality [2]. The ion exchange (IEX) process has been reported to allow for the selective and highly efficient removal of ammonium from wastewater whilst enabling nutrient recovery. For the latter,  $\text{NH}_4^+\text{-N}$  is concentrated in the regenerant solution from where it can be extracted as a valuable product [3]. One of the most efficient ion exchange media used for  $\text{NH}_4^+\text{-N}$  removal from wastewater are zeolites. Natural zeolites have been used for several applications [4], [5] including ammonium [6], [7] and heavy metals removal [8], [9], radioactive metals ions removal [10], toxic gas adsorption [11], in agrochemical [12] and construction industries [13], [14] as well as for biomedical application [5]. The natural zeolite most widely used is clinoptilolite which displays a high affinity for ammonium with capacities in the range 0.9-23.4 mg  $\text{NH}_4^+\text{-N/g}$  media (0.05-1.3 meq  $\text{NH}_4^+\text{-N/g}$  media) [1], [15]. Recently, Vocciante *et al.* [2] investigated the use of clinoptilolite in a 1000 L/h cation-exchange pilot plant reaching final effluent concentration of 5 mg  $\text{NH}_4^+\text{-N/L}$  with an ammonium removal around 75% [2]. Another media that has attracted attention is Zeoclere30. This clinoptilolite is already in the market for a price of 0.84£/kg (Mineral Supplies International Ltd., Sussex) and has shown good potential for ammonium removal, mostly applied in swimming pool filters [16].

Zeolites can be also engineered to achieve homogeneous granule size, high resistance to attrition and improved chemical composition towards achieving higher ammonium selectivity and exchange capacity. Synthetic zeolites, such as the synthetic zeolite Zeolite-N (chemical formula  $\text{K}_{12}\text{Al}_{10}\text{Si}_{10}\text{O}_{40}\text{Cl}_2\text{8H}_2\text{O}$  [17]), also referred as MesoLite [18], are obtained by modifying clay and other aluminium bearing minerals, e.g. kaolinites and montmorillonites [19]. Zeolite-N has been widely investigated at laboratory scale [20] and pilot scale [21] and has showed an ammonium exchange capacity up to 43-55 mg  $\text{NH}_4^+\text{-N/g}$  media (2.4-3.1 meq  $\text{NH}_4^+\text{-N/g}$  media) [15], [22], [23]. At pilot scale, a reduction >90% of ammonium was achieved in the centrate side stream [21]. When used for the treatment of sludge dewatering liquors, [22] >95% of

ammonium was removed. The high ammonium exchange capacity as well as the high mechanical strength [20] make the Zeolite-N suitable for applications in IEX plants for ammonium removal from wastewater. Additionally, after saturation, the zeolites can be regenerated to re-establish the initial ammonium exchange capacity [24]. Different regenerant solutions have been tested to optimise the regeneration process [24]. The most common regenerant are salts (NaCl [25] or in NaCl-NaOCl solution [26], [27]) and alkaline solutions (NaOH [28]) while other methods include bio-regeneration [29] and electrochemical regeneration [30]. According to the supplier of Zeoclere30, the optimal regeneration of this media is obtained by adding 14-15% hypochlorite ( $\text{ClO}^-$ ) solution to the media bed and leaving the solution for 12-24 hours [31] or by leaving the media for 5 days in NaCl 10% solution at ambient temperatures [16]. To decrease the environmental impact and costs of the IEX process, both the reuse of the media and the regenerant solution need to be investigated [32].

Despite the high efficiency, Zeolite-N is no longer available in the market which limits the operation of existing plants and forces the investigation of media replacement. When switching from one ion exchange media to another, it is important to consider the existing infrastructure to prevent large capital investments and changes in technical capabilities. This work investigated if existing ion exchange infrastructure could be easily adapted to Zeoclere30 for ammonium removal from municipal wastewater at demonstration scale, a plant previously designed for Zeolite-N specifications, i.e., empty bed contact time (EBCT) of 5 min and sodium chloride (NaCl) or potassium chloride (KCl) as regenerant.

## **4.2 Material and methods**

### **4.2.1 Zeoclere30**

Zeoclere30 (natural Clinoptilolite, Mineral Supplies International, MSI, UK) presented chemical formula  $(\text{MgCaNa}_2\text{K}_2)_{2.5}(\text{AlO}_2)_7(\text{SiO}_2)_{30}21\text{H}_2\text{O}$  [16] (Table 4.1). Zeoclere30 is sold in two different size: 0.8-1 mm and 2-4 mm. The 0.8-1 mm media were used in this work due to its higher surface area [33]. The media was sieved to remove any smaller particles ( $<0.8\text{mm}$ ) and then washed with deionized water to

remove any dust from its surface prior utilization in the ion exchange demonstration plant.

**Table 4.1. Chemical characterization of the natural zeolite Zeoclere30**

| %w/w       | Na <sub>2</sub> O | MgO | K <sub>2</sub> O | CaO | TiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> |
|------------|-------------------|-----|------------------|-----|------------------|--------------------------------|------------------|--------------------------------|
| Zeoclere30 | 1.4               | 0.9 | 3.9              | 1.5 | 0.1              | 1.2                            | 71.5             | 12.1                           |

#### 4.2.2 Municipal wastewater characterization

The municipal wastewater (Table 4.2) was obtained from Cranfield University wastewater treatment plant in the UK (2,840 population equivalents) after preliminary, primary and secondary treatment with trickling filters. The wastewater presented an ammonium concentration of 8.1±2.0 mg NH<sub>4</sub><sup>+</sup>-N/L, a pH of 7.1±0.2 and COD of 54±5.7 mg/L. Additionally, other ions (calcium, Ca<sup>2+</sup>, sodium, Na<sup>+</sup>, potassium, K<sup>+</sup>, magnesium, Mg<sup>+</sup>) that could interfere with the ammonium exchange capacity of the media [34] were measured and their concentrations are presented in Table 4.2.

**Table 4.2 Secondary effluent wastewater characteristic from Cranfield University WWTP fed to IEX demonstration plant**

|              | NH <sub>4</sub> <sup>+</sup> -N | Ca <sup>2+</sup> | Mg <sup>+</sup> | K <sup>+</sup> | Na <sup>+</sup> | PO <sub>4</sub> -P | SO <sub>4</sub> -S |
|--------------|---------------------------------|------------------|-----------------|----------------|-----------------|--------------------|--------------------|
| Conc. (mg/L) | 8.1±2.0                         | 69±14            | 7±0.7           | 16.9±0.1       | 60.2±14.6       | 5.9±0.1            | 75.4±6.2           |

#### 4.2.3 Demonstration plant system and operation

The demonstration plant (MionTec GmbH, Germany) consisted of a drum filter (SIBO Fluidra, Netherlands) for the removal of solids; compressed air diaphragm pump with float flow for measurement; PVC-U column with nozzle in the covers (0.2-2 mm) and air vent valves at the top and bottom and two manometers to measure pressure loss. The ammonium removal IEX column had internal diameter of 217 mm and height 1577 mm and it was filled with 35L (32 kg) of media. After an initial backwash, the wastewater was fed in downflow operation at 5 minutes empty bed contact time (EBCT). Three cycles were conducted treating 300 BV of wastewater



between regenerations using potassium chloride (KCl 10% wt., Easy Chemicals Ltd, Denbigh, UK) as regenerant. As suggested by the media supplier, 2 BV of regenerant brine were used. The solution was recirculated for 24 hours in upflow operation. Successively, sodium chloride (NaCl 10% wt., Easy Chemicals Ltd, Denbigh, UK) was used as regenerant solution and three different regeneration methods were tested: recirculation of 2 BV of NaCl 10% at pH 7 for 24h , recirculation of 2 BV of NaCl 10% at pH 10 for 24h and recirculation of 2 BV of NaCl 10% at pH 10 for 5 days. Three cycles of 300 BV of wastewater were conducted between each regeneration method (total 9 cycles).

#### 4.2.4 Monitored parameters

The ammonium exchange capacity ( $Q$ , mg  $\text{NH}_4^+\text{-N/g}$  media or meq  $\text{NH}_4^+\text{-N/g}$  media) of the media in each cycle was calculated as in Equation 4.1 [22] while the ammonium exchange capacity of the regenerant ( $Q_{\text{reg}}$ ) was calculated as in Equation 4.2 [35].

$$Q = \frac{\int_{V=0}^{V_{\text{fin}}} (C_{\text{influent}} - C_{\text{effluent}}) dV}{M} = \frac{\sum_0^n [(C_0 - C_n) * (V_n - V_{n-1})]}{M} \quad \text{Equation 4.1}$$

$$Q_{\text{reg}} = \frac{[C_{r,i} - C_{r,f}] * V_{\text{reg}}}{M} \quad \text{Equation 4.2}$$

where  $Q$  is the amount of ammonium ion on the surface of Zeoclere30;  $C_{\text{influent}}$  and  $C_{\text{effluent}}$  are the influent and effluent ammonium concentrations in wastewater (mg  $\text{NH}_4^+\text{-N/L}$ , meq  $\text{NH}_4^+\text{-N/L}$ );  $M$  is the mass of media (g);  $V$  is the volume of the wastewater treated in each cycle (L).  $Q_{\text{reg}}$  is amount of ammonium recovered during the regeneration (mg  $\text{NH}_4^+\text{-N/g}$  media or meq  $\text{NH}_4^+\text{-N/g}$  media);  $C_{r,i}$  and  $C_{r,f}$  are the concentrations of ammonium in the regenerant at the beginning and at the end of each cycle (mg  $\text{NH}_4^+\text{-N/L}$ , meq  $\text{NH}_4^+\text{-N/L}$ );  $V_{\text{reg}}$  is the volume of regenerant used (L). To monitor the effluent quality during the operation at demonstration scale, the ratio  $C_{\text{effluent}}/C_{\text{influent}}$  was calculated. The ammonium exchange efficiency (AEE) and the regeneration efficiency (RE) were calculated following Equation 2.3-2.5 [36].

$$M_{\text{retained in solid phase}} = M_{\text{fed}} - M_{\text{out}} \quad \text{Equation 4.3}$$

$$\text{AEE} = \frac{(M_{\text{fed}} - M_{\text{out}})}{M_{\text{fed}}} * 100 \quad \text{Equation 4.4}$$

$$\text{RE} = \frac{M_{\text{reg}}}{M_{\text{retained in solid phase}}} * 100 \quad \text{Equation 4.5}$$

where,  $M_{\text{fed}}$ ,  $M_{\text{out}}$  are the mass of ammonium ion in the wastewater the influent and effluent of the IEX demonstration plant (g), respectively;  $M_{\text{retained in solid phase}}$  and  $M_{\text{reg}}$  are the mass of ammonium ion retained by the Zeoclere30 and recovered during the regeneration phase (g), respectively. Considering that the regenerants were reused multiple times, to accurately calculate the regeneration efficiency, the ammonium concentration from previous cycles was taken into account.

#### 4.2.5 Analysis

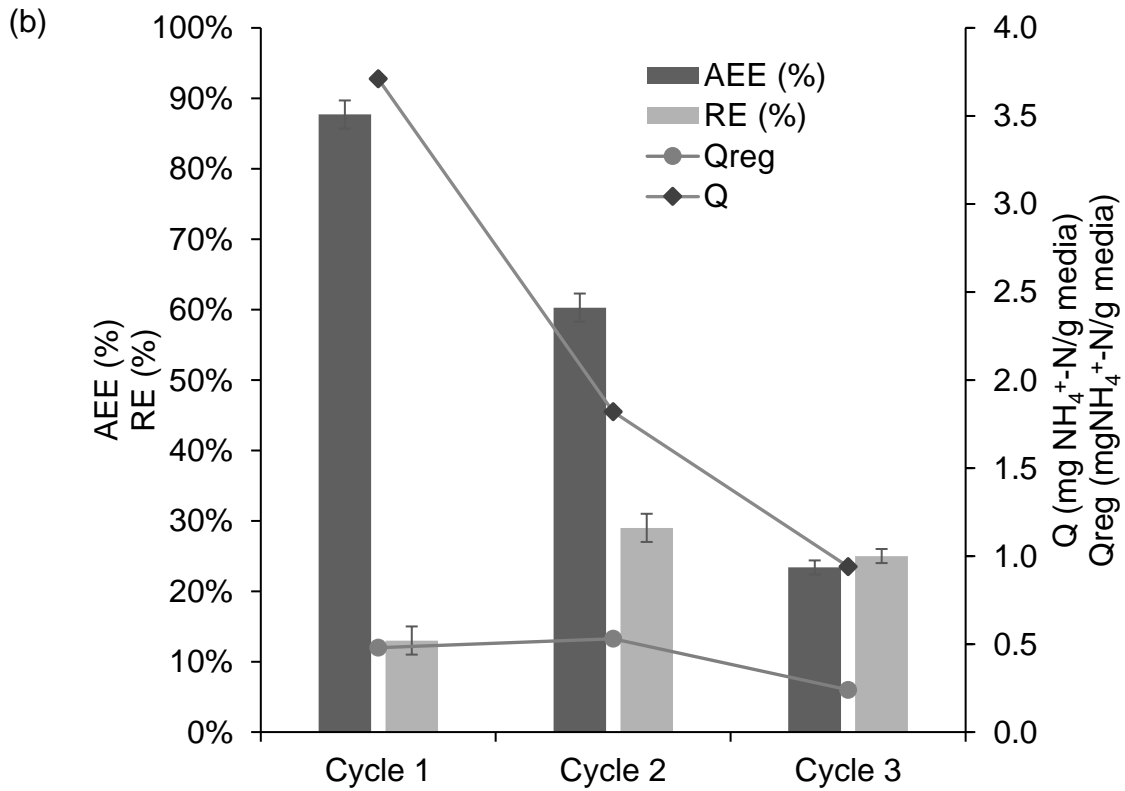
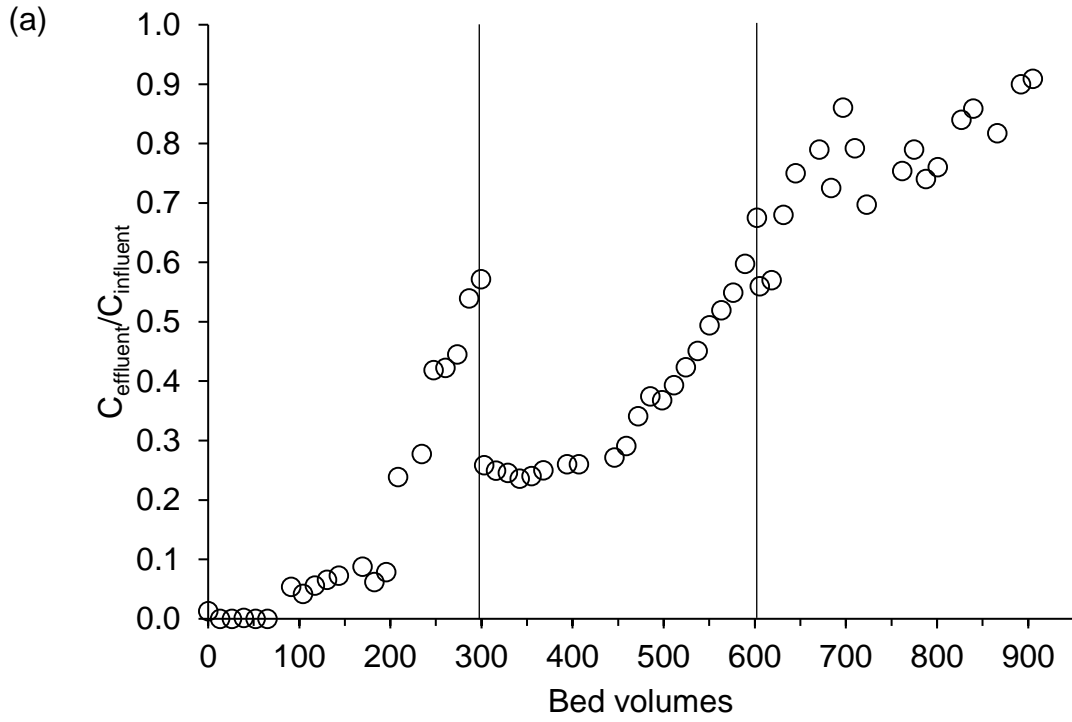
Samples were taken three times a day and the influent and effluent of the demonstration plant. Ammonium concentration was analysed using the Smartchem200 (AMS Alliance, Frépillon, France). Analysis of pH was performed using a pH portable meter (Jenway 3510 pH and conductivity meter, Camlab, UK), used on site. Calcium and COD were analysed using Spectroquant® Cell Test kit (Merk Millipore) according to manufacture protocol. Ions in wastewater were analysed following standard colorimetric analysis [37]. All the analysis were performed in duplicate.

## 4.3 Results

### 4.3.1 Ammonium exchange capacity of Zeoclere30

During the first cycle, Zeoclere30 kept  $C_{\text{effluent}}/C_{\text{influent}}$  below 0.1 for 195 BV (Figure 4.1a). This corresponded to an effluent concentration  $<1$  mg  $\text{NH}_4^+\text{-N/L}$  ( $<0.06$  meq  $\text{NH}_4^+\text{-N/L}$ ) (Figure 4.1a) starting from a  $C_{\text{influent}}$  of  $13.1 \pm 2.5$  mg  $\text{NH}_4^+\text{-N/L}$  ( $0.7 \pm 0.1$  meq  $\text{NH}_4^+\text{-N/L}$ ). Successively, the  $C_{\text{effluent}}$  increased, reaching 6 mg  $\text{NH}_4^+\text{-N/L}$  (0.3 meq  $\text{NH}_4^+\text{-N/L}$ ) after 300 BV ( $C_{\text{effluent}}/C_{\text{influent}}=0.6$ ) with a total of ammonium exchange efficiency (AEE) of 88% (Figure 4.1a).

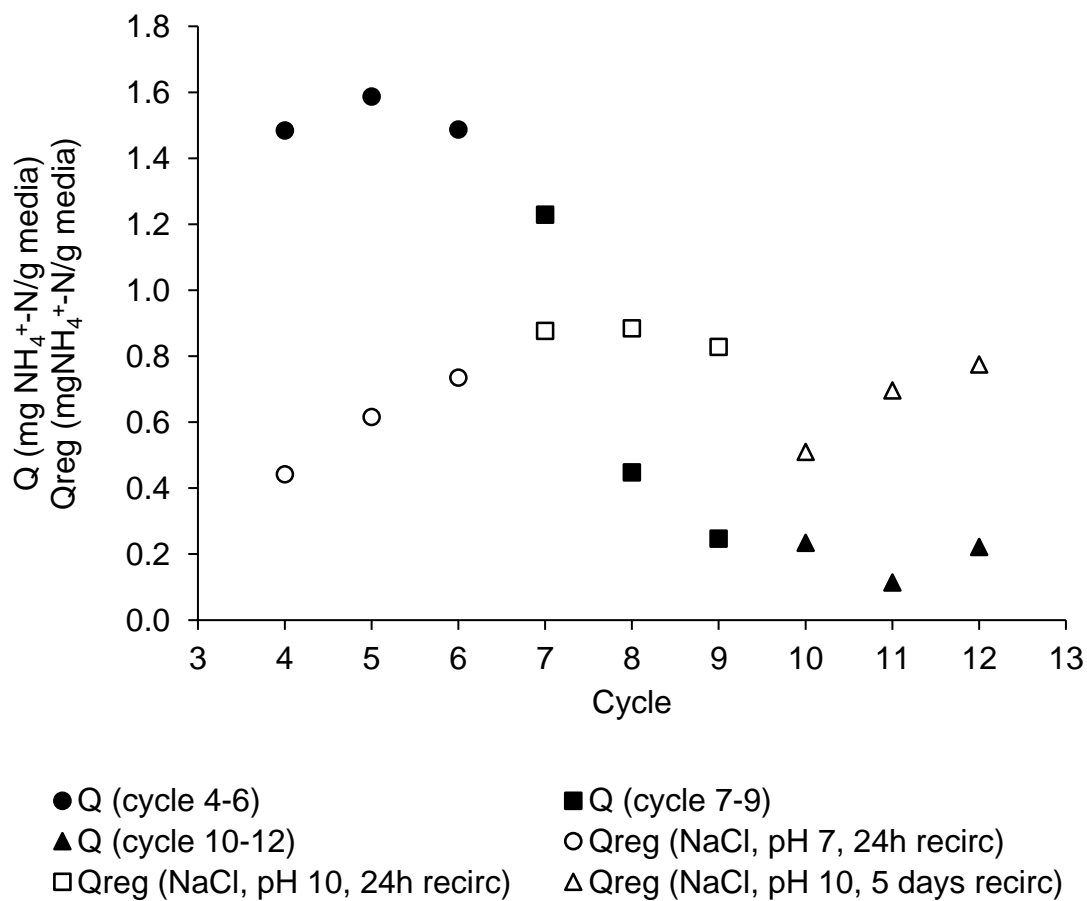
The regeneration with KCl 10% allowed for the recovery of 13% of the ammonium (Figure 4.1b). The second cycle presented a  $C_{\text{influent}}$  of  $10 \pm 1.2$  mg  $\text{NH}_4^+\text{-N/L}$  ( $0.6 \pm 0.1$  meq  $\text{NH}_4^+\text{-N/L}$ ) and, when the operation with wastewater were restarted, the concentration at the effluent was 1.7 mg  $\text{NH}_4^+\text{-N/L}$  (0.1 meq  $\text{NH}_4^+\text{-N/L}$ ) ( $C_{\text{effluent}}/C_{\text{influent}}=0.25$ ). The total AEE of the second cycle was 60% while the regeneration efficiency (RE) increased to 29%. During the third cycle ( $C_{\text{influent}}=13.6 \pm 1.9$  mg  $\text{NH}_4^+\text{-N/L}$ ,  $0.8 \pm 0.1$  meq  $\text{NH}_4^+\text{-N/L}$ ) the AEE decreased to 23% ( $C_{\text{effluent}}/C_{\text{influent}} > 0.6$ ) while 25% of the ammonium was recovered during regeneration (Figure 4.1b). The exchange capacities (Q) calculated for the three cycles were 3.7, 1.8, 0.9 mg  $\text{NH}_4^+\text{-N/g media}$  (0.21, 0.1 and 0.05 meq  $\text{NH}_4^+\text{-N/g media}$ ) respectively; on the other hand, the values of  $Q_{\text{reg}}$  were 0.48, 0.53 and 0.24 mg  $\text{NH}_4^+\text{-N/g media}$  (0.03, 0.03, 0.01 mg  $\text{NH}_4^+\text{-N/g media}$ ) respectively (Figure 4.1b).



**Figure 4.1. (a) Monitoring of the effluent quality (as  $C_{\text{effluent}}/C_{\text{influent}}$ ) obtained with Zeoclere30 (cycles 1-3, separated by a vertical line indicating that regeneration took place) treating secondary effluent wastewater and (b) ammonium exchange efficiency (AEE) and capacity (Q) of Zeoclere30 in municipal wastewater; regeneration efficiency (RE) and capacity ( $Q_{\text{reg}}$ ) obtained by treating Zeoclere30 with KCl 10% (2 BV, recirculated for 24h).**

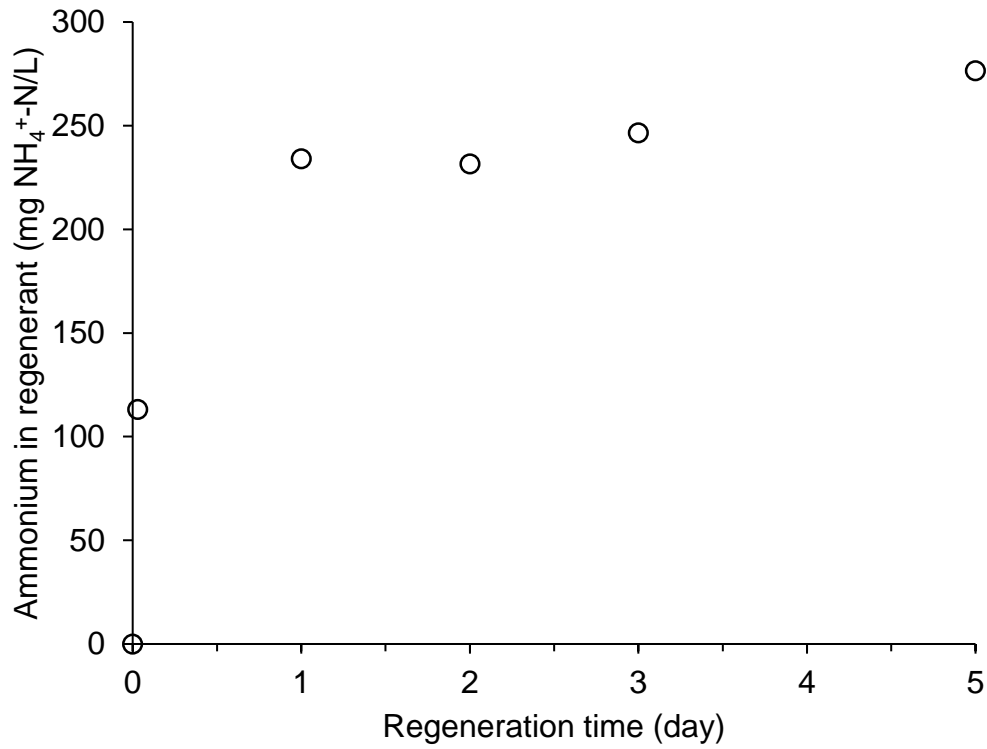
In Figure 4.2, the Q and  $Q_{\text{reg}}$  are presented for the cycles 4-12, where the media was regenerated with NaCl 10% in different conditions (pH 7-10, recirculation of 24h and 5 days). During cycle 4-6, the  $C_{\text{influent}}$  was  $13.6 \pm 3.3$  mg  $\text{NH}_4^+\text{-N/L}$  ( $0.8 \pm 0.2$  meq  $\text{NH}_4^+\text{-N/L}$ ) and the Q ranged between 1.8 and 1.5 mg  $\text{NH}_4^+\text{-N/g}$  media ( $0.1\text{-}0.08$  meq  $\text{NH}_4^+\text{-N/g}$  media) while the  $Q_{\text{reg}}$  increased from 0.4 to 0.7 mg  $\text{NH}_4^+\text{-N/g}$  media (from 0.02 to 0.04 meq  $\text{NH}_4^+\text{-N/g}$  media). These corresponded to an AEE of 40% and a RE of 5-6% by recirculating NaCl 10% at pH 7 for 24h.

Successively, the media was regenerated with a new solution of NaCl 10% at pH 10 (24h recirculation) for the cycles 7-9 with a  $C_{\text{influent}}$  of  $9.5 \pm 2.2$  mg  $\text{NH}_4^+\text{-N/L}$  ( $0.5 \pm 0.1$  meq  $\text{NH}_4^+\text{-N/L}$ ) (Figure 4.2). The AEE decreased from 34% in the 7<sup>th</sup> cycle (Q= 1.2 mg  $\text{NH}_4^+\text{-N/g}$  media, 0.07 meq  $\text{NH}_4^+\text{-N/g}$  media) down to 18% and 12% in the 8<sup>th</sup> and 9<sup>th</sup> cycles, respectively (0.5 and 0.3 mg  $\text{NH}_4^+\text{-N/g}$  media, 0.03 and 0.02 meq  $\text{NH}_4^+\text{-N/g}$  media) (Figure 4.2). The  $Q_{\text{reg}}$  was constant at around 0.9 mg  $\text{NH}_4^+\text{-N/g}$  media (0.05 meq  $\text{NH}_4^+\text{-N/g}$  media) in each regeneration cycle (5% regeneration efficiency). During the last three cycles, the  $C_{\text{influent}}$  was  $10.6 \pm 2.2$  mg  $\text{NH}_4^+\text{-N/L}$  ( $0.6 \pm 0.1$  meq  $\text{NH}_4^+\text{-N/L}$ ) and the calculated Q was 0.1-0.2 mg  $\text{NH}_4^+\text{-N/g}$  media ( $0.006\text{-}0.01$  meq  $\text{NH}_4^+\text{-N/g}$  media) (AEE=18-19%) while  $Q_{\text{reg}}$  increased from 0.03 to 0.04 mg  $\text{NH}_4^+\text{-N/g}$  media; however, the regeneration efficiencies were still low (3-4%).



**Figure 4.2 . Ammonium exchange capacity (Q) of Zeoclere30 and regeneration capacity (Q<sub>reg</sub>) in NaCl 10% at pH 7 (24h recirculation) and 10 (24h and 5 days of recirculation).**

Interestingly, when analysing the ammonium elution profile in 5 days regeneration (suggested by the supplier), a plateau was reached after 1 day, indicating that 5 days were not necessary for the regeneration of the Zeoclere30 (Figure 4.3).



**Figure 4.3 Ammonium ion elution profile in the NaCl 10% regenerant solution recirculated in upflow mode across the Zeoclere30 fixed bed for 5 days.**

## 4.4 Discussion

The suitability of Zeoclere30 to remove ammonium from secondary effluent wastewater was investigated in an ion exchange (IEX) demonstration plant (10 m<sup>3</sup>/day). Zeoclere30 could potentially replace Zeolite-N in existing IEX plants, as the latter is no longer available in the market. Zeoclere30 was tested under the existing IEX plant design specifications: an EBCT of 5 min [38] and sodium chloride (NaCl) or potassium chloride (KCl) as regenerants [34]. The maximum ammonium exchange capacity of Zeoclere30 in municipal wastewater (13.1±2.5 mg NH<sub>4</sub><sup>+</sup>-N/L) was 3.7 mg NH<sub>4</sub><sup>+</sup>-N/g media (0.2 meq NH<sub>4</sub><sup>+</sup>-N/g media) (Figure 4.1). In literature, according to the initial concentration (7-300 mg NH<sub>4</sub><sup>+</sup>-N/L), the ammonium exchange capacity of the clinoptilolite ranges between 0.36 and 12 mg NH<sub>4</sub><sup>+</sup>-N/g media (0.02-0.67 meq NH<sub>4</sub><sup>+</sup>-N/g media) [28], [34]. The ammonium exchange capacity of Zeoclere30 was substantially lower than the maximum value reported by the supplier in synthetic solution (NH<sub>4</sub>Cl 10%) which is 21.6-27 mg NH<sub>4</sub><sup>+</sup>-N/g media (1.2-1.5 meq NH<sub>4</sub><sup>+</sup>-N/g media) [16]. This reduction can be caused by the presence of competitive ions in wastewater which can affect the ammonium exchange capacity of the media [39]. In previous studies, the presence of multi-component matrix caused a decrease in the ammonium exchange capacity of natural zeolite up to 80% [34]. On the other hand, the ammonium exchange capacity of synthetic zeolites such as Zeolite-N is reported to be reduced by maximum 30% when comparing multi-component and mono-component solution [34]. Natural clinoptilolites present octahedrally coordinated Al<sup>3+</sup> while the synthetic zeolites present tetrahedrally coordinated Al<sup>3+</sup>, which results in increased selectivity and ammonium exchange capacity [20].

