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Resilience and life cycle assessment of ion exchange process for ammonium removal from municipal wastewater

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Abstract

This study was completed to understand the resilience of an ion exchange (IEX) process for its ability to remove variable ammonium (NH_4^+-N) loads) and to prove its environmental benefits through a life cycle assessment (LCA). The tertiary 10 m^3/day demonstration scale IEX was fed with variable NH_4^+-N concentrations (<0.006-26 mg NH_4^+-N /L) naturally found in municipal wastewater. Zeolite-N was used as ion exchange media and regeneration was completed with 10% potassium chloride (KCl). The influent NH_4^+-N concentration impacted the ion exchange capacity, which ranged from 0.9-17.7 mg NH_4^+-N/g media. When the influent concentration was <2.5 mg NH_4^+-N/L, the Zeolite-N released NH_4^+-N (up to 12%). However, the exchange increased up to 62% when the influent NH_4^+-N load peaked, confirming the resilience of the process. A 94% regeneration efficiency was obtained with fresh regenerant, however, with the increase of the mass of NH_4^+-N on the media, the regeneration efficiency decreased. An optimisation of the volume of brine and regeneration contact time is suggested. To further measure the benefits of the IEX process, an LCA was conducted, for a 10,000 population equivalent reference scenario, and compared with traditional nitrification-denitrification WWTP. The LCA revealed that IEX with regenerant re-use and NH_4^+-N recovery through a membrane stripping process resulted in reductions of: 25% cumulative energy demand; 66% global warming potential and 62% marine eutrophication potential, when compared to traditional WWTP. This work demonstrated that the IEX process is an efficient and an environmentally benign technology that can be widely applied in WWTPs.

Keywords

Ammonia removal; ammonia recovery; nutrients; synthetic zeolite; circular economy; Net-zero targets

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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 (Mines et al., 2007) and temperature (Jeppsson et al., 2006; Martin et al., 2014). 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 (Martin et al., 2014) in the wastewater. In particular, the ammonium (NH_4^+-N) concentration can range between 20 to 50 mg NH_4^+-N/L (Aboobakar et al., 2013 Perez et al., 2015) in the influent of a WWTP (Table 1). This variability is also observed through the different treatment stages of WWTP, including in the influent to secondary treatment process where the NH_4^+-N concentration has been reported to range between 0.1 and 25 mg NH_4^+-N/L (Aboobakar et al., 2013, Van Den Akker et al., 2010) (Table 1). Conventionally, nitrification and denitrification are used to remove NH_4^+-N from wastewater by oxidising NH_4^+-N to nitrate (NO_3^-) and reducing it to nitrogen gas (N_2) (Cruz et al., 2018). However, the high variability in the influent concentration is a major issue that limits the removal efficiency (Canellas et al, 2019a). It has been reported that an increase in total NH_4^+-N concentration by up to 80% (in the range of 0.15–1.8 mg/L) reduced the rate of nitrification in a trickling filter by 60%, when operated with high hydraulic loads (Mery et al., 2012). Effluent from secondary treatment processes are also affected, Zarate et al., 2018 reported a variation from 1.9 to 15.4 mg NH_4^+-N/L after treatment in the trickling filters of a 5500 population equivalent (pe) WWTP due to the impact of seasonal temperature variation on nitrification (Table 1). Besides temperature, Raboni et al., 2013, reported a daily variation in the denitrification efficiency from 40% to 78% depending on C:N ratio. Additionally, Yamashita et al., 2014 measured a variation from <0.5 to 20 mg NH_4^+-N/L at the effluent of trickling filter packed with foam ceramics for nitrification (Table 1). Hence, secondary effluent wastewater quality is not constant, and it suffers from great variability in ammonium concentrations (Table 1).

For this reason, to ensure high effluent quality in the discharged wastewater, there is a need for a flexible and resilient technology which can be adapted to the variability in the influent while ensuring efficient NH_4^+-N removal. At the same time, conventional biological removal processes pose an environmental concern due to the production of N_2O (a greenhouse gas) as an intermediate of aerobic NH_4^+-N oxidation (van der Hoek et al., 2018). As such, technologies that can remove ammonium with variable concentrations and have low GHG emissions are highly desirable. In particular, previous studies have considered the use of the ion exchange (IEX) as tertiary treatment process (Blaney et al., 2007). One of the most

efficient IEX media for NH_4^+-N removal is the synthetic zeolites, Zeolite-N (chemical formula $K_{12}Al_{10}Si_{10}O_{40}Cl_28H_2O$) (Mackinnon et al., 2012), which has shown NH_4^+-N removal efficiency >95% treating sludge dewatering liquors at laboratory scale (Mackinnon et al., 2010; Thornton et al., 2007).

Table 1. Variability of ammonium (NH_4^+-N) concentration in different stages of wastewater treatment.

Type of wastewater	Average (mg NH_4^+-N/L)	Min (mg NH_4^+-N/L)	Max (mg NH_4^+-N/L)	Notes	Ref
Influent/raw wastewater	37.7	30.0	50.0	Full-scale modelling study	Perez et al., 2015
Settled sewage	38.0	20.0	50.0	Full-scale nitrifying activated sludge treatment plant, UK	Aboobakar et al., 2013
Influent to aeration zones	15.3	8.0	20.0		
Influent of nitrifying trickling filter (NTF)	1.1	0.1	17.4	Pilot scale study, Australia	Van Den Akker et al., 2010
Effluent of secondary treatment process	7.4	1.9	15.4	Secondary process with trickling filters in a 5500 pe WWTP, UK	Zarate et al., 2018
Influent secondary treatment process	N/A	1-2	25	Secondary process with anoxic bioreactor packed with wood and iron + trickling filter packed with foam ceramics for nitrification, Japan	Yamashita et al., 2014
Effluent secondary treatment process	N/A	<0.5	20		
Effluent of domestic WWTP	N/A	<0.1	8.2	Secondary treatment process with a	Johnston et al., 2019

