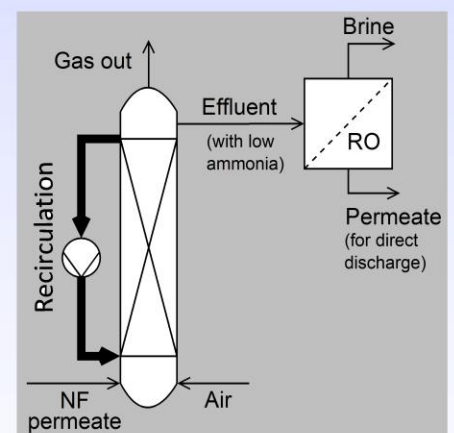Sreenivasan Ramaswami

High-rate nitrification of membrane-filtrated saline landfill leachate using fixed-bed biofilm reactors

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ABSTRACT

Ammonia in leachate forms the foremost concern in landfill management in the long-term. Leachates containing high ammonia concentrations (about 2 g/L NH_4^+-N or more) cannot be treated satisfactorily (to meet discharge limits, 70 mg/L total nitrogen) using reverse osmosis (RO) systems alone. The leachate from the landfill site at Ihlenberg (containing about 0.6 g/L NH_4^+-N, 6 g/L Cl^- and 0.8 g/L TOC) gets treated solely by a chain of high pressure membrane processes (RO-NF-RO) (NF: nanofiltration), aiming to achieve water recoveries over 95%. Insufficient ammonia rejection by the final RO stage however, hinders this plan. In this study, the possibility for ammonia removal by high rate nitrification using packed bed reactors was investigated for this scenario.

Batch trials were conducted over a period of about 400 days in four lab-scale packed bed reactors (PBR) – filled with three different media (coke, clay beads and PE carrier) (PE: polyethylene) – with dilutions of the different leachate matrices (RO retentate of raw leachate [3 g/L NH_4^+-N, 30 g/L Cl^- and 4 g/L TOC] and NF permeate of RO concentrate [2.2 g/L NH_4^+-N, 29 g/L Cl^- and 0.4 g/L TOC]) to identify a packing material and the process stream best suited for nitrification.

Maximum nitrification rates of about 570 and 1200 g NH_4^+-N/(m^3·d) were achieved in 1:4 to 1:2 dilutions of RO retentate and NF permeate, respectively. The organic compounds contained in the RO concentrate were found to cause nitrification inhibition. Coke media was found to be the most vulnerable to clogging owing to its ability to adsorb organics, followed by clay beads due its low bed porosity, whereas the PE carrier showed a long longevity. The potential to attain nitrification rates of up to about 1200 g NH_4^+-N/(m^3·d) in 1:4 diluted NF permeate was confirmed in further batch experiments (over a period of 4 months) using reactors filled with clay beads and PE carrier.

The practical application (continuous operation) was realised and studied using two lab-scale recirculating PBRs filled with PE carrier and clay beads. The trials were planned and conducted in two phases (lasting about 4 and 3 months, respectively): (a) to obtain stable operating conditions and identify any operational challenges; and (b) to investigate the effect of increasing wastewater chloride content and to demonstrate the practical application (treatability) with NF permeate.

The reactor packed with PE carrier outperformed the clay beads filled reactor during the initial continuous flow experiments with synthetic wastewater (resembling the permeate of the 2nd NF stage [0.4 g/L NH_4^+-N and 4 g/L Cl^-] at the landfill site). Due to insistent clogging (resulting from low bed porosity and uncontrolled biofilm growth), the clay beads-packed reactor demanded frequent washing to achieve the design performance, whereas the PE carrier-filled reactor offered stable and nearly complete nitrification at the design loading rate of about 925 g NH_4^+-N/(m^3·d) at 25°C.

A gradual stepwise increase in chloride concentration from 4 to 16 g/L (correspondingly, electrical conductivity increased from about 14 to 45 mS/cm) did not have any observable impact on the nitrification efficiencies of the reactors. The PE carrier-packed reactor operated with a mix of 1st and 2nd stage NF permeates from the landfill site (spiked with NaCl as per requirement) showed ammonia removals greater than 97% at loading rates of about 1100 g NH_4^+-N/(m^3·d) at 25°C, whereas the clay beads-filled reactor (without washing) fed with synthetic wastewater at loading rates of about 925 g NH_4^+-N/(m^3·d) gave nitrification efficiencies of about 70% (average) only.

Based on the findings from the continuous flow trials, a pilot-scale plant was conceptualised and commissioned at the Ihlenberg landfill site. The planning and layout of the demonstration plant is presented in this work.

KURZFASSUNG

Im Sickerwasser alter Deponien verursacht Ammonium die größte Besorgnis im Deponiemanagement. Alleine durch Umkehrosmose (UO) ist eine ausreichende Reinigung von Deponiesickerwässern, die hohe Konzentrationen an Ammonium (größer als 2 g/L NH_4^+-N) enthalten, nicht möglich, um die Grenzwerte (70 mg/L Gesamtstickstoff) für die Einleitung in Oberflächengewässer einzuhalten. Das Sickerwasser aus der Deponie Ihlenberg (mit ca. 0,6 g/L NH_4^+-N, 6 g/L Cl^- und 0,8 g/L TOC) wird ausschließlich mittels einer Reihe von Hochdruck-Membranverfahren (UO-NF-UO) (NF: Nanofiltration) behandelt, um Reinwassererträge von über 95% zu gewinnen. Aber der unzureichende Ammoniumrückhalt der letzten UO-Stufe verhindert das gewünschte Reinigungsziel. In dieser Arbeit wurde für diese Kombination von Membranverfahren die Möglichkeit der Ammoniumentfernung mittels einer zusätzlichen Hochleistungsnitrifikation in Festbettreaktoren untersucht.

Über einen Zeitraum von ca. 400 Tagen wurden vier Festbettreaktoren (FBR) im Labormaßstab – gefüllt mit den drei verschiedenen Füllmaterialien Koks, Blähton und PE-Träger (PE: Polyethylen) – mit Verdünnungen verschiedener Sickerwassermatrices (UO-Retentat des Rohsickerwassers [3 g/L NH_4^+-N, 30 g/L Cl^- und 4 g/L TOC] und NF Permeat des UO Konzentrats [2,2 g/L NH_4^+-N, 29 g/L Cl^- und 0,4 g/L TOC]) im Batchmodus betrieben, um sowohl ein passendes Füllkörpermaterial als auch den Teilstrom, der am besten für die Nitrifikation geeignet ist, auswählen zu können.

In den Batch-Versuchen wurden maximale Nitrifikationsraten von ca. 570 und 1200 g NH_4^+-N/(m³·d) mit 1:4- bis 1:2- Verdünnungen von UO-Retentat bzw. NF-Permeat erreicht. Die organischen Kohlenstoffverbindungen im UO-Konzentrat hemmten die Nitrifikation. Wegen der hohen Adsorptionskapazität für organische Stoffe zeigte das koksgefüllte Festbett das größte Risiko der Verstopfung. Nachstehend in Rang war der Reaktor, der mit Blähton (welcher die kleinste Porosität aufwies) gefüllt war. Der mit PE-Träger befüllte Reaktor hatte dagegen eine lange Betriebsdauer, ohne zu verstopfen. In weiteren Batchexperimenten mit ca. viermonatiger Betrieb Dauer in Reaktoren, die mit PE-Trägern und Blähton gefüllt waren, wurde das Potenzial für hohe Nitrifikationsraten (bis zu 1200 g NH_4^+-N·m^{-3}·d^{-1}) in 1:4 verdünntem NF Permeat bestätigt.

Zwei Festbettreaktoren einer mit PE-Trägern und der andere mit Blähton im Labormaßstab wurden für kontinuierliche Betriebsversuche verwendet, um die praktische Anwendung des Verfahrens zu untersuchen. Die Versuche wurden in zwei Phasen (Phase I: 4 Monate, Phase II: 3 Monate) durchgeführt, um: (a) stabile Betriebsbedingungen zu erreichen und etwaige operative Herausforderungen feststellen zu können, und (b) den Einfluss des Chlorid-Gehalts des Abwassers auf die Nitrifikation zu untersuchen und die praktische Anwendung mit dem NF-Permeat zu demonstrieren.

Die Nitrifikationsraten des mit dem PE-Träger befüllten FBRs übertraf die des blähtongefüllten Reaktors während der ersten Phase, in der die Versuche mit synthetischem Abwasser durchgeführt wurde, welches ähnliche Konzentrationen an NH_4^+-N und Cl^- (0,4 bzw. 4 g/L) wie das Permeat der zweitstufigen Nanofiltration am Deponieort enthielt. Aufgrund der Neigung zu Verstopfungen (infolge der geringen Porosität und des unkontrollierten Biofilmwachstums) zeigte der Blähton-FBR einen hohen Bedarf an regelmäßigem Spülen des Betts, um die mit der Bemessung angestrebten hohen Leistungen zu erreichen. Der FBR mit dem PE-Träger zeigte bei den bemessenen Belastungsraten von ca. 925 g NH_4^+-N/(m^3·d) und bei 25°C eine stabile annährend vollständige Nitrifikation.

Eine sukzessive schrittweise Erhöhung des Chlorid-Gehalts des Abwassers von 4 auf 16 g/L (bzw. der elektrischen Leitfähigkeit von 14 auf 45 mS/cm) hatte keinen erkennbaren Einfluss auf die Nitrifikationsleistungen der Reaktoren. Der mit PE-Träger befüllte FBR, der mit einem Gemisch von NF-Permeaten aus dem Deponieort (das mit NaCl angereichert wurde) betrieben wurde, zeigte Ammoniumentfernungen von über 97% bei Volumenbelastungsraten von ca. 1100 g NH_4^+-N/(m^3·d) bei einer Temperatur von 25°C. Der Blähton-FBR (ohne das Spülung des Festbetts) ergab aber bei Belastungsraten von ca. 925 g NH_4^+-N/(m^3·d) ebenfalls bei 25°C nur Nitrifikationseffizienzen von durchschnittlich 70%.

Basierend auf den Ergebnissen aus den kontinuierlichen Betriebsversuchen wurde eine Anlage im halb-technischen Maßstab am Ort der Deponie Ihlenberg konzeptioniert und in Betrieb genommen. Die Planung und die Auslegung der Demonstrationsanlage werden in dieser Arbeit präsentiert.

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LIST OF ABBREVIATIONS AND SYMBOLS

AOO	Ammonia oxidising organisms
AOX	Adsorbable organic halides
AS	Activated sludge
AWW	Institute of Wastewater Management and Water Protection
BAF	Biological aerated filter
BOD	Biochemical oxygen demand
BOD_5	Biochemical oxygen demand in 5 days
cBOD	carbonaceous BOD
COD	Chemical oxygen demand
df	Dilution factor
DO	Dissolved oxygen
d_p	Particle diameter
EC	Electrical conductivity
FA	Fulvic acids
FC	Flow controller
GAC	Granular activated carbon
HA	Humic acids
HDPE	High density polyethylene
HRT	Hydraulic retention time
IBC	Intermediate bulk container
ID	Inner diameter
$Kb_{8.2}$	Base neutralising capacity
$Ks_{4.3}$	Acid neutralising capacity

MBBR	Moving bed biofilm reactor
MBR	Membrane bioreactor
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
$N-NH_4^+$	Ammonium-nitrogen
$N-NO_2^-$	Nitrite-nitrogen
$N-NO_3^-$	Nitrate-nitrogen
NF	Nanofiltration
NOO	Nitrite oxidising organisms
ORP	Oxidation-reduction potential
PBR	Packed bed reactor
PE	Polyethylene
PN	Pressure nominal
PT	Pressure transmitter
PVC	Polyvinyl chloride
RBC	Rotating biological contactor
RL	Raw leachate
RO	Reverse osmosis
SBR	Sequencing batch reactor
SCBP	Suspended carrier biofilm process
SFBBR	Submerged fixed bed biofilm reactors
SS	Suspended solids
T	Temperature
TF	Trickling filter
TIC	Total inorganic carbon

TN	Total nitrogen
TOC	Total organic carbon
TSS	Total suspended solids
TUHH	Hamburg University of Technology
VARR	Volumetric ammonia removal rate
VFA	Volatile fatty acids

1   THE RESEARCH PROBLEM

The landfill Ihlenberg (commissioned in 1983), located about 15 km to the east of the north-German city Lübeck, is one of the largest co-disposal sites in Europe [1] and produces about 500 m³ of mature leachate per day. Since December 1989, the landfill operator (IAG - Ihlenberger Abfallentsorgungsgesellschaft mbH) has been treating the leachate[§] using disc-tube reverse osmosis (RO) systems (RTS Rochem Technical Services GmbH, Hamburg, Germany), operated at pressures of up to 120 bar, to attain clean water recoveries of about 80-85% [1,2].

Table 1 shows the values for some important parameters in the raw leachate (RL) and its RO concentrate, which is an excerpt from the elaborate analysis (see Table 12, Appendix) carried out by the project partner (RTS Rochem Technical Services GmbH) in July 2013. The RO retentate has high sulphate concentration since sulphuric acid is used during the RO process to prevent carbonate scaling. The RO permeate is discharged into nature through re-mineralisation basins and the retentate enriched with pollutants was until recently re-injected into the landfill. The recirculation of retentate was practised because it was one of the cheapest options [3,4].

Table 1. Values of some important parameters in the raw leachate from the Ihlenberg dumpsite and its RO concentrate [5].

Cations	in mg/L		Anions	in mg/L	
	RL	RO		RL	RO
Ca^{2+}	230	1200	Cl^-	5800	30000
K^+	1100	5800	$N-NO_2^-$	< 0.3	1.15
Mg^{2+}	81	350	$N-NO_3^-$	< 2	< 2
Na^+	3100	15800	$o-PO_4^{3-}-P$	4.5	15.6
$N-NH_4^+$	580	3000	SO_4^{2-}	560	13700
Sum parameters					
pH	8.0	7.5	EC (mS/cm)	23.5	92
ORP (mV)	210	190	$Ks_{4.3}$ (mmol/L)	56.5	131
COD (mg/L)	1900	11700	BOD_5 (mg/L)	740	960
TOC (mg/L)	840	4060	TN (mg/L)	588	3120

EC - electrical conductivity, ORP - oxidation reduction potential, $Ks_{4.3}$ - acid neutralising capacity

The current German regulation on landfills and long-term storage sites [6] prohibits the re-injection of mature leachates or their concentrates, thus mandating further treatment of the RO retentate or enhancement of the leachate treatment system. For this scenario, several methods and their combinations (as shown in Figure 1) were investigated within the framework of the research project. Some findings from these investigations have been published as papers in peer-reviewed journals (see List of Publications). It is widely reported [7–9] that an

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[§] Raw leachate after preliminary conditioning, more details can be found elsewhere [1].

integration of different physical-chemical and/or biological treatment methods is crucial for realising efficient handling of landfill leachates.
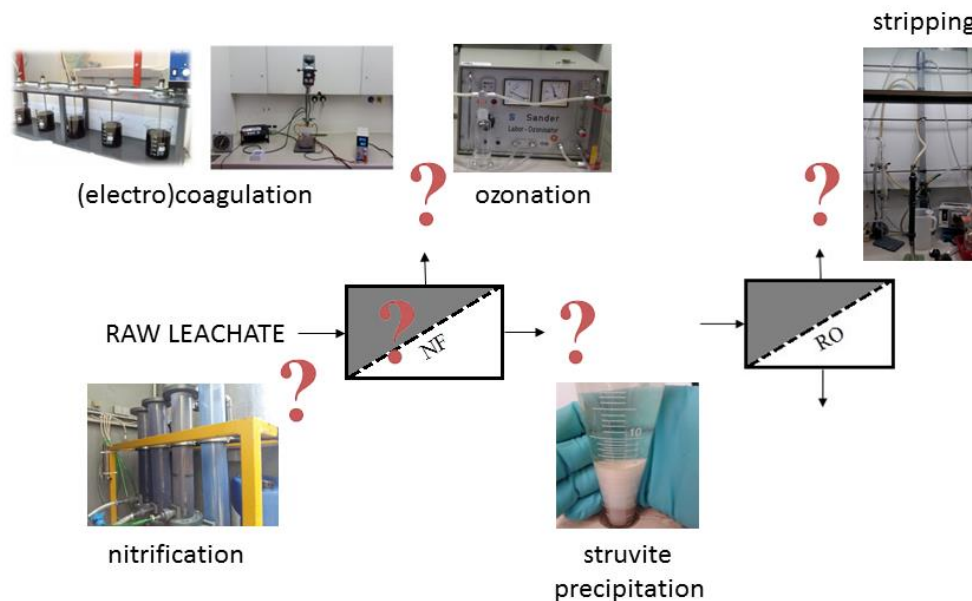
Figure 1. An overview of the different methods investigated within the project for treating the leachate.