Another important parameter to ensure high ammonium exchange capacity is the contact time between the wastewater and the media bed which is the time allowed for the ion exchange reaction [40]. While synthetic zeolites have been used at an EBCT of 1-15 minutes [34], natural zeolites usually require longer EBCT, ranging from 15 to 30 minutes with higher ammonium exchange capacity resulting from longer EBCT [41]. For this reason, it is suggested a more detailed study of the ammonium exchange capacity of the Zeoclere30 at longer EBCT. However, it is important to notice that



longer EBCT would require an adaptation of existing IEX infrastructure, such building multiple columns, increasing capital costs.

The results obtained from this study showed a regeneration efficiency (RE) of Zeoclere30 of maximum 29% with 10 BV of KCl 10% (Figure 4.1). Even lower values (max RE of 6%) were registered for the regeneration with NaCl 10% (Figure 4.2) both at pH 7 and 10. Interestingly, an increase in the  $Q_{reg}$  was detected in cycles 4-6 and 10-12 (Figure 4.2). In these cycles, the regenerant brines recovered the ammonium already present on the media surface which, however, was not efficient enough to ensure an increase in the ammonium exchange capacity of the media as evident by the fact that the  $Q$  of the Zeoclere30 did not increase. A drop in the  $Q$  was detected at cycle 8 indicating that the media had almost reached saturation. The capacity of being regenerated multiple times to restore the initial capacity is a crucial property of ion exchangers. From the literature, it is known that clinoptilolite can be regenerated with an efficiency ranging between 50-60% [28], [38], compared to synthetic zeolites, such as Zeolite-N, which can be regenerated with efficiency >95% [1]. The low regeneration efficiency of Zeoclere30 was potentially due to the incorrect regeneration operation. According to the supplier of Zeoclere30, in fact, the optimal regeneration of this media is obtained by adding 14-15% hypochlorite solution to the media bed and leaving the solution for 12-24 hours [31] or by leaving the media for 5 days in NaCl 10% solution at ambient temperatures [16]. The use of hypochlorite would represent a drawback to the implementation due to the possibility of corrosion of the ion exchange plant and the production of a hazardous waste. Moreover, the use of hypochlorite could limit the possibility of ammonium recovery from the saturated solution. On the other hand, the regeneration in NaCl was not efficient. Moreover, when analysing the ammonium elution profile over 5 days of regeneration with NaCl 10%, a plateau was reached after 1 day (Figure 4.3). To increase the regeneration efficiency, further studies should investigate the use of regenerant brine with pH above 10 [28] as well as the use of higher volumes of regenerant. In fact, in this study, 2 BV of brine were used, as the Zeoclere30 supplier suggests to use enough brine to cover the media bed. However, studies on the clinoptilolite regeneration have highlighted the need for 10-20 BV of regenerant to obtain 100% regeneration efficiency [42]. Such volumes, combined with the need of longer EBCT, would require an adaptation of the already existing

infrastructure to the new ion exchange media and potentially limit the continued operation of existing plants. Nevertheless, the availability in the market of Zeoclere30 and the low cost of production could justify future effort to test this media in different demonstration plant configurations.

## 4.5 Conclusion

- Zeoclere30 presented maximum ammonium exchange capacity of 3.7 mg  $\text{NH}_4^+\text{-N/g}$  media (0.21 meq  $\text{NH}_4^+\text{-N/g}$  media) in municipal wastewater. The maximum value reported by the supplier in synthetic solution ( $\text{NH}_4\text{Cl}$  10%) is 21.6-27 mg  $\text{NH}_4^+\text{-N/g}$  media (1.2-1.5 meq  $\text{NH}_4^+\text{-N/g}$  media) which proved the low selectivity for the ammonium in presence of competitive ions.
- The Zeoclere30 was tested at an EBCT of 5 minutes. However, longer EBCT (20-30 minutes) is usually used for natural zeolites and it should be tested to allow for a more efficient ammonium removal.
- The maximum regeneration efficiency of Zeoclere30 was 28%. Regeneration efficiency could be optimised by regenerating the media with 14-15% hypochlorite, according to the supplier indication and by increasing the bed volumes needed for the regeneration (10-20 BV). This however could damage existing infrastructure or lead to the production of hazardous chemical waste.
- A sever adaptation of the already existing infrastructure is needed for the use of Zeoclere30 as ion exchanger for ammonium removal. However, a suitable balance between capital (adding more IEX columns) and operational costs (media and regenerant costs) needs to be taken into consideration together with environmental impacts.

## 4.6 References

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## 5. COMPARISON OF METHODS TO RECOVER AMMONIA FROM BRINE GENERATED FROM WASTEWATER TREATMENT THROUGH ION EXCHANGE PROCESS

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### Abstract

Three different technologies were compared to recover ammonia (NH<sub>3</sub>) from ion exchange (IEX) regeneration brines: hollow fibre membrane contactor (HFMC), vacuum thermal stripping with rotary evaporator (VTS) and multi-component equipment vacuum thermal stripping (MVTs). The ammonia recovery efficiency (R<sub>NH<sub>3</sub></sub>), the ammonia losses and the purity of the recovered product were chosen as indicators of the competence of the technologies. When treating saturated IEX brine, the highest value of mass transfer coefficient (K<sub>L</sub>a) of HFMC, MVTs and VTS were 0.6 h<sup>-1</sup>, 0.7 h<sup>-1</sup> and 0.1 h<sup>-1</sup>, respectively, compared to 3.5 h<sup>-1</sup>, 1.7 h<sup>-1</sup> and 1.96 h<sup>-1</sup> when treating the synthetic solution (at pH=10). The highest ammonia recovery from IEX brine was obtained with the HFMC (99.8%), in comparison to 44% in MVTs and 19% in VTS. Additionally, higher rate of ammonia loss (J<sub>NH<sub>3</sub> loss</sub>) was measured at the VTS (24 mg/h) compared to the MVTs (15 mg/h). Concentrated ammonia solution was obtained by treating IEX brine with the MVTs and VTS with a concentration of 3.1 and 0.5 g NH<sub>4</sub><sup>+</sup>-N/L, respectively. The difference in concentration was connected to the higher water flux in the VTS (J<sub>H<sub>2</sub>O</sub> = 147 g/h) compared to the water flux in MVTs (J<sub>H<sub>2</sub>O</sub> = 51 g/h). Considering the higher recovery rate, the HFMC was selected as the most suitable method for the management of the saturated IEX brine. This method also

allowed for the recovery of ammonium sulphate which can be used as fertiliser. However, the high solubility of this product requires an investigation into the use of different acids to obtain a more stable product.

### **Keywords**

Ammonia recovery; ion exchange; regenerant brine; stripping; membrane; liquid-gas-liquid mass transfer.

## 5.1 Introduction

Ammonium ( $\text{NH}_4^+$ ) is the inorganic ion form of the majority of nitrogen (N) contained in municipal and industrial wastewater and its concentration can be efficiently reduced by using the ion exchange (IEX) process to achieve effluent concentrations  $<0.5 \text{ mg NH}_4^+\text{-N/L}$  [1]–[3]. However, the implementation of the process at full-scale is limited by the production of a highly concentrated brine, the management of which represents a significant environmental and economic challenge [4], [5]. In fact, if not effectively managed, the saturated regenerant has to be discarded as a hazardous waste with the high costs of the disposal (typically £65/ton) being economically prohibitive in the long-term [6]. For this reason, the conversion of brine waste to a usable resource has recently been investigated [7]. In particular, the possibility to recover ammonia ( $\text{NH}_3$ ) from the saturated brine allows for its reuse multiple times thus decreasing the chemical consumption [8]. Ammonia in the saturated brine exists in equilibrium between the ammonium ion ( $\text{NH}_4^+$ ) and free ammonia ( $\text{NH}_3$ ) [9]:



High values of pH and temperature will move the equilibrium to the left hand side with all the ammonia present as in its molecular form which is volatile and hence can be removed as ammonia gas [9] (Equation 5.2-5.3 [10]):

$$\alpha_{\text{NH}_3} = \frac{1}{1 + 10^{\text{pK}_a^s - \text{pH}}} \quad \text{Equation 5.2}$$

$$\text{pK}_{a,T}^s = \text{pK}_{a,298}^s + (0.0324(298 - T)) \quad \text{Equation 5.3}$$

where  $\alpha_{\text{NH}_3}$  is the fraction that is free ammonia within the total ammonia solution,  $\text{pK}_a^s$  is the negative logarithm of stoichiometric acid hydrolysis constant of ammonium ion,  $\text{pK}_{a,T}^s$  and  $\text{pK}_{a,298}^s$  are values of  $\text{pK}_a^s$  at temperature T and 298 K, respectively [10]. At pH 7 (typical pH in secondary wastewater [11]) almost 100% of the ammonium will be in ionic form ( $\text{NH}_4^+$ ) while, with an increase in the alkalinity of the solution, the molecular form  $\text{NH}_3$  becomes predominant with 100% of the  $\text{NH}_3$  present at pH 11 [3].

Removal of the free ammonia ( $\text{NH}_3$ ) through gas stripping can be accomplished in a number of technologies such as vacuum thermal stripping (VTS) and liquid-liquid membrane contactors (hollow fibre membrane contactor, HFMC) [12], [13]. These allow for the ammonia recovery from highly concentrated solutions as a high-purity product [10], [12], [14], [15].

The thermal stripping of the ammonia is obtained by increasing the temperature of the saturated solution, this causes more turbulence and reduces the boundary layer at the surface of the solution thus increasing ammonia mass transfer [10]. The boiling temperature can be reduced by applying a vacuum [16] thus reducing energy cost [17]. Vacuum thermal stripping (VTS) can be coupled with distillation to recover the stripped gas [14] where a cold solution is recirculated to cool the vapour (distillate) back into a liquid [18], [19]. With this procedure, ammonia gas ( $\text{NH}_{3(g)}$ ) can be recovered as aqueous ammonia ( $\text{NH}_{3(aq)}$ ), which is a valuable chemical widely used in plastics and textile manufacturing, food production and cleaning industry [20]. Alternatively, an acid reaction vessel can be incorporated in the process to recover a stable ammonium salt [21]. For example, by using sulfuric acid, ammonium sulphate ( $\text{NH}_4)_2\text{SO}_4$  has been recovered from raw hydrolysed and struvite-recovered urine (pH 9.2) [16] (boiling point of 65 °C and pressure of 270 mbar) as well as from anaerobically digested municipal sludge and dairy manure (pH 9) with a high recovery efficiency of up to 96% [10]. The process is commonly modelled as a first order rate process with a stripping rate coefficient of 0.1–0.2  $\text{h}^{-1}$  [14]. In laboratory scale experiments, vacuum thermal stripping of a saturated ammonia solution has been obtained with a rotary evaporator with recovery efficiency around 80% [22]. Rotary evaporators integrate the different components (vertical condenser, heating bath with for feed solution, receiving flask for recovered condensate, a vacuum pump and controller) in a single piece of equipment [19]. Practical vacuum thermal stripping is typically accomplished with independent stages from evaporation and distillation to provide better control (temperature and pressure) and ease of scale up (multi component vacuum thermal stripping, MVTTS).

The highly concentrated regenerant brine obtained in the IEX process is also suitable for treatment with hollow fibre liquid-liquid membrane contactors (HFMC) [23].

In this technology, the high pH (>9) of the brine favours the formation of free ammonia gas ( $\text{NH}_3(\text{g})$ ) which diffused through the gas filled microporous hydrophobic pores of the membrane, from the shell-side to the lumen-side [24]. Here, a strong acid solution promotes the precipitation of ammonia salts such as ammonium sulphate [24], ammonium nitrate or di-ammonium phosphate [25]. These salts can have application in the fertiliser industry according to their purity level [26]. Previous studies have used the HFMC to recover ammonia from wastewater (pH 11-12, initial concentration of 772 mg  $\text{NH}_4^+\text{-N/L}$ ) [27] as well as from concentrates formed during zeolite regeneration (2.1–2.7 g  $\text{NH}_3/\text{L}$ , pH 11-12) [23] with recovery efficiency higher than 98-99%. By recirculating the saturated brine multiple times around the membrane unit, it is possible to increase the liquid-gas-liquid mass transfer [28] while preventing the dispersion of one phase within another thanks to the hydrophobic nature of the pores of the membrane [24]. Membrane contactors are relatively simple to use, make the process rapid and more efficient as well as reduce the overall footprint due to the high specific surface area of the membrane at almost 10000  $\text{m}^2/\text{m}^3$  [22], [23]. Commonly, sulphuric acid is used to recover ammonium sulphate [24]. However, due its high solubility in water (75.13 g/100 g  $\text{H}_2\text{O}$  at 20°C), the recovered product can require evaporation of the acid solution and needs accurate control of the transport of water across the membrane [17].

To date, there have only been a few papers investigating ammonium recovery technologies for the management of saturated brine used for zeolite regeneration in wastewater treatment [4], [29], [30]. Further, no papers have, as yet, provided a comparison of (M)VTS and HFMC to enable a discussion of their relative suitability and prospects for use with ion exchange systems for the recovery of ammonia from wastewater. Therefore, the aim of this work was to compare trials treating two batches of ion exchange regenerant, one using a HFMC and the other (M)VTS systems to enable a direct comparison to be discussed. In both cases, a combination of synthetic and real brines was treated under conditions previously outlined as optimum for each technology. The results were then compared to assess the relative potential of the different options and offer a perspective on future outlook and development.

## 5.2 Materials and methods

### 5.2.1 Synthetic solutions

For the experiments using the HFMC, a synthetic ammonia solution was prepared diluting ammonium chloride ( $\text{NH}_4\text{Cl}$ , Fisher Chemicals, Loughborough, UK) in deionized water to obtain a solution with a concentration of 1000 mg  $\text{NH}_4^+\text{-N/L}$  and a pH that was adjusted between of 7-11 by adding sodium hydroxide. For the VTS and MVTs trials, the synthetic ammonia solution was prepared by diluting a stock solution (Ammonia 88532 – 34% sol., Woburn Chemical Ltd, Milton Keynes, UK) to the required concentration ( $564\pm 8$  mg  $\text{NH}_4^+\text{-N/L}$ ) at a pH of 10. The ammonia concentration and the chemical composition of the synthetic solution were chosen to simulate the real brine used at laboratory and demonstration scale.

### 5.2.2 Regenerant brine

For the HFMC experiments, regenerant brine was produced using sodium chloride in deionized water ( $\text{NaCl}$ , 10% wt., Fisher Chemicals, Loughborough, UK). The brine was used multiple times for the regeneration of an ion exchange (IEX) media (synthetic zeolite, Zeolite-N) in a laboratory scale fix-bed column filled with 50 mL of media. The IEX media was operated with municipal wastewater containing 25-50 mg  $\text{NH}_4^+\text{-N/L}$  to a breakthrough of 3 mg  $\text{NH}_4^+\text{-N/L}$  at an empty bed contact time (EBCT) of 10 minutes. A single batch of brine (10 bed volumes, BV) was reused 4 times in succession to regenerate the Zeolite-N at 10 minute EBCT up to a concentration of 890 mg  $\text{NH}_4^+\text{-N/L}$ . After each regeneration cycle, a calcium precipitate (calcium carbonate) was recovered by addition of soda ash (results not showed in this paper) from the IEX brine to avoid the build-up of calcium ions in the brine which could interfere with the media regeneration. The pH was increased to 11 with  $\text{NaOH}$  prior to treating the brine with the HFMC to adjust the fraction of free ammonia.

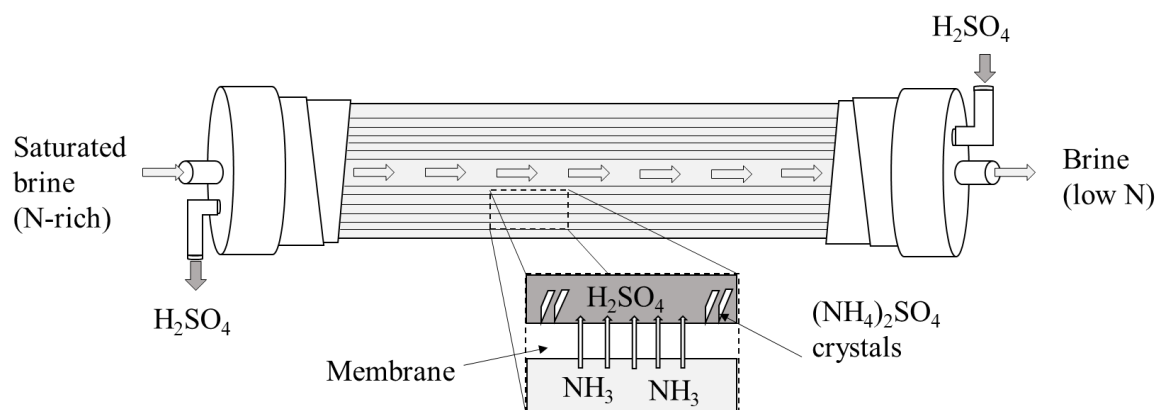
For the VTS and MVTs experiments, the regenerant brine was produced using potassium chloride in deionized water ( $\text{KCl}$  10% wt., Easy Chemicals Ltd, Denbigh, UK). The  $\text{KCl}$  brine was used multiple times for the regeneration of a column filled with Zeolite-N in a demonstration scale plant ( $10 \text{ m}^3/\text{day}$ ) until a concentration of around 580 mg  $\text{NH}_4^+\text{-N/L}$  was reached. The IEX media was operated in municipal wastewater

containing 13-20 mg  $\text{NH}_4^+\text{-N/L}$  to a breakthrough of 5 mg  $\text{NH}_4^+\text{-N/L}$ ; the media was regenerated 6 consecutive times by passing 10 bed volumes of KCl 10% through the column for 2 hours (13 min EBCT). The pH was adjusted to 10 with NaOH prior to the stripping experiments. A chemical characterization of the KCl brine revealed that the main compounds present in solution were potassium (47.6 g  $\text{K}^+\text{/L}$ ), calcium (1.2 g  $\text{Ca}^{2+}\text{/L}$ ) and ammonium (0.82 g  $\text{NH}_4^+\text{-N/L}$ ). The brine also presented magnesium and silicon (45.1 mg  $\text{Mg}^{2+}\text{/L}$  and 7.2 mg  $\text{Si}^+\text{/L}$ ) and traces of heavy metals (0.7-37  $\mu\text{g/L}$ ).

### **5.2.3 Ammonia recovery with HFMC**

#### **5.2.3.1 Equipment set up**

A commercial hollow fibre membrane contractor (HFMC) (Liqui-Cel® 1.7x5.5 MiniModule®, Membrana GmbH, Wuppertal, Germany) was used to strip ammonia from the concentrated solutions by contacting it with an acid stripping solution (sulfuric acid 2% wt., Fisher Chemicals, Loughborough, UK) (Figure 5.1). The HFMC comprised 7400 hydrophobic micro-porous propylene membrane fibres with inner and outer diameters of 220 and 300  $\mu\text{m}$ , respectively, a surface area of 0.79  $\text{m}^2$ , a mean pore diameter of 0.03  $\mu\text{m}$  and an effective length of 0.11 m. Flows were induced by two identical centrifugal pumps (Flojet HPR6/8, PS Components, Ontario) and controlled using four needle valves on the inlet and outlet of the HFMC shell and lumen (Platon, Domont, France). Sulfuric acid 2% was circulated through the fibre lumen at a flow of 40 mL/min while the ammonia-rich solution was fed counter-currently in the HFMC shell at a flow of 900 mL/min. Samples were taken from in-line luer-lock stop-cock valves (Cole-Parmer, USA) using a 5 mL syringe. The ammonium sulphate formed during transfer of  $\text{NH}_3$  from used brine to sulfuric acid was recovered by evaporation of the neutralised sulfuric acid solution after the recovery process.



**Figure 5.1 Schematic representation of hollow fibre membrane contactor (HFMC) used for ammonia recovery as ammonium sulphate.**

### 5.2.3.2 Operational set up

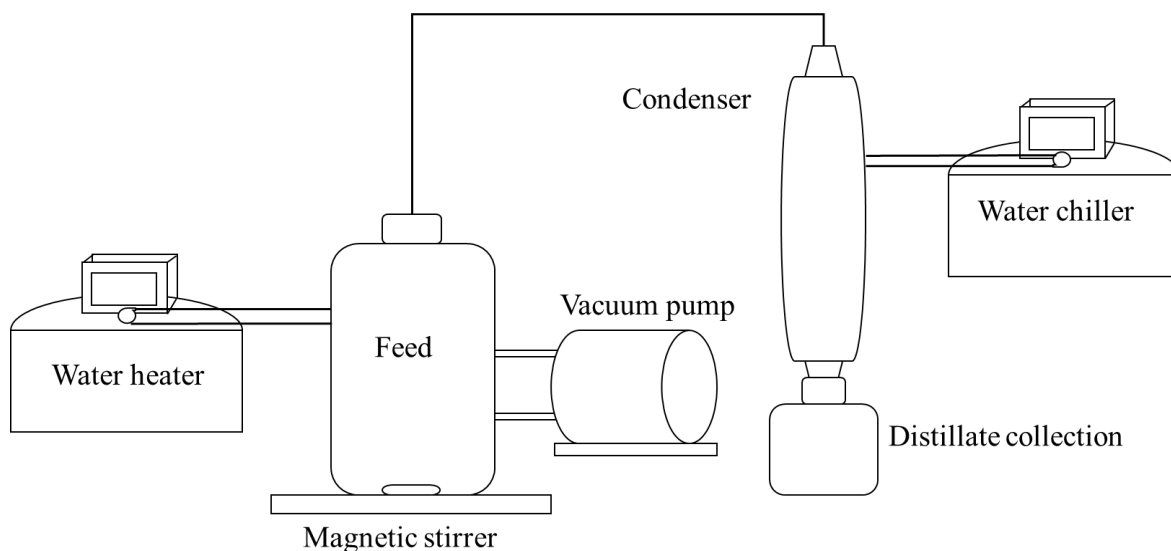
The experiments with the HFMC were performed first with synthetic brine to test the influence of pH and number of recirculations across the membrane on the ammonia recovery. The synthetic brine (1L), at different pH (7-11), was recirculated up to 100 times ( $N=100$ ). For the experiment with saturated IEX brine, the solution (pH=11) was recirculated up to 360 times. The experiments were conducted in duplicate.

## 5.2.4 Ammonia recovery with MVTs

### 5.2.4.1 Equipment set up

The multiple component vacuum thermal stripping (MVTs) system was tested using separated equipment for each step of the recovery process (Figure 5.2). This included: 500 mL evaporating flask for feed solution with heating jacketed – supplied by a recirculating water heater (MPC-K6, Huber, Offenburg, Germany) – and agitated using a magnetic stirrer (SB151, Stuart, Stone, UK) to distribute heat through the boiling solution. The surface area for evaporation was approximately  $8.0 \times 10^{-3} \text{ m}^2$  and the area-volume ratio was  $16 \text{ m}^2 \text{ m}^{-3}$ . The system also included a vacuum pump (ME-1C, Vacuubrand, Wertheim, Germany) and a vertical condenser (Inland Revenue Condenser, Scilabware Ltd., Stoke-on-Trent, UK) with surface area of  $2.5 \times 10^{-2} \text{ m}^2$  supplied with a recirculating water chiller (LT Ecocool 150, Grant Instruments, Cambridge, UK).





**Figure 5.2 Schematic representation of apparatus for vacuum thermal stripping including different components (MVTs).**

#### **5.2.4.2 Operational set up**

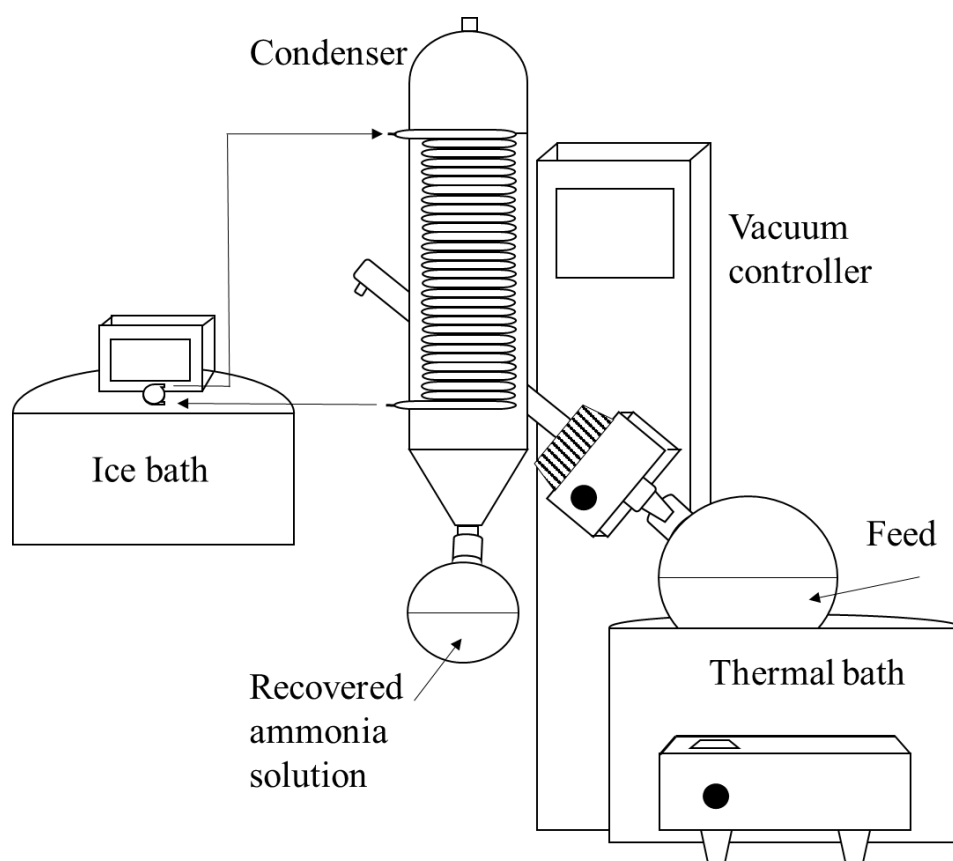
The operational set up of the experiments at the MVTs were chosen according to previous studies where the highest recovery was obtained by boiling the concentrated solution at 65-70°C and 250-280 mbar [14], [17]. Both synthetic solution and IEX brine (500 mL) were stabilized at  $T=69^{\circ}\text{C}$  and  $p=280\pm 5$  mbar for 30 minutes. The pressure was then decreased to  $p=250\pm 5$  mbar for 45 minutes while mixing at 920 rpm with  $T=69^{\circ}\text{C}$ . Vapour produced during boiling was drawn through a condenser supplied with 5°C water. At the end of each experiment, the final volume and the ammonia (as  $\text{NH}_4^+\text{-N}$ ) concentration were measured in both the treated and the recovered solution. All experiments were conducted in duplicate.

### **5.2.5 Ammonia recovery with VTS**

#### **5.2.5.1 Equipment set up**

The vacuum thermal stripping (VTS) system was also tested by using a rotary evaporator (Rotavapor R-200, Buchi Ltd, Oldham, UK) (Figure 5.3). This equipment included: a vertical condenser with condensing area of 0.15 m<sup>2</sup> (according to the supplier), an heating bath with a digital display, 1L evaporating flask for feed solution (approximately  $23\times 10^{-3}$  m<sup>2</sup> area for stripping), 500 mL receiving flask for the

recovered solution, a vacuum pump, and a pressure controller with a digital display. Additionally, an ice bath (Grant TC120, Grant Instruments Ltd, Cambridge, UK) was connected to the condenser to cool down the water. For all the experiments, the liquid feed was approximately 1L.



**Figure 5.3 Schematic representation of rotary evaporator used for ammonia recovery as concentrated solution through vacuum thermal stripping.**

### **5.2.5.2 Operational set up**

The temperature of the synthetic brine was set to 80°C and stabilised for 30 minutes at a vacuum pressure ( $p$ ) of 300±5 mbar reflecting the optimal temperature previously reported for the treatment of concentrated ammonia solution using a rotary evaporator [22]. The pressure was then decreased to 250±5 mbar [14] using the pressure controller monitors and the ammonia was recovered for 45 minutes, while mixing the feed solution at 200 rpm. During this experiment, the temperature of the water pumped into the condenser was kept between 3-7°C with a circulating ice bath thus allowing for a  $\Delta T$  of 73-77°C between the thermal bath and the condenser. The same

operational condition were used for the treatment of the IEX brine. All the experiment were conducted in duplicate.