	sequencing batch reactor, USA

After exhaustion of the NH_4^+-N exchange capacity, the media is regenerated, commonly by using high strength ionic brines such as sodium chloride (NaCl) or potassium chloride (KCl) (Malovanyy et al., 2014; Canellas et al., 2019b). In particular, previous studies confirmed KCl as a more effective regenerant solution than NaCl when regenerating Zeolite-N with efficiency between 72-94% and 64-68%, respectively (Canellas et al., 2019b; Huang et al., 2020). The brine can be used multiple times until saturation (Canellas et al., 2019b), however, once saturated, its disposal as a hazardous waste can constitute a cost limitation for the implementation of the IEX process at full scale (Huang et al., 2020). For this reason, the possibility to recover ammonia (NH_3) from the saturated brine has been recently investigate to increase the overall environmental and economical sustainability of the IEX process (Darestani et al., 2017; Guida et al., 2020). In particular, vacuum thermal stripping (Ukwuani et al., 2016) and membrane stripping (Sancho et al., 2017) represent potential processes for the brine management and for the recovery of the NH_4^+-N as valuable resource. In the vacuum thermal stripping process, the vacuum-induced boiling of saturated brine increases the transfer of the ammonia gas ($NH_{3(g)}$) to vapour bubbles (Tao et al., 2015) which are then condensed in an overall distillation process where $NH_{3(g)}$ is recovered as aqueous ammonia ($NH_{3(aq)}$), a valuable chemical (Zhang et al., 2019). On the other hand, in the membrane stripping process, the use of microporous and hydrophobic hollow fibres allows for the transfer of $NH_{3(g)}$ from shell-side of the membrane to the lumen-side where a strong acid solution promotes the precipitation of NH_4^+-N salts with application in the fertilizer industry (i.e. ammonium sulphate) (Boehler et al., 2015).

The possibility to reuse the same regenerant brine multiple times and recover the NH_4^+-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 NH_4^+-N concentration and an analysis of the environmental impact connected to the use of Zeolite-N for NH_4^+-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 NH_4^+-N concentrations. In particular, the resilience of the IEX was considered as its ability to maintain high removal capacities in a wide range of NH_4^+-N influent concentrations, i.e., by providing and maintaining an acceptable level of NH_4^+-N removal when faced with challenges to normal operation. Additionally, the work aimed 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 to investigate its potential in a holistic approach. The tool selected for such a comparison was a life cycle assessment, as this

assesses the potential environmental impacts of a product, process or system, it can account for related emissions and resource usage and it can facilitate the quantifications of the environmental impacts for comparative assessments (e.g., different processes) (Remy, 2017). 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) with tricking filters and rotating biological contactors included (Manuel Silva Dias, 2014). In particular, the data obtained from a demonstration scale plant (10 m^3/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. While demonstration scale research focussed on the issue of variation of NH_4^+-N influent concentration, the LCA used a hypothetical setup to explore the environmental profiles of IEX schemes *versus* a conventional WWTP.

2. Materials and methods

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 carbonaceous 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) in case of emergency 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 SM 1). The column (internal diameter of 307 mm, height of 1566 mm, total volume 116L) 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^3/day in downflow operation and empty bed contact time (EBCT) of 10 minutes (Huang et al., 2020). The EBCT was calculated considering the bed volume, V_R (L) and the flow rate in the bed, F (L/min) according to Equation 1 (Celik et al., 2001):

$$EBCT = V_R/F \qquad \text{Equation 1}$$

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) (i.e. a total of 690L) of 10% potassium chloride (10% KCl wt., Easy Chemicals Ltd, Denbigh, UK) (Canellas et al., 2019c) 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 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 batches of saturated regenerant solution were used for NH_4 recovery, then refreshed with new salt solution to balance ion losses during IEX process. 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 and displace the regenerant. The NH_4^+-N exchange capacity (AEC, mg NH_4^+-N/g media) after *n* samples was calculated according to Equation 2 (Thornton et al., 2007):

$$AEC = \frac{\int_{V=0}^{V_{fin}} (C_{in} - C_{out}) dV}{M} = \frac{\sum_0^n [(C_0 - C_n) \times (V_n - V_{n-1})]}{M} \quad \text{Equation 2}$$

where C_{in} and C_{out} are the influent and effluent NH_4^+-N concentration (mg NH_4^+-N/L); V is the volume of wastewater treated (L) at to time *n*, and *M* is the mass of Zeolite-N (g). The regeneration capacity Q_{reg} (mg NH_4^+-N/g media) was calculated according to Equation 3 (adapted from You *et al.* (You et al., 2016)):

$$Q_{reg} = \frac{[C_{r.i} - C_{r.f}] \times V_{r.treated}}{M} \quad \text{Equation 3}$$

where $C_{r.i}$ and $C_{r.f}$ are the NH_4^+-N concentration in the regenerant at the beginning and at the end of each regeneration cycle (mg NH_4^+-N/L); $V_{r.treated}$ is the volume of regenerant used (L) and M is the same as in Equation 2.

2.2. Wastewater characterization

The municipal wastewater fed to the ion exchange demonstration plant presented variable NH_4^+-N concentration with minimum and maximum values of 0.9 mg NH_4^+-N/L and 26 mg NH_4^+-N/L, respectively (shown in Supplementary Material (SM), Table SM 1). The pH was constant at around 7.1 while the average total suspended solids (TSS) concentration was 35±8 mg TSS/L during the entire period of operation. The main competing ions in wastewater that could interfere with the NH_4^+-N exchange, namely potassium, calcium, magnesium and sodium were measured at concentrations of 16.9±0.1 mg K^+/L, 69±14 mg Ca^{2+}/L, 7±0.7 mg Mg^{2+}/L and 60.2±14.6 mg Na^+/L, respectively (Table SM 1).