The project partner and the landfill operator plan to treat the retentate as illustrated in Figure 2. The scheme is based on previous research works [10,11], which were aimed at reducing the volume of retentate (to be re-injected previously) further using nanofiltration (NF). It is desired to handle the NF permeate using another RO stage (operated at about 200 bar) and thereby enhance the clean water recovery up to about 95 percent. However, as communicated by the project partner, the final RO stage would fail to reject ammonium ions sufficiently (since they are present in high concentrations in the NF permeate), making the RO-3 permeate unsuitable for direct discharge.
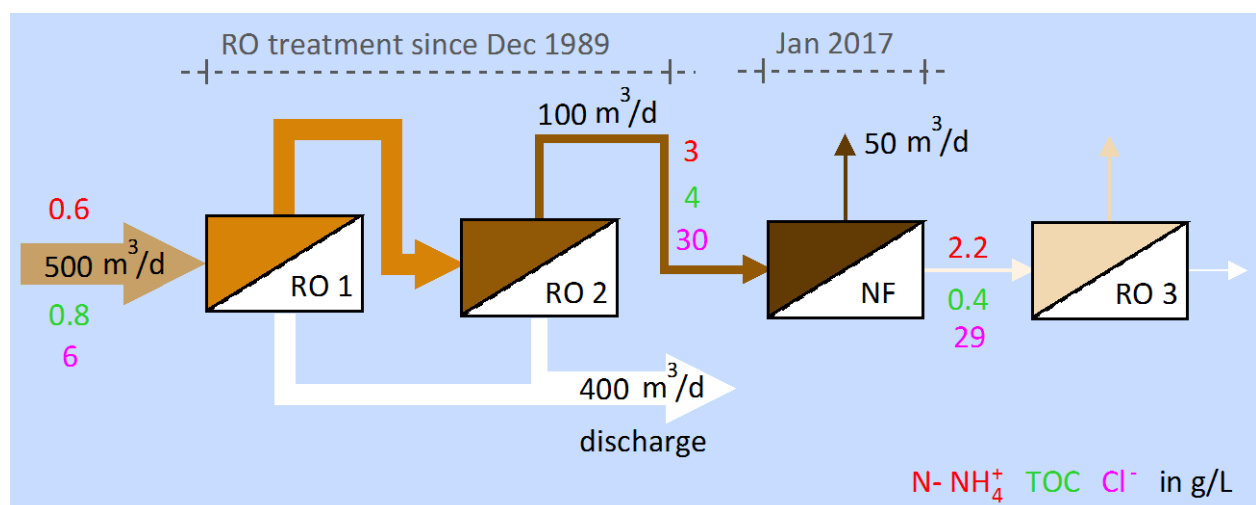
Figure 2. Proposed scheme for treating the leachate at the Ihlenberg dumpsite (approximate values for flow rates and concentrations of some relevant parameters are shown).

The project partner has communicated to the author that the final RO stage could reject nitrate ions better than ammonium ions (as also reported in some other sources [12–14]), since they have negative charge and a higher molecular weight than the latter. The aim of this research project was thus to achieve biological nitrification of the retentate of RO-2 or the permeate of NF stage (both of which have high salinities) so that the nitrogen species in the feed to RO-3 could predominantly be composed of nitrate ions and low ammonium-nitrogen concentrations.

Other ammonia removal technologies such as stripping [3,15,16] and chemical precipitation [17–19] centred on resource recovery were not of interest due to the bleak marketability perspectives of the recovered products – ammonium sulphate and magnesium ammonium phosphate, respectively. Also nitritation-ANAMMOX process was not considered because it demands long start-up times and high temperatures, and also shows failure risks and limited flexibility [20]. Furthermore, it requires more research for understanding the treatability of landfill leachates [3,21] compared to nitrification using suspended growth processes, which is better known, established and applied widely – also in full scale [22–25]).

This dissertation presents the results of the investigations focused on realising an efficient and robust nitrification system fitting to the scenario illustrated in Figure 2, paving way to the commissioning of a plant in half-technical scale at the landfill site.

2 INTRODUCTION

2.1 SOME GENERAL ASPECTS ABOUT LANDFILL LEACHATES

Landfill leachate – the wastewater formed from the percolation of precipitation[§] through the buried waste predominantly [26–28], and inherent moisture content and biochemical transformations of the discarded refuse [4] – is the most important environmental and public health concern arising from solid waste dumpsites. Unlike landfill gas, the production of polluted leachate is to be anticipated for more than 100 years after the closure of a waste tip [29–31], demanding collection and appropriate treatment so as to prevent the contamination of surrounding surface and ground waters. Generally characterised by high organics (ranging from biodegradable to recalcitrant and also comprising hazardous halogenated compounds) and ammonia content, additionally containing alkali/alkaline-earth metal ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, etc.), heavy metals (Ni^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, etc.) and inorganic anions (Cl^-, SO_4^{2-}, HCO_3^-, etc.) in varying proportions depending on the nature of the waste disposed, landfill leachates are unanimously regarded as one of the most polluted wastewaters. Due to the fact that both quality and quantity of leachate are highly variable (with climatic conditions, age of the landfill, the kind of refuse disposed of and therefore, from one site to another), choice of methods for its treatment becomes site-specific and challenging [3,4,32,33].

While leachate flow rate is the result of the water balance considering precipitation pattern and its infiltration, evaporation rates, surface runoffs, biodegradation and storage capacity [34–36], its composition depends mainly on the age of the landfill, type of waste and the quantity of leachate [3,4,28]. Table 2 shows the typical characteristics of leachates from landfills of different ages.

Table 2. Overview of variation in leachate composition with landfill age   (after [3,4,37]).

Parameter	Unit	Young	Intermediate	Old
Age	year	< 2	2-5	> 5
pH	-	< 6.5	6.5 – 7.5	> 7.5
COD	mg/L	> 10,000	3,000 – 10,000	< 3,000
BOD_5/COD	-	0.5 – 1.0	0.1 – 0.5	< 0.1
$N-NH_4^+$	-	high	high	high
Heavy metals	mg/L	> 2	< 2	< 2
Dominant organic fraction	-	80% VFA	5-30% VFA + HA + FA	HA + FA

VFA - volatile fatty acids, HA - humic acids, FA - fulvic acids

Owing to the fact that ammonium-nitrogen (compared to organic compounds) is stable under anaerobic (methanogenic) conditions; its concentration does not decrease with the ageing of a dumpsite [27,34,38] (see also Table 2), thus making it the major long-term pollutant in landfill leachates. Due to the effects including oxygen depletion, eutrophication and acute

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[§] Infiltration can be minimised by compaction of the dumped waste, increasing evaporation rates with vegetation covers or installing impermeable top sealing [34,36].

toxicity [39,40] resulting from its emissions, ammonia removal from landfill leachates demands the foremost concern in the long-run [27].

2.2   AMMONIA REMOVAL FROM LANDFILL LEACHATES USING NITRIFICATION

Although numerous technologies are technologically viable [3,4,21,41], nitrification-denitrification is considered to be by far the most cost-effective and widely applied method for nitrogen removal from landfill leachates [33,41–43].

Table 13 (in Appendix) presents a brief review of the past works on ammonia removal by nitrification from landfill leachates using different reactor types. The entries in Table 13 were carefully selected from the studies indexed/abstracted in Google Scholar, Web of Science, Scopus and Crossref, in which remarkable nitrification rates have been reported. Furthermore, care has been also taken to handpick studies that address particularly ammonia removal since majority of the works have laid focus on COD reduction [3,4].

Suspended growth processes – activated sludge (AS) and sequencing batch reactor (SBR) systems – are widely studied and applied for ammonia removal from landfill leachates [4,25,44,45]. This might be due to the fact that the knowhow of these processes (gained from the field of sewage treatment) is higher and better established compared to the attached growth processes (which has attracted high interest for municipal wastewater treatment during the last fifty years [46]). Analogous to the historical development in municipal wastewater treatment, BOD removal was initially the prime objective also for leachate treatment using suspended growth processes [47–49].

Knox [50] was one of the first workers studying nitrification of a mature landfill leachate extensively. A maximum nitrification rate of 508 $gN \cdot m^{-3}d^{-1}$ (at 13°C) was achieved in a pilot-scale AS system at the landfill site with a mixed liquor volatile suspended solids (MLVSS) concentration of about 3.9 g/L. The author experienced inadequate sludge settling and loss of biomass with effluent, which was reasoned to be due to the low BOD:N ratio of the leachate. The study also verified the influence of temperature on the nitrification process over a range from 0-24°C.

A combination of anaerobic (methanogenesis/denitrification in up-flow biofilm reactor) and aerobic (activated sludge) systems was studied by Im et al. [51] in lab-scale for treating a young leachate originating from a municipal waste landfill. With a hydraulic retention time (HRT) of about 4 days, they realised nitrification rates as high as 500 g NH_4^+-N/(m^3d) at 23°C in the aerobic reactor treating the effluent from the anaerobic reactor. In a recent study by Yusof et al. [52], complete nitrification was achieved at loading rates of about 2.56 kg NH_4^+-N$\cdot m^{-3} \cdot d^{-1}$ in a lab-scale AS reactor operated with 20 g TSS/L.

Amongst the suspended growth processes, the sequencing batch reactor (SBR) has been reported to be better suitable [43] and to be the widely applied variant for biological treatment (especially for nitrification-denitrification due to the operational flexibility the method offers

for the management of aerobic and anoxic conditions among other reasons) of landfill leachates [4,45]. In a pilot-scale SBR operated under field conditions, highest nitrification efficiency attained by Henderson et al. [53] was 93% ammonia removal at a loading rate of about 343 g NH_4^+-$Nm^{-3}d^{-1}$ (at 20°C). In a bench-scale study conducted by Doyle and co-workers [54] over a period of 2 years, the ability to achieve nitrification rates of up to 5.9 kg N/(m^3·d) was demonstrated using an SBR operated with 9.6 g MLSS/L enriched with highly acclimatised nitrifiers. However, such high volumetric rates are usually not realised in full scale suspended growth systems, with nitrification capacities typically being less than 200 g NH_4^+-N·m^{-3}·d^{-1} (K. Knox and H. Robinson, personal communication, Sardinia Symposium 2017). This also becomes evident from the design capacities or the rates achieved (being < 300 g NH_4^+-N·m^{-3}·d^{-1}) in the works in large scale [24,25,55–57].

The major bottleneck suffered by suspended growth processes applied to landfill leachate treatment is sludge bulking or inadequate settling and subsequent loss of biomass with the effluent [3,4,45,50,53,58]. It is also well known that the volumetric nitrifying capacity of a suspended growth system increases with increasing MLVSS concentration [54,59], which however, degrades the settling characteristics of the sludge [60].

Fixed-film processes, relying on microbiological processes occurring in biofilms attached to suitable support media, would be an attractive option for nitrification of landfill leachates compared to suspended growth processes. Although discovered prior to the suspend growth process (1893 vs. 1913) and biofilters were studied and installed in several locations around the world, the activated sludge process saw a widespread implementation for sewage treatment worldwide [46,61]. This explains why suspended growth processes have been widely used for leachate treatment in spite of the above-mentioned drawbacks.

With scientists worldwide keen on high rate processes for reducing reactor volumes and land requirements, fixed-film technologies regained popularity in the 1970s and the number of publications on the application of biofilm reactors for wastewater treatment have increased exponentially over the last few decades [61–64]. With high specific surface areas and the ability to immobilise the slow growing nitrifiers on the carrier media (preventing their wash out from the system) – thus offering very high biomass concentrations in the reactor and forming high rate systems – fixed-film reactors represent a highly desirable choice for nitrification of landfill leachates.

2.3   LEACHATE NITRIFICATION IN BIOFILM REACTORS

A comparison of nitrification in mature landfill leachate using pilot-scale (under field conditions at the landfill site) activated sludge and trickling filter (TF) was made by Knox [50]. The quality of the effluent (with regard to suspended solids) from the TF was shown to be superior to that from the AS. The author raised the necessity for a tertiary filtration step after AS in order to separate the biomass from the effluent and return it to the process (in order to ensure process stability).

Attached growth systems gained interest for leachate treatment in the 1990s. Numerous works spanning over the last two decades can be found in literature, focussing on COD (e.g. [58,65–67]) and ammonia removal [68–72] from landfill leachates using biofilm reactors. Table 13 (in appendix) highlights previous research reporting high nitrification rates in landfill leachates using fixed-film reactors.

Henderson and co-workers [53] compared the use of an SBR and a rotating biological contactor (RBC) in pilot-scale for nitrifying an old landfill leachate. The RBC in comparison to SBR not only offered higher volumetric nitrification rates (highest rates achieved in the study being about 890 versus 343 $gN \cdot m^{-3} \cdot d^{-1}$), but also a stable and reliable performance. The suspended solids content in the effluent from the RBC was lower and better settleable than that from the SBR. Both Knox [50] and Henderson et al. [53] also showed that the temperature dependence of nitrification in biofilm systems is much less pronounced compared to the suspended growth counterparts. Both studies concluded fixed-film systems to be superior and preferable over suspended growth processes for nitrification of landfill leachates (especially methanogenic ones having a low BOD:N ratio).

Several works [23,68,70,73] investigated the use of moving bed biofilm reactor (MBBR) or suspended carrier biofilm process for ammonia removal from leachates. It seems that these studies were driven by the progress on the application of MBBRs for municipal wastewater treatment [74,75]. Welander and co-workers studied nitrification of a mature leachate using MBBRs in lab [70] and pilot-scales [73]. Investigations with three different carrier materials in their laboratory-scale study revealed that the surface area available for biofilm growth and the surface characteristics of the support medium strongly influence the performance of a reactor.

The reactors filled (each 60% fill) with media with macro-surface areas of 200 and 390 m^2/m^3 showed similar volumetric nitrification capacities (265 $gN \cdot m^{-3} \cdot d^{-1}$ at 20°C), due to greater surface roughness of the former medium (although it had only about half the area as provided by the latter). The reactor containing carrier medium with the lowest specific macro-surface area (only 170 m^2/m^3) and only 10% fill, owing to the porous structure of the carrier material, offered the highest nitrification rate (953 g NH_4^+-$N \cdot m^{-3} \cdot d^{-1}$ at 20°C). The study also verified that the effect of temperature (over a range of 5-20°C) on nitrification in MBBRs is low. In their pilot-scale investigations with MBBRs at the landfill site, achieving maximum nitrification rates of about 288 and 576 $gN \cdot m^{-3} \cdot d^{-1}$ (at 17°C) in two parallel reactors filled (each 60% fill) with media having surface-to-volume ratios of 210 and 390 m^2/m^3 respectively, Welander et al. [73] clearly demonstrated the direct relationship between nitrification capacity and surface area available per unit reactor volume.

Horan and co-workers [71] conducted nitrification experiments with an old landfill leachate in granular activated carbon fluidised bed reactors (two stages in series) and compared it with trials using activated sludge systems. At an overall loading rate of 357 g NH_4^+-$N \cdot m^{-3} \cdot d^{-1}$ (at 20°C) and 1.41 kg COD/($m^3 \cdot d$), about 93% ammonia removal and 55% COD reduction (63% of which was estimated to be due to biodegradation) were achieved with the fluidised bed reactor

system. Nevertheless, the system showed poor suspended solids removal, thus necessitating a filtration step for the effluent. Due to nitrification inhibition, no ammonia removal was obtained in the AS reactors operated under similar ammonia loading rates and only about 20% COD reduction was observed.

The application of RBC for nitrification of mature landfill leachate was studied also by Spengel and Dzombak [76] and Kulikowska et al. [72] using lab-scale systems. At loading rates of 2.6 and 3.58 g NH_4^+-N·m^{-2}·d^{-1} (both at 20°C), respectively, remarkable ammonia removal percentages greater than 93 and 99% were attained. Loading and removal rates in RBCs are generally expressed per unit surface area. However, due to the fact that surface to volume ratio in RBCs are usually low [77,78], the volumetric removal rates achieved in these studies (432 and 244 g N·m^{-3}·d^{-1} respectively) were not very high.

Biological aerated filter (BAF) or submerged biofilter (which can fulfil BOD_5, N-NH_4^+ and SS removals, and may be considered analogous to a packed bed reactor, PBR), which offers high surface to volume ratios [77], is a widely used reactor type among the different attached growth process configurations for municipal wastewater treatment [79]. Only Jokela et al. [23] have addressed nitrification of landfill leachate using PBR to the best of author's knowledge. In their study, they have worked with N-NH_4^+ loading rates of up to 130 and 50 g·m^{-3}·d^{-1} in lab-scale and pilot scale reactors, respectively, but have not attempted to assess the maximum loading potential.