### 5.2.6 Data analysis

The stripping process is based on the transfer of ammonia from the liquid phase to the gas phase [13] following Fick's first law of diffusion as expressed by the Lewis-Whittman model Equation 5.4 [17]:

$$\frac{dC}{dt} = -K_L a (C - C_s) \quad \text{Equation 5.4}$$

where  $dC/dt$  is the rate of ammonia mass transfer (mg/L),  $K_L$  is the overall liquid-phase mass transfer coefficient (m/h),  $a$  is the area-volume ratio of the liquid (1/m),  $C$  is the concentration of free ammonia in liquid (mg/L) and  $C_s$  is the saturation concentration of free ammonia in liquid (mg/L) [9], [17]. Considering the ammonia concentration at time  $t=0$  ( $C_0$ , mg/L) and at time  $t$  ( $C_t$ , mg/L), Equation 5.4 can be rewritten as in Equation 5.5 [14], [17], [28]

$$t = -\frac{1}{K_L a} \ln\left(\frac{C_t}{C_0}\right) \quad \text{Equation 5.5}$$

which shows that a decrease in  $K_L a$  (1/h) leads to an increase in stripping time required to obtain a desired final ammonia concentration. Additionally, Equations 5.6-5.11 [31], [32] were used for the VTS and MVTs:

$$\Delta T = T_{\text{thermal bath}} - T_{\text{condenser}} \quad \text{Equation 5.6}$$

$$R_{\text{NH}_3} = \left( \frac{C_0 V_0 - C_t V_t}{C_0 V_0} \right) \times 100\% \quad \text{Equation 5.7}$$

$$J_{\text{H}_2\text{O}} = \frac{\Delta m_{\text{H}_2\text{O}}}{\Delta t} \quad \text{Equation 5.8}$$

$$C_{\text{loss,t}} V_{\text{loss,t}} = C_0 V_0 - C_t V_t - C_{\text{rec,t}} V_{\text{rec,t}} \quad \text{Equation 5.9}$$

$$J_{\text{NH}_3 \text{ loss}} = \frac{C_0 V_0 - C_t V_t - C_{\text{rec},t} V_{\text{rec},t}}{\Delta t} \quad \text{Equation 5.10}$$

$$J_{\text{NH}_3 \text{ rec}} = \frac{C_0 V_0 - C_t V_t - C_{\text{loss},t} V_{\text{loss},t}}{\Delta t} \quad \text{Equation 5.11}$$

where  $\Delta T$  is the difference in temperature between the thermal bath and the condenser ( $^{\circ}\text{C}$ );  $R_{\text{NH}_3}$  is the ammonia stripping efficiency (%),  $J_{\text{H}_2\text{O}}$  is the water flux recovered (g/h),  $\Delta m_{\text{H}_2\text{O}}$  (g) is the mass of water transferred from the brine to the condensate during the period  $\Delta t$  (h),  $J_{\text{NH}_3 \text{ loss}}$  and  $J_{\text{NH}_3 \text{ rec}}$  are the rate of ammonia loss and recovered (g/h),  $V_0$ ,  $V_t$  are the volumes of the brine at time  $t=0$  and time  $t$  (L) respectively,  $C_{\text{rec},t}$  and  $V_{\text{rec},t}$  are the concentration (mg/L) and volume (L) of the recovered solution at time  $t$ ,  $C_{\text{loss},t}$  and  $V_{\text{loss},t}$  are the concentration (mg/L) and the volume (L) of ammonia loss at time  $t$ ,  $C_t$  and  $C_0$  are the same as in equation 5.5.

### 5.2.7 Chemical analysis

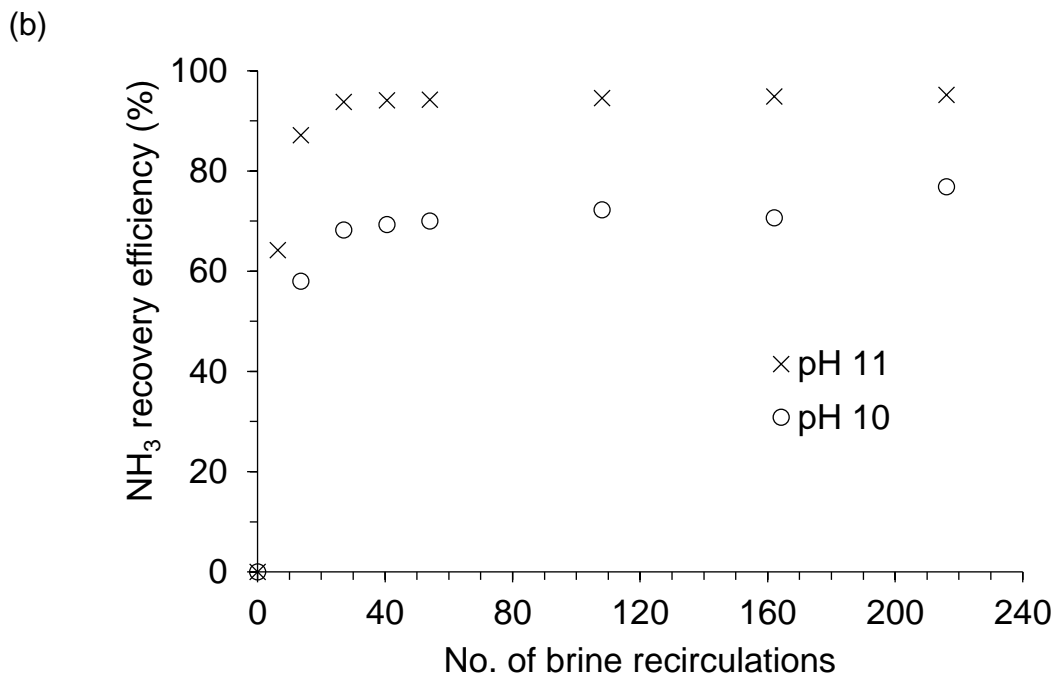
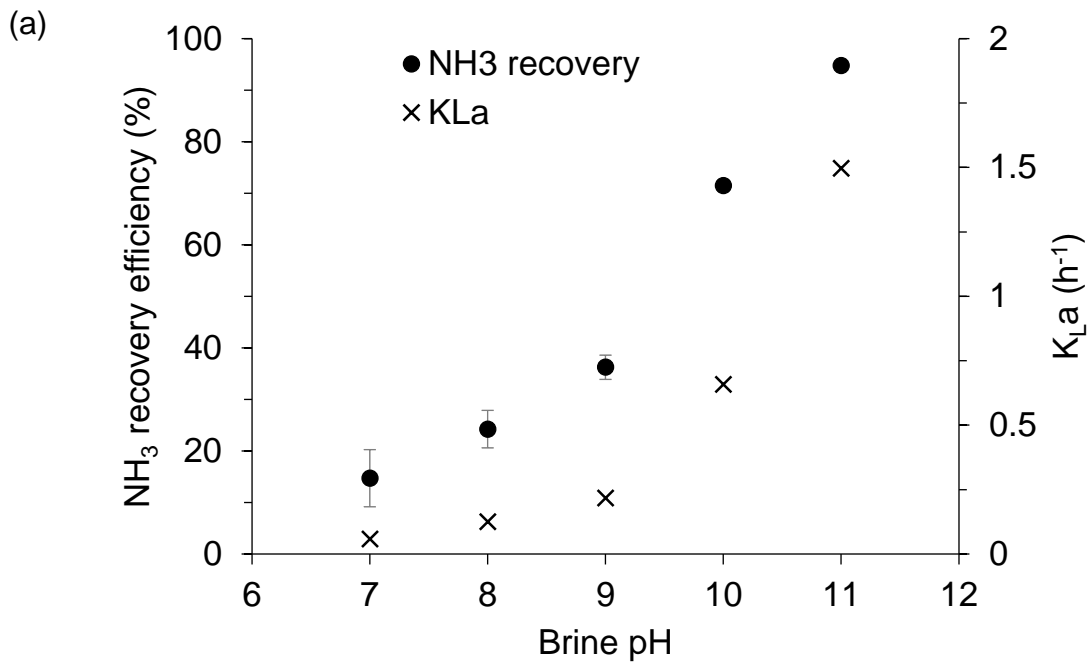
The ammonia concentration in the brine was measured with the Smartchem200 (AMS Alliance, France). The IEX brine and the recovered ammonia solution were analysed for heavy metals with the inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer NexION 450D). The chemical characterization of the product recovered from the IEX brine with the membrane was analysed with a scanning electron microscopy (SEM, Tescan Vega 3, large chamber, Kohoutovice, Czech Republic) including energy-dispersive X-ray spectroscopy (EDX). The pH was monitored using a pH meter (Jenway 3510 pH and conductivity meter, Camlab, UK).

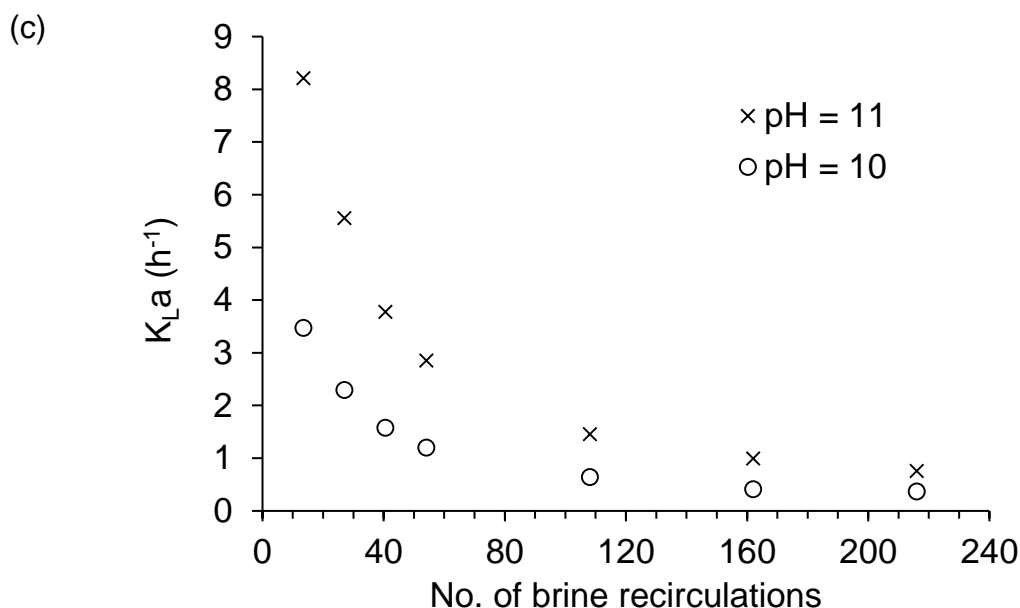
## 5.3 Results

### 5.3.1 Ammonia recovery with HFMC

#### 5.3.1.1 Effect of the pH and number of recirculations of synthetic brine in HFMC

The capability of HFMC to transfer ammonia from the synthetic brine was examined as a function of the brine pH, after 100 recirculations across the membrane (Figure 5.4a). The  $K_{La}$  increased with increasing pH with the highest value of  $1.5 \text{ h}^{-1}$  at  $\text{pH}=11$  which decreased to  $0.7 \text{ h}^{-1}$  at  $\text{pH}=10$ . These corresponded to ammonia recovery efficiencies after 100 recirculation of 95% and 72% respectively. Comparison to lower pH levels of 7-9 revealed significantly reduced recovery efficiencies of 15-36% corresponding to  $K_{La}$  values of  $0.1\text{-}0.2 \text{ h}^{-1}$ . The results confirmed the importance of pH as it controls the percentage of ammonia that exists as free ammonia available to be stripped [3]. Further investigation into the impact of the number of recirculations revealed pseudo stable removal levels occurred after only 27 cycles with recovery efficiencies of 68% and 94% at pH 10 and 11 respectively (Figure 5.4b). This corresponded to a 4 second residence time per pass for the brine flow and 30 minutes of operation overall. Extending the number of cycles did not significantly affect the ammonia recovery efficiency which were 77% and 95% after 216 cycles. The corresponding mass transfer coefficients decreased as a function of the number of cycles reflecting the decrease in transfer gradients as the ammonia was removed from the solution. To illustrate, the  $K_{La}$  decreased from  $3.5 \text{ h}^{-1}$  after 13 cycles down to  $0.37 \text{ h}^{-1}$  after 215 cycles when operated at pH 10 (Figure 5.4c). In comparison, operation at pH 11 resulted in a decrease of  $K_{La}$  from  $8.2 \text{ h}^{-1}$  to  $0.76 \text{ h}^{-1}$  for the same cycle numbers. Overall, this demonstrated the significance in a unit change in pH resulting in a doubling of the mass transfer coefficient.

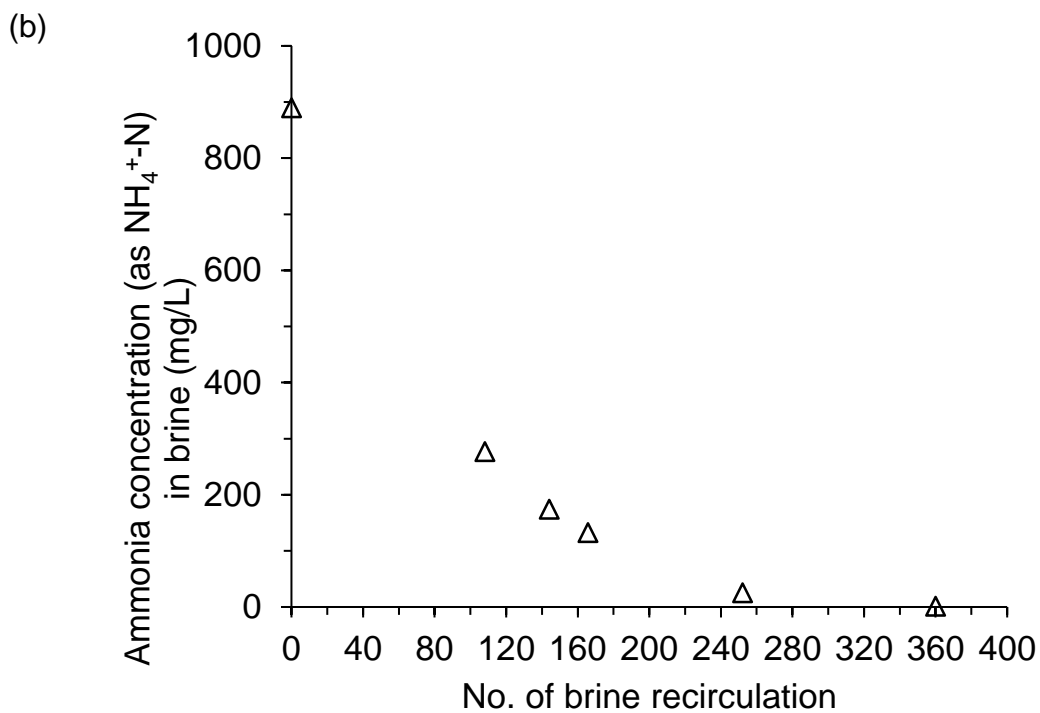
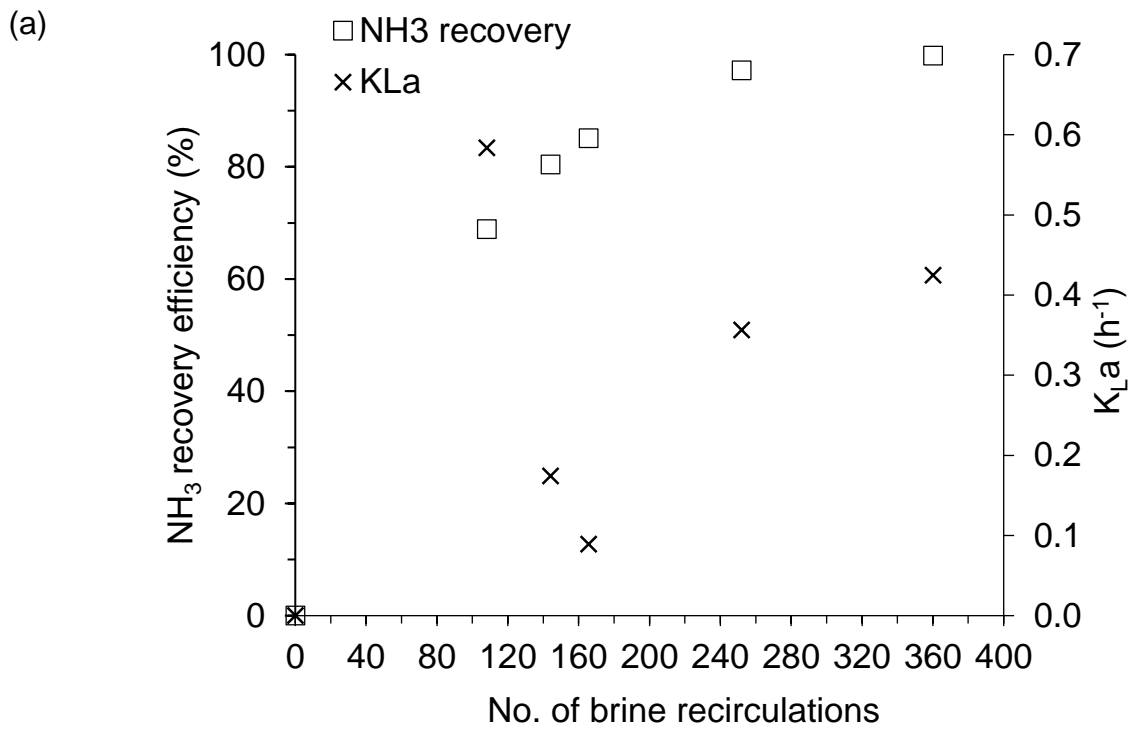




**Figure 5.4 Effect of (a) pH of the synthetic brine ( $C_{in} = 1000 \text{ mg NH}_4^+\text{-N/L}$ , 100 recirculation), and (b) number of recirculations of the synthetic brine (pH = 10 and 11) across membrane on  $\text{NH}_3$  recovery efficiency and (c) on mass transfer coefficient ( $K_{La}$ ,  $h^{-1}$ ).**

### 5.3.1.2 Ammonia recovery efficiency from IEX brine through HFMC

Treatment of the IEX brine (NaCl 10%, pH 11) resulted in a significantly different result (Figure 5.5). The ammonia recovery efficiency increased from 68.8% after 108 cycles up to 99.8% (complete recovery) after 360 cycles corresponding to a total operating time of 6.7 hours. The initial ammonia concentration of 890 mg  $\text{NH}_4^+\text{-N/L}$  was reduced down to 132 mg  $\text{NH}_4^+\text{-N/L}$  after 165 cycles and 25 mg  $\text{NH}_4^+\text{-N/L}$  after 250 cycles. The mass transfer coefficients ( $K_{La}$ ) were substantially lower than observed in the synthetic experiments and ranged between 0.09 and 0.58  $h^{-1}$  (Figure 5.5a). These levels were lower than the minimum observed before at 0.76  $h^{-1}$  with synthetic brine (Figure 5.4c) thus indicating that other ions present in the real regenerant brine have an impact on the ammonia recovery compared to the mono-component synthetic solution.



**Figure 5.5 (a) Impact of brine recirculations across the HFMC upon recovery of ammonia and overall mass transfer coefficient ( $K_{La}$ ) (b) and ammonia (as  $NH_4^+-N$ ) concentration in the treated brine.**



### 5.3.1.3 Ammonium sulphate recovered from HFMC

The dissolved ammonium sulphate that accumulated within the acid phase following contact with the used brine within HFMC was recovered as a solid product by evaporation of the acid phase (Figure 5.6a-b). The identity of the product was confirmed by EDX analysis and comparison of the pattern with literature data revealed a good purity product. Only elements comprising ammonium sulphate (atomic %: N=25.5%, O=55.6% and S=18.8%) were detected and in proportions close to that expected from the chemical formula of ammonium sulphate (atomic %: N=28.6%, O=57.1% and S=14.2%).

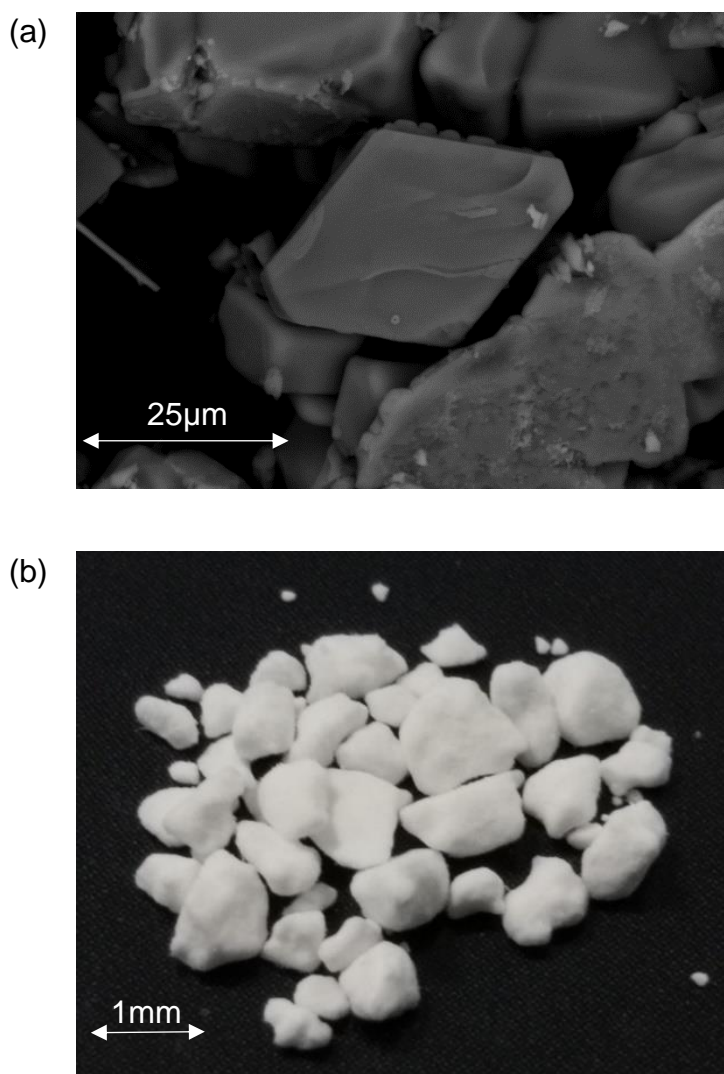


Figure 5.6 (a) SEM image of recovered crystalline product following dehydration from solution; (b) dried ammonium sulphate recovered from ion exchange (IEX) brine (NaCl 10%).

### 5.3.2 Ammonia recovery from synthetic and real solution with MVTs

Figure 5.7 compares the results of the MVTs in terms of rate of ammonia loss ( $J_{\text{NH}_3 \text{ loss}}$ ) and recovered ( $J_{\text{NH}_3 \text{ rec}}$ ) and the flux of recovered water ( $J_{\text{H}_2\text{O}}$ ) for synthetic and IEX brine at  $t=0.75\text{h}$ .

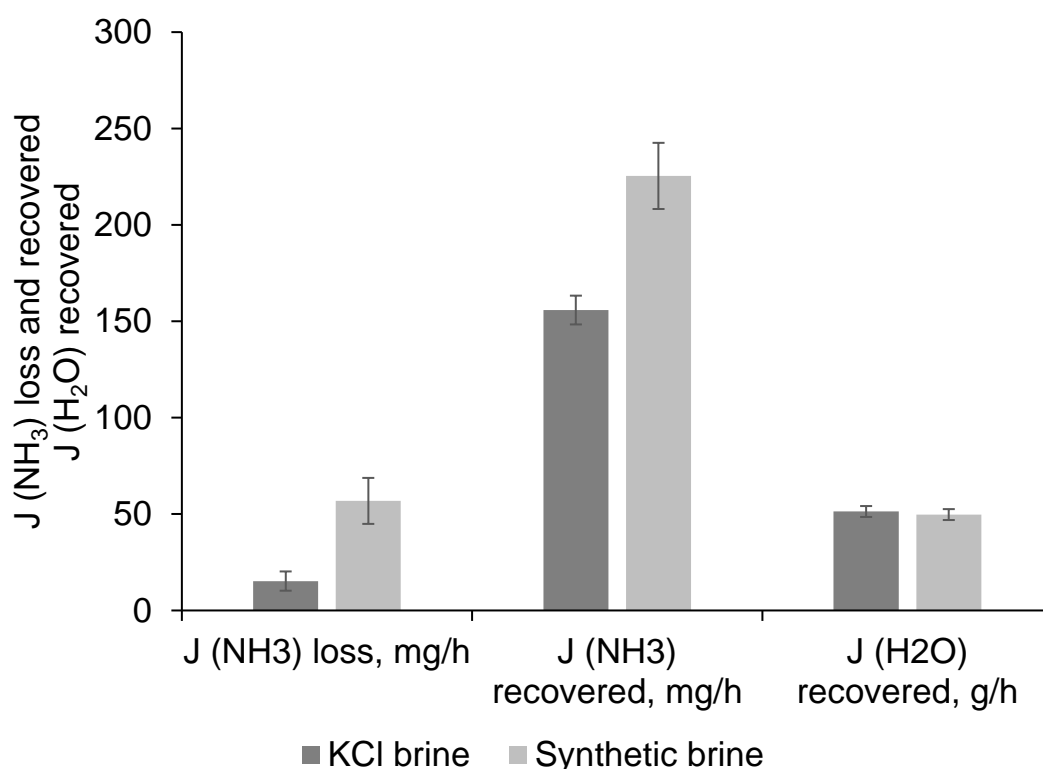


Figure 5.7 Ammonia recovered (mg/h), ammonia loss (mg/h) and water recovered (g/h) at the MVTs treating IEX brine (KCl,  $C_{\text{in}} = 580 \text{ mg NH}_4^+\text{-N/L}$ ,  $\text{pH}=10$ ) and synthetic solution ( $\text{NH}_4\text{Cl}$ ,  $C_{\text{in}} = 564 \pm 8 \text{ mg NH}_4^+\text{-N/L}$ ,  $\text{pH}=10$ ).

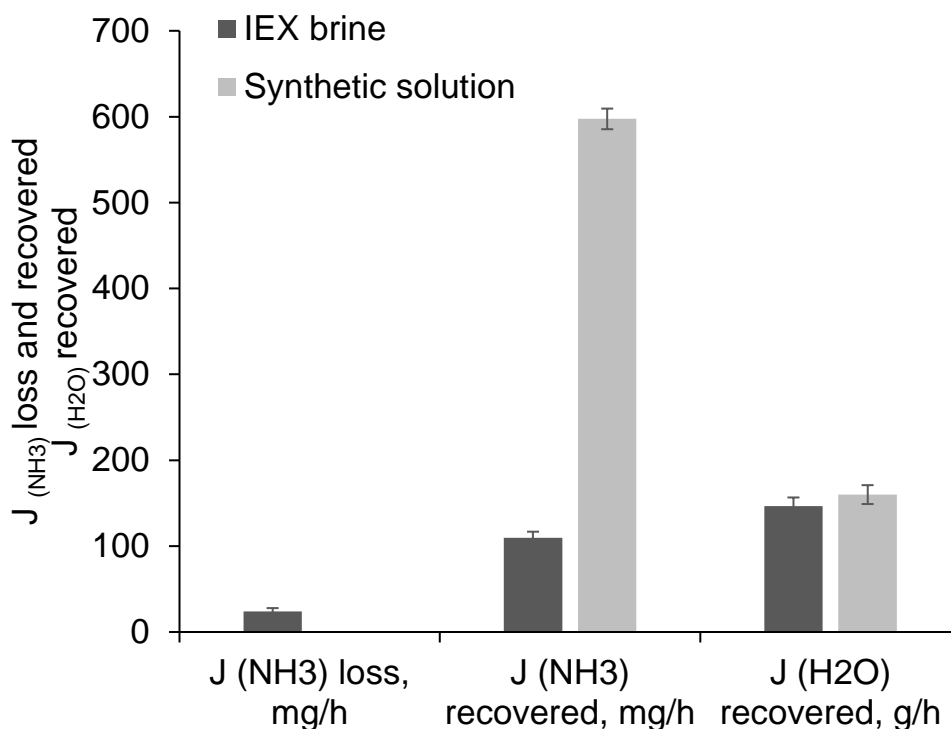
Ammonia recoveries of  $74 \pm 0.9\%$  and  $44 \pm 1.6\%$  were obtained when working with synthetic and IEX brine, respectively. These corresponded to recovery fluxes of 225 and 156 mg/h for synthetic and IEX brine, respectively. The corresponding mass transfer coefficients were  $1.7 \pm 0.05 \text{ h}^{-1}$  and  $0.7 \pm 0.04 \text{ h}^{-1}$  when treating the synthetic and IEX brines respectively, representing a reduction in transfer coefficient of 58% when moving to the more complex fluids associated with IEX brines. In addition, higher

ammonia loss ( $J_{\text{NH}_3 \text{ loss}}=57 \text{ mg/h}$ ) was obtained when treating the synthetic brine solution compared to the ammonia loss obtained from IEX brine ( $J_{\text{NH}_3 \text{ loss}}=15 \text{ mg/h}$ ). In contrast, similar water fluxes of 50-51 g/h were obtained (Figure 5.7) with a lower ammonia concentration in the recovered solution with the IEX brine ( $3.1\pm 0.3 \text{ g NH}_4^+\text{-N/L}$ ) compared to that when treating the synthetic solution ( $3.3\pm 0.2 \text{ g NH}_4^+\text{-N/L}$ ).

### 5.3.3 Ammonia recovery from synthetic and real brine with VTS

By treating the synthetic solution with a rotary evaporator, a  $J_{\text{NH}_3 \text{ rec}}$  of  $598\pm 12 \text{ mg/h}$  was measured (Figure 5.8) which is substantially higher than seen with the MVTS system (Figure 5.7). Additionally, no ammonia loss was measured but the  $J_{\text{H}_2\text{O}}$  was also much higher at  $160\pm 11 \text{ g/h}$ . The recovered ammonia solution had a concentration of  $2.5\pm 0.12 \text{ g NH}_4^+\text{-N/L}$  which corresponded to around 80% recovery efficiency with a  $K_{\text{La}}$  of  $1.96 \text{ h}^{-1}$ .

A much greater impact was observed with the VTS system when comparing synthetic and IEX brines. The equivalent data when using the IEX brine was a recovery efficiency of 19%, a  $J_{\text{NH}_3 \text{ rec}}$  of  $110\pm 7 \text{ mg/h}$ ,  $J_{\text{NH}_3 \text{ loss}}$  was  $24\pm 4 \text{ mg/h}$  and  $K_{\text{La}}$  was  $0.11 \text{ h}^{-1}$ . This represents a reduction in mass transfer coefficient of 94% indicating the VTS systems was much more impacted when treating the more complex IEX brine solution. The  $J_{\text{H}_2\text{O}}$  was  $147\pm 10 \text{ g/h}$  and a lower concentration in the recovered ammonia was obtained ( $0.51\pm 0.03 \text{ g NH}_4^+\text{-N/L}$ ).