2.3. Chemical analysis

Samples were taken from the demonstration plant daily. Chemical oxygen demand (COD), was analysed using Spectroquant® cell tests; ammonium (NH_4^+-N) was analysed using the Smartchem200 (AMS Alliance, France) (lower limit of detection (LOD) of 0.006 mg NH_4^+-N/L). The concentrations of Mg^{2+}, Cl^-, K+, Ca^{2+} and Na^+ were analysed using inductively coupled plasma- mass spectrometry (ICP-MS) (PerkinElmer NexION 350D). 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 (APHA, 2012).

2.4. Life cycle assessment

2.4.1 Goal, scope and scenarios definition

The life cycle assessment (LCA) is a widely used methodology to quantify environmental impacts of a technology (Amann et al., 2018). 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 of the art.

The LCA followed the method described in ISO 14040 (ISO 14040:2006(E), 2006) considering a WWTP with 10,000 population equivalent (pe) as a hypothetical case study. The goal of the LCA was to quantify potential environmental benefits of a WWTP scheme with IEX for nitrogen removal compared to a conventional WWTP scheme. For this purpose, the function of the different scenarios was related to the treatment of municipal wastewater for compliance with defined limit values for COD and NH_4^+-N in the discharged effluent (EEC Council, 1991). Consequently, the functional unit of the LCA was defined as "*the impact of a wastewater treatment process per population equivalent (pe) annually [impacts/pe×a]*". The system boundaries of the LCA included all processes of the WWTP, sludge treatment and disposal (Lin et al., 2016). In particular, the following processes were considered (Figure SM 2): wastewater treatment from raw wastewater to a defined effluent quality, including the IEX system and regeneration of IEX media; sludge thickening, digestion, dewatering, transport and disposal in agriculture; biogas valorisation in a combined heat and power (CHP) plant; and background processes required for the production of electricity, chemicals, and fuels and additional infrastructure for the IEX system. Nutrients delivered to agriculture via sludge application or via products recovered from IEX were credited considering avoided mineral fertiliser production ("avoided burden" approach).

Five different scenarios were taken into consideration in the comparative LCA (Table 2): in the reference scenario, COD and nitrogen (N) were removed in the trickling filter (nitrification/partial denitrification) while the IEX process was used as a post-treatment after trickling filter for the removal of NH_4^+-N in the scenarios 1 to 4. These scenarios describe different configurations of the regeneration process to explore their impact on the overall environmental footprint of the IEX process. As possible regenerants, potassium chloride (KCl) and sodium chloride (NaCl) were compared (Canellas et al., 2019b) while vacuum thermal stripping (VAC) and membrane stripping (MEM) were compared as recovery processes (Sancho et al., 2017; Ukwuani et al., 2016).

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 2019) (Table SM 2). 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. Background processes were modelled with datasets from Ecoinvent database v3.4 (Ecoinvent, 2017). The LCA was conducted by using the software *Umberto LCA+*, following an attributional approach. No allocation was required, as all impacts were attributed to the function of wastewater treatment. The temporal scope of the study refers to the actual situation in UK with current background process data (e.g., grid power mix).

Table 2. LCA scenarios for ammonium (NH_4^+-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	NH_4^+-N removal and recovery
Reference	Trickling filter	Trickling filter (with denitrification/nitrification)
1	Trickling filter	IEX-KCl-VAC
2		IEX-NaCl-VAC
3		IEX-KCl-MEM
4		IEX-NaCl-MEM

2.4.2. Environmental indicators

The environmental indicators considered were selected to represent major impacts of wastewater treatment, which are the efforts required for wastewater treatment (electricity, chemicals, transport, infrastructure) and their related life-cycle impact and the resulting water quality in WWTP effluent as direct emissions to the environment. To reflect these environmental impacts and benefits of a WWTP, the following midpoint indicators have been selected: cumulative energy demand (CED), global warming potential (GWP) and marine eutrophication potential (MEP). The CED (MJ/pe×a) considered the total non-renewable (fossil and nuclear) energy (Amann et al., 2018, VDI, 2012). The GWP considered all greenhouse gases (namely CO_2, CH_4 and N_2 O) expressed as CO_2 equivalent (kg CO_2 eq/pe×a) (Amann et al., 2018; Pachauri et al., 2007) and was estimated for a time horizon of 100 years. Finally, MEP (kg N eq/pe×a) was determined considering the effluent quality, following the approach in ReCiPe2016 (Huijbregts et al., 2017).

2.4.3 Inventory for the LCA

The input data for influent quality and efficiency of wastewater treatment in the reference and IEX scenarios was similar (Table SM 2). For the effluent quality, removal rates >95% for total solids (TS), >92 % for COD, >92% and >95% NH_4^+-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^3), trickling filter (0.19 kWh/m^3), and sludge treatment (thickening, digestion and dewatering) was assumed to be equal for all scenarios (Table SM 2). 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 IEX zeolite media, chemicals for the regenerant and for product recovery. The saturated Zeolite-N, enriched with NH_4^+-N, can theoretically be used as fertiliser at its end-of-life (Reháková et al., 2004). However, the amount of residual N on the media is expected to be minor compared to the overall amount of recovered N in the process due to the long lifetime of 5 years for the zeolite. Hence, impacts for end-of-life of the zeolite material have been neglected here. 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 NH_4^+ ion would replace one K^+ or Na^+ ion (Canellas et al., 2019b) which has to be replaced with fresh salt solution. In addition, 2% losses of the regeneration solution into WWTP effluent were estimated per year during backwash and flushing considering the results obtained with the demonstration scale plant (Table SM 2).