Existing literature on BAFs treating municipal wastewaters reports volumetric nitrification capacities of about 1.0-1.2 kgN·m^{-3}·d^{-1} for these systems. BAFs form the natural choice for wastewater treatment with stringent nutrient removal requirements especially when the available space is scarce [61,77,80]. The following key traits of packed bed reactors (or biological aerated filters), identifiable from the vast previous research on their application for the treatment of municipal and other industrial wastewaters [61,62,79,81–86], makes them attractive and promising for realising robust high rate nitrification of mature landfill leachates:

- high surface area per unit reactor volume and the ability to immobilise the slow growing nitrifying organisms (preventing wash out), resulting in compact systems with high biomass densities;

- the ability to offer high quality effluent with very low suspended solids concentrations (owing to the immobilisation of biomass, low excess sludge production and the filtering effect of the media) and thus eliminating the need for a clarifier;

- low temperature dependence of nitrifying biofilms and their ability to withstand temporal shock-loadings and stress due to inhibitors/toxins (which are characteristics common to landfill leachates) enabling a stable and reliable performance.

Due to these reasons, this dissertation has been centred on assessing the possibility for novel high rate nitrification of landfill leachate using aerated packed bed reactors. Considering the numerous studies (although mainly in lab and pilot scale) on the application of membrane bioreactors (MBR) for the treatment of landfill leachates reported in literature [87], it could be a potential solution to this problem faced by the conventional suspended growth processes. However, PBRs were chosen over MBRs for this study due to: the novelty in application, their competitiveness (learnt also from the first-hand previous experience on biofilm reactors at TUHH [88–90]) and benign nature.

2.4   AIM OF THIS STUDY

The objectives of this study were to:

- assess the potential of PBRs for high rate nitrification of mature landfill leachates,

- identify among RO retentate of raw leachate and NF permeate of RO concentrate, the stream suited for nitrification and characterise the matrix effects on the process,

- find a packing material that can deliver a stable and hassle-free operation,

- achieve stable and efficient nitrification with the identified stream in continuous flow,

- recommend and commission a suitable process configuration at half-technical scale at the landfill site.

3 MATERIALS

3.1   RO CONCENTRATE OF LANDFILL LEACHATE AND NF PERMEATE OF RO RETENTATE

For most of the study period, RO concentrate of raw leachate from the Ihlenberg landfill was delivered to the TUHH Institute of Wastewater Management and Water Protection (AWW) by RTS Rochem Technical Services GmbH. The samples were delivered in sealed 25 or 30 L HDPE containers in volumes ranging from 60 to 200 L (as per requirement), once or twice quarterly. All wastewater samples were stored at 4°C to keep any changes in composition to minimum.

During the first year of the research project, NF permeate was produced at the institute (from the supplied RO retentate) using an Effluent Treatment System packed with DOW FILMTEC NF270 membrane provided by RTS Rochem Technical Services GmbH. More details about the nanofiltration setup can be found elsewhere [91,92]. Thereafter, NF permeate was provided from the pilot scale nanofiltration plant treating the RO retentate at the landfill site. The NF permeate derived from the RO retentate is designated as "NF permeate" throughout the following text. Table 3 shows the range of the relevant parameters in the RO retentate and the NF permeate used in the project.

Table 3. Range of values for parameters measured in the RO concentrate of raw leachate and the NF permeate of RO retentate used in this study   [5].

Parameter	Unit	RO concentrate	NF permeate
Cl^-	mg/L	31500 ± 1000	30000 ± 1000
EC	mS/cm	96 ± 5	86 ± 3
$N-NH_4^+$	mg/L	3200 ± 200	2200 ± 200
pH	---	7.5 ± 0.2	7.7 ± 0.2
TN	mg/L	3400 ± 300	2400 ± 300
TOC	mg/L	3500 ± 500	370 ± 30

Synthetic NF permeate was prepared by dissolving known weights of ammonium chloride and sodium chloride in deionised water and used for the initial trials conducted in continuous flow reactor systems at TUHH, since large volumes of wastewater (ca. 50 L/d) were required. Once the nanofiltration stage was established in full scale at the landfill site (around March 2017), NF permeate was collected in 1000 L intermediate bulk containers (IBC) and transported to TUHH for the experiments.

3.2   PACKING MATERIALS

Hel-X® HXF12KLL (bio-carrier from recycled HDPE), Liapor® 8 4/8 (expanded clay beads) and Activated Lignite HOK®-grained (coke material) were purchased from Stöhr GmbH & Co.KG (Marktrodach, Germany), Liapor GmbH & Co. KG (Hallerndorf-Pautzfeld, Germany) and Rheinbraun Brennstoff GmbH (Frechen, Germany), respectively, to be investigated (in lab-scale at TUHH) for their suitability as packing material. Photographs of these materials and their

relevant physical characteristics (from respective manufacturer) can be seen in Figure 27 (in Appendix) and Table 4, respectively. For simplicity, the different packing materials shall hereafter be referred to as PE carrier, clay and coke respectively.

Table 4. Physical characteristics of packing materials and packed beds.

Attribute	Unit	PE carrier	Clay	Coke
Particle diameter	mm	12	4 - 8	1 – 3 [a]
Particle density	g/cm^3	n.a.	1.4	n.a.
Bed density	g/cm^3	0.15	0.8	0.47
Specific surface	m^2/m^3	859	800 - 900	4300 [a]
Bed porosity	---	0.85	0.55 [a]	0.7 [a]

a - [5], n.a. - not available

3.3 INNOCULUM

For the studies conducted at TUHH, return activated sludge (with about 6 g/L filterable suspended solids) was collected from the county wastewater treatment plant at Seevetal, Germany.

3.4 CHEMICALS

Ammonium chloride (Merck ACS grade, purchased from VWR Chemicals, Darmstadt, Germany) and food purity grade sodium chloride (table salt purchased from local supermarkets) were used for the preparation of synthetic NF permeate. Purified potassium carbonate (ca. 90%) or purified sodium carbonate (min. 98%) purchased from VWR Chemicals (Darmstadt, Germany) were used for controlling the pH by means of an automatic pH-controller. Laboratory grade sodium bicarbonate (min. 98%) purchased from VWR Chemicals (Darmstadt, Germany) was used for manual control of pH. All other chemicals used in the study were of analytical grade.

4   METHODS

4.1   PRELIMINARY EXPERIMENTS USING BENCH-SCALE REACTORS

The studies in the preliminary phase were constrained by the fact that the leachate might contain toxic/hazardous volatile organic compounds (like dioxins or other halogenated hydrocarbons), since the Ihlenberg landfill is a co-disposal dumpsite, which has accepted highly toxic waste (without records) in the past [93,94]. Therefore, it was of highest concern to take possible measures to minimise occupational hazards.

Due to this reason, the preliminary experiments were performed only with the nanofiltration permeate of RO concentrate, which would contain much lesser dissolved organics content (therefore, lower risks) compared to the RO retentate. These experiments were planned to help identify whether ammonia removal from these saline liquids via nitrification is possible at all. Parallelly, samples of RO retentate of the landfill leachate were submitted to the Central Laboratory of Analytical Chemistry of TUHH to be analysed for volatile chlorinated organic compounds concentration (using headspace gas chromatography with electron capture detector).
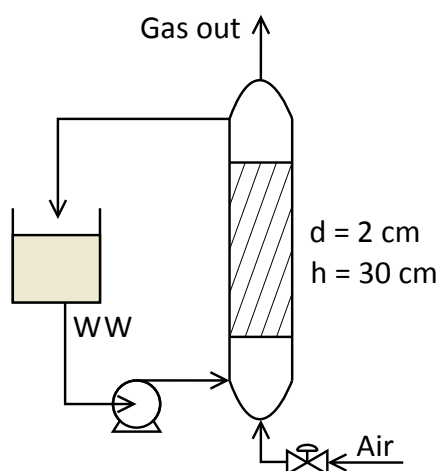
Figure 3. Schematic of the setup (left) and photograph of the fixed bed reactors (right) used for the preliminary experiments.

A schematic of the employed setup and a photograph of the reactors can be seen in Figure 3. Two transparent PVC columns (2.2 cm inner diameter) packed with expanded clay beads (bed height = 30 cm) were used as reactors. Other components of the setup included: 1 L glass bottles (reservoir), Masterflex variable speed peristaltic pumps (Model 7016, Cole-Parmer Instrument Company, Illinois, USA) and provision for aeration. A 1:25 dilution of return activated sludge in tap water (without substrate) was pumped overnight through the columns in order to inoculate them. Single trials were conducted with 1 L each of the NF permeate and a 1:2 dilution of the NF permeate. The wastewater solutions were pumped (with recirculation) at a flow rate of about 25 mL/min through the columns, which were aerated from the bottom.

Pressurised air (at 2 bar) was introduced at an ostensibly low flow rate into the reactors from the bottom. Samples were taken from the reservoirs on a regular basis and analysed for $N-NH_4^+$ concentration using Seal Auto-Analyser 3 following DIN 38406-5 [95].

4.2   EXPERIMENTS IN LAB-SCALE BATCH REACTORS

4.2.1   Trials for Identifying Suitable Wastewater Stream and Packing Media

Series of experiments were conducted over a period of about 500 days in lab-scale to find:

- the process stream (raw leachate, RO concentrate or NF permeate – from the scenario at the landfill site depicted in Figure 2) most suitable for nitrification, and
- an appropriate packing material (out of those described in section 3.2) for the reactor.

Four reactor setups (see schematic in Figure 4 and photographs in appendix, Figure 28) were established inside a fume hood (in order to minimise odour problems and possible health hazards). Figure 4 highlights and briefly explains the different components of the setup. The reactors were made out of transparent PVC-U pipes (110 mm outer diameter, 5.3 mm wall thickness, PN 10 bar) and were packed with different packing materials as shown in Table 5. Two out of three of these packing materials (clay beads and PE carrier), which are commercial products, were already available at the AWW, TUHH and were used in their previous works [89,90,96].

1. Packed bed reactor

2. Controlled using pH controller for two reactors and manually for the other two

3. Temperature, pH and dissolved oxygen measured using Hach HQ40D multi meter

4. 25 L HDPE reservoir for the wastewater

5. EHEIM Thermocontrol 25 W submersible heater (used only during winter season)

6. Totton NDP14/2 magnetically coupled chemical-resistant centrifugal pump

7. Manual control of aeration using a Serto elbow regulating valve to maintain DO at 2.7 ± 0.3 mg/L

Figure 4. Schematic of the reactor setup used for the lab-scale batch studies.

To inoculate the packed beds, 25 L of 1:25 dilution (in tap water) of return activated sludge were filled in the reservoirs and recirculated overnight through the reactors. After this, all four reactors were taken into operation.

At the start of each batch, 25 L of wastewater (dilutions of RO concentrate or NF permeate) were filled into each reservoir. The wastewater was continuously recirculated in up-flow mode through the reactors. Air was directly introduced at the bottom of the reactors in cocurrent fashion. Table 5 shows the attained superficial velocities (of water) in each setup, which correspond to flowrates in the range 330-390 L/h. Air flowrate into each reactor was adjusted manually so as to obtain a DO concentration of 2.7 ± 0.3 mg/L in the effluent. Dissolved oxygen, temperature and pH in the reactors were measured using a Hach Lange HQ40D multi meter. All experiments were conducted at ambient temperature (24 ± 3°C).

Table 5. Characteristics of the batch reactors.

Attribute	Reactor			
	R1	R2	R3	R4
Inner diameter (mm)	100	100	100	100
Bed height (mm)	450	465	460	480
Packing material	coke	coke	clay	PE carrier
Superficial velocity (m/h)	41.7	44.2	48.9	42.3

Starting from 2nd batch, the pH in each reactor setup was maintained at about 7.2 by dosing an alkali ($NaHCO_3$ or K_2CO_3). The pH in two reactors was controlled automatically using Bluelab pH Controllers purchased from Bluelab Corporation Limited (Tauranga, New Zealand) and was manually adjusted in the remaining two setups by adding known weights of $NaHCO_3$ on a regular basis (once or twice a day). Samples were withdrawn from each setup on a daily basis and were analysed for $N-NH_4^+$, TOC and TN concentrations. To facilitate material balance and to confirm nitrification, $N-NO_2^-$ and $N-NO_3^-$ concentrations were measured in selected samples.

A new batch was started when the NH_4^+-N concentration in the reactor setup was measured to be less than 15 mg/L (to avoid the reactors getting aerated without substrate). In case of the batch in one reactor system removing the entire ammonia earlier than the others, calculated amounts of NH_4HCO_3 were added to that particular setup and operation was continued, or the setup was turned off until the batch in other reactors came to an end. During unavoidable long periods of time when operation was not possible (for e.g. Christmas-New Year break), all setups were shutdown (both aeration and pump turned off), and the reactors were left filled with the wastewater from the on-going batch.

Experiments were conducted for about 500 days (in total) in batch mode over two phases. During this study period, backwashing of reactors was not performed. In the first phase (about 11 months), experiments were performed with dilutions of RO retentate and NF permeate to identify the possibility for treating the various streams (studying the influence of dissolved organics, NH_4^+-N concentration and salinity) and the associated advantages/disadvantages during operation. By the end of 11 months, 3 out of 4 reactors (all but one packed with PE carrier) were plugged and this marked the beginning of the second phase of experiments.

The packings from the clogged reactors were taken out and were filled with fresh packing material. Based on the experiences from the first phase, studies in phase 2 were planned to be carried out only with clay and plastic packing materials. Thus, reactors R1 and R2 were packed with expanded clay beads and reactor R3 with PE carrier. These reactors were inoculated as described before. Trials in the second phase were carried out with dilutions of NF permeate only (on the basis of the findings from phase 1). Since NF permeate was not readily available in large quantities, some batches in phase 2 were conducted with a synthetic wastewater (having desired $N-NH_4^+$ and Cl^- concentrations) prepared from mixing calculated volumes of stored urine (5400 mg NH_4^+-N/L, conductivity 31 mS/cm) and weights of table salt (NaCl) in deionised water. Experiments were conducted for a period of about 4 months without any backwashing.

4.2.2   Validation of Nitrification Rates before Continuous Flow Trials

Once ammonia oxidation rates of about 1 kg $N/(m^3 \cdot d)$ or more were achieved in all four reactors, the setup was disassembled (packing materials were taken out) and modified[§]. The reactors packed with materials of a kind were combined (end-to-end in series) to give two reactor systems each having a bed height of 1.2 m resulting in a reactor volume of 9.42 L (see photograph in appendix, Figure 29). In other words, reactors R1 and R2 were joined using a flange connection to give one long reactor with clay packing, and likewise R3 and R4 forming a single reactor with PE carrier. As a consequence of the increase in the total head of the system, the delivery rate of the pump decreased to about 140 L/h (corresponding to about 18 m/h up flow velocity). Otherwise, the experimental setup and conditions used for this part of the study were very similar to that in lab-scale batch studies (Figure 4).

Experiments were conducted in batch mode using synthetic wastewater with different initial $N-NH_4^+$ concentrations (prepared by dissolving appropriate quantities of NH_4Cl and NaCl in deionised water) to validate nitrification rates before taking the reactors into continuous mode. Trials were conducted in duplicate with initial $N-NH_4^+$ concentrations ranging from 50-400 mg/L. Chloride concentrations in these trials were maintained at about 2 g/L. Multiple small volume samples were continually drawn during each batch and analysed for $N-NH_4^+$ (to facilitate the estimation of ammonia removal rates) and TN concentrations. Depending on the initial $N-NH_4^+$ concentration, the batch times ranged between 3 and 28 hours. For the time gaps between the batches or during weekends, calculated amounts of NH_4HCO_3 were added to the reservoir as substrate.