**Figure 5.8 Ammonia recovered (mg/h), ammonia loss (mg/h) and water recovered (g/h) at the VTS treating IEX brine (KCl,  $C_{in} = 580 \text{ mg NH}_4^+\text{-N/L}$ ,  $\text{pH}=10$ ) and synthetic solution ( $\text{NH}_4\text{Cl}$ ,  $C_{in} = 564 \pm 8 \text{ mg NH}_4^+\text{-N/L}$ ,  $\text{pH}=10$ ).**

### **5.3.4 Chemical characterization and purity of ammonia solution recovered from VTS and MVTS from IEX brine**

The chemical characterization of the recovered ammonia solution obtained by treating IEX brine with VTS and MVTS systems revealed a good quality product (Table 5.1). The MVTS ammonia solution presented a lower concentration of heavy metals (0.1-30  $\mu\text{g/L}$ ) and higher concentrations of calcium (55 mg/L), silicon (16.3 mg/L) and potassium (1.2 mg/L). In comparison, the ammonia solution recovered by the VTS systems contained heavy metals in the range of 0.2-108  $\mu\text{g/L}$  with traces of potassium and silicon (0.3-0.5 mg/L, respectively) and 4 mg/L of calcium. In particular, much higher levels of copper, magnesium and zinc were carried over into the recovered solution when using the VTS system.

**Table 5.1 Chemical characterization of ammonia solution recovered with MVTS and VTS.**

|      | <b>Calcium</b> | <b>Potassium</b> | <b>Silicon</b> | <b>Copper</b> | <b>Magnesium</b> | <b>Zinc</b> | <b>Aluminium</b> | <b>Arsenic</b> |
|------|----------------|------------------|----------------|---------------|------------------|-------------|------------------|----------------|
|      | <i>mg/L</i>    | <i>mg/L</i>      | <i>mg/L</i>    | <i>µg/L</i>   | <i>µg/L</i>      | <i>µg/L</i> | <i>µg/L</i>      | <i>µg/L</i>    |
| MVTS | 55.3           | 1.2              | 16.3           | 30.3          | 14.5             | 4.4         | 17.1             | 2.1            |
| VTS  | 4.0            | 0.3              | 0.5            | 108.0         | 92.6             | 35.0        | 19.3             | 1.1            |

## 5.4 Discussion

In this study, HFMC, MVTS and VTS were assessed for their relative suitability to recover ammonia from synthetic solutions and IEX brines used as part of an ion exchange process for ammonia removal and recovery. Due to experimental limitations, the brine used for the HFMC was different from the one used for (M)VTS in terms of concentration and chemical composition, making a direct comparison between the recovery efficiencies of the technologies challenging. The most direct comparison is made through the mass transfer analysis with  $K_{La}$  values at pH 10 during the synthetic trials with values of  $3.5 \text{ h}^{-1}$ ,  $1.7 \text{ h}^{-1}$  and  $1.96 \text{ h}^{-1}$  for the HFMC, MVTS and VTS respectively. Raising the pH to 11 increased the  $K_{La}$  of the HFMC to  $8.2 \text{ h}^{-1}$  (Figure 5.4c), representing an enhancement factor of 2.3, emphasising the importance of pH on the stripping rate due to the differences in the free ammonia fraction that exists. To illustrate, the percentage of the ammonia that exists as free ammonia at equilibrium at pH 10 and 11 is 80% and 98% respectively, assuming  $20^\circ\text{C}$  [22].

The equivalent transfer coefficients when treating IEX brines were  $0.6 \text{ h}^{-1}$ ,  $0.7 \text{ h}^{-1}$  and  $0.1 \text{ h}^{-1}$  for HFMC, MVTS and VTS, respectively. The value obtained at VTS agreed with the mass transfer coefficient reported in literature ( $0.1\text{--}0.2 \text{ h}^{-1}$  [14]) for the ammonium recovery from anaerobic digestate. The HFMC trials were conducted at pH 11 whereas the (M)VTS trials were conducted at pH 10. Adjusting the HFMC based on the enhancement factor observed during the synthetic trials would reduce the  $K_{La}$  to  $0.26 \text{ h}^{-1}$ . Accordingly, the reduction in  $K_{La}$  was similar for the HFMC and the MVTS systems at 60% and 59% respectively. In contrast, a much greater reduction was observed for the integrated VTS system where the  $K_{La}$  was reduced by 95%. The reduction in mass transfer observed when treating IEX brines with HFMC and (M)VTS is attributed to the impact of the other ions in the water. For instance, the IEX brine used during the (M)VTS trials was rich in magnesium and silicon ( $45.1 \text{ mg Mg}^{2+}/\text{L}$  and  $7.2 \text{ mg Si}^+/\text{L}$ ) as well as containing traces of heavy metals ( $0.7\text{--}37 \text{ }\mu\text{g}/\text{L}$ ). Metal cations are known to lead to the formation of metal amine complexes [10], [14] which exhibit much lower volatilities and hence decrease the stripping performance [33]. This idea is supported by the presence of higher levels of copper, magnesium and zinc in the

recovered ammonia solution from the VTS system which suffered the greatest reduction in  $K_{La}$ . The impact of this is to increase the time required to transfer the available ammonia (Equation 5.5). In the case of the HFMC system, this resulted in an increase in the number of recirculations required to recovery 100% of the ammonia from 27 ( $t=0.5$  h) in the synthetic solution to 360 ( $t=6.7$  h) in the IEX brine (Figure 5.5b). The equivalent in the case of the (M)VTS systems is a reduction in ammonia recovery for a fixed time period. In the case of the MVTS system, this represented a change from 74% to 44% in the recovery efficiencies compared to the VTS system where the change was from 80% to 19% when working with synthetic and real brine, respectively. Additionally, the difference in  $K_{La}$  between the synthetic and real solutions could be attributed to the higher solids concentration and viscosities of the latter [34]. These values were not calculated for the real brines in this work. However, it could be hypothesised that the multiple reuse of the brine as regenerant solution for zeolites, used to treat wastewater, could have increased its viscosity due to remaining solids on the media surface [35]. A future more in-depth analysis could investigate the impact of the increased viscosity of the brine on the mass transfer coefficients though the calculation of the *alpha factor* as reported in Fernández *et al.* [34].

The overall effectiveness of (M)VTS systems depends on the operating conditions namely the vacuum pressure, the temperature of the IEX brine as well as of the cooling solution in the condenser [17] and the mixing of the brine [19]. The comparison of the MVTS and VTS provides an assessment of this, with the MVTS being more controllable. This was observed in relation to a higher ammonia recovery flux ( $J_{NH_3\ rec} = 156$  mg/h) and lower ammonia loss rate ( $J_{NH_3\ loss} = 15$  mg/h) compared to the values observed for the VTS system ( $J_{NH_3\ rec} = 110$  mg/h,  $J_{NH_3\ loss} = 25$  mg/h) (Figure 5.7-5.8). Key differences in the current trials were the efficiency of mixing in the two systems (with the MVTS allowing for much better mixing) as well as the difference in temperature of the solution (80°C and 69°C for the VTS and MVTS, respectively). The importance of these conditions relates to more consistent and gradual heat distribution avoiding an abrupt onset of evaporation in a process called *bumping*. The impact of which is greater carryover of water as evidenced by the respective water flux rates of 51 g/h (MVTS) and 147 g/h (VTS) (Figure 5.7-5.8).

All three processes resulted in the recovery of ammonia either in a concentrated liquid form or as a metal salt. In the case of the HFMC, this can be taken ultimately to the production of a high-purity solid (Figure 5.6). However, due to its high solubility (75.13 g/100 g H<sub>2</sub>O [17]), the recovery of the solid product required evaporation of the acid phase and the recovery process would require the minimization of both transport of water and heat from a stripper to the acid solution [17]. As an alternative, the production of liquid fertiliser using HFMC has been investigated [23], [26], [35]. For instance, Licon *et al.* [25] studied the possibility to recover liquid fertiliser (ammonium nitrate, NH<sub>4</sub>NO<sub>3</sub>, and diammonium phosphate, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>) from ion exchange brine regenerant (1-3 g N/L) using a HFMC with an ammonia recovery >98% [25]. Similarly, Sancho *et al.* [23] recovered ammonium nitrate and di-ammonium phosphate (2-5% wt N) from a solution of NaOH (2-3 g N/L) used to regenerate Clinoptilolite [23]. In fact, reported trials with recovered ammonia from anaerobic digestion effluent were able to generate a solution with an N content of 5-10% wt, from initial ammonia concentrations in the solution of 1.7-4.0 g/L [35]. In the current case, the (M)VTS systems generated ammonia solutions with a maximum concentration of 3.1 g/L with MVTS and 0.5 g/L with VTS. When recovered in this form, the solution has many applications such as plastics, textiles and cleaning industries [20]. Moreover, due to its high refrigerant power, ammonia can substitute organic chlorofluorocarbons as refrigeration gas in large refrigerating machines [36].

Both HFMC and (M)VTS systems were shown to be effective for the recovery of ammonia from IEX brines. The systems have a number of challenges that require consideration for further development. In the case of the HFMC, a major disadvantage is related to the possibility of fouling of the pores of the membrane caused by particulates (i.e. solids) in the brine solution which could limit the mass transfer and result in possible breakage of the fibres [7]. Accordingly, if the brine presents high concentration of solids, Wäeger-Baumann and Fuchs [37] suggested a pre-treatment step with micro- or ultra- filtration to ensure long lifespan of the membrane [37]. Nevertheless, the membranes have a finite lifespan and would eventually need to be replaced thus increasing the cost of the treatment. According to Darestani *et al.* [7], the cost of the technology is also impacted by the type of solution that is being treated with the HFMC as this will define the number of modules required for the treatment



and, therefore, the capital cost. Moreover, the scale-up of the technology should also consider costs connected to the recovered product, i.e. volatility of the fertiliser, production of sodium hydroxide to obtain the required pH as well as transport costs [7].

The equivalent challenge for the (M)VTS system is the energy requirements for heating the brine and driving the vacuum system. Compared to thermal stripping, the vacuum can reduce the energy cost as a result of lower heating requirement [17], however, according to Tao *et al.* [16], the energy requirements for vacuum stripping still account for 87.2% of the total cost of the technology. The heat requirement can be effectively meet through the use of waste heat dissipated from thermal hydrolysis coolers (in the case of advanced anaerobic digestion) and un-utilised waste heat from combined heat and power production, although this is yet to be demonstrated. Recent estimates have indicated this could equate to as much as 40% of the energy produced from biogas on wastewater sludge processing sites and so looks promising [22].

A direct comparison of the total costs requirements of the ammonia recovery from saturated IEX brine through HFMC and (M)VTS has not been performed in this work. However, future work should focus on this to better estimate the viability of the technologies at bigger scale. Overall, considering the ammonia recovery efficiency obtained in this work and the technology readiness level, the HFMC is suggested as the preferred method. However, it is important to consider that other challenges also remain which can interfere with the scale-up of HFMC for ammonia recovery such as the analysis of viable commercialisation pathway. To increase the market value of the recovered product, alternative acids should be tested to investigate the possibility of recovering different ammonium salt (solids or liquid) with higher market values (such as  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2(\text{HPO}_4)$  solutions) for potential use as liquid fertilisers.

## 5.5 Conclusions

- The ammonia stripping efficiency depends on the ratio of free ammonia present in solution and hence pH. Operation below pH 10 (80% free ammonia) become ineffective and are maximised at pH 11 (98% free ammonia).
- Significant reduction in transfer coefficient are generated from real IEX brines (0.6 h<sup>-1</sup>, 0.7 h<sup>-1</sup> and 0.1 h<sup>-1</sup> for HFMC, MVTS and VTS) compared to synthetic solution (3.5 h<sup>-1</sup>, 1.7 h<sup>-1</sup> and 1.96 h<sup>-1</sup> for HFMC, MVTS and VTS) due to the presence of metal ions, which form metal amine complexes. This leads to an increase in the required time to recover the available ammonia.
- The effectiveness of vacuum thermal stripping system requires good mixing and temperature control to enable gradual thermal gradients, avoiding bumping in the fluid which leads to high levels of water carryover. The better control of the MVTS resulted in higher ammonia recovery flux ( $J_{\text{NH}_3 \text{ rec}} = 156 \text{ mg/h}$ ) and lower ammonia loss rate ( $J_{\text{NH}_3 \text{ loss}} = 15 \text{ mg/h}$ ) compared to the values observed for the VTS system ( $J_{\text{NH}_3 \text{ rec}} = 110 \text{ mg/h}$ ,  $J_{\text{NH}_3 \text{ loss}} = 25 \text{ mg/h}$ ).
- HFMC was selected as preferred method for the treatment of saturated IEX brine. However future studies are needed to investigate the recovery of different ammonium salt (solids or liquid) with high market values (such as NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> solutions) for potential use as liquid fertilisers.

## 5.6 References

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## 6. DEMONSTRATION OF ION EXCHANGE TECHNOLOGY FOR PHOSPHORUS REMOVAL AND RECOVERY FROM MUNICIPAL WASTEWATER

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### Abstract

An hybrid anion exchanger (HAIX) demonstration plant was fed with a wastewater flow of 10 m<sup>3</sup>/day to investigate changes in orthophosphate (PO<sub>4</sub>-P) adsorption capacity over an extended period of operation and to establish an efficient regenerant management. Hydroxyapatite was recovered from the NaOH 2% (w/v) regenerant and its reusability was assessed in order to reduce chemical costs. The municipal wastewater contained an average of 6 mg PO<sub>4</sub>-P /L and it was reduced to below 0.3 mg PO<sub>4</sub>-P/L in the HAIX plant, after 430 bed volumes, with an adsorption capacity of 4.1 mg PO<sub>4</sub>-P/g resin. Subsequently, the regenerant was reused up to 5-8 times, reaching 785 mg PO<sub>4</sub>-P/L. Nevertheless, the reuse of the regenerant resulted in a decrease of the PO<sub>4</sub>-P adsorption capacity to 1.5 mg PO<sub>4</sub>-P/g resin which was also affected by the organic matter accumulated in the HAIX. For this reason, a regeneration of the resin with NaCl was suggested to avoid fouling of the HAIX, resulting in a 16% increase in adsorption capacity. Up to 95% of the PO<sub>4</sub>-P was recovered by adding calcium hydroxide in the saturated NaOH regenerant solution. The hydroxyapatite recovered was analysed for impurities and it was found not to contain pathogens or organic pollutants and respected the legal limits on the heavy metals imposed in several countries for its use as fertiliser. After the recovery of the hydroxyapatite, the NaOH was reused as regenerant solution, ensuring high effluent quality of <0.2 mg PO<sub>4</sub>-P/L. This study confirmed the advantages of ion exchange technology for the removal of PO<sub>4</sub>-P from municipal wastewater offering a solution



which ensures both a high effluent quality and a circular economy approach due to the recovery of the  $\text{PO}_4\text{-P}$  as a valuable product.

### **Keywords**

Phosphorus removal, phosphorus recovery, calcium phosphate, ion exchange, regenerant management, circular economy, resource recovery

## 6.1 Introduction

Orthophosphate (as  $\text{PO}_4\text{-P}$ ) concentrations in municipal wastewater treatment plants (WWTPs) range between 4 and 12 mg  $\text{PO}_4\text{-P/L}$  [1]. This  $\text{PO}_4\text{-P}$  needs to be removed to ensure that stringent discharge limits, imposed by the Water Framework Directive and enforcing phosphorus (P) concentration as low as  $<0.1$  mg/L in effluent [2], are met. Different technologies can be applied in WWTPs [3] but the overall increasing demand for P [4] has moved the attention towards those that can allow for both removal and recovery of P [5]. To evaluate the applicability of such technologies many factors need to be considered, including: operational and maintenance costs, final effluent quality, sludge production, chemical consumption, purity of the recovered product and environmental impact of the technology such as greenhouse gas emissions. One type of technology which can meet the tighter consents limit for P discharge [6] with low energy consumption and moderate environmental impact [7], [8] is based on using ion exchange resin (IEX). Ion exchange technologies have been applied to remove a wide range of chemicals such as nitrate [9], ammonium [10], arsenic [11], phosphorus [7] from water and wastewater [12]. In particular,  $\text{PO}_4\text{-P}$  can be selectively removed from wastewater using resins [13], [14] such as inorganic ion exchangers, polymeric hydrogels or polymeric ligand exchanger [1]. These resins can be successively regenerated after saturation, commonly using a high pH brine solution (such as NaOH) thus restoring their initial capacity [15].

A selective IEX resin which has been widely used for the efficient  $\text{PO}_4\text{-P}$  removal is composed of a hybrid polymeric base [12] where hydrated ferric oxide nanoparticles (HFO-NP) have been dispersed, usually referred to as hybrid anion exchanger (HAIX) [7], [16]. Due to the Donnan membrane exclusion effect, the polymeric anion exchanger allows enhanced permeation of anions, such as  $\text{PO}_4\text{-P}$ , within the polymer phase due to its high concentration of fixed positive charges of  $\text{FeOH}_2^+$  [17]. More in particular, previous studies have confirmed that 90% of the capacity of the resin for phosphorus is due to the ferric nanoparticles with the other 10% is related to the exchange component [18]. The process for the preparation of the HAIX was developed at Lehigh University and it has since been commercialized by Layne Christensen and Purolite Company in the US [17]. The previous work conducted on HAIX describes  $\text{PO}_4\text{-P}$  removal from municipal wastewater [6], [19], surface waters with high

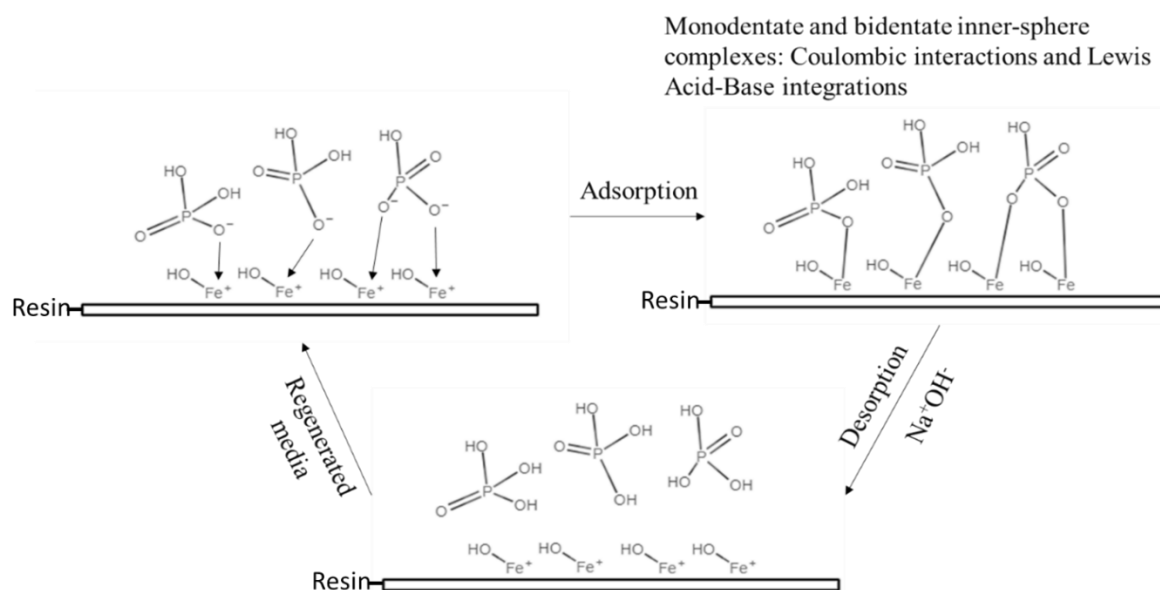
concentration concentrations of natural organic matter [20], urban wastewater treatment plant sludge liquor [6], primary and secondary effluent wastewater [18] (Table 6.1). In these laboratory scale experiments, the HAIX removed up to 95% of the PO<sub>4</sub>-P present in wastewater with high affinity for the PO<sub>4</sub>-P in presence of competitive ions compared to other selective resins [20] with a capacity up to 14.4 mg P/g resin according to the initial PO<sub>4</sub>-P concentration [6] (Table 6.1) .

**Table 6.1 Laboratory scale experiments using HAIX for the removal of PO<sub>4</sub>-P from synthetic and real wastewater.**

| HAIX resin supplier              | Treated solution                    | Initial PO <sub>4</sub> -P conc. | Adsorption capacity                                     | Regen. efficiency                  | Experiment scale                                                                   | Ref. |
|----------------------------------|-------------------------------------|----------------------------------|---------------------------------------------------------|------------------------------------|------------------------------------------------------------------------------------|------|
| SolmeteX Co., Massachusetts      | Sludge liquor, municipal wastewater | 350 mg/L                         | 14.2-14.4 mg P/g resin                                  | 95% (regen. 1M NaOH)               | Batch test; Packed bed column test (45 cm height and 1.5 cm diameter glass column) | [6]  |
| SolmeteX Co., Massachusetts      | Real and synthetic wastewater       | 4.8 mg/L                         | 0.29-0.51 mg P/g resin (13% of the exhaustive capacity) | 88% (regen. 2%-5% NaCl-2%-5% NaOH) | Batch test; Fixed-bed columns (20 cm height and 1.5 cm diameter)                   | [7]  |
| SolmeteX Co., Massachusetts      | Municipal wastewater                | 4 mg/L                           | 3.4-6.3 mg P/g resin                                    | N/A (regen. NaCl-NaOH)             | Fixed-bed columns (0.03-1.0 m length and 15 and 500 mm diameter)                   | [19] |
| Layne Christensen Company, Texas | Secondary wastewater effluent       | 100 mg/L                         | 7-9.7 mg P/g resin                                      | 90% (regen. 4% NaOH)               | Fixed-bed columns (2.5 cm diameter)                                                | [18] |
| Layne Christensen Company, Texas | Synthetic solution                  | 5 mg/L                           | N/A                                                     | >90% (regen. NaCl 2%)              | Batch experiments                                                                  | [13] |

|                                  |                            |              |     |                        |                                                               |      |
|----------------------------------|----------------------------|--------------|-----|------------------------|---------------------------------------------------------------|------|
|                                  |                            |              |     | and NaOH 2%)           |                                                               |      |
| Layne Christensen Company, Texas | Organic-rich surface water | 132-250 µg/L | N/A | 80% (regen. NaCl-NaOH) | Fixed-bed column (50 mm height - 10 mm diameter glass column) | [20] |

HAIX effectively removed  $\text{PO}_4\text{-P}$  within a pH range of 6-8 [12] where the divalent anion  $\text{HPO}_4^{2-}$  and the monovalent anion  $\text{H}_2\text{PO}_4^-$  are present and can therefore create an inner sphere complexed with HFP-NP via Lewis acid (metal oxides) – base (orthophosphate anion) interactions (Figure 6.1) [16], [21]. An alkaline solution can be used to deprotonate the HFO-NP whereas polymeric base requires brine regeneration as with common IEX processes [18] (usually NaOH 2% - NaCl 2% [13]). The regeneration of the HAIX resin concentrates >90% of the adsorbed  $\text{PO}_4\text{-P}$  into the regenerant solution [6], [15], [18], [22].



**Figure 6.1 Schematic illustrating the formation of monodentate and bidentate inner-sphere complexes between orthophosphate ( $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ ) and iron HFO-NP surface groups and regeneration with NaOH solution.**

The saturated regenerant solution can be further processed for  $\text{PO}_4\text{-P}$  recovery [15]. Struvite crystallisation is often applied for  $\text{PO}_4\text{-P}$  recovery from different wastewaters and it has been widely studied [23]–[25]. However, the successful

crystallization depends on the pH,  $Mg^{2+}$  and  $NH_4^+$  concentrations, temperature, and mixing energy [24], [26], and regenerant solutions do not have the suitable characteristics for struvite formation. Recently, the recovery of calcium phosphate has gained attention due to the lower cost and simplicity of the process [25], [27]. Depending on the operational condition, different forms of calcium phosphate can be obtained, namely hydroxyapatite ( $Ca_5(PO_4)_3(OH)$ ) [28], octa calcium phosphate ( $Ca_4H(PO_4)_3 \cdot 3H_2O$ ) [25], tricalcium phosphate ( $Ca_3(PO_4)_2$ ) [25], monohydrogen phosphate ( $CaHPO_4$ ) or brushite ( $CaHPO_4 \cdot 2H_2O$ ) [29]. According to Ansari *et al.* [27], the efficiency of the recovery mainly depends on the initial P concentration in the treating solution with higher concentration resulting in higher recovery. This makes the process suitable for the management of the IEX regenerant solution as the NaOH saturated with  $PO_4-P$  can be used to recover calcium phosphate.

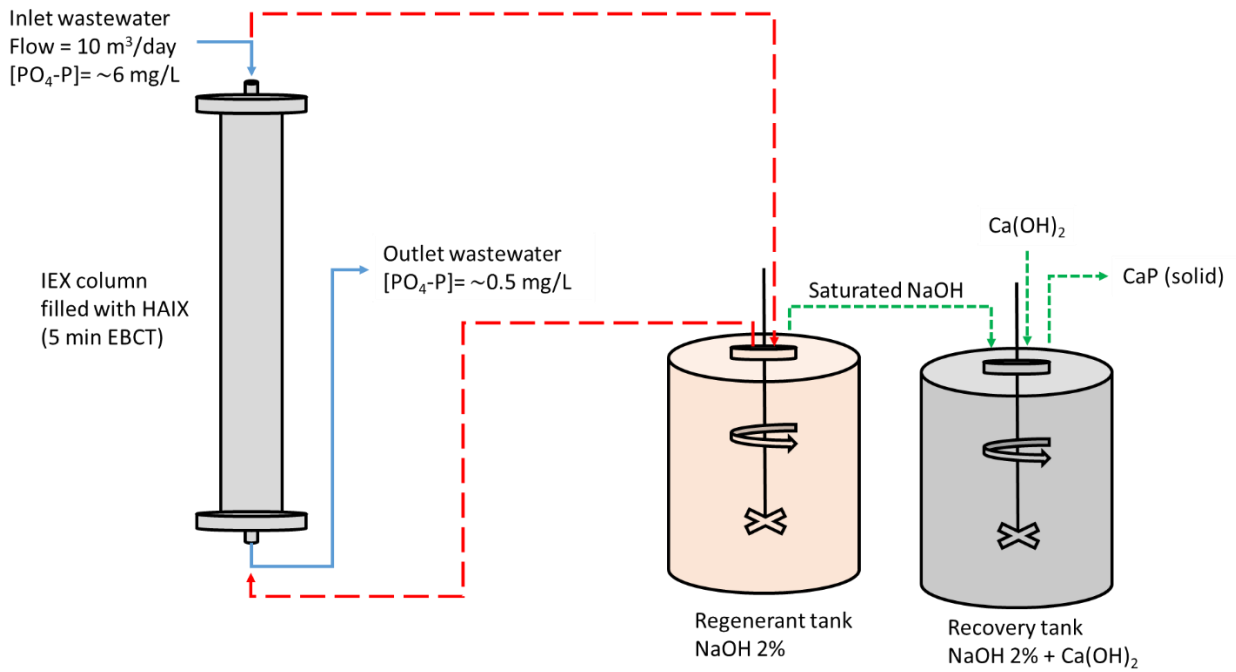
To date, HAIX resins have been investigated for P removal at laboratory scale [15], [16], [22] with promising results (Table 6.1), but there is a need to investigate the application of the technology in WWTP at larger scale, over extended operation whilst establishing an efficient regenerant management solution. Hence, this study investigates changes in  $PO_4-P$  adsorption capacity over an extended period of operation (under fixed conditions to establish the consistency of performance), regenerant reuse and calcium phosphate recovery in a demonstration IEX plant fed with  $10 \text{ m}^3/\text{day}$  of secondary treated municipal wastewater over a period of 2 years.

## **6.2 Materials and methods**

### **6.2.1 Resin and secondary wastewater**

The resin, HAIX-LayneRT (hereinafter referred to simply as HAIX), was purchased from Layne Christensen Company, Texas, United States. It is a commercially available resin mainly used for arsenic removal from contaminated groundwater [11], [30]. The HAIX base material is a strong base anion exchange resin (macroporous, with a quaternary ammonium functional group [30]), within which hydrated ferric oxide nanoparticles have been dispersed to enhance the selectivity for phosphorus [13]. The average particle diameter was 0.69 mm [19]. The secondary treated wastewater originated from Cranfield University WWTP, after preliminary, primary and secondary treatment that ensured solids and chemical oxygen demand (COD) removal.

The demonstration plant was manufactured to the required specifications by MionTec GmbH (Germany) and assembled on site (Figure 6.2). It consisted of a drum filter, a compressed air diaphragm pump with float flow measurement and air flow regulator to adjust the pump's flow rate, a PVC-U column, two manometers to measure pressure loss and sampling points. The IEX column had an internal diameter of 22 cm and a height of 158 cm and it was filled with 35L of HAIX (24 kg), up to a height of 95 cm, 60% of the total height, to allow for resin expansion during backwash and regeneration procedures.



**Figure 6.2 Schematic representation of demonstration plant.**

The IEX column was fed with wastewater in downflow operation at a flow rate of 10 m<sup>3</sup>/day (416.7 L/h) equivalent to an empty bed contact time (EBCT) of 5 minutes, that was suggested as the optimal in previous studies [31]. The PO<sub>4</sub>-P concentration at the influent and effluent was monitored daily by taking samples from the designated valves. The regeneration of the resin was performed with 10 bed volumes (BV) of NaOH 2% (w/v) solution in upflow operation at 400 L/h. The column was drained before and after the regeneration started. The regenerant was kept homogenous by a mixer installed on the regenerant storage tank. At the end of the regeneration, the total volume of the regenerant was collected in the storage tank to be reused and the column was backwashed with tap water for 30 minutes before a new adsorption cycle was started.

### 6.2.2 Operating parameters

Considering the bed volume, BV (L), and the flow rate in the bed, F (L/min), it was possible to calculate the empty bed contact time (EBCT), according to Equation 6.1 [32]:

$$\text{EBCT} = \text{BV}/F \quad \text{Equation 6.1}$$

The orthophosphate adsorption capacity ( $Q$ , mg PO<sub>4</sub>-P/g resin) after  $n$  samples and desorption capacity ( $Q_{reg}$ , mg PO<sub>4</sub>-P/g resin) of the HAIX in each cycle was calculated as in Equations 6.2 [33] and 6.3 [34]:

$$Q = \frac{\int_{V=0}^{V^{fin}} (C_{in} - C_{out}) dV}{M} = \frac{\sum_0^n [(C_0 - C_n) * (V_n - V_{n-1})]}{M} \quad \text{Equation 6.2}$$

$$Q_{reg} = \frac{[C_{r,i} - C_{r,f}] * V_{reg}}{M} \quad \text{Equation 6.3}$$

where  $C_{in}$  and  $C_{out}$  are the initial and final orthophosphate concentration in wastewater (mg PO<sub>4</sub>-P/L);  $M$  is the mass of resin (g);  $V$  is the volume of the wastewater treated in each cycle (L);  $C_{r,i}$  and  $C_{r,f}$  are the orthophosphate concentrations in the regenerant at the beginning and at the end of each cycle (mg PO<sub>4</sub>-P/L);  $V_{reg}$  is volume of regenerant (L).