The input data for the LCA also considered the direct emissions of greenhouse gases (Table SM 2). For the reference scenario, direct N_2O emissions were estimated to be 1% of TN influent concentration of the biological stage, based on a linear correlation between TN removal and N_2O emission factors (Parravicini et al., 2016). The LCA also considered direct $NH_{3(g)}$ emissions during the biological treatment (assumed 0.6% of NH_4^+-N at the influent (Jossa et al., 2015)). For the IEX scenarios, no N_2O 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 (ATV, 2000). Elimination efficiencies for the centralised dewatering liquor treatment were estimated at 90% for COD, 99% for NH_4^+-N, 80% TN via denitrification (ATV, 2000).

For the sludge and product application in agriculture, the dewatered sludge was considered suitable for agricultural application (Colón et al., 2014) and it is the preferred sludge disposal route in the UK, where the study took place. For the crediting of nitrogen in the sewage sludge and IEX products, diammonium phosphate was credited as a substituted mineral fertilizer, and its production impact subtracted as avoided burden in the overall impact score. The substitution potential of nutrients in relation to mineral fertilizer were calculated according to factors from the chamber of Agriculture Lower Saxony (Landwirtschaftskammer Niedersachsen, 2020; Jossa et al., 2015). For nitrogen, an accounting rate of 25% for sewage sludge and 100% for ammonium sulphate or ammonia solution was considered (Landwirtschaftskammer Niedersachsen, 2020).

The direct emissions into groundwater and air due to product and sludge application in agriculture were estimated for the non-utilized fraction (Huijbregts et al., 2017). Direct emissions of $NH_{3(g)}$ connected to nutrient application were assumed to be 10.7% and 6.2% of TN in sludge and conventional fertiliser, respectively (Hutchings et al., 2016; Strogies et al., 2016). Direct emissions of N_2O and NO_2 were assumed to be 1.0% and 1.2% of the TN, respectively (Hutchings et al., 2016; Strogies et al., 2016). Emissions of nitrogen to groundwater were calculated at 7.9% of TN (Ecoinvent, 2017). The datasets for background

processes are shown in Supplementary Material (Table SM 2 and Table SM 3) and refer to the global market or European market. Data quality of this LCA has been qualitatively assessed as medium to high for most parts, except for the ammonia recovery process where more estimates and assumptions were needed as these are new areas of research and development, and hence there is a higher uncertainty associated with that part of the LCA (Table SM 4).

3. Results

3.1 Ammonium diurnal and seasonal variability

The NH_4^+-N concentration at the influent of the IEX demonstration plant was influenced by diurnal and seasonal variations. Figure 1a shows the diurnal NH_4^+-N concentration in the influent wastewater for nine different daily profiles (selected randomly from all the data available, including summer and winter). Overall, the NH_4^+-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 1a). Additionally, the profiles also presented different ranges of NH_4^+-N variation with some cycles presenting higher values at around 14 mg NH_4^+-N/L and other presenting maximum values of 3 mg NH_4^+-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 1b). During winter, lower temperatures of 5-8°C, impacted nitrification (Roy et al., 2017) and the wastewater entering the IEX demonstration plant contained up to 26 mg NH_4^+-N/L. During summer, the wastewater temperature increased up to 20°C, full nitrification was observed in the trickling filters and the NH_4^+-N concentration reaching the IEX demonstration plant was 0.5-1 mg NH_4^+-N/L (Figure 1b).