4.3   STUDIES IN CONTINUOUS FLOW SYSTEMS

Upon achieving ammonia oxidation rates of about 900 g $N/(m^3 \cdot d)$ from the validation trials, the setup was modified (to have continuous in and outflows) as shown in Figure 5, which

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[§] This was planned as a transition step towards achieving continuous flow reactors.

represents a line diagram of the experimental setup and a block diagram of the reactor. A photograph of the setup is available in the appendix (Figure 30).
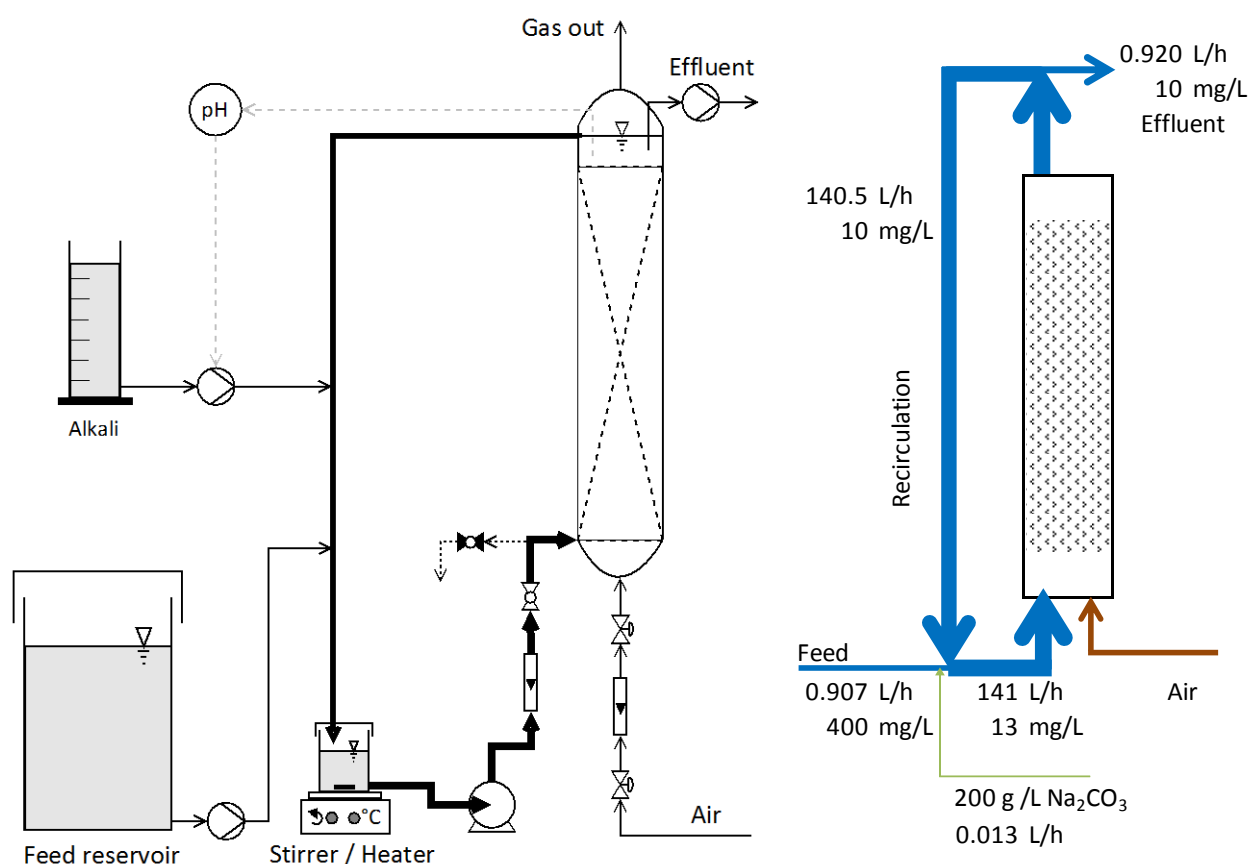
Figure 5. Experimental setup used for continuous flow studies (left), simplified version with design flowrates and concentrations (right).

Each reactor setup consisted of a 25 L HDPE container (as feed reservoir), a Watson-Marlow 323S-313D peristaltic pump (as feed pump), an IKAMAG® RCT magnetic stirrer hot plate (for ensuring a homogeneous inflow and maintaining the temperature during winter), a Totton NDP14/2 centrifugal pump (for recirculation), the reactor (of the same dimensions as described in chapter 4.2.2, packed with clay or PE carriers), a Bluelab pH controller (with alkali contained in a measuring cylinder), a Heidolph Pumpdrive 5001 (as effluent pump) and a facility for aeration.

Small sample volumes were collected on a daily basis (mostly twice per day) from the feed line (after the feed pump), from the 1 L Duran Schott bottle placed on the stirrer/heater (as inlet sample) and from the effluent line. The following parameters were measured in the various samples collected: $N-NH_4^+$, TN and TOC in the feed; $N-NH_4^+$ in the inlet; and $N-NH_4^+$, $N-NO_2^-$, $N-NO_3^-$, TN and TOC in the effluent. DO was measured (in the liquid phase just above the packing) using a Hach HQ 40D Multimeter and maintained at 4.5 ± 1.0 mg/L by adjusting the air flow rate manually. During the study period, the temperature (measured along with DO) was maintained at 25 ± 4°C. The pH controller was supplied with 200 g/L solution of K_2CO_3 or Na_2CO_3 in a 2 L measuring cylinder, the consumption of which was monitored on a daily basis.

Experiments in this phase of the project were conducted in two parts: (i) starting-up the reactors making initial trials with synthetic wastewater, and (ii) studying the effect of chloride content. The initial trials were aimed at bringing both reactors to stable operating conditions and validating the applicability of the high rate nitrification concept. After the initial trials using synthetic wastewater, the reactor packed with PE carrier was fed with NF permeate collected from the full-scale on-site membrane treatment plant, which had been upgraded (as shown in Figure 6) in the meantime. The effect of salinity on nitrification was investigated in both fixed bed reactors – feeding the clay beads-filled PBR with synthetic wastewater and the reactor containing PE carrier with NF permeate – by gradually increasing the wastewater NaCl content maintaining a constant N-NH$_4^+$ loading rate.
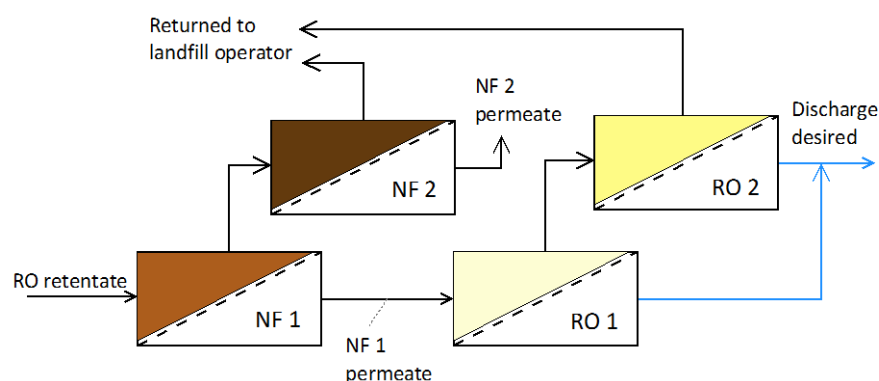
Figure 6. Schematic of the extended treatment system (at landfill site) for handling the RO concentrate of raw leachate.

Table 6 shows the values for important parameters analysed in the two NF permeates. The membrane materials were changed towards the end of part-one studies (section 4.3.1); as a result of which, the composition of NF1 and NF2 permeates changed. NF2' permeate (once) and later a mix (about 120 L NF1'' and 780 L NF2'') of the permeates (twice), containing about 400 mg/L N-NH$_4^+$ and about 4 g/L Cl$^-$, were transported (once a month – three times in total: labelled as permeate I, permeate II and permeate III – 900 L each) from Ihlenberg to TUHH.

Table 6. Measured values for the relevant parameters in the NF permeates.

Parameter	until May 2017		from May 2017 *		Unit
	NF 1'	NF2'	NF1''	NF2''	
TOC	320	430	1030	75	mg/L
TIC	190	150	270	120	mg/L
N-NH$_4^+$	2100	440	2100	140	mg/L
Cl$^-$	32000	3900	34000	900	mg/L
EC at 20°C	85	17	90	4.3	mS/cm

* Due to change of membrane materials in May 2017, the composition of NF permeates had changed.
TIC - total inorganic carbon

4.3.1 Initial Continuous Flow Trials – Starting Up

Both reactors were taken into operation with synthetic wastewater prepared by dissolving calculated amounts of NH$_4$Cl and NaCl in deionised water. The composition of the feed

wastewater was set at 400 mg N-NH$_4^+$/L and 4 g Cl$^-$/L (similar to the then-existing NF2 permeate, i.e. NF2' see Table 6). The nitrogen loading rates for the reactors were estimated such that an N-NH$_4^+$ concentration of 10 mg/L may be obtained in the effluent (using an ammonia oxidation capacity of 900 g N/(m^3·d) and a reactor volume of 9.42 L). For these operating conditions, the required N-NH$_4^+$ loading rate was about 925 g·m^{-3}·d^{-1} (N-NH$_4^+$ mass flow rate = 0.363 g/h and feed flowrate = 907 mL/h). Correspondingly, about 13 mL/h of 200 g/L Na$_2$CO$_3$ (106 g Na$_2$CO$_3$ would be theoretically consumed for every 14 g N-NH$_4^+$ oxidised) would be theoretically necessary to buffer the system (see Figure 5 right).

This part of the project focussed on validating the applicability of the concept for achieving desired results; that is, operating the reactors with high recirculation ratios, low ammonium-nitrogen concentrations, high N-NH$_4^+$ loading rates, short hydraulic retention times and high salinity. The reactors were taken into operation after filling the system with 38 mg/L solution of NH$_4$Cl in deionised water (10 mg N-NH$_4^+$/L). After about 20 days of operation, the reactors were dismantled and flexible rubber air diffusers (to have a better distribution and to produce finer bubbles for enhancing the oxygen transfer rates) were introduced into both of them (see photograph in appendix, Figure 31). Experiments were also conducted to investigate the effect of N-NH$_4^+$ loading rate (by increasing the N-NH$_4^+$ concentration in the feed) on the performance of the system. Towards the end of this study phase, the reactor with PE carrier was started to be fed with NF2 permeate collected from the landfill site (NF2'' permeate after adjustment of N-NH$_4^+$ and Cl$^-$ concentrations, see 4.3.2).

From these initial trials with the reactors over a period of about 4 months (127 days), it was also possible to identify other operational challenges. Due to increases in pressure drop across the bed (observed as decrease in recirculation flow rate), the reactor filled with clay packing was washed twice (on days 60 and 79) during this period. Washing was performed using pressurised water from the central cold water facility (at ca. 14°C), flushing the reactor at flow rates up to 500 L/h. Washing was done for about 5 min (without air sparging) and 20 min (with air at flow rates of about 100 L/h, to produce scouring), respectively, on days 60 and 79.

4.3.2 Investigating the Effect of Chloride Content

To study the influence of salinity on the process, trials were conducted for a period of about 100 days (after the 127 days initial trials) wherein the Cl$^-$ content in feed water was gradually increased up to 16 g/L maintaining a constant N-NH$_4^+$ loading rate. The clay beads packed PBR was operated with synthetic wastewater§ whereas the PE carrier filled PBR was fed with NF permeate of RO retentate collected (once a month, three times in total, 900 L each) from the landfill site (which was aimed to serve as a characterisation and validation of the operation with real wastewater). The experimental setup, methods and analyses were the same as before (see section 4.3).

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§ Since the PE carrier was found to outperform clay beads during previous experiments and also due to the need for greater transportational efforts to obtain more NF permeate.

Studies with the PE carrier-packed reactor were planned to be conducted with NF2 permeate (with low salinity) so as to have the possibility to gradually increase the chloride content in steps (by adding NaCl to it) maintaining a constant $N-NH_4^+$ loading rate. For the first time, NF2'' permeate was transported (assuming[§] it to be NF2'). Upon realising that the NH_4^+-N and Cl^- concentrations in the collected permeate deviated from the experimental design, calculated amounts of NH_4Cl and $NaCl$ were dissolved into the collected permeate so as to achieve NH_4^+-N and Cl^- concentrations of about 400 and 4000 mg/L, respectively. For the second and third time, a mix of about 120 L NF1'' and 780 L NF2'' permeates (as per calculation, to have about 440 mg $N-NH_4^+$/L) were collected.

For the first 37 days of this phase, the PE carrier-filled reactor was fed with the adjusted NF2'' permeate (about 0.4 g/L $N-NH_4^+$, 4 g/L Cl^- and a loading rate of 925 $g \cdot m^{-3} \cdot d^{-1}$). The reactor was operated with the permeate mix unaltered (containing about 0.4 g/L $N-NH_4^+$, 6 g/L Cl^-) at a loading rate of about 925 $g \cdot m^{-3} \cdot d^{-1}$ from days 38-73. Trials between days 74 to 91 and 91 to 100 were conducted with feed chloride concentrations of 11 and 16 g/L, respectively, by dissolving appropriate amounts of table salt into the permeate mix.

The reactor packed with expanded clay beads was run with synthetic wastewater, also during this 3 months period. The feed reservoir and loading rate were maintained at 400 mg $N-NH_4^+$/L and 925 $g/(m^3 \cdot d)$, respectively. However, the chloride concentration in the wastewater was stepped up progressively from 4 to 8, 12 and 16 g/L every (approximately) 3 weeks to study its effect on the process.

A sort of passive backwash was carried out about once in three weeks (by shutting the inlet valve after the rotameter and draining about 0.5-1 L water from the reactor through the drain valve) for both reactors so as to remove the solids trapped at the inlet zone of the bed, thereby relieving the pressure loss partially.

4.3.3 Modelling the Continuous Flow Reactor Using OpenModelica

A simple code (see Appendix E) was written in OpenModelica to model the process and to calculate the steady state concentrations of nitrogen parameters ($N-NH_4^+$, $N-NO_3^-$ and TN) and inert species (Na^+, K^+ and Cl^-) in the system. The model considers the setup as a continuously stirred tank reactor with recycle (see Figure 7). The model serves the purpose of calculating the steady state concentrations of abovementioned species in the effluent, which could be used to compare with and verify the experimental results. Complete nitrification was assumed for a given set of conditions (stated in Section 4.3.1 and depicted in Figure 5) like feed flow rate; concentration of $N-NH_4^+$ in feed; ammonia oxidation rate; reactor volume and up flow velocity. The growth or decay of biomass, possible inhibitions (due to free ammonia, nitrous acid, salinity and/or organics) and limitations due to diffusion (of substrate and/or oxygen) were not considered in the simulation.

[§] The changing of membrane materials at the landfill site (correspondingly, the change in compositions of permeates) was not communicated to the author.

Concentrations: $N-NH_4^+$, $N-NO_3^-$, TN, Na^+ and Cl^-

Inputs to the model:
Feed: flow rate, concentrations
Buffer: flow rate, concentrations
Reactor: diameter, height, up-flow velocity, nitrification rate

Output: steady state concentrations in effluent
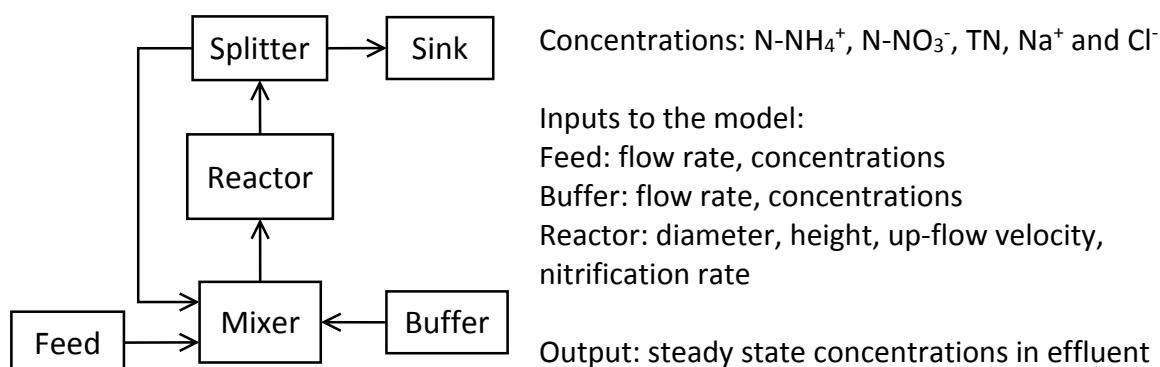
Figure 7. Block diagram of the OpenModelica model and variables/parameters considered in the model

4.4 WASTEWATER ANALYSES

Table 7 shows the parameters, which were systematically (or most frequently) measured (following the German standard methods [95]) in the samples throughout the study. TOC in the samples were measured via the difference method. COD was measured only for selected samples using Hach Lange cuvette tests (LCK114 or LCK014) following the standard procedure DIN 38409-H41-H44 [95]. Due to high chances for interference of COD analysis with chloride ions [97,98], which are contained in very high concentrations in the leachate from Ihlenberg (see Table 1), TOC has been widely used throughout the study for the characterisation of dissolved organics. For measuring nitrate-nitrogen concentration in the samples, cuvette tests were preferred over the determination using a double-beam photometer due to their robustness towards chloride interference [99].

Table 7. Important parameters measured in the samples throughout the study.

Parameter	Procedure	Instrumentation
$N-NH_4^+$	DIN 38406-5	Jasco - V-550 UV/vis spectrophotometer
$N-NO_2^-$	DIN EN 26777	Jasco - V-550 UV/vis spectrophotometer
$N-NO_3^-$	DIN 38405 D9	Hach Lange - DR3900 photometer and LCK339 cuvette
TN	DIN EN 12260	Analytik Jena - Multi N/C 3000 analyser
TOC	DIN EN 1484	Jena Analytik - Multi N/C 3000 analyser

Acid neutralising capacities ($Ks_{4.3}$) of the leachate matrices were measured following the German Standard Method DIN 38409-7 [95]. Determination of total inorganic carbon (TIC) and chloride concentrations were done using Jena Analytik - Multi N/C 3000 analyser (alongside TOC analysis) and Hach Lange cuvette test LCK 311, respectively.