The adsorption and regeneration efficiency (AE and RE, respectively) were calculated following Equations 6.4, 6.5 and 6.6 [35].

$$M_{\text{retained in solid phase}} = M_{\text{fed}} - M_{\text{out}} \quad \text{Equation 6.4}$$

$$AE = \frac{(M_{\text{fed}} - M_{\text{out}})}{M_{\text{fed}}} * 100 \quad \text{Equation 6.5}$$

$$RE = \frac{M_{\text{reg}}}{M_{\text{retained in solid phase}}} * 100 \quad \text{Equation 6.6}$$

where  $M_{\text{fed}}$ ,  $M_{\text{out}}$  are the mass of orthophosphate in the wastewater the influent and effluent of the IEX demonstration plant (g), respectively;  $M_{\text{retained in solid phase}}$  and  $M_{\text{reg}}$  are the mass of orthophosphate retained by the HAIX and recovered during the regeneration phase (g), respectively. Considering that the regenerants were reused multiple times, to accurately calculate the regeneration efficiency, the orthophosphate concentration from previous cycles was taken into account.



### 6.2.3 Investigation of the accumulation of organics on the resin

To test the effect of organic matter on the adsorption capacity of the HAIX, 4 g of resin were taken from the top of the column. The resin was regenerated with 400 mL of NaOH 2% for 1 hour, mixing at 100 rpm orbital shaker (SSL1, STUART, UK). Successively 2 g of the regenerated resin were treated with NaCl 5% (1 hour at 100 rpm), adding 100 mL/g resin. The regenerated resin (both NaOH 2% and NaOH 2% + NaCl 5%) was used to treat wastewater with an initial concentration of 4.3 mg PO<sub>4</sub>-P/L in a batch test. For this, 1 gram of resin was added to 100 mL of wastewater and left in agitation at 100 rpm overnight. The orthophosphate concentration and the chemical oxygen demand (COD) were analysed in the regenerants (NaOH and NaCl) before and after the regeneration and in the wastewater, before and after the adsorption.

### 6.2.4 Recovery process

The orthophosphate saturated regenerant solution (NaOH 2%) was used to test the recovery process at two different Ca:P ratios. A calcium hydroxide (Ca(OH)<sub>2</sub>) solution (300 g/L) was added to 600 mL of saturated regenerant to achieve Ca:P molar ratios of 2 and 3, based on the reaction stoichiometry. The solutions were mixed at 75 rpm (Phipps and Bird PB-700 jar tester, Richmond, USA) at room temperature (18°C) for 6 hours. Samples were taken after 1, 2, 4 and 6 hours. After 1 hour of settling, the samples were filtered using filter syringes (Sartorius 0.2 µm retention syringe filter, 26 mm diameter) and the orthophosphate concentration was measured in each sample. The experiment was conducted in triplicate.

The recovery of orthophosphate from the IEX demonstration scale plant was done in batch. Fifty litres of saturated regenerant solution were mixed with a solution of 300 g/L of Ca(OH)<sub>2</sub> at a Ca:P ratio of 3. The solution was mixed for 24 hours and the samples were taken after each hour. The precipitate was successively filtered (polypropylene filter bags, 50 µm), washed with deionized water and dried in the oven overnight at 100°C.

### 6.2.5 Chemical analysis

During adsorption phase, samples of the effluent were collected using an ISCO autosampler (3700 Standard Portable Sampler, Teledyne Isco) while manual sampling

three times a day was used for the influent wastewater. The samples were filtered using Whatman Filters (22 µm pores diameter) before all the analysis were performed to remove any solids in solution. If storage was needed, the samples were kept refrigerated at 4°C. Orthophosphate (PO<sub>4</sub>-P) concentration, pH, temperature and chemical oxygen demand (COD) were monitored regularly. During regeneration (desorption phase), samples of NaOH were taken before and after the regeneration and pH, calcium and orthophosphate concentrations were measured.

Orthophosphate concentration was analysed using the Smartchem200 (AMS Alliance, Frépillon, France). Analysis of pH and temperature were performed using pH and temperature portable meters (Jenway 3510 pH and conductivity meter, Camlab, UK), used on site. Calcium and COD were analysed using Spectroquant® Cell Test kit (Merk Millipore) according to manufacture protocol. Anions and cations in wastewater were analysed following standard colorimetric analysis [36]. Metals were analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) [37]. Analysis of the total suspended solids (TSS) was performed according to Standard Methods (Standard Methods 2540D). The recovered product was weighted and analysed with a scanning electron microscope (SEM, Tescan Vega 3, large chamber, Kohoutovice, Czech Republic) and X-ray diffraction (XRD, Siemens D5000 powder diffraction set-up, theta/2 theta configuration, Munich, Germany) for chemical characterisation.

## **6.3 Results**

### **6.3.1 Wastewater characterisation**

The secondary wastewater fed to the IEX demonstration plant presented an average orthophosphate (PO<sub>4</sub>-P) concentration of around 6 mg PO<sub>4</sub>-P/L and total phosphorus (TP) of 6.6 mg TP/L (Table 6.2). Other ions in the wastewater were also measured as they can interfere in the adsorption process or competed for adsorption sites in the HAIX and the concentrations are shown in Table 6.2. The pH was stable at around 7.1±0.2 while the COD was 54±5.7 mg/L. The wastewater temperature varied between 6 to 25°C while total suspended solids (12.7±5 mg TSS/L) and column head loss were very consistent throughout the operations of the demonstration plant.

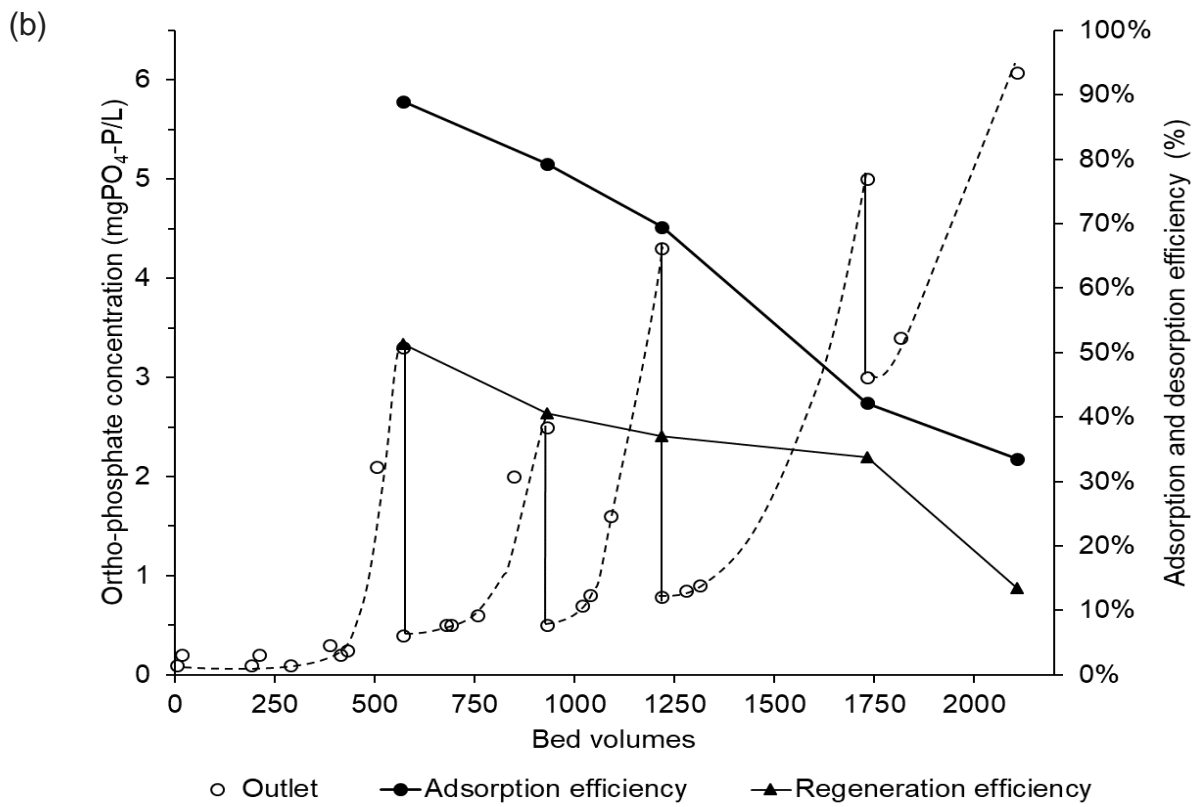
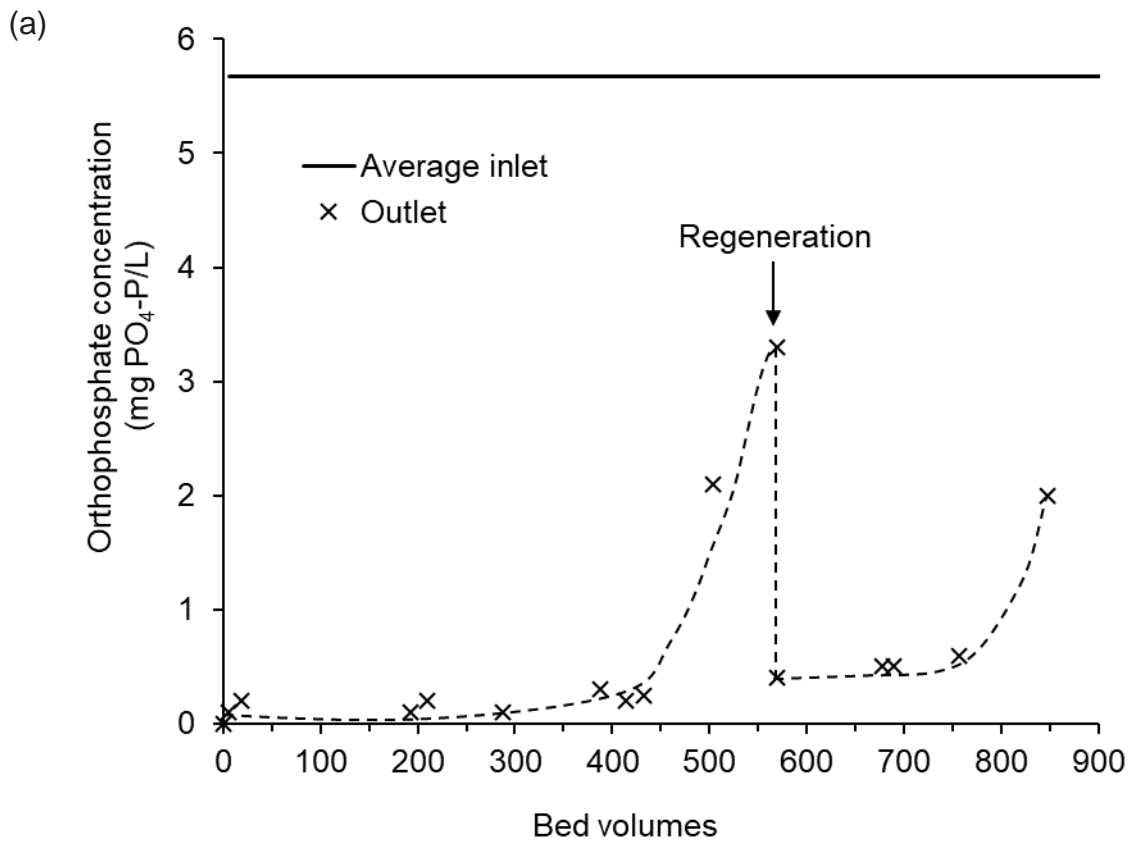
**Table 6.2 Characterisation of the secondary treated wastewater fed to the IEX demonstration plant.**

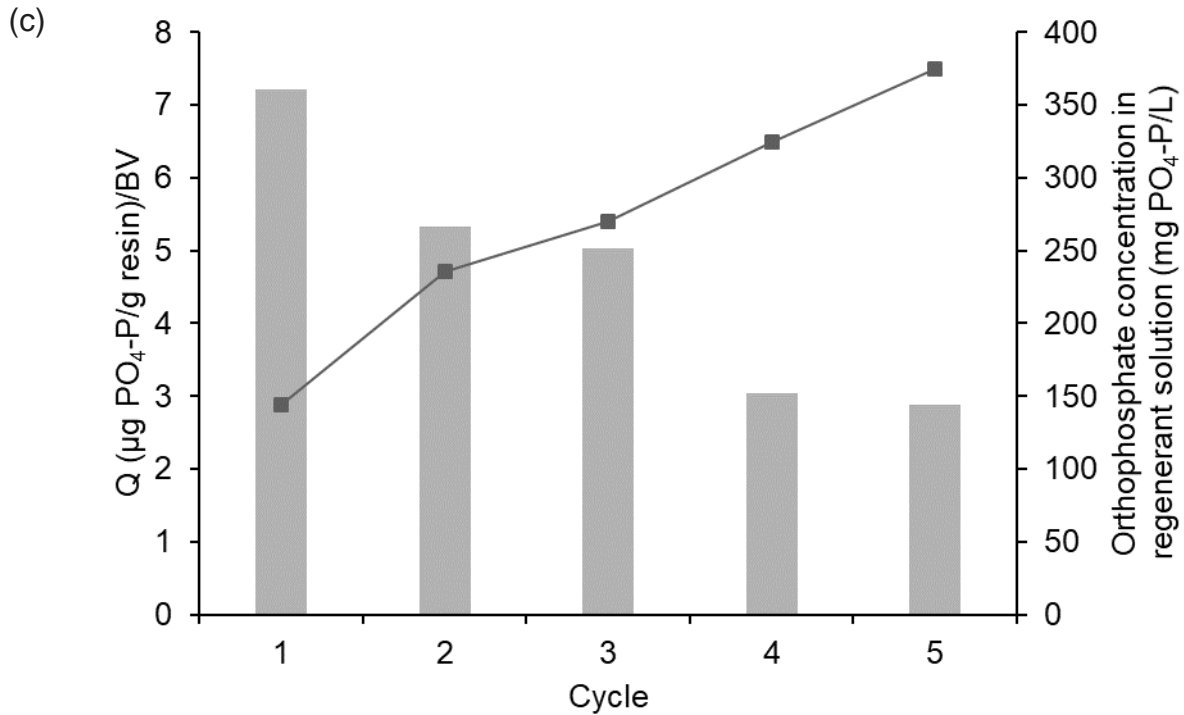
| <b>Pollutant</b>    | PO <sub>4</sub> -P | TP          | SO <sub>4</sub> -S | NH <sub>4</sub> -N | Na          | K            | Ca        | Cl           | NO <sub>3</sub> |
|---------------------|--------------------|-------------|--------------------|--------------------|-------------|--------------|-----------|--------------|-----------------|
| <b>Conc. (mg/L)</b> | 5.9<br>±0.1        | 6.6<br>±0.2 | 75.4<br>±6.2       | 8.1<br>±2.0        | 60<br>±14.6 | 16.9<br>±0.1 | 69<br>±14 | 75.6<br>±9.6 | 141<br>±4.9     |

### 6.3.2 Orthophosphate removal from wastewater

When operating the demonstration plant with fresh HAIX resin, the effluent PO<sub>4</sub>-P concentration was kept below 0.3 mg PO<sub>4</sub>-P/L for 430 bed volumes (Figure 6.3a). The HAIX resin removed up to 90% of the PO<sub>4</sub>-P, yielding an adsorption capacity of 4.1 mg PO<sub>4</sub>-P/g resin. About 51.3% of the adsorbed PO<sub>4</sub>-P was recovered in the regenerant solution, corresponding to a Q<sub>des</sub> of 2.1 mg PO<sub>4</sub>-P/g resin. The same regenerant was reused for the following four cycles and the adsorption capacity gradually decreased down to 1.5 mg PO<sub>4</sub>-P/g resin (33% adsorption efficiency) in the fifth cycle (Figure 6.3b). The efficiency of the regeneration decreased from 51.3% in cycle 1 to 13% in cycle 5 (Figure 6.3b). The bed volumes treated before breakthrough decreased from 430 BV in cycle 1 to 83 BV in cycle 5, indicating that both the resin and the regenerant reached saturation.

The effluent orthophosphate concentration was 0.4 mg PO<sub>4</sub>-P/L in the second cycle and was kept below 0.6 mg PO<sub>4</sub>-P/L for 186 BV. However, with the continual decrease in the regeneration efficiency after each cycle, the adsorption efficiency was the resin was reduced and the effluent reached 3 mg PO<sub>4</sub>-P/L at the beginning of the fifth cycle (Figure 6.3b). At the same time, the orthophosphate concentration in the regenerant solution increased from 144 mg PO<sub>4</sub>-P/L after the first cycle up to 375 mg PO<sub>4</sub>-P/L in the fifth cycle (Figure 6.3c). To normalize the data according to the bed volumes (BV) treated, the orthophosphate adsorption capacity per BV of wastewater treated was calculated (Figure 6.3c). The capacity gradually decreased from cycle 1 (7.2 µg PO<sub>4</sub>-P/g resin/BV) to cycle 5 (2.9 µg PO<sub>4</sub>-P/g resin/BV).



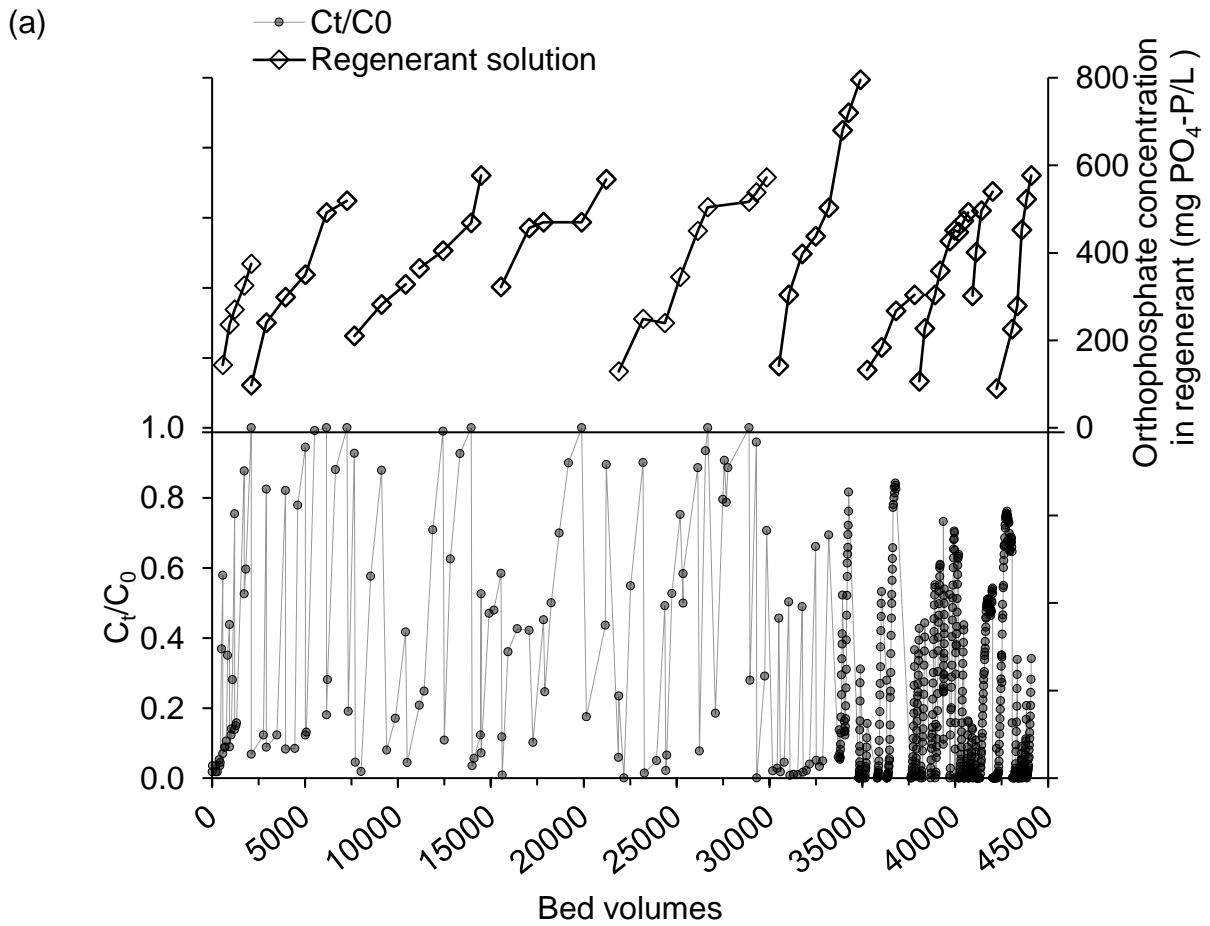


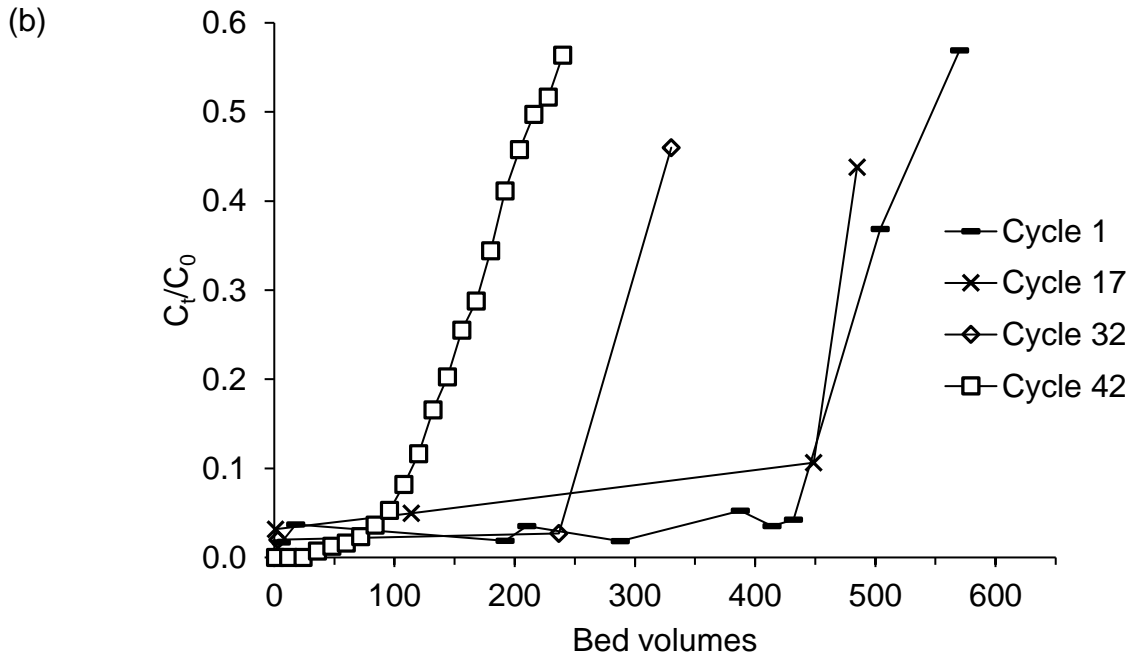
**Figure 6.3 (a) Orthophosphate removal from municipal wastewater ( $C_{in}=5.7$  mgPO<sub>4</sub>-P/L) using fresh hybrid anion exchanger (HAIX) and regeneration with NaOH 2% (10 bed volumes); (b) impact of reusing the same regenerant solution multiple times upon HAIX adsorption capacity (Q), vertical lines represent regeneration; (c) Q per bed volume (Q/BV) of wastewater treated and increase in concentration of the regenerant solution after each regeneration cycle.**

### 6.3.3 Long-term operation of the IEX technology

The longevity and robustness of the IEX technology was investigated by reusing the HAIX resin over an extended period of time. Figure 6.4a presents the  $C_t/C_0$  (effluent concentration at time  $t$ /influent concentration at time  $t=0$ ) during entire period of operation of the demonstration plant (63 cycles) and the increase in the concentration PO<sub>4</sub>-P in the regenerant. The NaOH was reused up to 5-8 times reaching a concentration of 785 mg PO<sub>4</sub>-P/L. When the efficacy of the regeneration fluid was no longer apparent, the solution was stored for the recovery process and reused or a new solution was prepared (Figure 6.4a). Figure 6.4b presents the breakthrough curves of cycles 1, 17, 32, 42 after regeneration with fresh regenerant. After the regeneration with fresh regenerant solution, when the adsorption cycles were initiated, the  $C_t/C_0$  was below 0.1 (Figure 6.4b). Nevertheless, the prolonged use of

the HAIX resin decreased the amount of bed volumes treated before breakthrough. In fact, while for cycle 1 the  $C_t/C_0$  was kept below 0.1 for almost 450 BV, the same  $C_t/C_0$  was reached after 108 BV in cycle 42 indicating a loss in the adsorption capacity over time (Figure 6.4b).

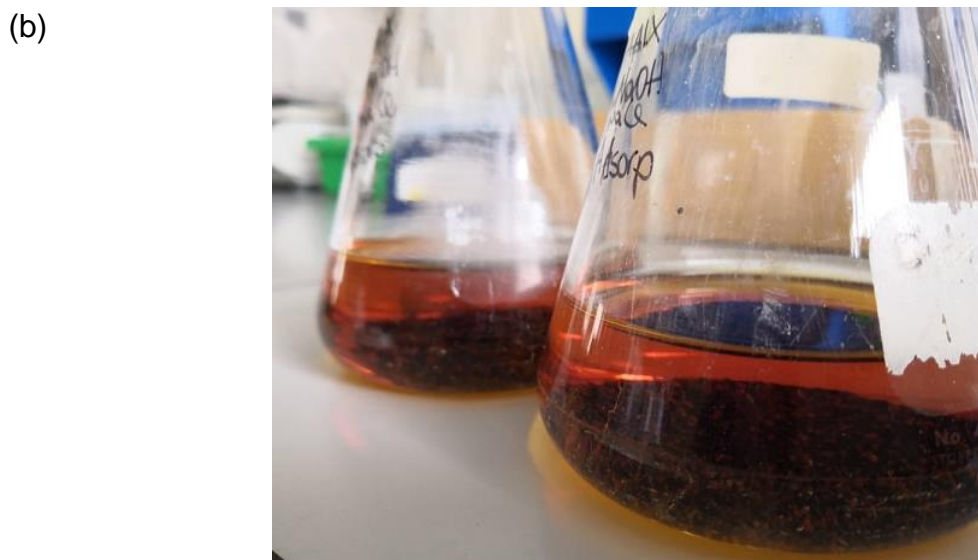
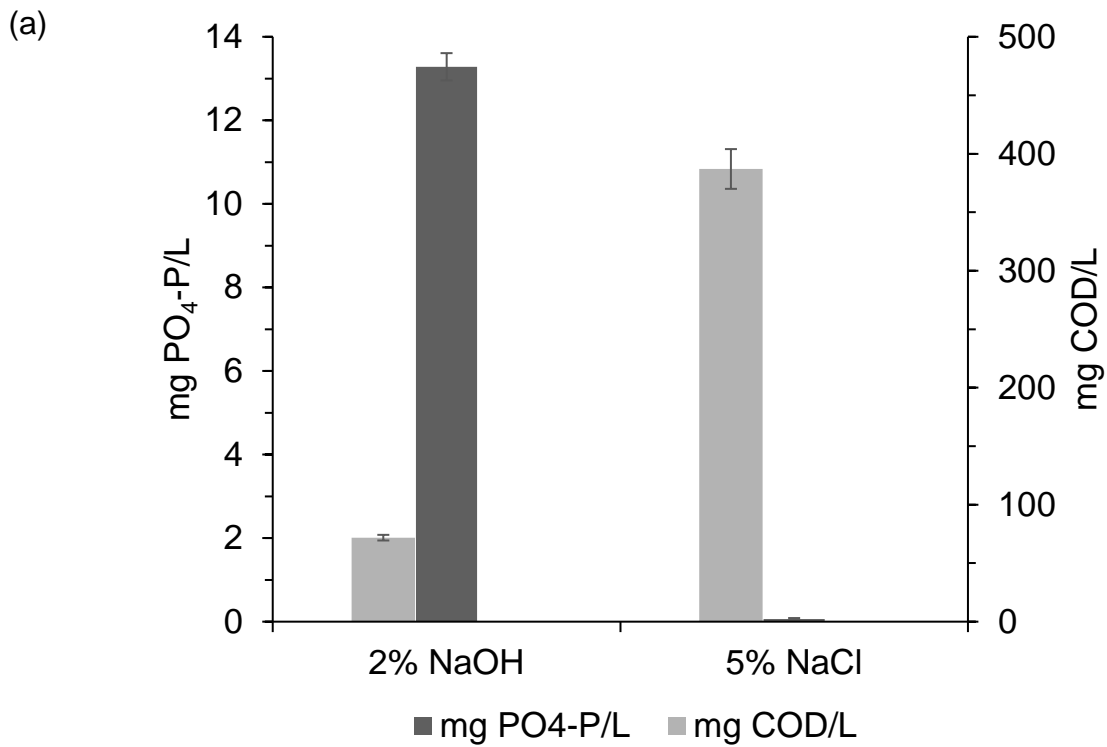




**Figure 6.4 (a)  $C_t/C_0$  for all the cycles performed at demonstration scale (63 cycles) and increase in orthophosphate concentration in the regenerant solution (NaOH) obtained by multiple reuse; (b) impact of reusing the same HAIX resin multiple times upon number of bed volumes treated between breakthroughs for cycle 1, 17, 32 and 42.**

### 6.3.4 Investigation of the accumulation of organics on the resin

The HAIX was also observed to remove around  $26 \pm 10\%$  of the influent COD during the entire period of operation. To investigate the impact of organics on resin capacity, a laboratory scale experiment was performed. When the resin was regenerated with NaOH 2%, about  $13.28 \pm 0.33$  mg  $\text{PO}_4\text{-P/L}$  and  $71.8 \pm 2.4$  mg COD/L were desorbed and released in the regenerant (Figure 6.5a). When the resin was regenerated with NaCl 5%, an additional  $0.06 \pm 0.03$  mg  $\text{PO}_4\text{-P/L}$  and  $387 \pm 17$  mg COD/L were released. The higher amount of organic matter in solution was confirmed by the evident brown colour of the NaCl solution after regeneration (Figure 6.5b). As a result, the resin regenerated with NaOH and NaCl presented adsorption capacity of  $0.43 \pm 0.0$  mg  $\text{PO}_4\text{-P/g}$  resin, 16% higher of the capacity of the resin regenerated with only NaOH ( $0.35 \pm 0.02$  mg  $\text{PO}_4\text{-P/g}$  resin).