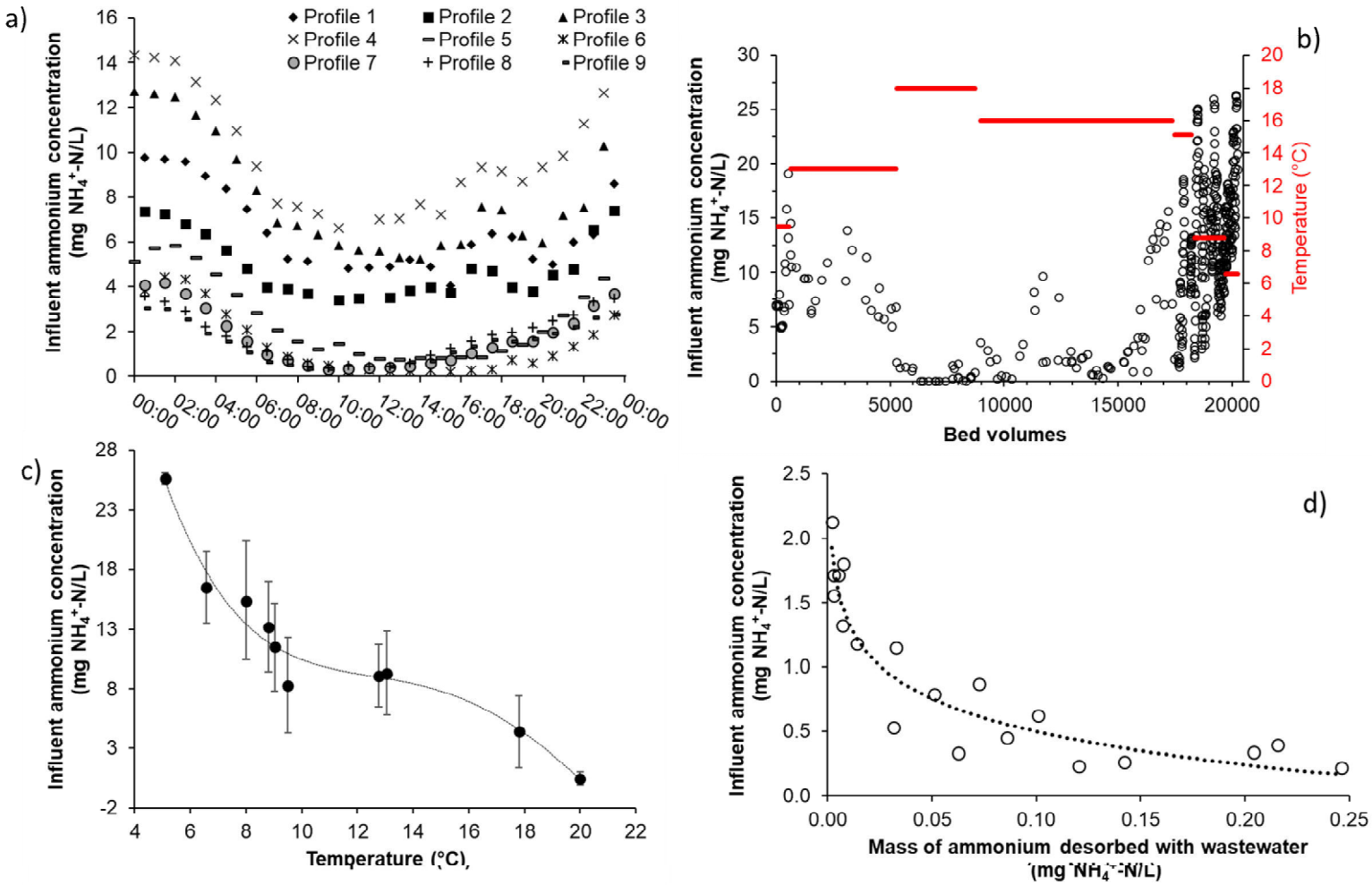

Figure 1 a) Diurnal and b) seasonal variability in the ammonium (NH_4^+-N) concentration in the secondary effluent wastewater, fed to the ion exchange (IEX) demonstration plant; c) influent profile and temperature variation during operation of the IEX demonstration plant and d) NH_4^+-N desorption (mg NH_4^+-N/g media) with wastewater when $C_{influent}$<2.5 mg NH_4^+-N/L.

Figure 1c shows the NH_4^+-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_4^+-N influent concentration ($C_{influent}$<3 mg NH_4^+-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 1c).

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

In total, 9 cycles of NH_4^+-N uptake and regeneration were performed with different influent concentration of the wastewater (<0.006-26 mg NH_4^+-N/L) (Figure 1c) fed to the

demonstration plant and consequently different NH_4^+-N exchange capacities (AEC) were measured (Table 3). During the first cycle, the influent concentration was 8.3±4.0 mg NH_4^+-N/L (mass load- 320 g NH_4^+-N) and an AEC of 3.9 mg NH_4^+-N/g media (0.2 meq NH_4^+-N/g media) was measured with an NH_4^+-N exchange efficiency of 96%. During the second cycle, the influent concentration was 9.0±2.6 mg NH_4^+-N/L, however, due to an increase in the volume of wastewater treated (mass load - 2339.4 g NH_4^+-N), an AEC of 15.3 mg NH_4^+-N/g media (0.85 meq NH_4^+-N/g media) was registered (ammonium exchange efficiency of 51%) (Table 3). Successively, the influent concentration decreased to 0.5±0.6 mg NH_4^+-N/L and the AEC dropped to -2.5 mg NH_4^+-N/g media (0.14 meq NH_4^+-N/g media) indicating a release of the NH_4^+-N into the wastewater (Table 3). However, in the following cycle, the average influent concentration increased again to 4.4±4.4 mg NH_4^+-N/L and the measured AEC was 17.1 mg NH_4^+-N/g media (0.95 meq NH_4^+-N/g media) with an NH_4^+-N exchange efficiency of 62% (Table 3). Overall, a good correlation (R_2 = 0.95) between influent mass load and ammonium exchange efficiency was observed (Figure SM 3).

Importantly, a decrease of the $C_{influent}$ to <2.5 mg NH_4^+-N/L resulted in a release of the NH_4^+-N from the Zeolite-N to the wastewater (cycle 3 in Table 3 and Figure 1d). The highest release (0.25 mg NH_4^+-N/g media, 0.014 meq NH_4^+-N/g media) was registered when $C_{influent}$ was 0.22 mg NH_4^+-N/L (Figure 1d).

For the first 800 bed volumes of wastewater treated (average $C_{influent}$ = 8.3±4 mg NH_4^+-N/L, Table 3), the effluent concentration was kept below 2 mg NH_4^+-N/L (Figure 2a). After 1300 bed volumes, the effluent profile reached a plateau and it stabilized at a concentration of 5 mg NH_4^+-N/L (Figure 2a). For the following cycles, the NH_4^+-N effluent profiles mirrored the NH_4^+-N influent concentration. As an example, Figure 2b shows the profiles in cycles 8-9.

During cycle 8, three influent NH_4^+-N loading peaks were registered at 19, 11 and 13 mg NH_4^+-N/L, the corresponding maximum effluent concentration was 7.3, 6.1 and 8.2 mg NH_4^+-N/L. During cycle 9, the high variability in NH_4^+-N at the influent concentration (16.5±4.2 mg NH_4^+-N/L) caused an effluent quality between 4.6 and 12.6 mg NH_4^+-N/L (Figure 2b).

Table 3. 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 NH_4^+-N	Influent mass load	NH_4^+-N exchange capacity	NH_4^+-N exchange efficiency

	m^3	mg NH_4^+-N/L	g NH_4^+-N	mg NH_4^+-N/g media	%
1	37.4	8.3±4.0	319.9	3.9	96
2	249.8	9.0±2.6	2339.4	15.3	51
3	237.7	0.5±0.6	105.4	-2.5	-
4	580.9	4.4±4.4	2165.8	17.1	62
5	58.8	9.3±4.7	452.9	1.6	28
6	12.8	15.3±7.8	198.7	0.9	34
7	41.8	13.2±5.5	537.9	4.3	62
8	25.5	11.5±3.7	291.6	1.4	39
9	36.4	16.5±4.2	624.1	4.3	54