5   RESULTS AND DISCUSSIONS

5.1   PRELIMINARY EXPERIMENTS USING BENCH-SCALE REACTORS

Figure 8 shows the observed reduction in ammonium-nitrogen concentrations in the NF permeate of the RO retentate during the preliminary experiments in bench scale fixed bed reactors with recirculation. At this stage, the decrease in ammonium concentrations was considered to signify a potential for nitrification of the NF permeate, although the possibility of ammonia removal by stripping cannot be excluded since neither pH nor $N\text{-}NO_3^-$ concentration was measured in these rudimentary trials.
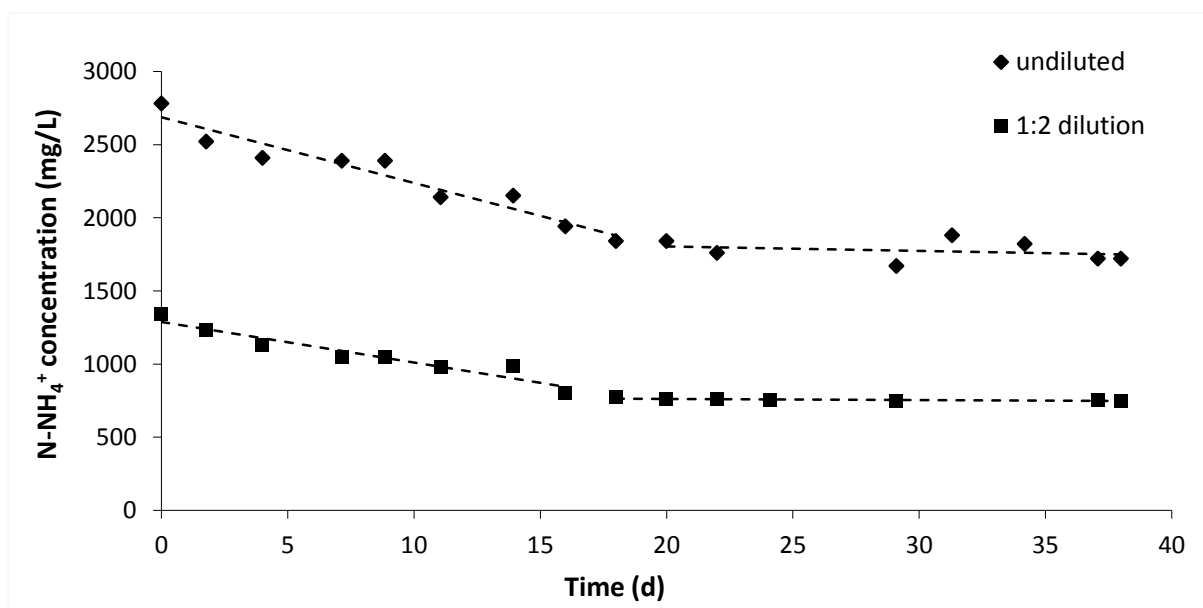
Figure 8. Ammonia reduction during nitrification of the NF permeate in the preliminary batch experiments.

Volatile chlorinated organic compounds content in the RO concentrate was measured (by the Central Laboratory of Analytical Chemistry of TUHH) using solid phase micro-extraction of headspace with subsequent gas chromatography with electron capture detection to be below the detection limit (0.01 mg/L). With this, safe operating procedure for the landfill leachate could be established. For ensuring occupational safety, lab-scale trials were planned to be executed inside an enclosed chamber with forced ventilation.

5.2   EXPERIMENTS IN LAB-SCALE BATCH REACTORS

5.2.1   Trials for Identifying Suitable Wastewater Stream and Packing Media

Trials in this part of the project were aimed at investigating the possibilities for treating the different streams (viz. raw leachate, RO concentrate of raw leachate and NF permeate of the RO retentate) and identifying a suitable packing material amongst the ones chosen for this study. This section presents the most important findings from the experiments with batch reactors which formed decisive factors for further studies.

5.2.1.1   Phase 1: Wastewater Matrix - Differences in Alkalinity content

Since raw leachate was not available for this research, a 1:5 dilution of RO concentrate (in deionised water) was considered as a simulation of the raw leachate. It has to be noted, that raw leachate gets concentrated about 5 times by the RO process (80-85% water recovery) at the landfill site. Figure 9 shows the observations from reactors R1 and R2 (both packed with coke material) during the first two batches, wherein R1 was fed with a 1:5 dilution of RO concentrate and reactors R2 to R4 were operated with dilutions of NF permeate. pH was not controlled in R1 during both batches, whereas in R2 to R4, pH was controlled during the 2nd batch (but not in the first) by adding known weights of $NaHCO_3$.
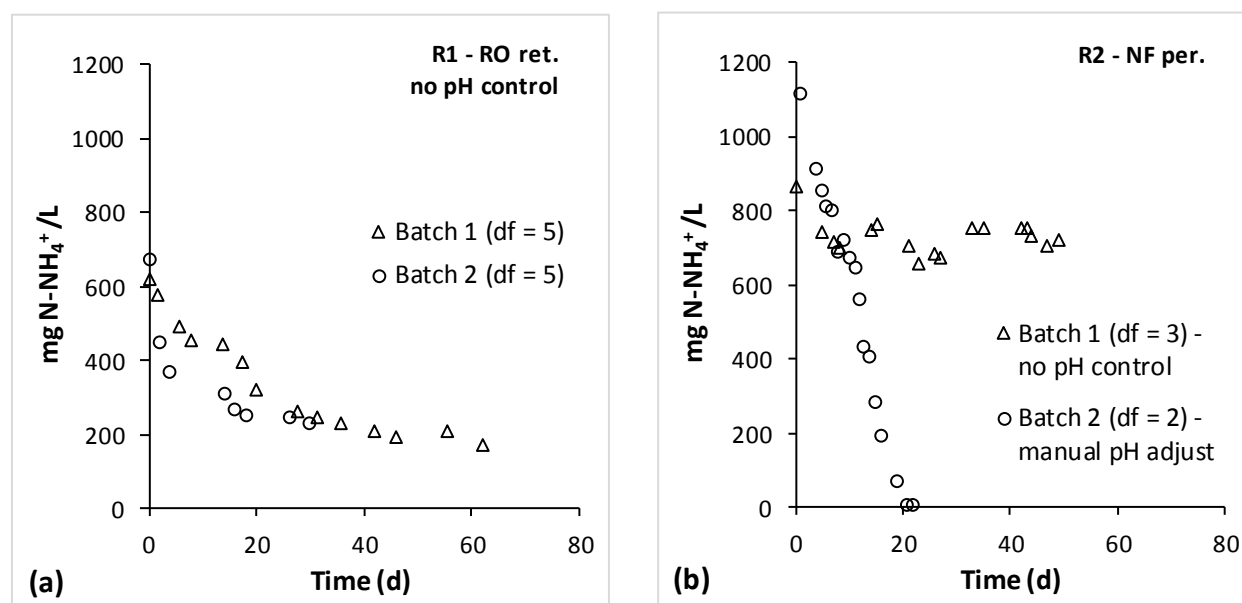
Figure 9. Observations from the first two batches conducted with reactors R1 and R2 (both containing coke packing) - (a) R1 fed with dilutions of RO retentate and both batches without pH control; (b) R2 fed with dilutions of NF permeate and pH controlled in 2nd batch alone   [df - dilution factor].

These results indicate the necessity of alkalinity (which is lacking in NF permeate) for achieving complete ammonia removal. Literature [100,101] suggests that NF membranes can achieve high (>80%) bicarbonate rejection. Therefore, with NF permeate, only about 15% ammonia removal was attained during the first batch (without the addition of external alkalinity); whereas more than 99% removal could be obtained with the control of pH (by adding $NaHCO_3$) in the 2nd batch (Figure 9b). In the case with 1:5 dilution of RO retentate, its inherent alkalinity has driven the nitrification process until being consumed completely (Figure 9a).

Figure 10a (showing a gradual decline in pH from about 8.8 to 6.0 in reactor setup R1 during the 2nd batch) and 9b (illustrating the interconnectedness of pH and nitrifiers' activity represented by DO concentration) support this reasoning further. Other studies [102,103] suggest that nitrification rates are highest within the pH range of 7.2-8.0 and decline outside these limits (sharply below 7.1 and beyond 8.5). A comparison of the trends in Figure 9a and

Figure 10a suggests that addition of external alkalinity might have driven the nitrification process in 1:5 dilution of RO retentate to completion.

In reactor R2, which was operated with a 1:3 dilution of NF permeate during batch 3, the DO concentration, pH and temperature in the reactor were recorded every 15 minutes over a period of two days. A constant air flow rate into the reactor and temperatures of 26.7 ± 0.6 °C were maintained during this period. Under these conditions, the observed increase in DO concentration with decrease in pH (see Figure 10b) can only mean a decrease in ammonia oxidation rate as concluded from the following mass balance:

Accumulation (measured as DO concentration) in the system   =   Mass of oxygen entering the system   −   Mass of oxygen consumed by nitrifiers
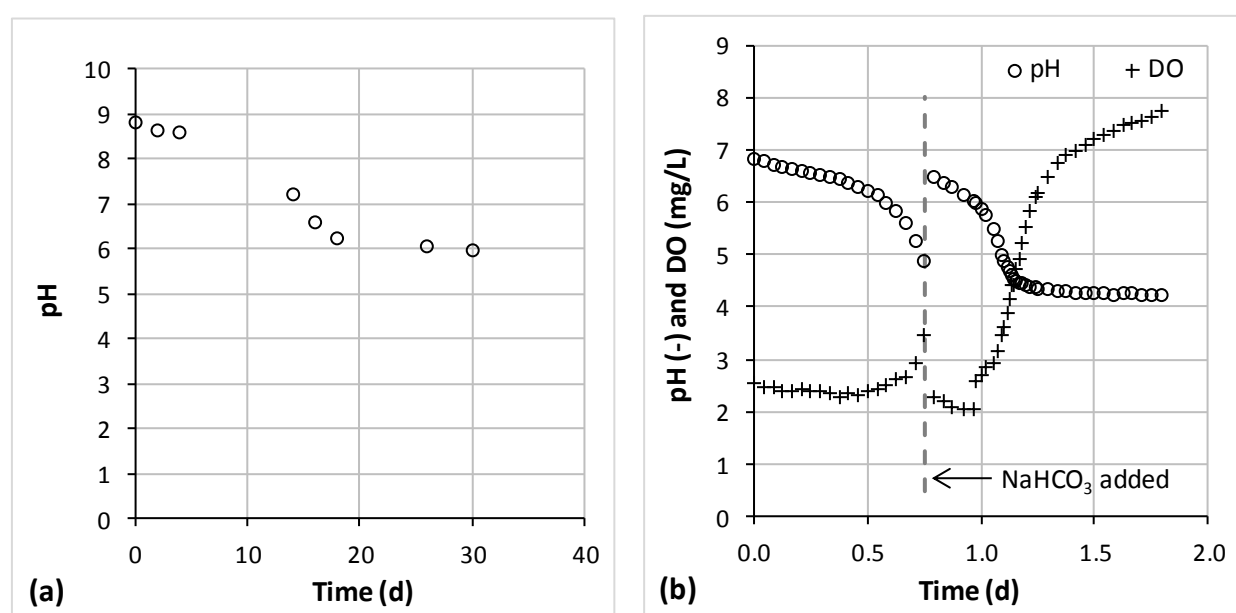
Figure 10. (a) Measured decline in pH during nitrification process in reactor R1, batch 2; (b) Illustration showing the dependence of nitrification (indicated by DO concentration) on pH in reactor R2, batch 3.

Analysis of acid neutralising capacities of RO retentate and NF permeate revealed values of about 123 and 9.6 mmol H^+/L, respectively. Correspondingly, TIC concentrations of 1385 ± 32 and 188 ± 16 mg/L (115 and 16 mmol/L) were measured in RO retentate and NF permeate, respectively. This means larger external alkali source demands for complete nitrification of NF permeate compared to RO retentate. From the numerous batch experiments performed in the first phase, it was found that (on an average) 3.9 ± 0.8 and 6.3 ± 0.6 mg $CaCO_3$ are required for each mg $N-NH_4^+$ oxidised in RO retentate and NF permeate, respectively. Due to the lack of buffer capacity in NF permeate, its nitrification demands an amount of alkalinity almost equal to the theoretical requirement of 7.14 mg $CaCO_3$/ mg $N-NH_4^+$ to be externally added.

5.2.1.2   Phase 1: Wastewater Matrix - Effect of Dissolved Organics

Availability of enough alkalinity to buffer the system is indeed preferable, so that the expenses on external alkali source can be minimised. However, the nitrification rates (for

similar N-NH$_4^+$ initial concentrations) achieved with dilutions of RO concentrate were significantly smaller compared to those with dilutions of NF permeate (see Figure 11).

Figure 11a shows and compares the curves for ammonium reduction obtained in coke material packed reactors R1 (with diluted RO concentrate) and R2 (with dilutions of NF permeate) during the initial 4 months of operation. The removal rates achieved in R1 for N-NH$_4^+$ starting concentrations of about 600 and 1200 mg/L were 35 and 68%, respectively, lower than those attained in R2. Likewise, the nitrification rate in reactor setup R3 (packed with clay beads, after about 7 months of operation) leapt from about 325 g·m^{-3}·d^{-1} (when operated with five-fold diluted RO retentate) to about 580 g·m^{-3}·d^{-1} (about 78% higher), when fed with 1:4 dilution of NF permeate in subsequent batch (see Figure 11b).
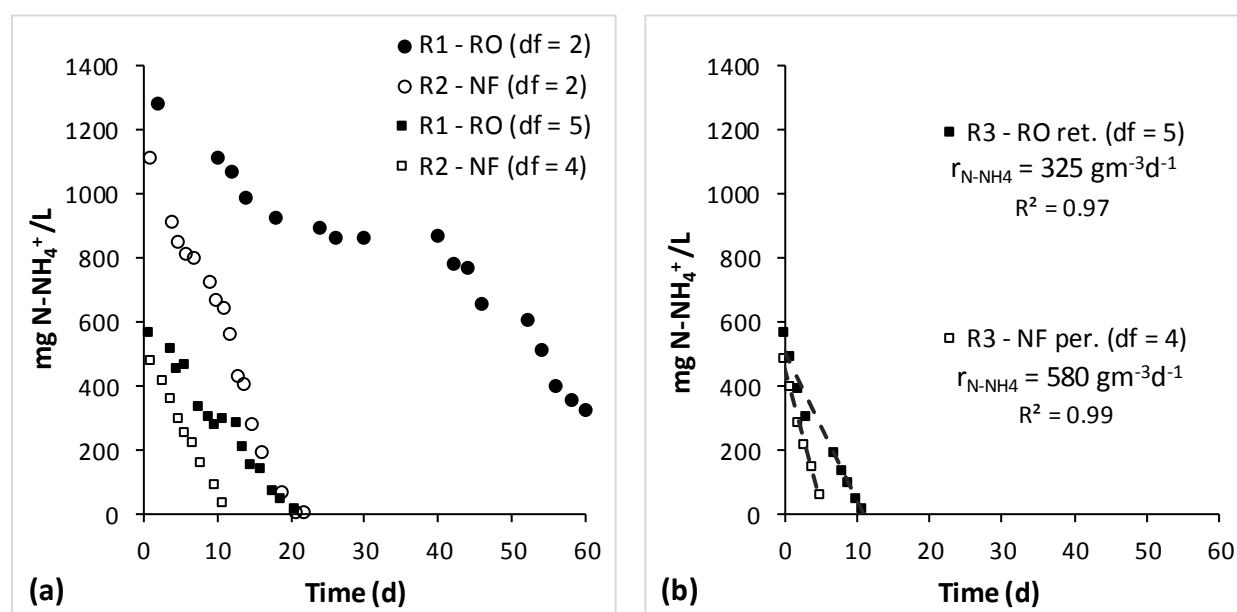
Figure 11. Influence of leachate matrix at similar N-NH$_4^+$ start concentrations: (a) from the trials performed with reactors R1 and R2 fed with dilutions of RO retentate and NF permeate, respectively, during the initial 4 months; (b) after about 7 months of operation, from trials performed with reactor R3 fed with diluted RO concentrate and diluted NF permeate in consecutive batches. §

Considering that the salinities of RO retentate and NF permeate are comparable (Table 3) and that the heavy metals' concentrations in RO retentate is negligible [19], the organic fraction of the RO concentrate can be reasoned to have posed an inhibition to the nitrifiers. The original RO concentrate showed TOC concentrations of 3500 ± 500 mg/L. Nanofiltration of the RO retentate resulted in significant (about 90%) TOC removal. It has been widely reported in literature [3,4] that humic substances contained in old leachates inhibit biological treatment processes. The inhibitory nature of organic compounds contained in the RO concentrate was further verified by conducting a set of experiments in sequencing batch reactors (see Appendix D).