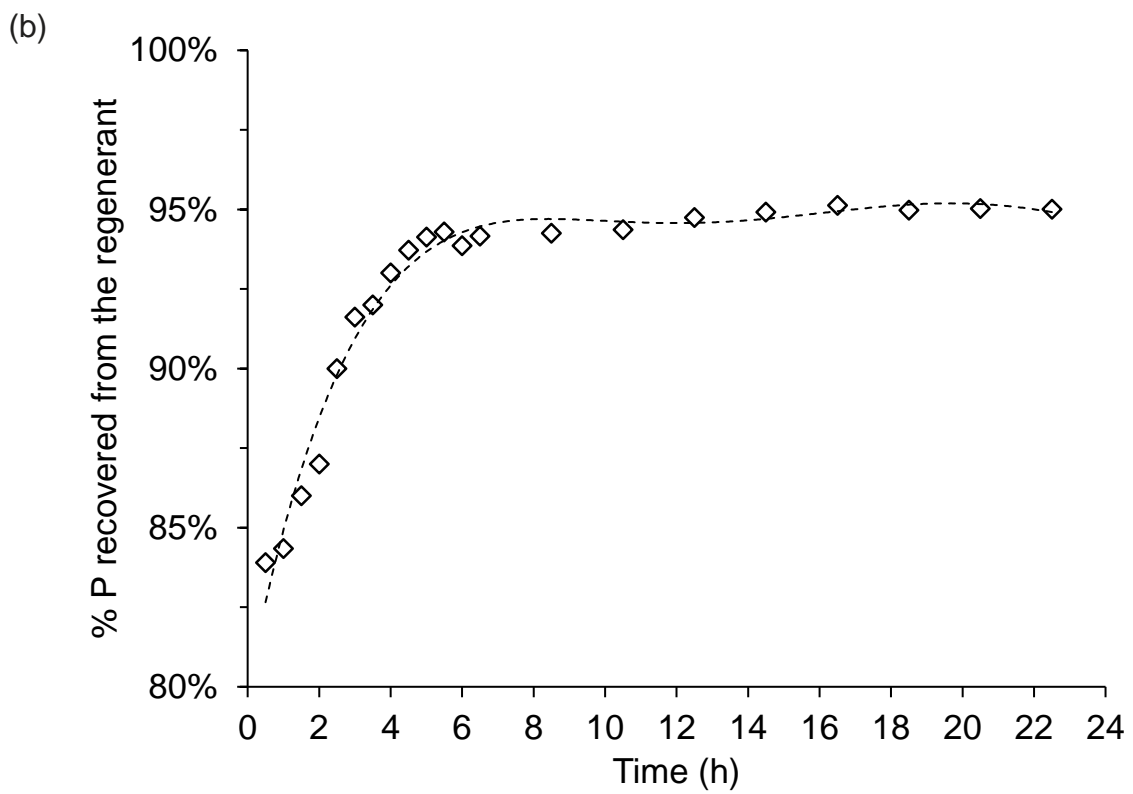
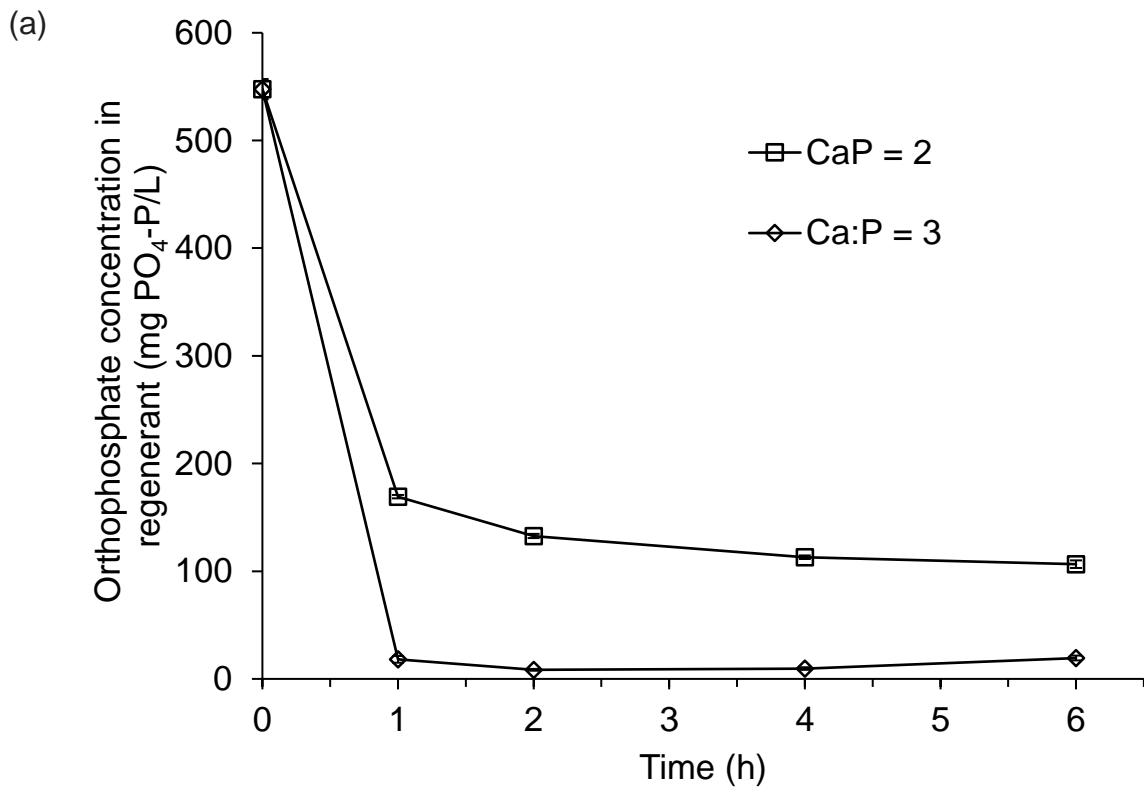
**Figure 6.5 (a) Orthophosphate and COD released from HAIX resin treated with NaOH 2% + NaCl 5% and (b) brown colour characteristic of organic matter in NaCl 5% solution after HAIX regeneration.**

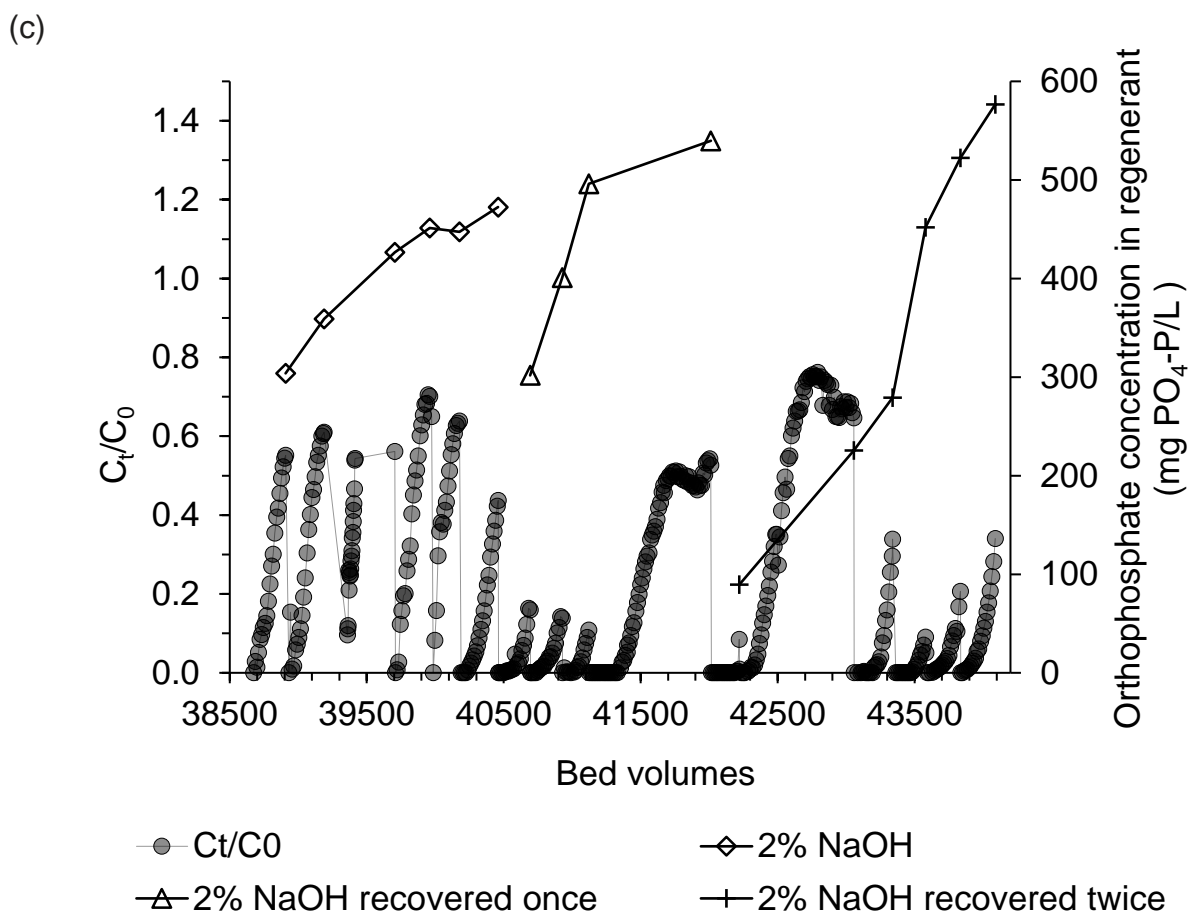


### 6.3.5 Phosphorous recovery from saturated HAIX solution

Reusing the same regenerant for 8 cycles increased the orthophosphate concentration up to 785 mg PO<sub>4</sub>-P/L. The addition of Ca(OH)<sub>2</sub> to a molar Ca:P ratio of 3 allowed for the recovery of 98% of the mass of PO<sub>4</sub>-P, after 1 hour of mixing (Figure 6.6a). In comparison, 69% of the orthophosphate present in solution was recovered after the addition of Ca(OH)<sub>2</sub> to a Ca:P ratio of 2, while a maximum recovery of 80.5% was obtained after 6 hours of mixing (Figure 6.6a). The concentration of orthophosphate in the NaOH regenerant decreased to 19.4±2.2 mg PO<sub>4</sub>-P/L and 106.5±3.5 mg PO<sub>4</sub>-P/L after the recovery with Ca:P ratios of 3 and 2, respectively. The pH of the regenerant solution before the recovery was 12.74 and final values of 12.75 and 12.83 were registered after the recovery with Ca:P of 3 and 2, respectively. Following the experiment to investigate the Ca:P ratio, batches of 50L of saturated regenerant were treated with Ca(OH)<sub>2</sub> at a Ca:P ratio of 3. As presented in Figure 6.6b, a plateau was reached after 6 hours of mixing (94% of recovery) and the PO<sub>4</sub>-P concentration decreased from 684±16 mg PO<sub>4</sub>-P/L to 42±2 mg PO<sub>4</sub>-P. At the same time, the calcium concentration in the regenerant solution was 0.4±0.01 mg Ca<sup>2+</sup>/L indicating that almost the total mass of calcium added as Ca(OH)<sub>2</sub> had precipitated.

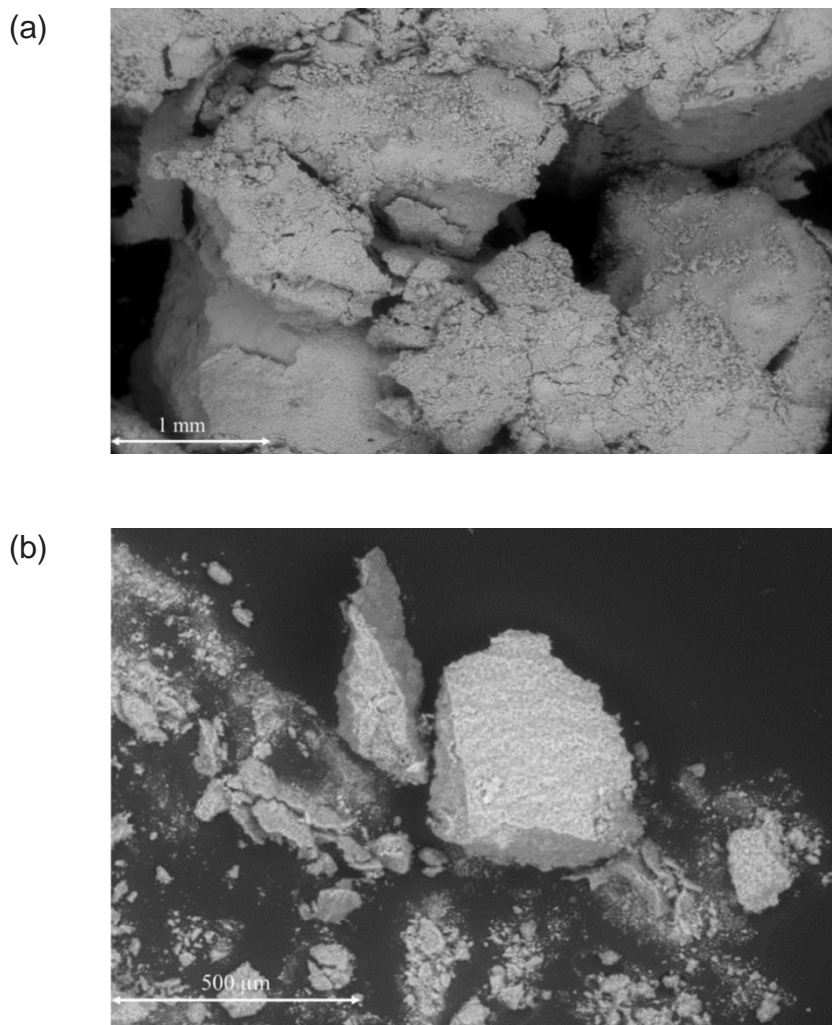
The recovery of the calcium phosphate allowed for the reuse of the NaOH as regenerant solution for the HAIX at demonstration scale (Figure 6.6c). In particular, as presented in Figure 6.6c, after the recovery, it was possible to regenerate the resin to keep  $C_t/C_0 < 0.2$  for 230-240 bed volumes. The recovery was repeated after four regeneration cycles (final concentration of NaOH of 539 mg PO<sub>4</sub>-P/L). The NaOH treated twice for the recovery was again reused as regeneration solution for the following six regeneration cycles maintaining a  $C_t/C_0$  below 0.2 for up to 228 bed volumes (Figure 6.6c).





**Figure 6.6 (a) Decrease in concentration of the regenerant solution (NaOH) following addition of calcium hydroxide to saturated NaOH at Ca:P molar ratio of 2 and 3 and (b) phosphorus (P) recovery from 50 L batch from saturated NaOH solution following addition of calcium hydroxide up to a Ca:P molar ratio of 3; (c) reusability of the recovered NaOH as regenerant solution at demonstration scale.**

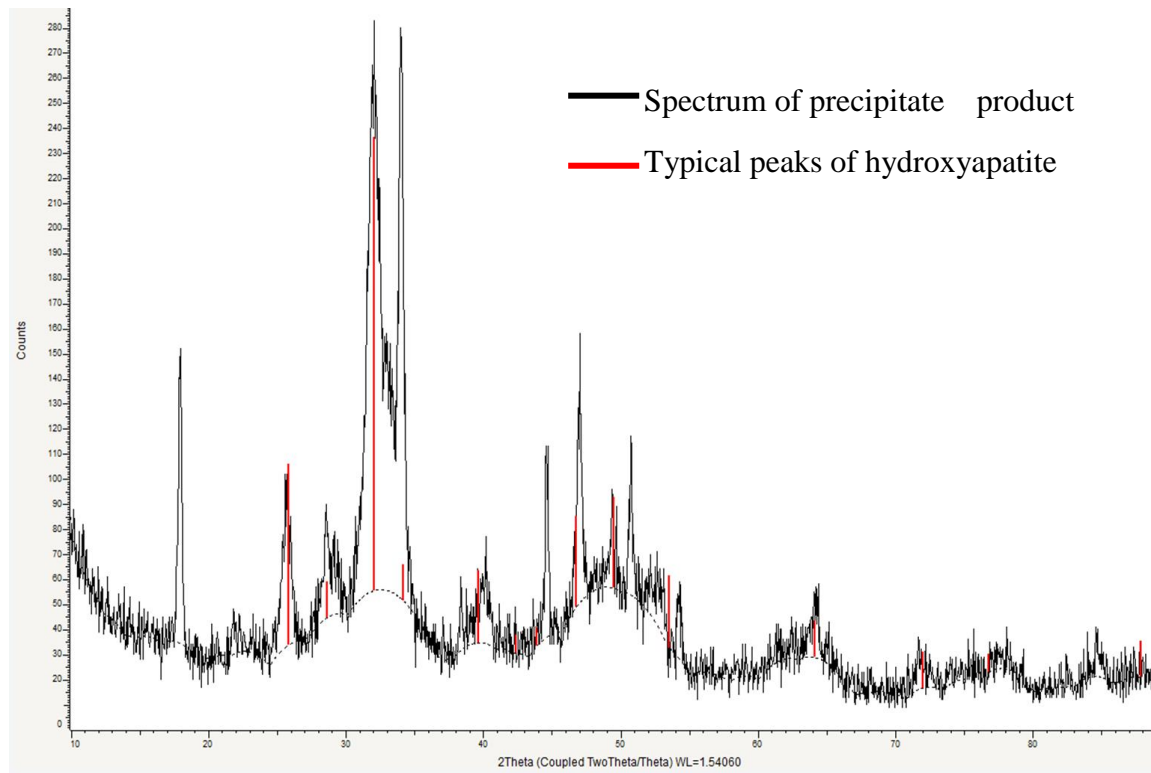
A total of 0.45 kg of precipitate was recovered from 50 L of saturated regenerant. The scanning electron microscope (SEM) analysis revealed an amorphous crystal structure and the EDX indicated a composition of 5.7% P, 15.1% Ca (in weight %) (Figure 6.7 and Table 6.2). The Ca:P ratio was 2.7, very close to dosed Ca:P ratio of 3. The XRD analysis showed that the recovered precipitate was similar to hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) as shown by the comparison against the standard from literature [38] (Figure 6.8a). The recovered hydroxyapatite was also analysed for impurities and it showed no pathogens (total coliforms and *Escherichia coli* <0 cfu/g), low concentrations of metals and the investigated organic pollutants were below the detection limits (Table 6.3).



**Figure 6.7 (a-b) Scanning electron microscope pictures of recovered product, identified as hydroxyapatite.**

**Table 6.3 Scanning electron microscope analysis: element composition (% weight) of calcium phosphate precipitate from saturated NaOH treated with calcium hydroxide.**

| <b>Element</b>  | O    | Ca   | C    | P    | Na   | Si   | Mg   | S    | Al   |
|-----------------|------|------|------|------|------|------|------|------|------|
| <b>Weight %</b> | 63.0 | 15.1 | 12.7 | 5.7  | 2.6  | 0.4  | 0.2  | 0.2  | 0.1  |
|                 | ±0.5 | ±1.1 | ±1.0 | ±0.0 | ±0.2 | ±0.0 | ±0.1 | ±0.0 | ±0.0 |



**Figure 6.8 X-ray diffraction spectrum of calcium phosphate precipitate from saturated NaOH treated with calcium hydroxide (Ca:P=3) compared to hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>).**

**Table 6.4 Pathogens, metals and organics analysis of hydroxyapatite recovered from saturated regenerant.**

| Pollutant |                         | Concentration (µg/g) |
|-----------|-------------------------|----------------------|
| Pathogens | Total coliforms         | 0                    |
|           | <i>Escherichia coli</i> | 0                    |
| Metals    | Aluminium (Al)          | 4×10 <sup>5</sup>    |
|           | Cadmium (Cd)            | 2.4×10 <sup>4</sup>  |
|           | Chromium (Cr)           | 8×10 <sup>3</sup>    |
|           | Copper (Cu)             | 3.6×10 <sup>4</sup>  |
|           | Iron (Fe)               | 9.2×10 <sup>5</sup>  |

|                    |                         |                   |
|--------------------|-------------------------|-------------------|
|                    | Lead (Pb)               | $2.4 \times 10^3$ |
|                    | Mercury (Hg)            | $4 \times 10^2$   |
|                    | Nickel (Ni)             | $1.2 \times 10^4$ |
|                    | Potassium (K)           | $7.2 \times 10^5$ |
|                    | Zinc (Zn)               | $7.2 \times 10^4$ |
| Organic pollutants | Benzene                 | $4 \times 10^5$   |
|                    | Acenaphthene            | $<4 \times 10^4$  |
|                    | Acenaphthylene          | $<4 \times 10^4$  |
|                    | Anthracene              | $<4 \times 10^4$  |
|                    | Benzo (a) anthracene    | $<4 \times 10^4$  |
|                    | Benzo (g,h,i) perylene  | $<4 \times 10^4$  |
|                    | Benzo (a) pyrene        | $<4 \times 10^4$  |
|                    | Benzo (b) fluoranthene  | $<4 \times 10^4$  |
|                    | Benzo (k) fluoranthene  | $<4 \times 10^4$  |
|                    | Chrysene                | $<4 \times 10^4$  |
|                    | Dibenz (a,h) anthracene | $<4 \times 10^4$  |
|                    | Fluoranthene            | $<4 \times 10^4$  |
|                    | Fluorene                | $<4 \times 10^4$  |

|  |                             |                    |
|--|-----------------------------|--------------------|
|  | Indeno (1,2,3) cd<br>pyrene | <4×10 <sup>4</sup> |
|  | Naphthalene                 | <4×10 <sup>4</sup> |
|  | Phenanthrene                | <4×10 <sup>4</sup> |
|  | Pyrene                      | <4×10 <sup>4</sup> |
|  | PAH, Total                  | <4×10 <sup>4</sup> |
|  | 4-n-Nonylphenol             | N/S                |
|  | 4-Nonylphenol<br>(Tech)     | N/S                |

## 6.4 Discussion

To obtain high effluent quality in presence of competitive ions in municipal wastewater, there is the need of an adsorptive resin with high selectivity for orthophosphate ( $\text{PO}_4\text{-P}$ ). The wastewater treated in this study contained 75 mg  $\text{SO}_4\text{-S/L}$ , 141 mg  $\text{NO}_3\text{/L}$  and 76 mg  $\text{Cl/L}$ , while the orthophosphate concentration was 6 mg  $\text{PO}_4\text{-P/L}$  (Table 6.2). This confirmed the typical composition of secondary effluent wastewater, where competing ion such as  $\text{SO}_4\text{-S}$ ,  $\text{NO}_3$  and  $\text{Cl}$  are usually present in higher concentration than  $\text{PO}_4\text{-P}$  [31], [39]. In particular, the high concentration of  $\text{SO}_4\text{-S}$  can act as strong competitor for the  $\text{PO}_4\text{-P}$  adsorption due to the similarity in atomic weight and valence between the two molecules [1], [16]. The hybrid anion exchanger (HAIX) was proved to have high selectivity in presence of competing ions [15], [31], thanks to the quaternary ammonium groups on the polymeric base and the hydrated ferric oxide nanoparticles dispersed on the resin [17] (Figure 6.1). In this study, up to 430 bed volumes of wastewater could be treated before breakthrough with a capacity of 4.1 mg  $\text{PO}_4\text{-P/g}$  resin working with an EBCT of 5 minutes (Figure 6.3a). This is in agreement with previous studies completed with EBCT of 4 min (capacity up to 3.8 mg  $\text{PO}_4\text{-P/g}$ ) [19]. HAIX ensured up to 90% of the removal of  $\text{PO}_4\text{-P}$  from the wastewater maintaining high effluent quality for multiple cycles [18]. The capacity obtained in this work was comparable with values reported in literature of 0.29-14.4 mg  $\text{PO}_4\text{-P/g}$  resin, depending on the initial  $\text{PO}_4\text{-P}$  concentration wastewater [6],[7],[18] (Table 6.1).

Up to 63 cycles of adsorption/desorption were performed at demonstration scale (Figure 6.4a). During regeneration at alkaline pH, the hydrated ferric oxide nanoparticles are deprotonated and negatively charged thus ensuring  $\text{PO}_4\text{-P}$  desorption [15]. However, the efficiency of  $\text{PO}_4\text{-P}$  removal while reusing the resin was affected by both the reuse of the same regenerant solution (Figure 6.3b) and the long-term operation (Figure 6.4). The multiple reuse of the regenerant resulted in a decrease of the regeneration efficiencies and in the reduction of the available adsorption sites. Consequently, a loss in capacity from 7.2  $\mu\text{g PO}_4\text{-P/g resin/BV}$  to 2.9  $\mu\text{g PO}_4\text{-P/g resin/BV}$  after the fifth reuse of the regenerant was detected (Figure 6.3b). The success of the ion exchange process relies on restoring the initial adsorption capacity of the resin after each regeneration cycle over a long-term operational period. In this study, by using the same resin over an extended period of times, a reduction in



the adsorption capacity was detected (Figure 6.4). This indicated that the resin lifespan was reduced when subjected to intensive operation that was linked to the removal of organics. During the entire period of operation, a constant COD removal of  $26\pm 10\%$  was measured. This corroborates with previous studies [18] and highlights the importance of taking into consideration the accumulation of organic matter on the resin surface. This, in fact, can occupy the sorption sites and, at the same time, limit the mass transfer on the resin surface and, when not removed, will eventually foul the HAIX and result in loss of capacity [17]. During the conventional regeneration with NaOH, the organic matter is only partially desorbed. At laboratory scale, when the HAIX was regenerated with NaOH 2%, 71 mg COD/L were desorbed, however, when after regeneration with NaCl 5%, the COD desorbed were 387 mg COD/L (Figure 6.5). This aligned with the study from SenGupta [17] that suggests the soaking of the resin in NaCl at slightly high temperature ( $40^{\circ}\text{C}$ ) facilitates the desorption of organics. After the regeneration with NaCl 5%, the HAIX presented higher regeneration capacity ( $0.43\pm 0.0$  mg $\text{PO}_4\text{-P/g}$  resin) compared to the resin regenerated with only NaOH 2% ( $0.35\pm 0.02$  mg  $\text{PO}_4\text{-P/g}$  resin). This proves that the organics have an impact on the capacity of the resin and, therefore, a periodic regeneration with NaCl is required. Successively, the NaCl brine and the organics can be separated by nanofiltration, electrodialysis or ion exchange technologies [40], [41]. This would ensure the recovery of the brine for its reuse and allow for the recovery of natural organic matter (NOM) (i.e. humic acids and low molecular weight (LMW) organics [40]). In particular, there is a recent interest in the recovery of humic substances for their application in the agricultural industry due to their beneficial effects on soil quality and plant growth [42]. Additional studies on the possibility to recover organics from saturated IEX brine should be performed as well as their recovery as valuable products.

The temperature of the wastewater registered during the entire period of operation, varied between 6 and  $25^{\circ}\text{C}$ . Although the impact of temperature could not be clearly established in this investigation, previous studies reported no influence of the temperature upon the orthophosphate uptake [17]. Lee *et al.* [15] reported similar breakthrough curves for the orthophosphate adsorption with HAIX at 7, 23 and  $37^{\circ}\text{C}$ . This represents one of the advantages of the IEX technologies compared to biological processes where low temperature can have an impact on the microbial growth and, as a consequence, on a decrease in the efficiency of the process [15]. Additionally,

the IEX process is considered adequate for water and wastewater treatment thanks to its simplicity of operation, no need of start-up time and resilience towards any fluctuation of the influent concentrations [17].

However, an effective management of the regenerant solution is the limiting step for the implementation of the ion exchange process at bigger scale. The disposal of saturated regenerant as hazardous waste represents a cost (typically £65/ton [8]) and environmental concern [8], [16]. For this reason, the recovery of the regenerants is critical to ensure sustainability and economic feasibility of the IEX process. In this work, the orthophosphate content in the NaOH regenerant solution reached up to a concentration of 785 mg PO<sub>4</sub>-P/L after multiple reuse of the regenerant solution. The regenerant management entailed mixing with calcium hydroxide for the recovery of calcium phosphate. The most effective recovery was obtained with Ca:P=3 (98%) after 1 hour (compared to 80.5% with Ca:P=2). Working at demonstration scale with a flow of 10 m<sup>3</sup>/day, a total of 75 kg/year of recovered hydroxyapatite were estimated. Depending on the quantity of the recovered product, niche applications for the hydroxyapatite can be found, especially in market sectors interested in investing in circular economy. In particular, the hydroxyapatite can be used as agricultural and ornamental crop fertiliser [8]. However, the marketability of the product depends on its purity (level of pathogens, heavy metal and organics) which represents a restriction for the utilization of such a product as fertiliser due to legal limits. In particular, the most common pathogens (*Escherichia coli* and total coliforms) were not found in the hydroxyapatite produced (Table 6.3) while the organics were mostly below the detection limit. Particular attention needs to be put on the level of metals such as cadmium, chromium, copper, lead, mercury, nickel and zinc, which are regulated at different limits depending on the country [43]. When comparing the metals content of the recovered product with known regulation limits for fertilisers, the metals concentration in the precipitate were found to comply with regulations for product use as fertilisers in China [44], Turkey [43] and the new proposed European Union (EU) limits [45] (Table 6.5). Therefore, it can be concluded that the hydroxyapatite produced can have a potential in the market as fertiliser. Additionally, hydroxyapatite has been used for the remediation of water and soils contaminated with heavy metals such as zinc, lead as well as cadmium [46], [47].