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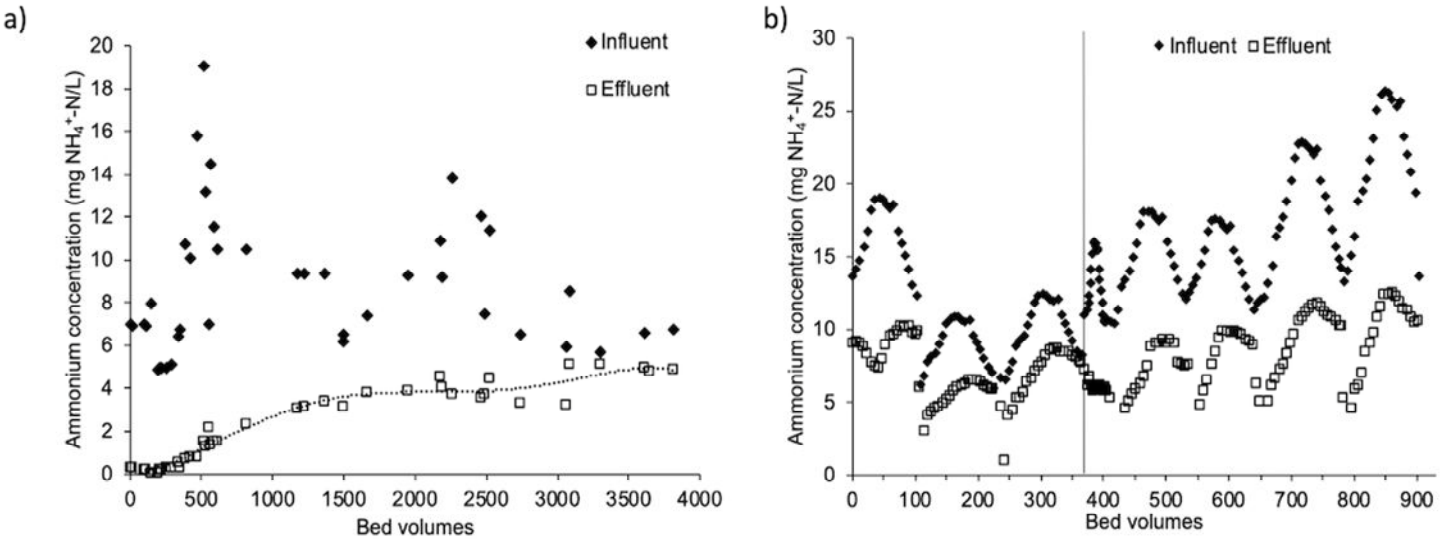

Figure 2. a) Breakthrough curve obtained during the first cycle with Zeolite-N at demonstration scale; b) correlation between ammonium influent concentration and effluent profiles in cycles 8 and 9 (vertical line represents the regeneration).

In the first cycle at demonstration scale, 94% of the total amount of NH_4^+-N in the media was recovered in the regeneration phase (Table SM 5). For the following cycles (cycle 2-cycle 9), the regeneration efficiencies depended on the mass of NH_4^+-N in the media, which was a result of the mass of NH_4^+-N removed from wastewater and the mass recovered in the previous regeneration cycles (Table SM 5). During cycles 1-6, the mass remaining in the media after the regeneration increased up to 1282.3 g NH_4^+-N and as a result, the efficiency

of regeneration decreased to 22%. The NH_4^+-N concentration of the 10% KCl regenerant brine increased from 140 mg NH_4^+-N/L to 520 mg NH_4^+-N/L from the cycle 1 to 6 while from cycle 6 to 9, the concentration in the brine reached 700 mg NH_4^+-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 NH_4^+-N, respectively (Table SM 5).

3.3. Results of life cycle assessment

Figure 3 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×a, 33 kg CO_2 eq/pe×a and 2.1 kg N eq/pe×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 3a). This accounted for 320 MJ/pe×a and 263 MJ/pe×a for the IEX scenarios with KCl-VAC and NaCl-VAC, respectively. On the other hand, if excess heat was considered available (Neugebauer et al., 2015), the net CED for the IEX-KCl-VAC and IEX-NaCl-VAC was 138 and 80 MJ/pe×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×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_4^+ from the saturate brine compared to the amount of KCl (Table 3).

Regarding the GWP, the IEX process scenarios presented a net improvement when compared to the reference scenario (Figure 3b). 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_2 eq/pe×a. If no excess heat was available, the GWP of these scenarios slightly increased up to 23 and 20 kg CO_2 eq/pe×a, respectively. In comparison, the implementation of the membrane stripping for the NH_4^+-N recovery resulted in a GWP of 14 and 11 kg CO_2 eq/pe×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 kg N eq/pe×a which corresponded to a

62% reduction compared to the MEP of the reference scenario (2.1 kg N eq/pe×a) (Figure 3c). In Table SM 6, 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_2 eq/pe×a, respectively) and the sludge dewatering and transportation (58 MJ/pe×a and 2.2 kg CO_2 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_2 eq/pe×a) and sludge application (2.2 kg CO_2 eq/pe×a) (Table SM 6). 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_2 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 (Table SM 6). 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 CO2 eq/pe×a), the heat for the VAC process (11.1 kg CO2 eq/pe×a) and the sulfuric acid production for the MEM process (1.4 kg CO_2 eq/pe×a) (Table SM 6). 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.