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§ The flat segment in the curve R1 - RO (df = 2) was due to failure in pH control, which was done manually, over a weekend (causing a freezing of nitrifiers' activity). Nitrification rate for this trial was estimated using the first segment of the curve.

According to the packing material properties and type of operation, the reactors were getting clogged one after another (Section 5.2.1.3). After reactors R1 and R2 were plugged, operation of reactor setups R3 and R4 were continued till 11th and 13th months, respectively. With the further development of the biofilms during this period, nitrification rates of up to about 570 and 1200 $g \cdot m^{-3} \cdot d^{-1}$ were attained for (1:4, 1:3 and 1:2) dilutions of RO concentrate and NF permeate, respectively. Also in this phase, organic compounds caused RO retentate's dilutions to be less efficiently nitrified than those of NF permeates. Attempts to treat non-diluted RO retentate failed miserably. Besides nitrification inhibition, RO concentrate presented excessive foaming and increase in pH (due to CO_2 stripping) when aerated. Trials with undiluted NF permeate were not conducted.

5.2.1.3   Phase 1: Characterisation of Packing Material Properties

During the initial batches (or start-up phase), the reactors packed with coke material (viz. R1 and R2) were found to perform slightly better (about 30% higher oxidation rates for the same wastewater matrix) than the reactors filled with clay (R3) and plastic (R4) packing materials. Reactors R3 and R4 showed similar activities or trends.

However, the differences in nitrification rates diminished with time (or with the proliferation of nitrifiers in the four media) and all four reactors displayed comparable efficiencies when fed with the same wastewater matrix (differences were to be observed only due to the inhibition caused by organics). The initial higher nitrification rate in coke material might have been due to its size (smaller particle diameter and thus larger specific surface compared to other materials, see Table 4) and shape (irregular and rugged, see Figure 27) characteristics, as a result of which the nitrifiers could colonise faster on them [61,104,105].

In addition to higher ammonia oxidation rates during the initial stages, the coke-packed beds showed abilities to remove (adsorb) up to about 90% of the dissolved organics contained in RO-5x (model raw leachate). Again with time, once the breakthrough capacities of the beds were exceeded, the TOC reductions observable in all four reactor setups were very similar. At this stage, about 40% removal in TOC was observed (fitting quite well with the BOD_5/COD ratio of 0.39 in raw leachate, see Table 1) when the reactors were operated with 1:5 dilution of RO retentate.

The following media and wastewater characteristics were found to have a great influence on the long-term operability of the reactors:
  - adsorption capacity of the packing material,
  - presence of dissolved organics in the wastewater, and
  - porosity of the packed bed.

Since the reactors were not backwashed during the study, they got plugged (photographs of the packing materials, which were taken out from the reactors, can be found elsewhere [5]) in the following time order: R1 (after about 6 months) < R2 (8 months) < R3 (11 months). The observed sequence in clogging could be reasoned as follows: Reactors R1 and R2 were packed

with coke material, which has a high adsorption capacity [106]. As a result, they were vulnerable to clogging due to adsorption of organics and the subsequent proliferation of heterotrophic organisms [107]. R1 was blocked faster than R2 possibly because R1 was operated only with dilutions of RO concentrate, whereas R2 was fed alternately with dilutions of organics-lean NF permeate also. Despite the low bed porosity of clay packing (0.55 compared to 0.7 for coke material), R3 was operable longer likely due to its low TOC adsorption capacity. Reactor R4 packed with PE carrier, having negligible adsorption capacity and a high bed porosity (0.85), did not suffer from any clogging. Thus, clay beads and PE carrier, due to their longer operability and durability, were chosen for the investigations to be conducted in Phase 2.

It is known that the presentation of ammonia oxidation rates development (implying biofilm development) vs. time is highly reasonable. However, due to the following two reasons, it will not be presented for Phase 1:

- The reactors were not fed with just one type of wastewater (except during the initial 4 months). Since the reactors were alternately fed with dilutions of RO retentate and NF permeate (which was partly also due to the non-availability of NF permeate at times), the organisms were subjected to highly varying stress conditions resulting in fluctuations in nitrification activities.

- Water flow rate, which has a profound influence on nitrification rate (see Appendix C), could not be tracked. The decrease in water up-flow velocities, due to progressive clogging of the packed beds, was not measured. Thus, although a development of biofilm was existent, the clogging of the reactors could have counteracted the increase in ammonia oxidation rates.

Analyses of the different nitrogen parameters ($N-NH_4^+$, $N-NO_2^-$, $N-NO_3^-$ and TN) during the experiments in Phase 1 revealed the achievement of complete nitrification (with $NO_3^--N_{end} \approx NH_4^+-N_{start}$, $N-NO_2^-$ mostly < 10 mg/L and $TN_{start} \approx TN_{end}$) in the batches.

5.2.1.4 Phase 2: Further Batch-trials with NF permeate for Establishing an Efficient Biocenosis

Since the goal of the project was to achieve nitrification in continuous mode, operating at steady state concentrations close to discharge limit (about 10 mg/L), trials were not conducted with undiluted NF permeate. In this phase, experiments were conducted only with dilutions (mainly 1:4) of NF permeate [or with synthetic wastewater when NF permeate was not available] with the aim to achieve stable biofilms, thereby attaining high volumetric ammonia oxidation rates. The influence of chloride-content on the process was decided to be investigated at a later stage.

Figure 12 shows plots of volumetric ammonia oxidation rates vs. time (or biofilm age) for the four different reactors. It is to be reminded that reactors R1, R2 and R3 were filled with virgin packing materials (and inoculated as before) for the trials in Phase 2, and operation in R4 was

simply continued (as it did not suffer any blockage). Furthermore, the reactors were operated in batch fashion, with each batch mostly starting on Mondays or Tuesdays (and sustained over weekend by adding calculated amounts of substrate (stored urine or NH_4HCO_3), see section 4.2). Volumetric ammonia removal rates (VARR) were calculated using the respective ammonia reduction rate from each batch.
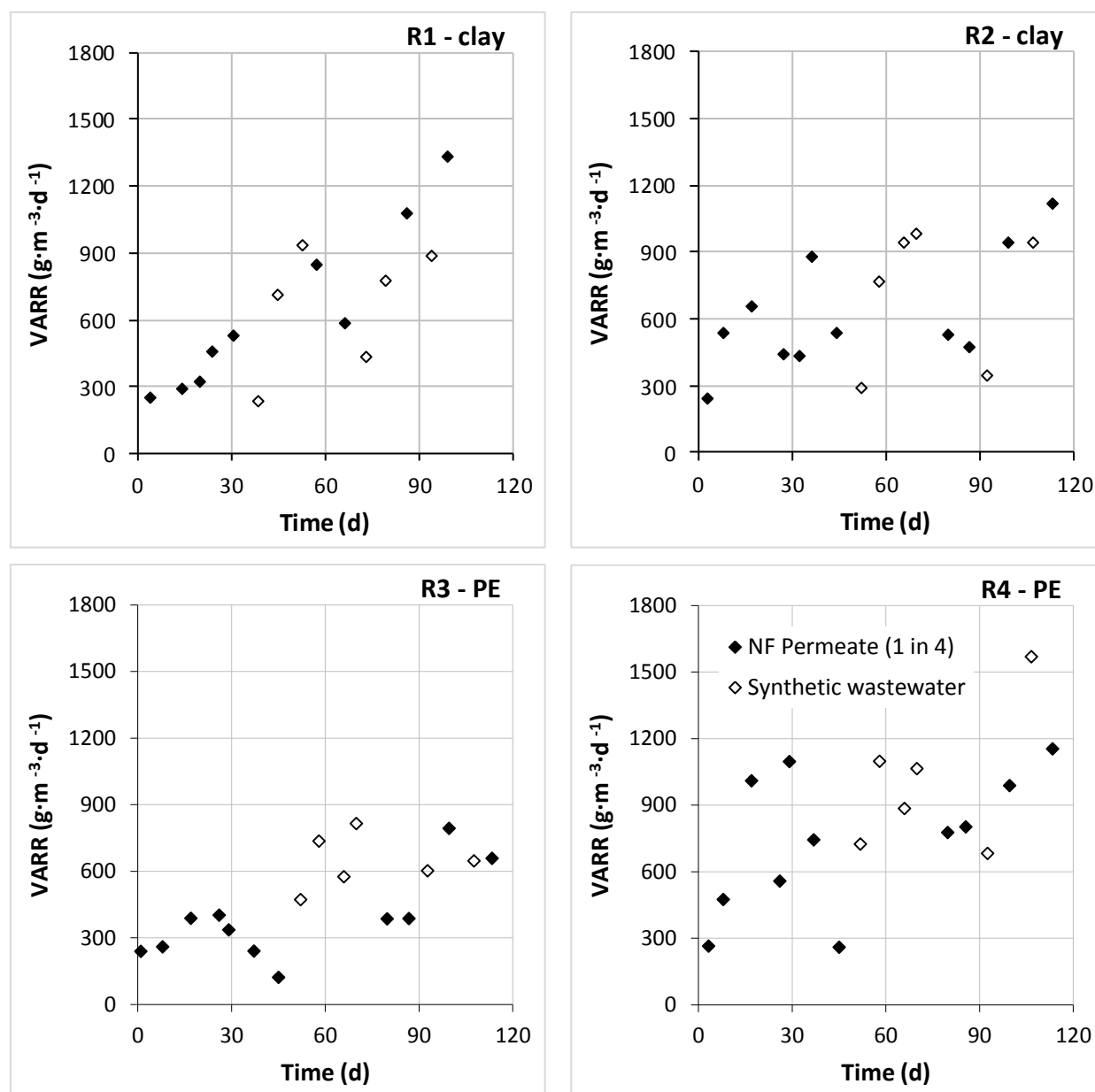
Figure 12. Tracking the increase in volumetric ammonia removal rates (VARR) with time.

As expected, the volumetric oxidation rates increased with time, although with considerable fluctuations. These deviations in nitrification may be attributed to changes in wastewater composition (for instance, differences in delivered NF permeate and the use of synthetic wastewater) and at times due to lack of optimal pH control. In short, these trials proved the possibility to achieve high nitrification rates with dilutions of NF permeates paving the stones for the conceptualisation of the continuous flow reactor systems.

As in phase 1, the achievement of complete nitrification could be verified also during the trials in Phase 2 from the analyses of the different nitrogen parameters (N-NH$_4^+$, N-NO$_2^-$, N-NO$_3^-$ and TN).

5.2.2   Validation of Nitrification Rates before Continuous Flow Trials

Figure 13 shows the nitrification rates attained during the batch trials in the reactors fabricated for continuous operation mode (from joining the two clay- and the two PE carrier-filled reactors, having mature biofilms, end-to-end into two longer reactors) for continuous flow operation. Water up-flow rates remained fairly constant (130-140 L/h) in both PBR systems during these experiments providing up-flow velocities of about 18 m/h. Both reactors showed lower VARRs during the first three batches compared to the individual reactors (Figure 12), which were combined. This is supposed to be due to the detachment and loss of nitrifiers during the removal and refilling of the packing materials. However, the reactor filled with clay beads had recovered its activity within 10 days of operation (see Figure 13), offering nitrification rates mostly higher than 900 g/(m^3·d) although with some fluctuations.
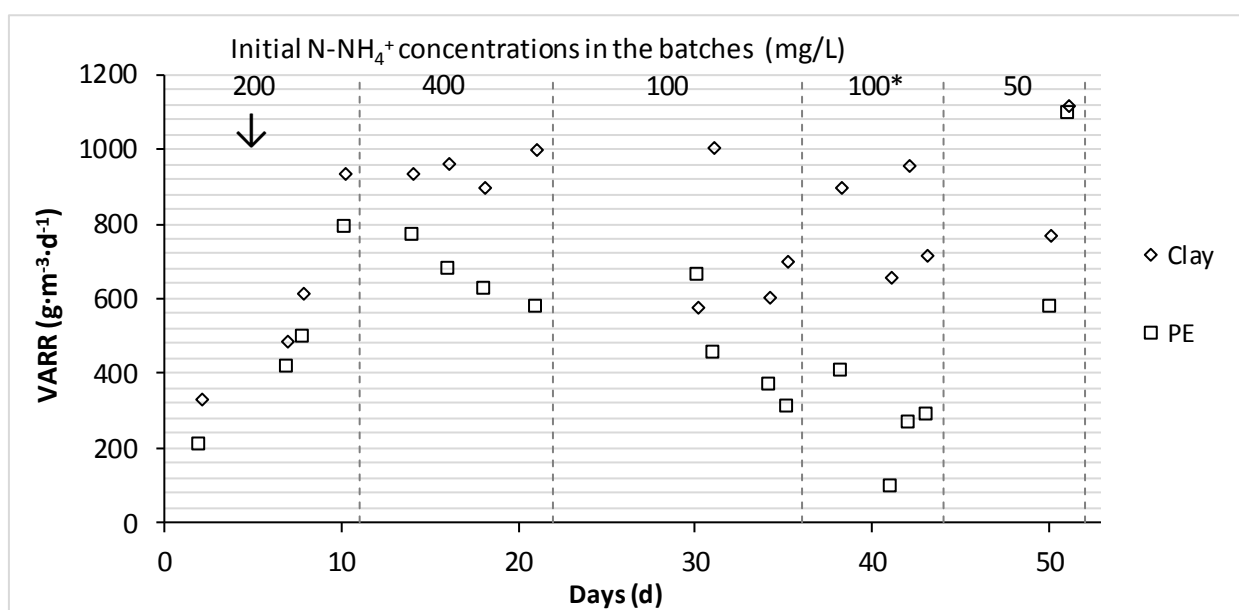
Figure 13. Validation of nitrification rates in batch trials (before switching to continuous flow operation) using synthetic wastewater solutions at different N-NH$_4^+$ start concentrations and diluted NF permeate (4th phase 100*).

Contrasting to the reactor filled with clay beads, the nitrification capacity of PE carrier packed reactors was found to steadily decline from 10 to 40 days of operation. The continuous decrease in activity was due to the washout of nitrifiers from the bed. Although this reason was not evident during this phase of the work, it was possible to validate it at a later stage when the phenomenon recurred. A re-development of the biofilm was observable (from the increase in VARR) after 40 days of operation.

The start N-NH$_4^+$ concentration of the batches did not have any influence on the nitrification rates. Lack of impact of starting ammonia concentration was also observed in the experiments

using sequencing batch reactors with suspended biomass (see Appendix D) and also reported by Kim et al. [108] and Mahne et al. [109]. Based on these (Figure 13) and previous trials (Figure 12), a volumetric ammonia removal capacity of 900 g NH_4^+-N/(m^3·d) was considered as a basis for the conceptualisation of continuous flow trials.

5.3   STUDIES IN CONTINUOUS FLOW SYSTEMS

5.3.1   Continuous Flow Trials – Starting Up

5.3.1.1   Experiences from the Clay Beads-filled Packed Bed Reactor

Figure 14 shows the performance of the reactor filled with clay beads during the initial operation phase with synthetic wastewater over a period of 127 days. Until day 28, N-NH_4^+ removal rate (parallelly, also percentage removal) was found to decrease slowly from about 900 to 500 g·m^{-3}·d^{-1} (see Figure 14b). Correspondingly, the ammonia concentration in the system was increasing (Figure 14a). After the introduction of the diffuser (for improving the distribution of air in the reactor), the VARR of the reactor had improved up to 1000 g·m^{-3}·d^{-1} resulting in a decrease in the N-NH_4^+ concentration in the reactor effluent reaching 3-5 mg/L during days 48-50. Very low concentrations in the effluent during these days were also a consequence of the slight reduction in the loading rate. The low effluent ammonia concentrations in this period indicated the optimal functioning of the reactor at the designed capacity.

To rectify the decline (of about 40%) in recirculation flow rate (which can lead to a reduction of nitrification performance), the reactor was subjected to washing for about 5 minutes on day 60. Up-flow velocity could be restored to about 15 m/h after washing, although, only for a couple of days. Due to low bed-porosity, the reactor bed acted as a depth filter entrapping the dislodged biomass during operation. After the intensive washing of the packed bed on day 79 lasting for about 20 minutes, ammonia oxidation rates increased to about 1200 g·m^{-3}·d^{-1}. However, the removal capacity started dwindling again as the up-flow rates declined gradually (signifying an increase in pressure drop across the reactor resulting from the uncontrolled growth of biofilm [110]).

Clogging of the clay beads packing due to biofilm growth gets aggravated due to its low initial bed porosity. From these results, it becomes evident that a reactor filled with clay beads must be subjected to regular washing (or backwashing) in order to achieve high nitrification rates. The improvement seen in ammonia oxidation rate after the introduction of diffuser tubes could also have been caused by the remotion of excess biomass from the bed resulting from the removal and re-filling of clay beads.