**Table 6.5 Heavy metals legal limit from different countries (namely European Union [45], China [44], Turkey [43]) (adapted from [43]).**

|          | Legal limit ( $\mu\text{g}/\text{kg}$ ) |                   |                   | Concentration in precipitate |
|----------|-----------------------------------------|-------------------|-------------------|------------------------------|
|          | European Union                          | China             | Turkey            | $\mu\text{g}/\text{kg}$      |
| Cadmium  | $6.0 \times 10^4$ <sup>a</sup>          | $1.0 \times 10^4$ | N/A               | $2.4 \times 10^4$            |
| Chromium | $2.0 \times 10^3$                       | $5.0 \times 10^5$ | $2.7 \times 10^5$ | $8.0 \times 10^3$            |
| Copper   | N/A                                     | N/A               | N/A               | $3.6 \times 10^4$            |
| Lead     | $1.5 \times 10^5$                       | $1.5 \times 10^5$ | N/A               | $2.4 \times 10^3$            |
| Mercury  | $2.0 \times 10^3$                       | $5.0 \times 10^3$ | N/A               | $4 \times 10^2$              |
| Nickel   | N/A                                     | N/A               | $1.2 \times 10^5$ | $1.2 \times 10^4$            |
| Zinc     | $1.2 \times 10^5$                       | N/A               | $1.1 \times 10^6$ | $7.2 \times 10^4$            |

<sup>a</sup>  $6.0 \times 10^4$  first 3 years;  $4.0 \times 10^4$   $\mu\text{g}/\text{kg}$ , following 9 years

After the hydroxyapatite recovery, it was possible to reuse the NaOH as regenerant solution for the HAIX. In fact, after regeneration with the NaOH used for the recovery, it was possible to reach again a good effluent quality ( $C_t/C_0 < 0.2$ ) thus proving the reusability of the regenerant solution (Figure 6.6c). However, it is important to highlight that the multiple reuse of the regenerant solution after the recovery of the hydroxyapatite can have an impact on the purity of the recovered product. To indicate, additional studies on the hydroxyapatite obtained from the NaOH recovered twice, revealed an increase in the concentration of heavy metals (namely chromium, copper, nickel, potassium and zinc) up to 78% compared to the concentration in the hydroxyapatite recovered from the NaOH treated once which could limit the implementation of the product in the fertiliser industry. The results from this work confirmed the feasibility of IEX to efficiently remove P from wastewater and recover it in with a sustainable circular approach which is not found in conventional biological (EBPR) processes [8]. This work demonstrated that the HAIX is suitable for long-term operation of IEX technology and effluent quality  $< 0.3$  mg  $\text{PO}_4\text{-P}/\text{L}$  can be maintained for a significant number of bed volumes. However, an efficient regeneration of both the hydrated ferric oxide nanoparticle (with NaOH) and the polymeric base of the resin (with NaCl) is needed to ensure the long-term applicability the process and avoid the

reduction of the adsorption capacity and lifespan of the resin. Additionally, it was proved that more than 95% of the P in municipal wastewater can be recovered as hydroxyapatite from the saturated regenerant solution (NaOH) by adding calcium hydroxide to a Ca:P molar ratio of 3 in less than 6 hours.

## 6.5 Conclusions

- The IEX demonstration scale plant with HAIX resin removed up to 90% of the PO<sub>4</sub>-P present in the wastewater and maintain high effluent quality (<0.3 mg PO<sub>4</sub>-P/L) at an EBCT of 5 minutes.
- The adsorption capacity of the resin over multiple cycles was affected by the reuse of the regenerant solution (NaOH 2%) which caused a loss in capacity from 7.2 µg PO<sub>4</sub>-P/g resin/BV to 2.9 µg PO<sub>4</sub>-P/g resin/BV after the fifth reuse of the regenerant.
- COD was removed by the HAIX (26%) which caused a slow fouling of the resin and impacted the adsorption capacity over extended periods of operation. A scattered regeneration with NaCl is needed to increase the adsorption capacity of the resin.
- Up to 95% of the PO<sub>4</sub>-P was recovered by adding Ca(OH)<sub>2</sub> to the saturated regenerant to a Ca:P molar ratio of 3 in less than 6 hours. The recovered product was identified as hydroxyapatite. It respected the limits of metals concentration existing in different countries and can be used as fertiliser. A total recovery of 75 kg/year of hydroxyapatite was estimated for the 10 m<sup>3</sup>/day demonstration plant.
- Following the recovery, it was possible to regenerate the HAIX resin and the C<sub>t</sub>/C<sub>0</sub> at the beginning of the adsorption cycle was kept below 0.2 confirming the reusability of the regenerant solution.

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## 7 DISCUSSION

The aim of this PhD thesis was to underline the mechanisms of removal and recovery of ammonium ( $\text{NH}_4^+$ ) and phosphorus (as  $\text{PO}_4^{3-}$ ) from wastewater through the ion exchange (IEX) process in order to optimise the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  removal efficiency and maximise their recovery from IEX regenerant brines, when working at demonstration scale over an extended period of time.

### 7.1. Ammonium removal and recovery

The most important environmental challenges towards the implementation of a circular economy scheme in the wastewater cycle [1] are connected to the need of reducing the ammonium in wastewater down to low concentration ( $<1 \text{ mg NH}_4^+\text{-N/L}$  [2]), and enabling its recovery. Additionally, the need to strengthen the global response to the threat of climate change requires a technology with reduced carbon footprint which can help the water sector reaching carbon neutrality [3]. As presented in Chapter 1, conventional biological technologies are focused on the removal of ammonium from wastewater effluents but present limited possibility for the recovery and have recently risen environmental concerns due to the production of nitrous oxide ( $\text{N}_2\text{O}$ ) as intermediate [4], a greenhouse gas with a global warming potential approximately 310 times higher than carbon dioxide ( $\text{CO}_2$ ) [5].

Results presented from Chapter 2, 3 and 5, showed that the ion exchange (IEX) process can represent a sustainable and efficient alternative for the ammonium removal and recovery from secondary treated wastewater. In particular, following laboratories and demonstration scale studies, the synthetic Zeolite-N was confirmed as the most suitable media for application in IEX processes due to the high resilience and ammonium exchange capacity (up to  $17.1 \text{ mg NH}_4^+\text{-N/g media}$ ) (Chapter 5) and high mechanical strength ( $0.03\%$  loss/month) (Chapter 2). However, Zeolite-N is no longer available in the market which forces the investigation of replacement media. In particular, a suitable candidate to replace Zeolite-N should have similar selectivity towards ammonium ions as well as similar Al/Si as this affects the ion exchange capacity of the media (Chapter 2). Zeolite6, produced following the same protocol as

Zeolite-N [6], showed similar ammonium exchange capacity (0.9 mg NH<sub>4</sub><sup>+</sup>-N/g media) as Zeolite-N (1.1 mg NH<sub>4</sub><sup>+</sup>-N/g media) in laboratory scale experiments with secondary effluent wastewater. However, the low mechanical strength of this media forced the stopping of the operation of the demonstration plant due to intensive breakage (10% loss/month) (Chapter 2). This highlighted the need to improve the production process of synthetic zeolites and the necessity to obtain a strong media which can be suitable for long-term operations while, at the same time, maintaining efficient ammonium exchange capacity. In Chapter 4, due to its availability on the market and low cost in production, the natural clinoptilolite Zeoclere30 was presented as ammonium exchange media. However, the results from the operation at demonstration scale proved that Zeoclere30 is still not a competitive ion exchanger in terms of ammonium exchange capacity. In particular, the EBCT and regeneration have to be optimised to ensure high ammonium exchange capacity as well as an efficient regeneration. The efforts towards the identification of a new media which could substitute Zeolite-N were justified in Chapter 3 which proved that the IEX process is a resilient technology capable to adapt to daily and seasonal variation in the ammonium concentration of the wastewater (<0.006-26 mg NH<sub>4</sub><sup>+</sup>-N/L). This, in fact, constitutes one of the main drawbacks of the conventional biological treatments as these are affected by loading peaks [7].

Although the IEX process for ammonium removal looks promising, the necessity to produce the regenerant brine and dispose it (typically £65/ton [4]) as hazardous waste is not considerate suitable for the long-term operation. For this reason, in Chapter 5, hollow fibre membrane contactor (HFMC), vacuum thermal stripping at the rotary evaporator (VTS) and multicomponent vacuum thermal stripping (MVTs) technologies were compared for their relative ammonium recovery efficiencies from the saturated regenerant brine. This could in fact reduce the chemical consumption of the process by ensuring the multiple reuse of the regenerant brine and, at the same time, allowing for the recovery of a high purity product (ammonium sulphate/concentrated ammonia solution). More in particular, when comparing the HFMC and the (M)VTS technologies, the first was detected as the most efficient technology to recover ammonia from concentrated solution (recovery efficiency of 100%). On the other hand, VTS presented higher ammonia loss and therefore required an accurate control of the

operational conditions (i.e. the temperature of the thermal bath and the vacuum pressure). Moreover, the energy required for the heat of the saturated solution and to power vacuum pumps increased the environmental impact of the process (Chapter 3). Nevertheless, the life cycle assessment (LCA) analysis conducted in Chapter 3 proved the environmental benefits linked to the use of the IEX process as tertiary process for ammonium removal from wastewater. The IEX process (with NaCl used as regenerant brine and membrane stripping as recovery technique) resulted in savings of 25% cumulative energy demand, a reduction of 66% of the global warming potential and of 62% of the marine eutrophication potential, when compared with traditional nitrification-denitrification technology (Chapter 3).

## **7.2. Phosphorus removal and recovery**

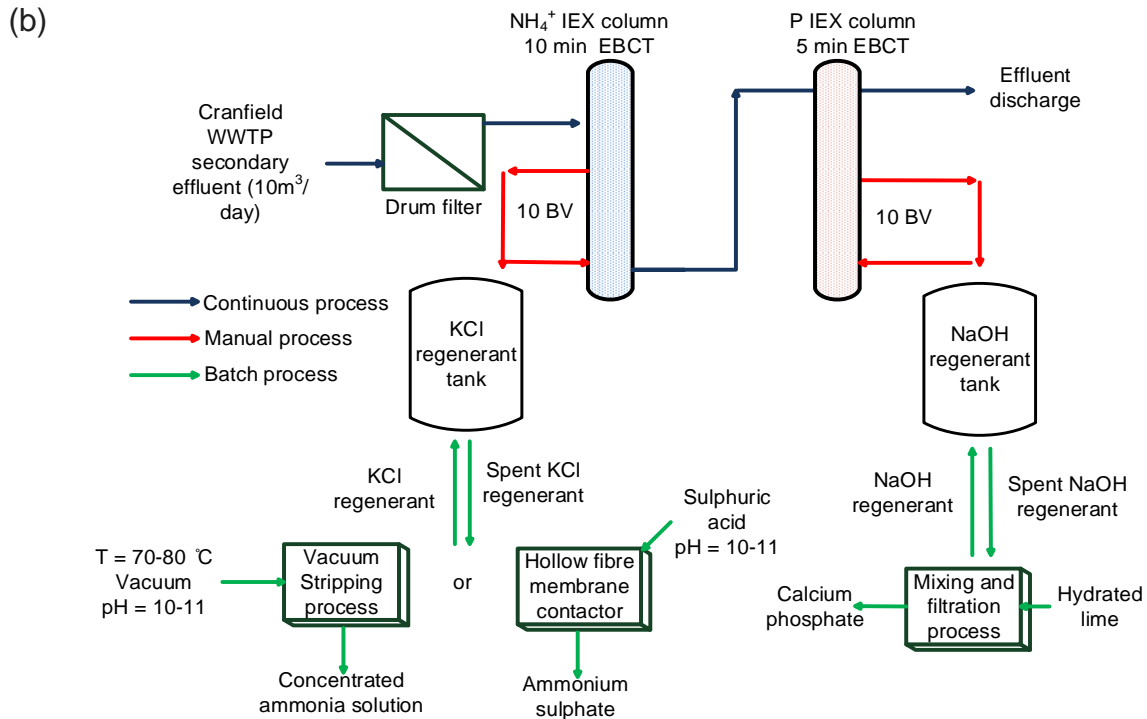
The use of hybrid anion exchanger (HAIX) resin for phosphorus (as orthophosphate,  $\text{PO}_4\text{-P}$ ) removal from wastewater is a well-known process which has been intensely studied [8]–[10] and confirmed in this work where HAIX removed  $\text{PO}_4\text{-P}$  from secondary effluent wastewater down to low concentration ( $<0.1$  mg  $\text{PO}_4\text{-P/L}$ ) (Chapter 6). This work, however, represented a step forward towards the use of the HAIX as tertiary treatment process for the  $\text{PO}_4\text{-P}$  removal as it proved that the resin can be continuously used for multiple cycles over a period of 2 years (total of 63 cycles) at demonstration scale. To maintain a consistency in the  $\text{PO}_4\text{-P}$  adsorption capacity over multiple cycles, it was concluded that a wash of the resin in sodium chloride (NaCl) is needed periodically to avoid the fouling of the resin caused by the organic matter present in wastewater. At the same time, this work also proved that the saturated regenerant solution (sodium hydroxide, NaOH) can be used for the recovery of an high purity product (hydroxyapatite). The regenerant was reused up to 8 times before reaching saturation (concentration of 785 mg  $\text{PO}_4\text{-P/L}$ ) and, following the recovery of the hydroxyapatite (a valuable fertiliser [11]), its regeneration capacity was restored. This proved that the treated regenerant brine could be reused multiple times thus reducing the chemical consumption and environmental impact of the process [4]. Therefore, it was concluded that this technology offers a route to efficiently remove  $\text{PO}_4\text{-P}$  from wastewater and recover it in with a sustainable circular approach which is not found in conventional biological (EBPR) processes [4].

### 7.3. Ammonium and phosphorus removal and recovery

The work presented in this PhD thesis significantly moved the ion exchange process higher in the technology readiness level by investigating the removal and recovery of both ammonium (as  $\text{NH}_4^+\text{-N}$ ) and phosphorus (as  $\text{PO}_4\text{-P}$ ) at demonstration scale for a long period of time. Over almost 2.5 years, the operation at demonstration scale (Figure 7.1) allowed for the study of different parameters, which were monitored for the entire period of operation and would need to be taken into consideration in future implementation of the IEX process (Table 7.1).

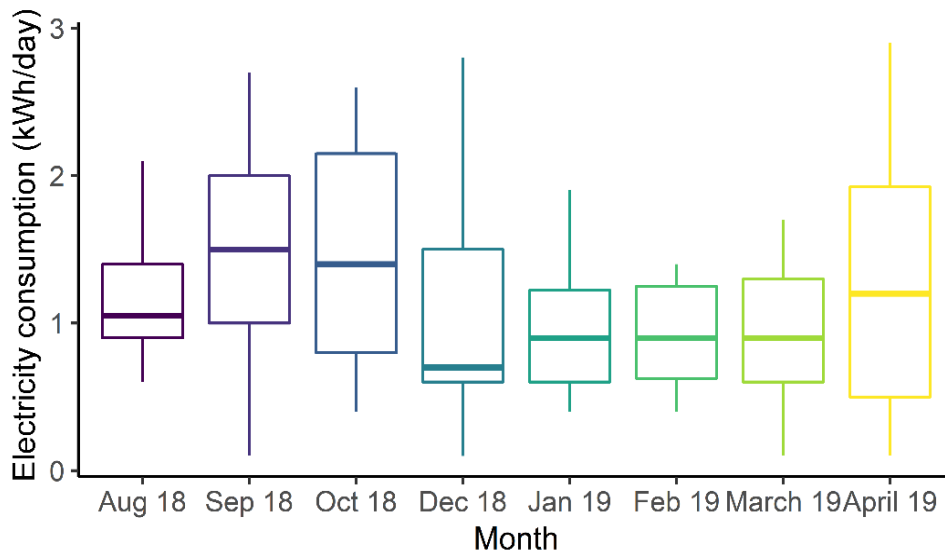
(a)





**Figure 7.1 (a) Ion exchange demonstration plant for ammonium and phosphorus removal with storage tanks for regenerant brines and (b) schematic representation of ammonium and phosphorus removal and recovery operations.**

The IEX process was proved adequate for wastewater treatment thanks to its simplicity of operation, no need of start-up time, resilience towards any fluctuation of the influent concentrations (Chapter 3) and low environmental impact (Chapter 3) related to lack of greenhouse gas (GHG) emission and low energy demand. In the IEX process, these are mainly connected to the electricity required for the running of the plant (nutrients removal and recovery and resin regenerations) and for the production of IEX resin and regenerants (Chapter 3). In particular, moving forward towards an environmentally sustainable circular economy, the reduction in GHG emission (namely CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub>) is a crucial advantage of the IEX process compared to conventional biological processes. Additionally, the electricity consumption of the IEX demonstration plant (Figure 7.1) was monitored during the operation (ENERWATER Wellness TechGroup©) and resulted in an average of 1.17±0.068 kWh/day, i.e., 0.12±0.01 kWh/m<sup>3</sup> (Figure 7.2). This was mainly due to the influent pump and the drum filter as the mixers were only used when the regeneration or calcium phosphate recovery were taking place.



**Figure 7.2 Boxplot monthly energy consumption (kWh/day) of IEX demonstration plant (ammonium and phosphorus removal and recovery) for the period August 2018-April 2019.**

Potentially, the IEX process can be used to treat any type of wastewater as long as this presents adequate nutrients concentration and low solids. These, in particular, can cause clogging and packing of the resin bed which, therefore, will required more frequent backwashes which could damage the resin and require its replacement and impact the overall cost of the system (Table 7.1). The demonstration plant used in this work was designed to have the ammonium removal column before the phosphorus removal one (Figure 7.1). This was intentional as the zeolite could act as additional filter for solids removal prior the phosphorus removal through HAIX. In fact, due to their small dimension (0.69 mm, Chapter 6), the HAIX beads are more affected by residual solids than the zeolites and therefore more prone to packing. If the phosphorus removal through HAIX alone were required, the column would need to be preceded by the complete solids removal (i.e. via sand filtration).

When considering the implementation of the IEX process in existing wastewater treatment plant, the infrastructures will need to be adapted to the available IEX resin. This was confirmed in Chapter 4 where the empty bed contact time, EBCT (10 minutes) and regeneration operation (10 bed volumes of KCl 10%) previously optimised for Zeolite-N were found not suitable for the natural Zeoclere30 which



required longer EBCT and hypochlorite (14-15% w/w) as regenerant solution (not suitable due to its high corrosivity). The optimisation of the EBCT is a crucial factor to ensure the efficiency and applicability of the IEX process (Chapter 3 and 6). More in particular, for the HAIX resin, a longer EBCT would reduce the frequency of regenerations thus reducing the cost and environmental impact connected to the production of saturated regenerant brine.

The success of the implementation of the IEX process at bigger scale depends on the possibility to maintain high removal capacity, and therefore high effluent quality ( $<0.1$  mg  $\text{PO}_4\text{-P/L}$  and  $<1$  mg  $\text{NH}_4^+\text{-N/L}$  [12],[2]), over multiple cycles. It was demonstrated that such concentration can be reached by using HAIX and Zeolite-N, however, as the demonstration plant was operated manually, it was difficult to monitor the effluent quality which caused the variability of the effluent concentrations and a lack of consistency between the cycles. For this reasons, to fully demonstrate the benefits of the IEX process, it is suggested the use of an automated plant to monitor the effluent quality and start the regeneration phase when the desired effluent concentration is reached.

As presented in this work, the implementation of the IEX process at bigger scale can be hindered by the production of highly concentrated brines (around 700 mg  $\text{NH}_4^+\text{-N/L}$  in KCl, Chapter 5, and 700 mg  $\text{PO}_4\text{-P/L}$  in NaOH, Chapter 6) which represent both an economic and environmental impact [4]. Therefore, an accurate management of the regenerant operation and brines is needed. The saturated brines can be treated for the recovery of nutrients, which has the double advantage of ensuring the reusability of the brines and recovering the nutrients as valuable products. However, for the management of the Zeolite-N brine (KCl), the recovery process has just been tested at laboratory scale (Chapter 5) and, therefore, its application at bigger scale and the possibility to reuse the brine solution require further studies. On the other hand, the recovery of the calcium phosphate from the saturated NaOH and the possibility to reuse the brine has been tested at demonstration scale (Chapter 6). Future studies are nevertheless needed to study the decrease in the product purity connected to multiple treatment of the saturated brine (Table 7.1). Once optimised, the nutrients recovery could increase the environmental benefits and economic sustainability related to the implementation of IEX process in existing WWTP (Figure

7.3). The recovered calcium phosphate and ammonium sulphate/concentrated ammonia solution can in fact find application in the chemical sector or in the fertiliser industry, both as separate products or combined in a nutrient-rich fertiliser. Further applications of the concentrated ammonia solution include its use in the cleaning sector, in plastics and textile manufacturing [13], as an absorbent for H<sub>2</sub>S and CO<sub>2</sub> in biogas purification and upgrading [14] and in microbial protein production [15], [16] (Figure 7.3). These applications will need to be further investigated. Importantly, the afterlife of the ion exchange resins and their disposal require further studies. Zeolite-N, saturated with both NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> ions (depleting nutrients [17]), could be used as fertiliser (Figure 7.3) which would improve the overall benefits of the IEX process (Chapter 3). On the other hand, HAIX could pose a risk when disposed into landfill, as Fe<sup>3+</sup> can be reduced to Fe<sup>2+</sup> thus causing leaching of toxic contaminants [18]. For this reason, an efficient disposal technique is needed and should focus on obtaining a safe final product with minimum waste volume.

**Table 7.1 Operating parameters and recommendation when using the IEX process from ammonium and phosphorus removal and recovery.**

|                    | <b>Ammonium</b>                                                                                                                             | <b>Phosphorus</b>                          | <b>Comment</b>                                                                                                                |
|--------------------|---------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|
| Process            | Ion exchange                                                                                                                                | Adsorption/Ion exchange                    |                                                                                                                               |
| Operational flow   | 10 m <sup>3</sup> /day                                                                                                                      | 10 m <sup>3</sup> /day                     | Possibility to scale-up the system                                                                                            |
| Media supplier     | Zeolite-N: no supplier in the market<br>Zeolite1-6: BYK, Additives & Instrument (UK)<br>Zeoclere30: Mineral Supplies International Ltd (UK) | HAIX: Layne Christensen Company (USA)      | The availability of the media in the market is the limiting step towards the scale-up of the process                          |
| Type of wastewater | Secondary treated (with trickling filters)                                                                                                  | Secondary treated (with trickling filters) | Potentially different types of wastewater can be treated as long as they present low solids and high nutrients concentrations |
| Temperature (°C)   | 7-20                                                                                                                                        | 7-20                                       | The process is not directly affected by temperatures variation                                                                |

|                                     |                                                                                                 |                                      |                                                                                                                                                                                                                                   |
|-------------------------------------|-------------------------------------------------------------------------------------------------|--------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| COD in feed (mg/L)                  | 30-55 mg/L                                                                                      | 30-55 mg/L                           | The organics in the wastewater can affect the adsorption efficiency of the HAIX by fouling the resin                                                                                                                              |
| pH                                  | 6-7.5                                                                                           | 6-7.5                                | The IEX process depends on the pH of the wastewater as this controls the amount of the ionic form of ammonium and phosphorous available for the ion exchange                                                                      |
| Nutrients concentration feed (mg/L) | Seasonal and diurnal variation of the concentration (0-26 mg NH <sub>4</sub> <sup>+</sup> -N/L) | Stable at ~6 mg PO <sub>4</sub> -P/L | Variation in the influent concentration can impact the ion exchange capacities; however, the IEX process has proved good resilience                                                                                               |
| Total suspended solids (mg/L)       | As low as possible to avoid clogging                                                            | As low as possible to avoid clogging | A high concentration of solids will cause clogging and packing of the media bed and will require more frequent backwashes which could damage the resin and impact the cost of the system (more frequent replacement of the resin) |
| Empty bed contact time              | 10 minutes (synthetic zeolites)                                                                 | 5 minutes                            | In this work, the operational parameters of the IEX demonstration plant (EBCT and regenerant                                                                                                                                      |

|                                      |                                                                                            |                                                               |                                                                                                                                                                                                                                                                                                                                                                                |
|--------------------------------------|--------------------------------------------------------------------------------------------|---------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                      | ~20-30 minutes (or higher)<br>(natural zeolites)                                           |                                                               | solution) were chosen according to the previous laboratory studies [7], [12]. When implementing the IEX process with different resins, an accurate evaluation of the infrastructures and operational conditions will be required                                                                                                                                               |
| Regenerant brine                     | KCl 10%<br>NaCl 10%                                                                        | NaOH 2%<br>NaCl 5% (to remove organics)                       |                                                                                                                                                                                                                                                                                                                                                                                |
| Bed volumes of regenerant brine used | 10                                                                                         | 10                                                            |                                                                                                                                                                                                                                                                                                                                                                                |
| Removal efficiencies                 | Expected: >90%                                                                             | Expected: >90%                                                | Factors affecting the removal efficiencies were: the reuse of the regenerant solution (which affects the efficiency of regeneration and the possibility to restore the initial adsorption capacity of the resin after each regeneration cycle); the variability in the ammonium influent concentration for the Zeolite-N; the fouling of the HAIX due to organics accumulation |
|                                      | Obtained: 40-94%                                                                           | Obtained: 30-90%                                              |                                                                                                                                                                                                                                                                                                                                                                                |
| Concentration effluent (mg/L)        | 0-17 mg NH <sub>4</sub> <sup>+</sup> -N/L according to the influent ammonium concentration | It can be kept <0.1 mg PO <sub>4</sub> -P/L by decreasing the | An accurate control of the bed volumes of wastewater treated between regeneration is needed to ensure the desired high effluent                                                                                                                                                                                                                                                |

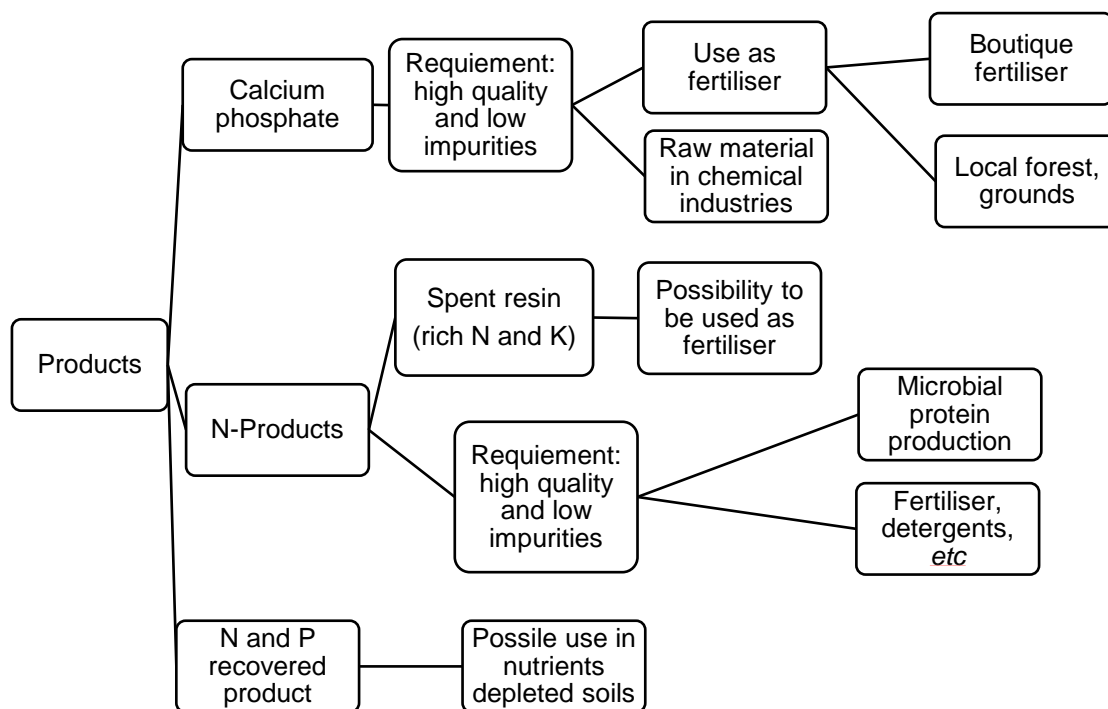
|                                                                        |                                                             |                                                                                                                                                                      |                                                                                                                                                    |
|------------------------------------------------------------------------|-------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                                        |                                                             | number of BV treated between regeneration                                                                                                                            | quality. This number of bed volumes should be adapted while reusing the resin multiple times                                                       |
| Bed volumes (BV) between regenerations                                 | 500-800 BV according to the influent ammonium concentration | Fresh resin: 430 BV.<br>For the following cycles, the reduction of the removal efficiencies required regeneration after 200-250 BV to maintain high effluent quality |                                                                                                                                                    |
| Maximum number of regeneration cycles performed at demonstration scale | 9 cycles                                                    | 63 cycles                                                                                                                                                            | With an accurate control of the regeneration routine and the use of a strong media, the IEX process is suitable for long term period of operations |
| Number of times the same                                               | 1-2 times                                                   | 5-8 times                                                                                                                                                            | In the case of the regenerant for Zeolite-N, top-up of fresh KCl is needed to ensure an efficient regeneration capacity, after each regeneration.  |

|                                                                             |                                                                                                     |                                                                                                            |                                                                                                                                                                                                                                       |
|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| regenerant can be re-used                                                   |                                                                                                     |                                                                                                            | For the HAIX regenerant, pH adjustment can be needed to ensure an efficient regeneration capacity, after each regeneration                                                                                                            |
| Maximum nutrients concentration in the regenerant obtained for recovery     | 580 mg NH <sub>4</sub> <sup>+</sup> -N/L                                                            | 785 mg PO <sub>4</sub> -P/L                                                                                | The high nutrients concentration in the regenerant solution will facilitate and improve the recovery. However, the efficiency of the regeneration needs to be considered as this is impacted by the reused of the regenerant solution |
| Number of times the same regenerant can be re-used after nutrients recovery | -                                                                                                   | 2 times                                                                                                    | Multiple reuse of the regenerant could impact the purity of the recovered product                                                                                                                                                     |
| Recovered products                                                          | Ammonium sulphate ((NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ); concentrated ammonia solution | Calcium phosphate (as hydroxyapatite, Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> ) | Purity of the products, applicability in the market and possible end-users need to be considered                                                                                                                                      |

|                                                              |                                                                                                                                                                                                                                      |                                                                                                                                                                                                                                                 |                                                                                                                                                                                                                                                                                                                                                                                    |
|--------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                              |                                                                                                                                                                                                                                      |                                                                                                                                                                                                                                                 | for the future application of the recovered products                                                                                                                                                                                                                                                                                                                               |
| Recovery processes                                           | <ul style="list-style-type: none"> <li>• Hollow fibre membrane contactor (HFMC)</li> <li>• Vacuum stripping process (VTS)</li> <li>• Multicomponent vacuum stripping process (MVTTS)</li> </ul>                                      | Addition of calcium hydroxide (Ca(OH) <sub>2</sub> ), mixing and filtration                                                                                                                                                                     | Recovery conditions need to be considered for the environmental impact, CAPEX and OPEX of the recovery processes                                                                                                                                                                                                                                                                   |
| Amount of recovered product per m <sup>3</sup> of regenerant | 100 L (concentrated ammonia solution)                                                                                                                                                                                                | 9 kg (as hydroxyapatite)                                                                                                                                                                                                                        | The amount of recovered products depends on the volume of regenerant solution treated and on the possibility to scale up the recovery techniques. The volume of product obtained from the saturated regenerant solution and the purity are two major factors that need to be taken into consideration for future application of the IEX process for nutrients removal and recovery |
| Purity of the product                                        | <ul style="list-style-type: none"> <li>• Ammonium sulphate recovered from HFMC: N=25.5%, O=55.6% and S=18.8% (atomic %)</li> <li>• Concentrated ammonia solution recovered from MVTTS: Calcium: 55.3 mg/L; Potassium: 1.2</li> </ul> | No pathogens (total coliforms/ <i>Escherichia coli</i> ); Organics below detection limits; heavy metals: Aluminium: 4×10 <sup>5</sup> µg/kg; Cadmium: 2.4×10 <sup>3</sup> µg/kg; Chromium; 8×10 <sup>3</sup> µg/kg; Copper: 3.6×10 <sup>4</sup> |                                                                                                                                                                                                                                                                                                                                                                                    |



|  |                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                                                              |  |
|--|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|
|  | <p>mg/L; Silicon: 16.3 mg/L;<br/>Copper: 30.3 µg/L;<br/>Magnesium: 14.5 µg/L;<br/>Zinc: 4.4 µg/L; Aluminium:<br/>17.1 µg/L; Arsenic 2.1 µg/L</p> <ul style="list-style-type: none"> <li>• Concentrated ammonia solution recovered from VTS: Calcium: 4.0 mg/L;<br/>Potassium: 0.3 mg/L;<br/>Silicon: 0.5 mg/L; Copper: 108.0 µg/L; Magnesium: 92.6 µg/L; Zinc: 35.0 µg/L;<br/>Aluminium: 19.3 µg/L;<br/>Arsenic 1.1 µg/L</li> </ul> | <p>µg/kg; Iron: 9.2×10 µg/kg;<br/>Lead: 24×10<sup>3</sup> µg/kg;<br/>Mercury: 0.4×10<sup>3</sup> µg/kg;<br/>Nickel: 12×10<sup>3</sup> µg/kg; Zinc:<br/>72×10<sup>4</sup></p> |  |
|--|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|



**Figure 7.3 Possible exploitation of the products recovered from saturated ion exchange regenerant brines.**

It is expected that this work will result in the commissioning of numerous demonstration plants, which will investigate the removal and recovery of both ammonium and phosphorus at different scale. In particular, the ion exchange technology could represent a viable option for ammonia and phosphorus removal from the effluent of the anaerobic membrane reactor (anMBR) thus substituting the conventional activated sludge process which leaves less opportunity for the nutrient recovery and requires higher costs. More in particular, according to a recent study [4], the combination of anMBR and IEX (10,000 pe municipal WWTP treating settled wastewater) resulted in a capital expenditure (CAPEX) and total operational expenditure (OPEX) of 3.6 M£ and 177k£/year, respectively [4]. This represented a decrease of 9% and 44% of the CAPEX and OPEX, respectively, when compared to a scenario with biological nutrient removal and iron dosing [4]. The economic advantages and possibility for resource recovery of anMBR+IEX will be further investigated at the Sernal Sewage Treatment Works (Severn Trent Water) in the framework of the NextGen European project (2018-2022). Additionally, the results obtained from this work have attracted the interests of several companies (Severn

Trent Water, ACWA and Cirtec) which are interested in implementing the process and installing ion exchange demonstration plants around Europe.