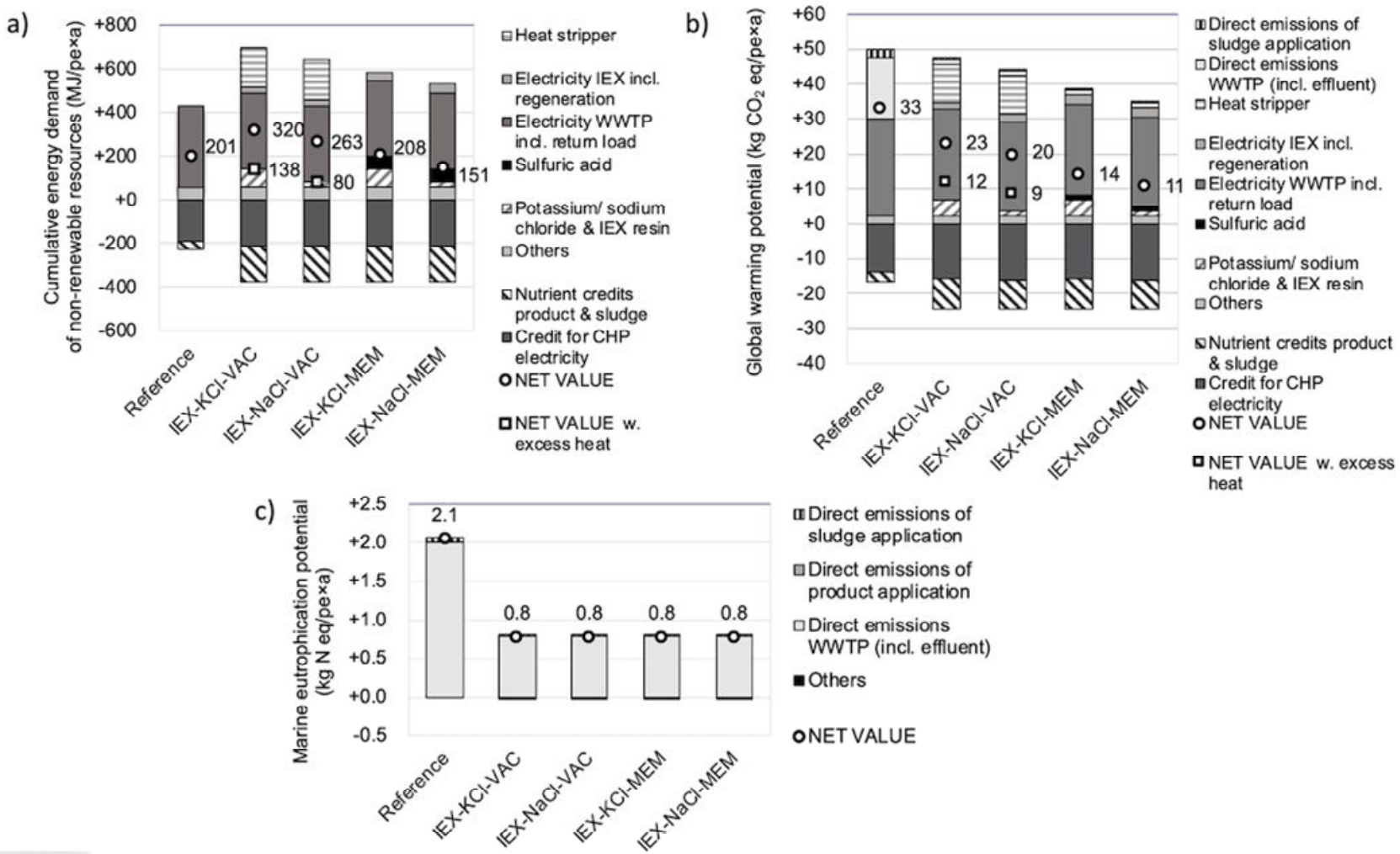

Figure 3. a) Cumulative non-renewable energy demand, b) global warming potential and c) marine eutrophication potential of reference scenario (biological ammonium removal) and IEX exchange process scenarios (ammonium removal and recovery). "Others" refers to polymer for dewatering, additional infrastructure for the IEX system and sludge transportation.

4. Discussion

The secondary treated wastewater presented an ammonium (NH_4^+-N) concentration ranging from 0 to 26 mg NH_4^+-N/L (Figure 1d). The diurnal and seasonal variability was related with the temperature, which affected the efficiency of nitrification in the trickling filters used for secondary treatment. 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 NH_4^+-N concentration by maintaining high removal capacities. Zeolite-N maintained an effluent concentration below 2 mg NH_4^+-N/L (Figure 2b) 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 (105.4-2339.4 g NH_4^+-N) which was a result of the variable influent concentrations and the volumes of wastewater treated (Table 3). The classical ion exchange reaction on the surface of the media (R) between two ions with equal charges (A^+ and B^+) is expressed by equation 4 (Sengupta, 2017):

$$RB^+ + A^+ \leftrightarrow RA^+ + B^+$$ Equation 4

At equilibrium, the electrochemical potential of A^+ and B^+ is equal for both the ion in the exchanger and in the aqueous phase (Sengupta, 2017). Higher NH_4^+-N concentrations in the aqueous phase (A^+) increase the driving force so that the NH_4^+-N ions can be exchanged with cations (B^+) on the surface of the media (Millar et al., 2016; Wang et al., 2006). As a result, AEC of 15.7-17.1 mg NH_4^+-N/g media (0.87-0.95 meq NH_4^+-N/g media) were measured when the influent mass load was 2166-2339 g NH_4^+-N. On the other hand, the AEC was 0.9-1.4 mg NH_4^+-N/g media (0.05-0.08 meq NH_4^+-N/g media) when the amount of ammonium fed to the demonstration plant decreased (199-292 g NH_4^+-N) (Table 3). 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 mg NH_4^+-N/g media (0.02-2.7 meq NH_4^+-N/g media) with influent concentration increasing from 2 to 1000 mg NH_4^+-N/L (Thornton et al., 2007). More in particular, a comparison to literature revealed that the AEC of the Zeolite-N can be increased up to 55 mg NH_4^+-N/g media (3.1 meq NH_4^+-N/g media) when treating wastewater with ammonium concentrations up to 1500 mg NH_4^+-N/L (Mackinnon et al., 2003).