Figure 14c shows the concentrations of the different nitrogen species in the feed reservoir and the effluent from the reactor, illustrating a material balance for nitrogen around the reactor. It can be seen that the ammonia removed was oxidised completely to nitrate in the last 30 days of the study period. Till day 55, nitrate-nitrogen concentration in the samples was
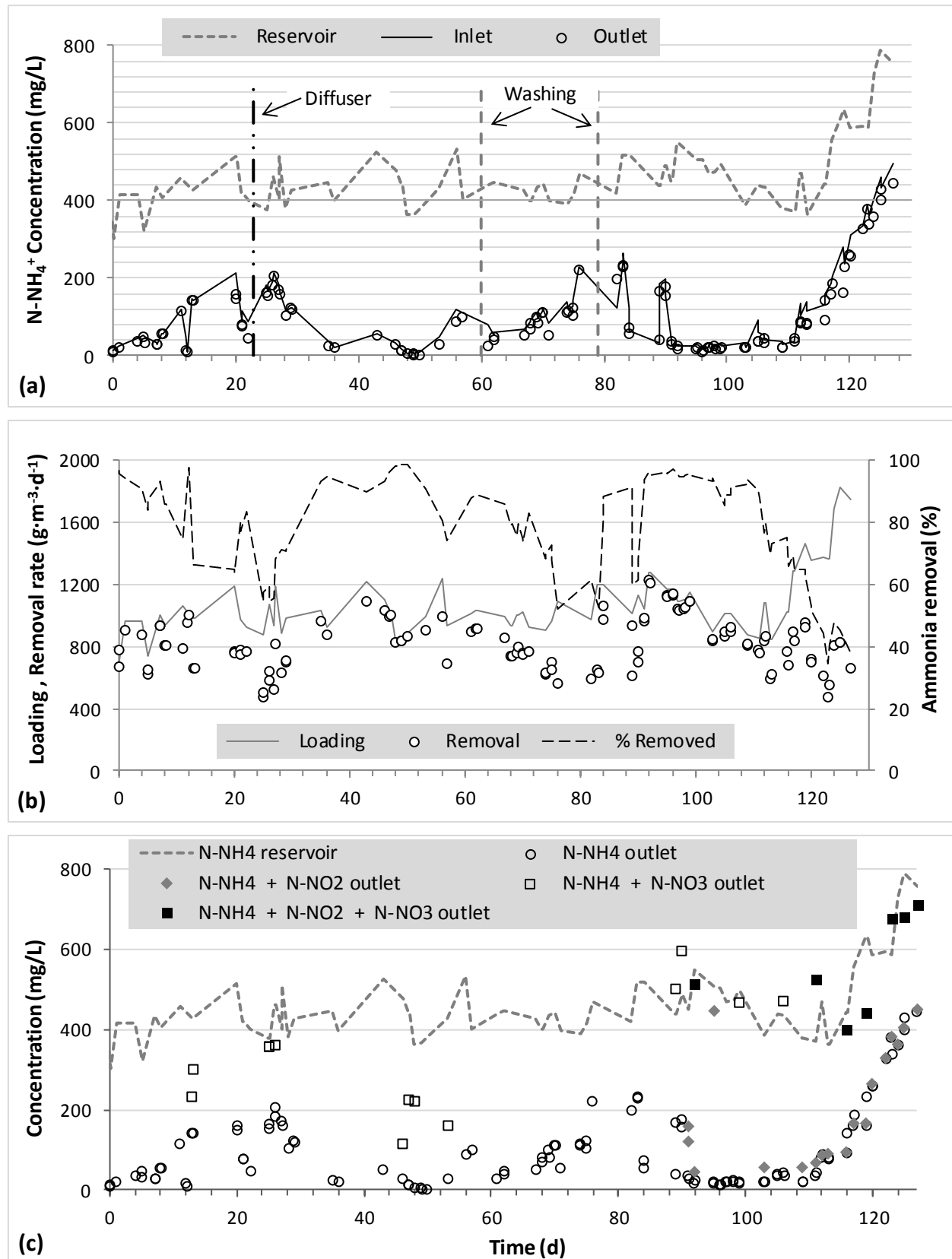
Figure 14. Experiences from the PBR filled with clay beads during the initial continuous flow trials with synthetic wastewater: (a) NH$_4^+$-N concentrations in the feed reservoir, reactor inlet and outlet; (b) Applied NH$_4^+$-N loading rates and obtained removal rates; (c) Nitrogen balance - species in feed reservoir and reactor outlet.

[Reactor bottom was opened and diffuser was introduced on Day 23 (Figure 31). The reactor was washed on Days 60 and 79 (see section 5.3.1).]

measured using a Seal Autoanalyser (details can be found elsewhere [99]) which has a lower recovery rate compared to the cuvette test. The observed low nitrate-nitrogen concentrations until day 55 must have been due to sub-estimation and the transformation of nitrate to nitrite during sample storage[§]. Thereafter, determination of nitrate-nitrogen was accomplished using cuvette tests within a couple of hours after sampling.

Regular measurement of nitrite-nitrogen in the effluent samples was started from day 90, since the sum of $N-NH_4^+$ and $N-NO_3^-$ concentrations in the effluent from the PE carrier filled reactor was not complying with the achieved ammonia removal (see Figure 15c). Accumulation of nitrite had occurred during the days 90-98 which was caused by an accidental increase in the temperature to 33°C (this was also observed in the reactor filled with PE carrier, see chapter 5.3.1.2). It is well known that ammonia oxidising organisms (AOO) have much higher specific growth rates compared to nitrite oxidising organisms (NOO) at temperatures above 30°C resulting in higher nitritation rates [111,112]. Soon after temperature was controlled at 25 ± 3°C (by adjusting the heater properly), nitrite concentration in the system decreased and was measured to be low (< 10 mg/L $N-NO_2^-$) as can be seen from the overlap of $N-NH_4^+$ and the sum of $N-NH_4^+ + N-NO_2^-$ concentrations in Figure 14c.

Ammonium-nitrogen concentration in the feed wastewater of the clay beads-filled reactor was increased in steps from about 400 to 600 mg/L and from 600 to 800 mg/L on days 117 and 124, respectively, in order to: (1) assess the influence of loading rate and maximum removal capacity, and (2) also confirm that the nitrite accumulation (during the days 90-98) that happened in PE carrier-filled reactor (see 5.3.1.2) was mainly due to temperature increase (and not necessarily due to increase in $N-NH_4^+$ loading rate). The $N-NH_4^+$ concentration in the reactor effluent was shown to increase fairly linearly during this phase with increasing ammonia concentrations in the feed suggesting that the reactor had reached its maximum loading potential. The $N-NO_3^-$ concentration in the effluent was slowly decreasing which follows the gradual decrease in removal capacity as seen in Figure 14b. Nitrite-nitrogen concentrations in the effluent were < 10 mg/L suggesting that the high temperature (>30°C) during days 90-98 was the sole reason for the accumulation of nitrite in the reactor.

5.3.1.2 Experiences from the packed bed reactor filled with PE carrier

Performance of the PE carrier-filled reactor during the initial continuous phase (the first 127 days period) is depicted in Figure 15. With lower ammonia removal capacities compared to the clay beads-filled reactor, the PE media initially failed to offer the desired performance. This was because the biofilm in PE carrier was washed out to a greater extent during (and after) the packed-bed removal and re-filling events. The decline in nitrification rates can be markedly seen after both removal-refilling events in the research project: (1) during the trials for the

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[§] Sometimes, the samples were stored (refrigerated) for a couple of days since the measurement device could be operated only once per week adding to inaccuracies.
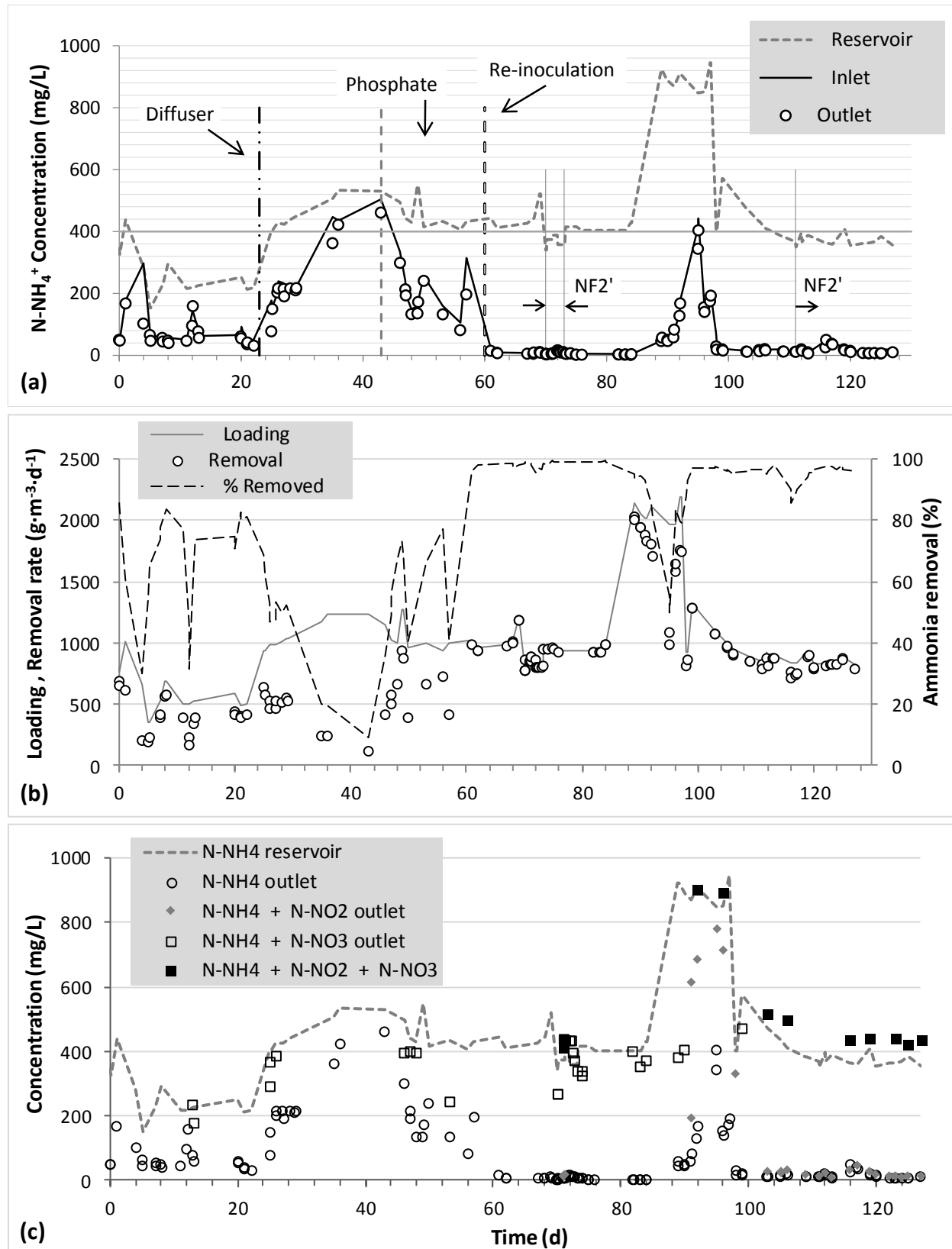
Figure 15. Experiences from the PE carrier-filled PBR during the initial continuous flow trials: (a) NH$_4^+$-N concentrations in the feed reservoir, reactor inlet and outlet; (b) Applied NH$_4^+$-N loading rates and obtained removal rates; (c) Nitrogen balance - species in feed reservoir and reactor outlet.

[Reactor bottom was opened and diffuser was introduced on Day 23 (Figure 31). Na$_3$PO$_4$ (10 mg P/L) was added to the feed reservoir between days 43 and 60. The reactor was re-inoculated with the backwash water from the other reactor filled with clay beads on day 60. NF2': between days 70-73 and from day 111 the reactor was operated with NF2' permeate obtained from the landfill site, and otherwise with synthetic wastewater.]

validation of VARR (Figure 13) [§] and (2) after the introduction of the diffuser into the continuous reactor (Figure 15b).

The ammonia removal capacity of the reactor was increasing from about 200 g N/(m³·d) on day 4 (the estimated high VARRs on day 0 were due to the fact that the reactor was taken into operation with a starting concentration of 10 mg N-NH$_4^+$/L) to 600 g NH$_4^+$-N·m^{-3}·d^{-1} until the installation of the diffuser on day 23, after which it plummeted to about 110 g NH$_4^+$-N·m^{-3}·d^{-1} on day 43. With the provision of a phosphate source (which in minute quantities is essential for the sustenance of nitrifying biofilms [113]) from day 43, the lack of which was initially thought to be the possible reason for the underperformance of the reactor, the VARR improved (see Figure 15b). Particularly after re-inoculation on day 60, nitrification rates of about 1 kg NH$_4^+$-N·m^{-3}·d^{-1} (about 98% removal) could be achieved, realising outlet concentrations of about 8 mg NH$_4^+$-N/L.

To demonstrate the concept and feasibility of high rate nitrification in packed bed reactors to the project partners (so as to affirm for the planning and implementation of a demonstration scale reactor), the reactor with PE carrier was fed with NF2' permeate instead of synthetic wastewater (under the same feed flow conditions as in the phase when synthetic wastewater was used, offering a similar NH$_4^+$-N loading rate) during the days 70-73. Ammonia removal during these days was larger than 95% (by and large higher than 98%). Signs of a temporary shock lasting for about 24 hours, likely due to the organics in the NF permeate, were observed as a small peak in the reactor inlet and outlet N-NH$_4^+$ concentrations (see Figure 16a). Figure 16b shows the accumulation and leaching of permeate organics (measured and simulated values) in/from the system. The simulation was run with a minor adaptation of the Modelica code, defining organics as inert with boundary conditions (if 69.98 < time < 72.77 then TOC reservoir = 425 mg/L, else TOC reservoir = 0). It can be seen that the simulated values represent the actual concentrations quite well. The reduction in N-NH$_4^+$ concentration in the outlet to 5 mg/L on day 73 and further to < 2 mg/L on day 74 (correspondingly, the increase in percentage removal to > 99%) signifies that the nitrifying organisms in the reactor could well adapt to the organics contained in the NF2' permeate.

Between days 75 and 84, the percentage ammonia removal in the reactor was consistently greater than 99% resulting in N-NH$_4^+$ concentrations < 6 and < 3 mg/L in the influent and effluent, respectively. To avoid any limitation of ammonia for nitrification and to identify the maximum removal capacity of the reactor, the loading rate was doubled on day 85 by doubling the N-NH$_4^+$ concentration in the feed reservoir. It was hypothesised that the maximum VARR could be estimated from the N-NH$_4^+$ and N-NO$_3^-$ concentrations in the effluent once a steady-state is achieved. However, the temperature of the system increased accidentally to about 33°C causing an imbalance of ammonia and nitrite oxidation rates resulting in accumulation of nitrite in the system (see Figure 15c). With high N-NO$_2^-$ concentrations (> 500 mg/L), N-NO$_3^-$ and

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[§] The ammonia removal capacities of the PE carrier were as good as those of the clay beads packing during the lab-scale batch experiments (see Figure 12).