#### **7.4. Future work**

- Synthetic zeolites production: it is suggested the production of more spherical media to limit the presence of eventual sharp edges which could have an impact on both the resistance to attrition and compression.
- Vacuum thermal stripping: the temperature of the heating bath, the vacuum pressure and the mixing of the saturated should be optimised as these have an impact on the ammonia loss and the overall recovery efficiency of the process.
- Reusability of the regenerant brines after the nutrient recovery should be investigated to demonstrate that the regeneration capacity of the brines can be restored following multiple recovery treatments.
- Characterisation of the organics which have an impact on adsorption capacity of HAIX to optimise the removal and prevent the fouling of the resin.
- Optimisation of the EBCT during the operation with Zeolite-N (both in wastewater and during regeneration phase) to improve the ammonium exchange efficiency.
- Investigate the possibility to integrate the ion exchange process as treatment for the effluent of anaerobic membrane reactor (anMBR).
- Marketability of the recovered products: applications of the concentrated ammonia solution in different sectors (cleaning, plastics and textile manufacturing, biogas purification and microbial protein production).

#### **7.5. Contribution to knowledge**

Overall, this work has contributed to identification and optimisation of ion exchange process for the removal and recovery of ammonium and phosphorus from secondary effluent wastewater and to the development of an environmentally sustainable method to manage the ion exchange regenerant brine. Table 7.2 summarizes the contributions to knowledge of the PhD thesis.

**Table 7.2. Contribution to knowledge of the PhD thesis.**

|                              | <b>What has been confirmed?</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <b>What has advanced knowledge?</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
|------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Theoretical knowledge</b> | <ul style="list-style-type: none"> <li>▪ Synthetic zeolite Zeolite-N can be used for an efficient and selective removal of ammonium from wastewater (Chapter 2 and 5).</li> <li>▪ Hybrid anion exchanger can be used for an efficient and selective removal of phosphorus from wastewater (Chapter 6).</li> <li>▪ Ammonium variability in secondary effluent wastewater is very significantly impacted by seasonal and diurnal temperature variations due to the efficiency of the nitrification during the secondary treatment (Chapter 3).</li> </ul> | <ul style="list-style-type: none"> <li>▪ The optimal ammonium exchange media to be used for extended period of time must ensure good effluent quality (&lt;1 mg NH<sub>4</sub><sup>+</sup>N/L), high mechanical strength to limit the media losses and resilience to variation in the influent wastewater concentration (Chapter 2 and 3).</li> <li>▪ The IEX process with NaCl used as regenerant solution and the membrane stripping process as recovery technique presented higher environmental benefits (-25% cumulative energy demand, -66% global warming potential, -62% marine eutrophication potential) compared to the biological ammonium removal process via nitrification/denitrification (Chapter 3).</li> </ul> |

|                                  |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
|----------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p><b>Empirical evidence</b></p> | <ul style="list-style-type: none"> <li>▪ The variability in the ammonium concentration in the influent wastewater affected the ammonium exchange capacity of the Zeolite-N (Chapter 3).</li> <li>▪ The ammonia stripping efficiency depends on the ratio of free ammonia present in solution with the highest free ammonia (90-99%) present at pH &gt;10-11. To indicate, at the hollow fibre membrane contactor, a mass transfer coefficient (<math>K_{La}</math>) of <math>1.5 \text{ h}^{-1}</math> was registered while treating synthetic solution at pH 11 compared to <math>K_{La}</math> of <math>0.66 \text{ h}^{-1}</math> at pH 10, down to <math>K_{La}</math> of <math>0.06 \text{ h}^{-1}</math> at pH 7 (Chapter 5).</li> </ul> | <ul style="list-style-type: none"> <li>▪ Zeolite-N presented high resilience to variable ammonium influent concentration (<math>&lt;0.006\text{-}26 \text{ mg NH}_4^+\text{-N/L}</math>) with ammonium exchange capacities ranging from <math>0.9 \text{ mg NH}_4^+\text{-N/g media}</math> to <math>17.7 \text{ mg NH}_4^+\text{-N/g media}</math> (Chapter 3).</li> <li>▪ The mass of ammonium present in the media, and consequently the ammonium concentration in the influent, is the key factor influencing the IEX process efficiency while the reuse of the regenerant is a secondary factor (Chapter 3).</li> <li>▪ The Zeoclere30, used as ion exchanger media at demonstration scale, showed a maximum capacity of <math>3.7 \text{ mg NH}_4^+\text{-N/g media}</math> at an EBCT of 5 minutes in secondary effluent wastewater (Chapter 4).</li> <li>▪ At demonstration plant, up to 90% of the <math>\text{PO}_4\text{-P}</math> present in the wastewater was removed and high effluent quality (<math>&lt;0.3 \text{ mg PO}_4\text{-P/L}</math>) was maintained at an EBCT of 5 minutes for 430 bed volumes (Chapter 6).</li> </ul> |
|----------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

|                    |                                                                                                                                  |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |
|--------------------|----------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                    |                                                                                                                                  | <ul style="list-style-type: none"> <li>▪ The reuse of the same regenerant solution (NaOH) for HAIX regeneration caused a loss in capacity from 7.2 <math>\mu\text{g PO}_4\text{-P/g resin/BV}</math> to 2.9 <math>\mu\text{g PO}_4\text{-P/g resin/BV}</math> after the fifth reuse of the regenerant (Chapter 6).</li> <li>▪ COD was removed by the HAIX (26%) which caused a slow fouling of the resin and impacted the adsorption capacity over extended periods of operation (Chapter 6).</li> <li>▪ Following the recovery, it was possible to regenerate the HAIX resin and the <math>C_t/C_0</math> at the beginning of the adsorption cycle was kept below 0.2 confirming the reusability of the regenerant solution (Chapter 6).</li> <li>▪ The recovered concentrated ammonia solution/ammonium salt and hydroxyapatite recovered from saturated KCl and NaOH, respectively, presented high purity (Chapter 5 and 6) making them suitable for applications in the fertiliser and chemical industries.</li> </ul> |
| <b>Methodology</b> | <ul style="list-style-type: none"> <li>▪ The cumulative energy demand (CED) required for the vacuum thermal stripping</li> </ul> | <ul style="list-style-type: none"> <li>▪ The production process (temperature, time and dimension of the kiln during calcination) impacted the</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |

|  |                                                                             |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
|--|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  | <p>can be minimized by using excess heat available on site (Chapter 3).</p> | <p>variability of the mechanical strength of the synthetic zeolites (Chapter 2).</p> <ul style="list-style-type: none"> <li>▪ When switching from one ion exchange resin to another, an adaptation of the infrastructures and operational conditions is needed to ensure high ion exchange efficiency (Chapter 4).</li> <li>▪ Compared to the vacuum thermal stripping at rotary evaporator (VTS), the multi-component vacuum thermal stripping (MVTs) was easier to control in regards to the temperature of the thermal bath and condenser as well as to the vacuum pressure. This resulted in a reduction of the ammonia loss (<math>J_{NH_3 \text{ loss}}=15 \text{ mg/h}</math>) in the MVTs compared to the VTS (<math>J_{NH_3 \text{ loss}}=24 \text{ mg/h}</math>) (Chapter 5).</li> <li>▪ A regeneration with NaOH 2% + NaCl 5% of HAIX saturated with organic matter resulted in a 16% increase in adsorption capacity at laboratory scale (Chapter 6)</li> <li>▪ Calcium hydroxide (<math>Ca(OH)_2</math>) can be added to the saturated NaOH regenerant to a Ca:P molar ratio of 3</li> </ul> |
|--|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

|  |  |                                                                                                                |
|--|--|----------------------------------------------------------------------------------------------------------------|
|  |  | to recover up to 95% of the PO <sub>4</sub> -P in solution as hydroxyapatite in less than 6 hours (Chapter 6). |
|--|--|----------------------------------------------------------------------------------------------------------------|



## 7.6. References

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## 8 CONCLUSION

The overall conclusions of this PhD thesis are presented with respect to the PhD objectives presented in Chapter 1.

**Objective 1. To evaluate of ammonium exchange capacity and mechanical strength (resistance to attrition and compression) of synthetic zeolites (Zeolite1-6) against natural (clinoptilolite) and engineered zeolite, Zeolite-N, use as reference ion exchange resin for ammonium removal from wastewater.**

- Zeolite6 and Zeolite2 showed increased maximum AEC (4.7 and 4.5 meq  $\text{NH}_4^+$ -N/g media, respectively) when compared to Zeolite-N (4.3 meq  $\text{NH}_4^+$ -N/g media).
- In secondary effluent wastewater ( $C_{\text{initial}} = 0.7$  meq/L), Zeolite1, 2 and 6 showed AEC of 0.05 meq  $\text{NH}_4^+$ -N/g media, similar to Zeolite-N (0.06 meq  $\text{NH}_4^+$ -N/g media). The slight increase of AEC in Zeolite-N can be due to the lower Si/Al ratio (1.5) compared Zeolite1-6 (Si/Al=1.7-2).
- All the media showed lower reusability during the 10 cycles of batch test when compared to Zeolite-N.
- When compared to Zeolite-N, the natural clinoptilolite showed higher mechanical strength, Zeolite3 and 6 showed higher resistance to attrition while Zeolite4 and 6 showed higher resistance to compression. The variability of the mechanical strength of the synthetic zeolites was attributed to the difference in the production process (temperature, time and dimension of the kiln during calcination).
- This study highlighted the importance of producing synthetic zeolites with mechanical strength to reduce media loss during operations (10% loss/month with Zeolite6 in the demonstration scale plant). In particular, a media with more spherical shape would reduce eventual sharp edges which could have an impact on both the resistance to attrition and compression.

**Objective 2. To understand the resilience of the Zeolite-N in an ion exchange demonstration-scale process for its ability to respond to variable ammonium loadings and to prove the environmental benefits of using the ion exchange process for ammonium removal through a life cycle assessment.**

- The variability in the influent of secondary treatment as well as seasonal and diurnal temperature variation affect the efficiency of nitrification. This results in loading peaks in secondary effluents. The ammonium ( $\text{NH}_4^+\text{-N}$ ) variability (<0.006 and 26 mg  $\text{NH}_4^+\text{-N/L}$ ) affected the  $\text{NH}_4^+\text{-N}$  exchange capacity which ranged from 17.7 mg  $\text{NH}_4^+\text{-N/g}$  media, down to 0.9 mg  $\text{NH}_4^+\text{-N/g}$  media.
- Due to ammonium exchange equilibrium between the media and the wastewater, with influent concentration below 0.5 mg  $\text{NH}_4^+\text{-N/L}$ , the Zeolite-N released the ammonium up taken in previous cycles into the wastewater causing an increase of the ammonium effluent concentration. The use of an automated system is suggested to better control the effluent quality.
- The ammonium present in the media affected the efficiencies of regeneration. After the first cycle (94% regeneration efficiency), due to the accumulation of ammonium on the media, the maximum efficiency of regeneration was 39%. An optimisation of the volume of brine and the contact time between the brine and the media is suggested.
- The LCA revealed that the optimal scenario in terms of CED, GWP and MEP was the IEX-NaCl-MEM scenario. This presented -25% CED (mainly connected to the savings in electricity demand of the biological treatment stage), -66% GWP (due to the reduction in the production of greenhouse gases), -62% MEP (due to the different defined TN values in the effluent) compared to the reference scenario.
- The CED of the IEX-KCl-VAC and IEX-NaCl-VAC was mainly related to heat needed to bring the saturated brine to boiling point which can be minimized by using available excess heat in WWTPs (CED from 320 to 138 MJ/pe $\times$ a for IEX-KCl-VAC; from 263 to 80 MJ/pe $\times$ a for IEX-NaCl-VAC).
- Switching from potassium chloride (KCl) to sodium chloride (NaCl) for the regeneration process resulted in a substantially lower CED and lower GWP in all the scenarios.

**Objective 3. To investigate the possibility to use a demonstration scale plant, previously commissioned for the removal of ammonium from secondary effluent wastewater with Zeolite-N, for the operation with Zeoclere30 (natural clinoptilolite) under the existing IEX plant design specifications (i.e. an empty**

**bed contact time of 5 min and sodium chloride or potassium chloride (KCl) as regenerant brines).**

- Zeoclere30 presented maximum ammonium exchange capacity of 3.7 mg NH<sub>4</sub><sup>+</sup>-N/g media in municipal wastewater. The maximum value reported by the supplier in synthetic solution (NH<sub>4</sub>Cl 10%) is 21.6-27 mg NH<sub>4</sub><sup>+</sup>-N/g media which proved the low selectivity for the ammonium in presence of competitive ions.
- The Zeoclere30 was tested at an EBCT of 5 minutes. However, longer EBCT (20-30 minutes) is usually used for natural zeolites and it should be tested to allow for a more efficient ammonium removal.
- The maximum regeneration efficiency of Zeoclere30 was 28%. Regeneration efficiency could be optimised by regenerating the media with 14-15% hypochlorite, according to the supplier indication and by increasing the bed volumes needed for the regeneration (10-20 BV). This however could damage existing infrastructure or lead to the production of hazardous chemical waste.
- A sever adaptation of the already existing infrastructure is needed for the use of Zeoclere30 as ion exchanger for ammonium removal. However, a suitable balance between capital (adding more IEX columns) and operational costs (media and regenerant costs) needs to be taken into consideration together with environmental impacts.

**Objective 4. To develop a science based understanding of different ammonium (as ammonia, NH<sub>3</sub>) recovery techniques from saturated brines regenerant solution by establishing gas/liquid mass transfer coefficients of: (1) thermal vacuum stripping and distillation using a rotary evaporator and (2) a multi-component equipment and (3) liquid-liquid mass transfer technology (hollow fibre membrane contactor).**

- The ammonia stripping efficiency depends on the ratio of free ammonia present in solution and hence pH. Operation below pH 10 (80% free ammonia) become ineffective and are maximised at pH 11 (98% free ammonia).
- Significant reduction in transfer coefficient are generated from real IEX brines (0.6 h<sup>-1</sup>, 0.7 h<sup>-1</sup> and 0.1 h<sup>-1</sup> for HFMC, MVTS and VTS) compared to synthetic solution (1.5 h<sup>-1</sup>, 1.7 h<sup>-1</sup> and 1.96 h<sup>-1</sup> for HFMC, MVTS and VTS) due to the presence of

metal ions, which form metal amine complexes. This leads to an increase in the required time to recover the available ammonia.

- The effectiveness of vacuum thermal stripping system requires good mixing and temperature control to enable gradual thermal gradients, avoiding bumping in the fluid which leads to high levels of water carryover. The better control of the MVTS resulted in higher ammonia recovery flux ( $J_{\text{NH}_3 \text{ rec}} = 156 \text{ mg/h}$ ) and lower ammonia loss rate ( $J_{\text{NH}_3 \text{ loss}} = 15 \text{ mg/h}$ ) compared to the values observed for the VTS system ( $J_{\text{NH}_3 \text{ rec}} = 110 \text{ mg/h}$ ,  $J_{\text{NH}_3 \text{ loss}} = 25 \text{ mg/h}$ ).
- HFMC was selected as preferred method for the treatment of saturated IEX brine. However future studies are needed to investigate the recovery of different ammonium salt (solids or liquid) with high market values (such as  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  solutions) for potential use as liquid fertilisers.

**Objective 5. To investigate changes in phosphorus (as  $\text{PO}_4\text{-P}$ ) adsorption capacity of an hybrid anion exchanger (HAIX) over an extended period of operation, regenerant re-use and calcium phosphate recovery in a demonstration IEX plant fed with  $10 \text{ m}^3/\text{day}$  of secondary treated municipal wastewater over a period of 2 years.**

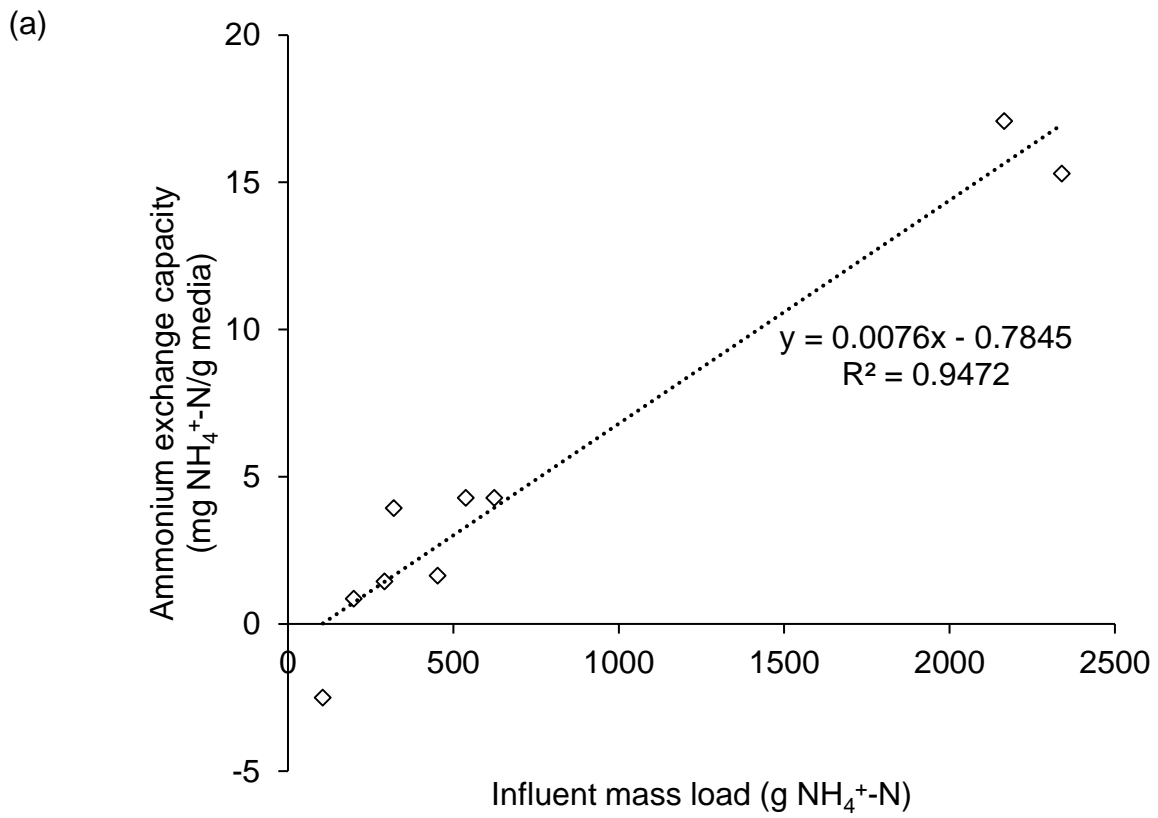
- The IEX demonstration scale plant with HAIX resin removed up to 90% of the  $\text{PO}_4\text{-P}$  present in the wastewater, maintain high effluent quality ( $<0.3 \text{ mg PO}_4\text{-P/L}$ ) at an EBCT of 5 minutes.
- The adsorption capacity of the resin over multiple cycles was affected by the reuse of the regenerant solution (NaOH 2%) which caused a loss in capacity from  $7.2 \mu\text{g PO}_4\text{-P/g resin/BV}$  to  $2.9 \mu\text{g PO}_4\text{-P/g resin/BV}$  after the fifth reuse of the regenerant.
- COD was removed by the HAIX (26%) which caused a slow fouling of the resin, and impacted the adsorption capacity over extended periods of operation. A regeneration with NaCl is needed to increase the adsorption capacity of the resin.

**Objective 6. To understand the influence of mixing time and calcium/phosphate (Ca:P) ratio on the phosphorus recovery from the HAIX regenerant solution (saturated NaOH) by precipitation with hydrated lime,  $\text{Ca}(\text{OH})_2$ , and to investigate the purity of the recovered product.**

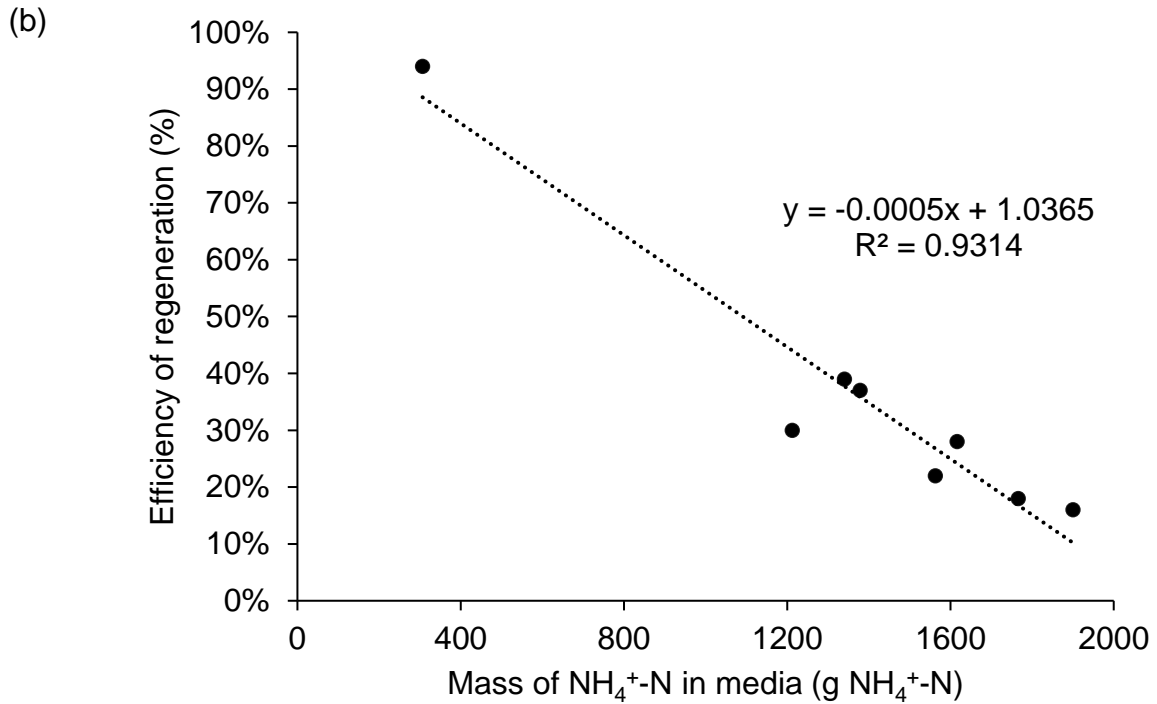
- Up to 95% of the  $\text{PO}_4\text{-P}$  s was recovered by adding  $\text{Ca}(\text{OH})_2$  to the saturated regenerant to a Ca:P molar ratio of 3 in less than 6 hours.
- The recovered product was identified as hydroxyapatite and it respected the limits of metals concentration existing in different countries and can be used as fertiliser. A total recovery of 75 kg/year of hydroxyapatite was estimated for this 10 m<sup>3</sup>/day demonstration plant.
- Following the recovery, it was possible to regenerate the HAIX resin and the  $C_t/C_0$  at the beginning of the adsorption cycle was kept below 0.2 confirming the reusability of the regenerant solution.

## A. APPENDIX

### A.1 Effect of ammonium influent load on Zeolite-N ammonium exchange capacity at demonstration scale







**Figure A.1 (a) linear correlation between the influent NH<sub>4</sub><sup>+</sup>-N load and NH<sub>4</sub><sup>+</sup>-N exchange capacity of Zeolite-N during 9 cycles at demonstration scale and (b) linear correlation between the mass of NH<sub>4</sub><sup>+</sup>-N on Zeolite-N before the regeneration and regeneration efficiency.**

## A.2 Background data for LCA

Background processes were modelled with datasets from Ecoinvent database v3.4 [1]. The related datasets are shown in Table A1 and refer to the global market [GLO] or European market [EU]. For electricity, the market mix of the UK was applied. Material demand for additional infrastructure was accounted only for the IEX stage. A rough estimation of the additional infrastructure for the IEX was made and included 0.5 tons of stainless steel, 0.5 of reinforcing steel, 10 m<sup>3</sup> of concrete and 5 tons of PE. The corresponding lifetimes of the equipment were estimated to 25 years for concrete, 20 years for steel and 5 years for PE according to the German working group of federal states on water (LAWA) [2].

**Table A.1 Datasets for background data considering dataset from UK, global market (GLO), European market (EU) and rest of the World (RoW).**

| <b>Process</b>            | <b>Dataset [1]</b>                                             | <b>Remarks</b>                                                 |
|---------------------------|----------------------------------------------------------------|----------------------------------------------------------------|
| Electricity               | market for electricity, medium voltage [UK]                    | For all operational electricity demand and credits from biogas |
| Heat                      | Heat production, natural gas, at boiler modulating <100kW [EU] | Heat for ammonium stripping                                    |
| Sulfuric acid             | market for sulfuric acid [GLO]                                 | Acid to produce ammonium sulphate                              |
| Potassium chloride        | market for potassium chloride [GLO]                            | For regeneration solution                                      |
| Sodium chloride           | market for sodium chloride, brine solution [GLO]               | For regeneration solution                                      |
| Cationic media            | market for cationic media [GLO]                                | Media                                                          |
| Ammonia solution (100% N) | diammonium phosphate, as N, at regional storehouse [EU]        | Credit for recovered ammonium                                  |
| Truck transport           | transport, freight, lorry 16-32 metric ton, EURO5 [EU]         | Sludge transports                                              |
| Nitrogen                  | diammonium phosphate, as N, at regional storehouse [EU]        | Fertiliser credit for N in sludge in agriculture               |
| Concrete                  | market for concrete [RoW]                                      | Infrastructure material for IEX foundation                     |
| Stainless steel           | steel production, electric, chromium steel 18/8 [RoW]          | Infrastructure material for IEX                                |
| Reinforced steel          | reinforcing steel production [RoW]                             | Infrastructure material for IEX                                |

|    |                                                      |                                 |
|----|------------------------------------------------------|---------------------------------|
| PE | polyethylene production, low density, granulate [EU] | Infrastructure material for IEX |
|----|------------------------------------------------------|---------------------------------|

### A.3 References

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