Interestingly, when the influent concentration decreased below 2.5 mg NH_4^+-N/L, the ammonium on the Zeolite-N was desorbed with the wastewater (Figure 2) due to the equilibrium presented in Equation 4. In particular, the selectivity of Zeolites towards different cations is $K^+ > NH_4^+ > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+}$ (Zorpas et al., 2010). Therefore, with low NH_4^+-N concentration, due to the shift in the ion exchange equilibria (Miladinovic et al.,

2008), it is expected for the Zeolite-N to release NH_4^+-N and uptake other cations present in wastewater at higher concentrations (such as 17 mg K^+/L, 69 mg Ca^{2+}/L, 7 mg Mg^{2+}/L and 60 mg Na^+/L, Table SM 5). The release of NH_4^+-N caused by a drop in the influent concentration was previously detected by Hankins et al., (2004) while using clinoptilolite for the NH_4^+-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 (<1 mg NH_4^+-N/L (EEC Council, 1991)), 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 were reflected in the effluent profile. Importantly, the ammonium release could limit the technology suitability to meet tighter effluent permits 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_4^+-N in the media resulting from the NH_4^+-N influent concentration and load and the NH_4^+-N accumulated from previous cycles (R^2=0.93, Figure SM 3 and Table SM 5). The maximum amount of NH_4^+-N that was recovered in the regenerant brine was 378 g NH_4^+-N (cycle 9, Table SM 5) 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 (Canellas et al., 2019b). 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 SM 5). 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 re-use of the regenerant is a secondary factor. In this work, 10 BV of brine were used as regenerant solution (Canellas et al., 2019c) 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 (Malovanyy et al., 2013).
As a consequence of the need for regeneration, the application of the ion exchange process often entails a significant chemical consumption (Zhang et al., 2017), costs and environmental impact connected to the disposal of the saturated brine as hazardous waste (Huang et al., 2020), 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 (Ukwuani et al, 2016) to ensure the economic feasibility of the process by allowing for the reusability of the brine (Huang et al., 2020). 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 (Darestani et al., 2017; Ukwuani et al., 2016). 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 4).

Table 4. 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×a	201	320 (+59%)	138 (-31%)	263 (+30%)	80 (-60%)	208 (+3%)	151 (-25%)
GWP	kg CO_2 eq/pe×a	33	23 (-30)	12 (-60%)	20 (-39%)	9 (-72%)	14 (-58%)	11 (-66%)
MEP	kg N eq/pe×a	2.1	0.8 (-62%)		0.8 (-62%)		0.8 (-62%)	0.8 (-62%)

In this case, the net CED was 151 MJ/pe×a compared to 201 MJ/pe×a obtained from the reference scenario. This reduction was due to the possibility to recover the NH_4^+-N as

ammonium sulphate ($(NH_4)_2SO_4$) which can be used in the fertilizer industry (Lubensky et al., 2019). The difference in CED between the IEX-KCl-MEM and IEX-NaCl-MEM scenarios (208 and 151 MJ/pe×a, respectively) was due to the higher energy required for the production of KCl compared to NaCl (Ecoinvent, 2017). Considering that one ion of NH_4^+ in the media is substitute with one K^+ or one Na^+ in the regenerant, the required quantity of KCl (5.3 kg KCl/kg NH_4^+) was higher than the quantity of NaCl (4.2 kg KCl/kg NH_4^+) (Table 4); 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), this has been identified as a more efficient regenerant for Zeolite-N (Canellas, et al., 2019b) 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 SM 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 (Ukwuani et al., 2016). Importantly, the need for additional heat could be reduced by applying the recovery process to an anaerobic digester recirculation line (Anwar et al., 2016). In fact, if excess heat (recovered from heat pumps and exchangers and the use of digester gas in CHP systems (Neugebauer et al., 2015)) 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 (Ukwuani et al., 2016) 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_2, N_2O and CH_4 (Huang et al., 2020)) and lack of resource recovery (Lin et al., 2016) which resulted in a global warming potential of 33 kg CO_2 eq/pe×a. In comparison, the IEX scenarios accounted for 9-23 kg CO_2 eq/pe×a (Table SM 6). According to Huang et al., (2020), 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., (2016), confirmed that the IEX process had the lowest GWP when compared to Anammox process and conventional nitrification and denitrification (Lin et al., 2016).

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_4^+-N loads can cause eutrophication of the waterways (Huang et al., 2018), Lin *et al.* noticed that the environmental footprint of the IEX process for NH_4^+-N removal is mainly due to the phosphorus emission (Lin et al., 2016). 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. Therefore, to increase the certainty of the LCA, it is necessary to perform additional studies or expand the data sources to limit the estimations associated with the ammonia recovery processes as these carries higher uncertainty (Table SM 4) and including additional emerging technologies for wastewater treatment such as mainstream anammox or aerobic granular sludge for a comparison with the IEX process.

5. Conclusions

The variability in the influent of secondary treatment as well as seasonal and diurnal temperature variation affect the efficiency of nitrification. In this work, this resulted in peaks in NH_4^+-N concentration in the effluent of secondary processes (0 and 26 mg NH_4^+-N/L). Under such conditions, the NH_4^+-N exchange capacity of Zeolite-N ranged from 0.9 to 17.7 mg NH_4^+-N/g media. Due to ammonium exchange equilibrium between the media and the wastewater, with influent concentration below 2.5 mg NH_4^+-N/L, the Zeolite-N released the NH_4^+-N up taken in previous cycles into the wastewater causing an increase of the NH_4^+-N effluent concentration. The use of an automated system is suggested to better control the effluent quality. Additionally, the NH_4^+-N present in the media affected the efficiencies. An optimization of the volume of brine and the contact time between the brine and the media is suggested.

When considering the environmental impact of the IEX process, 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×a for IEX-KCl-VAC; from 263 to 80 MJ/pe×a for IEX-NaCl-VAC). Additionally, switching from KCl to NaCl for the regeneration process resulted in a substantially lower CED and lower GWP in all the scenarios.

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