N-NH$_4^+$ concentrations in the effluent were found to decrease and increase, respectively. On day 98, loading rate was reduced to about 900 g NH$_4^+$-N·m^{-3}·d^{-1} and wastewater temperature was adjusted to 25 ± 3°C by stepping-down the heater. Steady-state with normal operating efficiency (low N-NH$_4^+$ and N-NO$_2^-$ in the effluent, and N-NO$_3^-$ outlet ≈ N-NH$_4^+$ reservoir) could be regained within about 5 days.
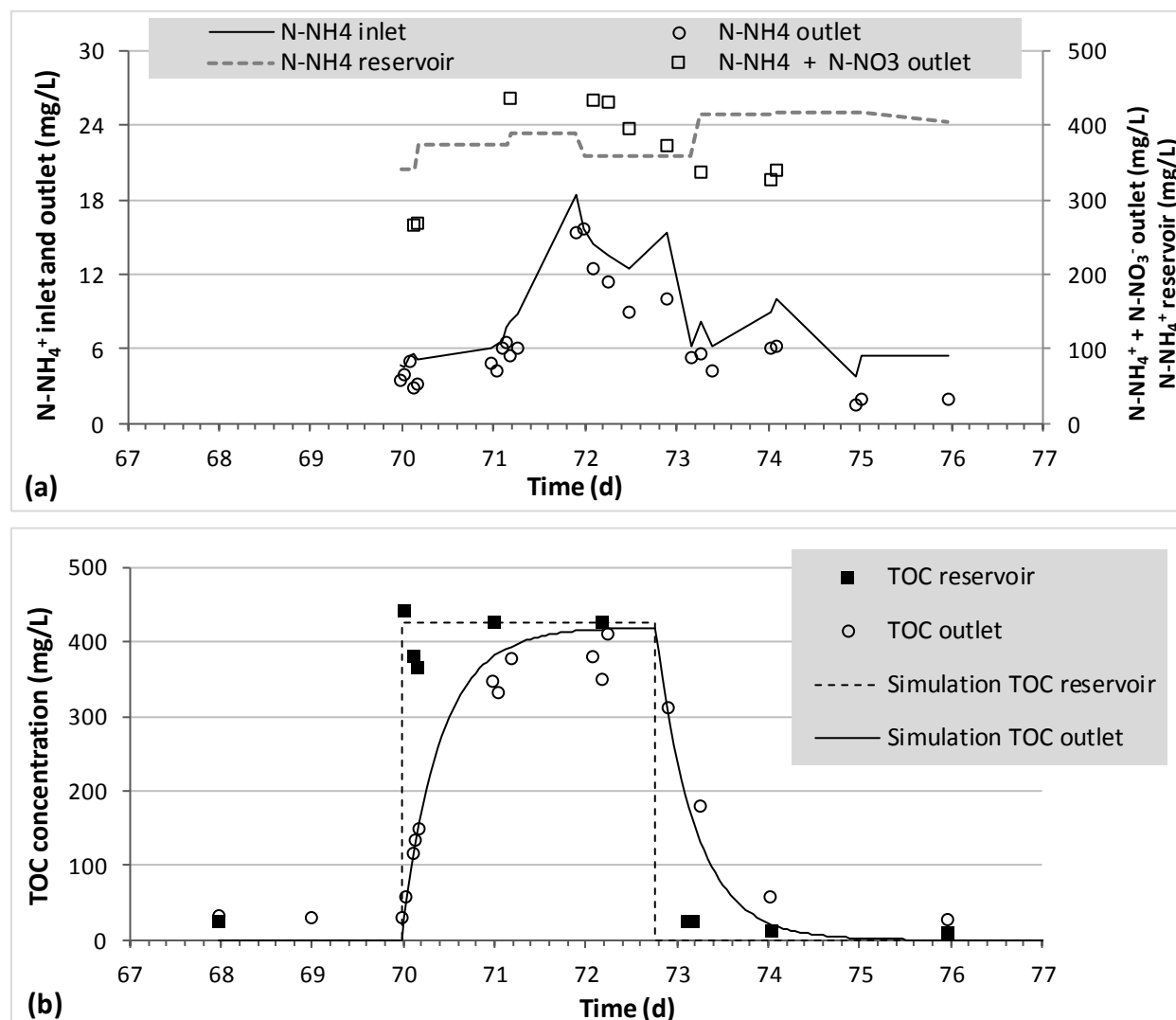
Figure 16. PE carrier-filled PBR fed with NF2' permeate between days 70-76: (a) temporal stress for the nitrifiers seen as a peak in inlet and outlet N-NH$_4^+$ concentrations, (b) accumulation and wash-out of organic compounds.

Upon realising stable and complete nitrification with synthetic wastewater for about two weeks (from day 98 to 111), the reactor was again fed with the NF2' permeate collected from the landfill site starting from day 111. The nitrifying organisms in the column ostensibly suffered inhibition temporarily as before, which could be markedly seen from the dip in percentage removal between the days 113 and 120 (Figure 15b). Again, the organisms were able to acclimatise to the NF2' permeate as can be seen from the increase in removal efficiency. The reactor offered by and large percentage removals higher than 96% with outlet N-NH$_4^+$ concentrations mostly < 10 mg/L.

Figure 15c shows the measured values for N-NH$_4^+$ concentrations in feed and outlet, and N-NO$_3^-$ and N-NO$_2^-$ concentrations in outlet for this study phase, also serving the purpose of material balance for nitrogen. Similar to the observations in the reactor packed with clay beads, nitrite-nitrogen concentrations in the effluent were low (< 10 mg/L) except for the days 91-98, when temperatures of about 33°C were recorded in the system. After re-inoculation, the reactor offered reliable and efficient nitrification (except the period of accidental nitrite accumulation) without the risk of clogging which took place in the clay beads-filled reactor. The raw data from the initial continuous flow trials can be found in Table 14 (in appendix).

5.3.2 Modelling Using OpenModelica

Simulation results of the Modelica code (Appendix E) are presented in Figure 17. The simulation (run for the initial 5 days) generated the concentration profiles for the different nitrogen and inert species from the starting-up of the continuous nitrification reactor depicted in Figure 5 (for the operating conditions explained in section 4.3.1) with an acclimatised biocenosis until the development of steady state conditions. For the considered feed and buffer

(a)

(b)
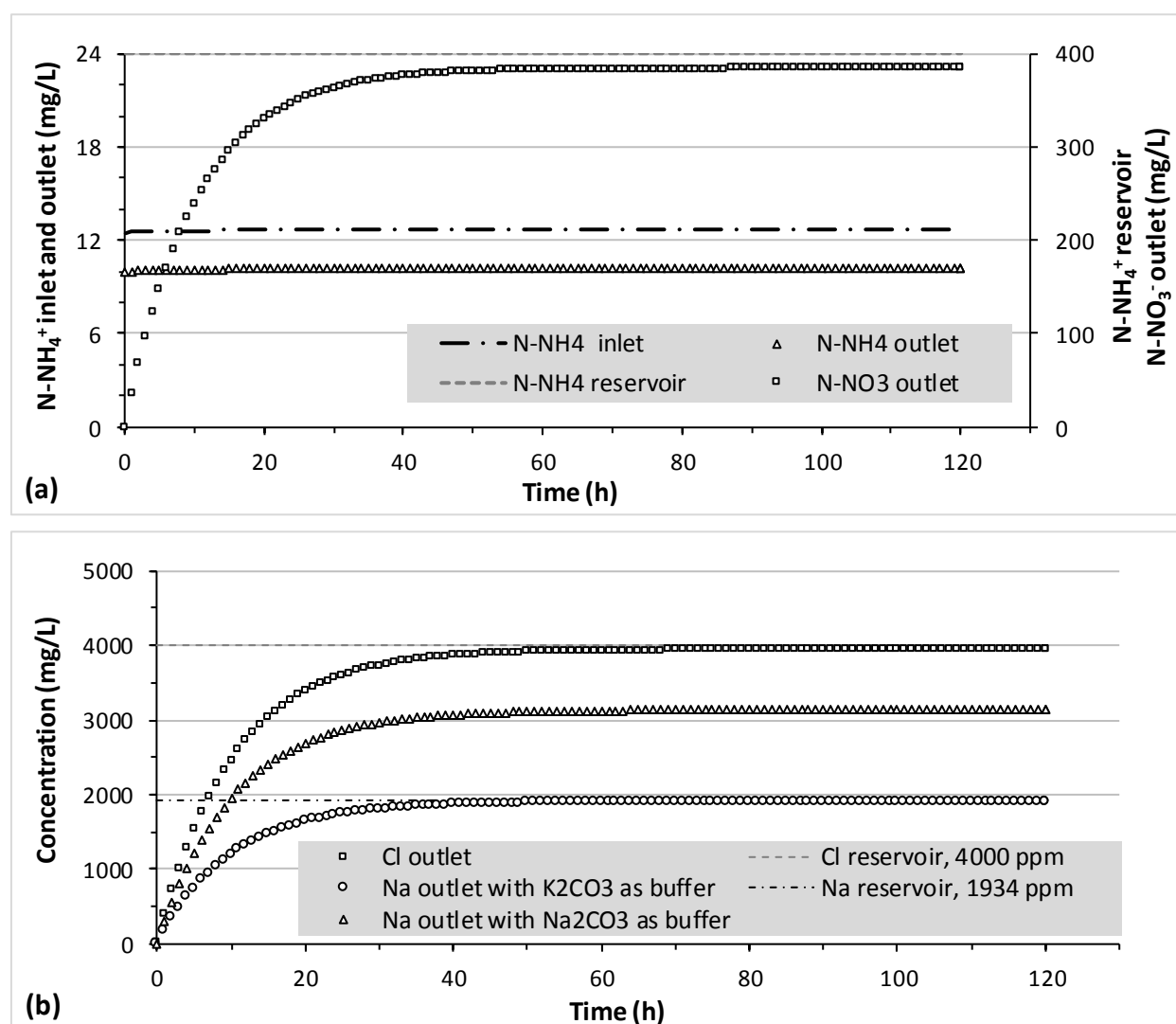
Figure 17. Simulation results from the mathematical model of the reactor system: concentrations of (a) nitrogen species, (b) inert ions.

concentrations, nitrification rate and hydrodynamic conditions, the steady state concentrations of $N-NH_4^+$, $N-NO_3^-$, Na^+ and Cl^- in the reactor outlet were calculated to be 10, 384, 3133 and 3943 mg/L, respectively. The sum of residual ammonium-nitrogen and nitrate-nitrogen concentrations in the effluent was calculated to be slightly lower than the feed $N-NH_4^+$ concentration due to the dilution caused by the buffer solution.

Likewise, effluent chloride concentration approaches the concentration in feed wastewater suggesting the tendency of inert solutes to accumulate and equilibrate in the system. Due to the use of Na_2CO_3 as buffer, Na^+ concentration in the effluent is higher compared to its concentration in the feed. Figure 17b also shows the concentration profile of Na^+ ions in the effluent when K_2CO_3 is used as buffer, in which case, the trend is similar to that of Cl^- ions.

The model in its current form also has the ability to suggest the time lag between a change in the feed composition and the achievement of a new steady state. For the scenario of starting-up (as described in section 4.3.1), with 900 g NH_4^+-$N·m^{-3}·d^{-1}$ nitrification rate and the hydrodynamic conditions applied in the model, the time derivatives of $N-NO_3^-$ and Cl^- concentrations decrease to less than 2 mg/(L·h) after about 31 and 54 hours, respectively. Thus, an estimate of about 2 days (see also Figure 16b) can be drawn for the lag phase, which has served in judging the steady-state attainment in this research. Another important application of the model during this study was in determining the nitrification rate of the reactors (by trial and error) for given feed and outlet $N-NH_4^+$ concentrations, simulating the effluent nitrate-nitrogen concentration and validating it versus the measured $N-NO_3^-$ concentration.

5.3.3 Investigating the Effect of Chloride Content

5.3.3.1 <u>Results from the Continuously Operated PE Carrier-filled PBR Fed with NF permeate</u>

Figure 18 (raw data in Table 15, appendix) shows the results from the about 100 days lasting period during which the reactor was operated with NF permeate of RO retentate collected from the landfill site. NF permeate was shipped thrice (in 900 L volumes, designated as Permeate I, II and III, respectively) during the study period (see section 4.3.2) and the trials have been demarked (Permeate II shaded in light grey) accordingly (see Figure 18a). Furthermore, chloride content was gradually increased in steps (marked by dashed vertical lines) from about 4 to 16 g/L during the same period.

It may be seen from Figure 18a that the ammonium-nitrogen concentration in the outlet was mostly less than 10 mg/L, corresponding to removal percentages greater than 97% (see Figure 18b). The two events of ammonium-nitrogen accumulation in the system (or peak in the inlet and outlet $N-NH_4^+$ concentrations), namely around days 116 and 154, should be attributed to the dissolved organic compounds contained in the NF permeate as seen previously (Figure 16). The drop in ammonia removal percentage was particularly higher after the mix of NF1'' and NF2'' permeates was fed to the reactor on day 149. This can be explained by the fact that the NF1'' permeate has a high organics content (see Table 6).
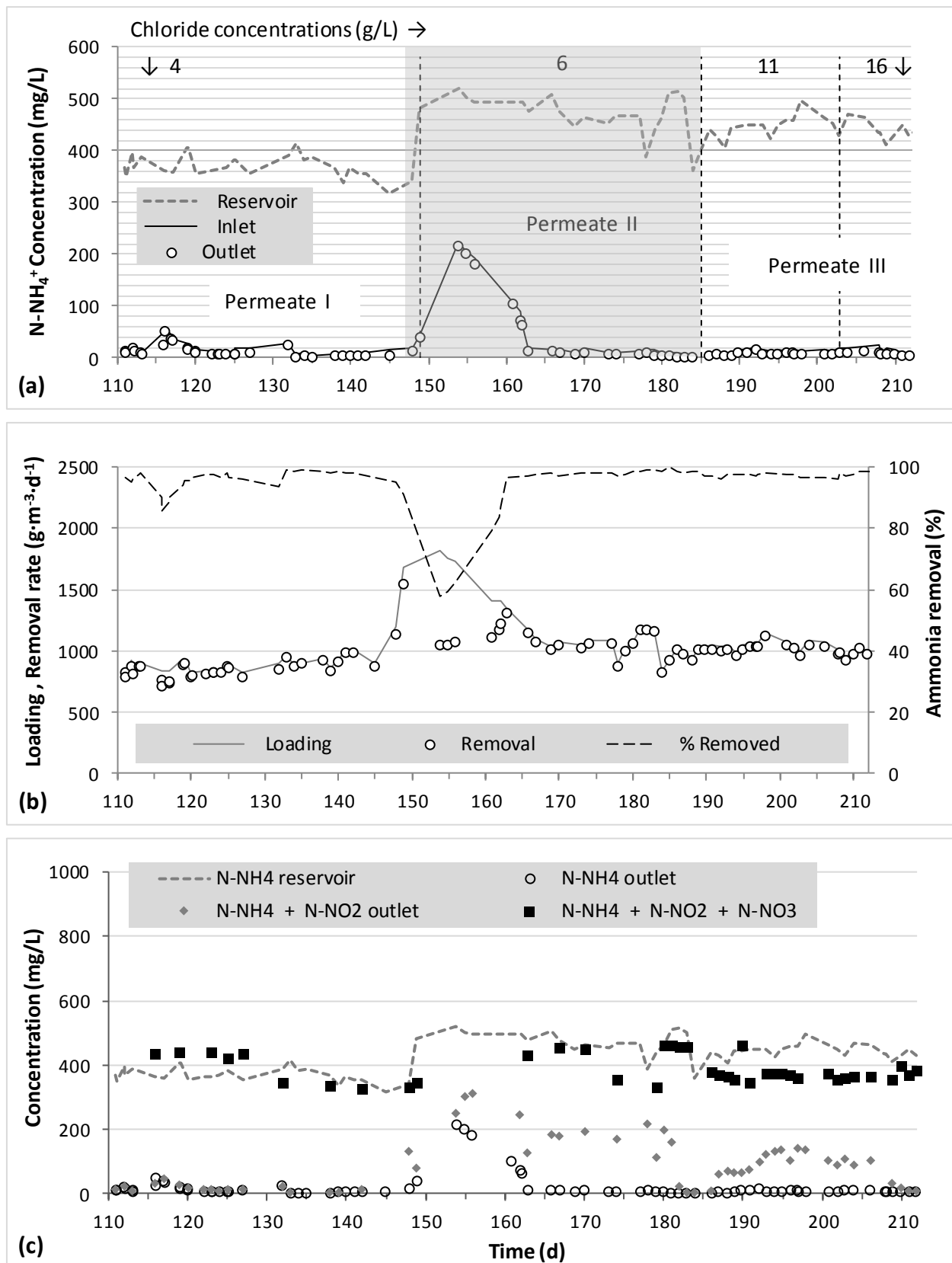
Figure 18. Performance of the PE carrier-filled reactor when fed with NF permeate under increasing chloride concentrations: (a) NH₄⁺-N concentrations in the feed reservoir, reactor inlet and outlet; (b) Applied NH₄⁺-N loading rates and obtained removal rates; (c) Nitrogen balance - species in feed reservoir and reactor outlet.

[The period operated with permeate II has been shaded in light grey in Figure 18a. The step-by-step increment in chloride content in feed water has been depicted using dashed vertical lines.]

Furthermore, accumulation of nitrite was observed when the reactor was fed with the permeate mix (see Figure 18c) which correlated ostensibly to a good extent with the TOC content of the wastewater (Figure 19). It is interesting to see that:

- the AOOs could acclimatise to the dissolved organic compounds since an ammonium-nitrogen peak was not to be seen with permeate III.

- the activity of the NOOs was not affected by permeate I, but by permeates II and III (latter contained about 13% (v/v) NF1'' permeate).

The bell-shaped curve for TOC concentrations over time (Figure 19) during the phase, when permeate II was fed to the reactor, could have resulted from the fact that the wastewater in the feed reservoir was not agitated or mixed and thus susceptible to settling or stratification of the high molecular weight humic molecules. Based on the nitrite-nitrogen-values curve (also being fairly bell-shaped), it is possible that nitrite accumulation might not have occurred if this stratification phenomenon had not happened (resulting in the observed temporal spike in feed TOC concentrations). It is also possible that nitratation could be hindered if the reactor was fed with higher volume ratios of NF1'':NF2'' permeates or that the NOOs might acclimatise as well.
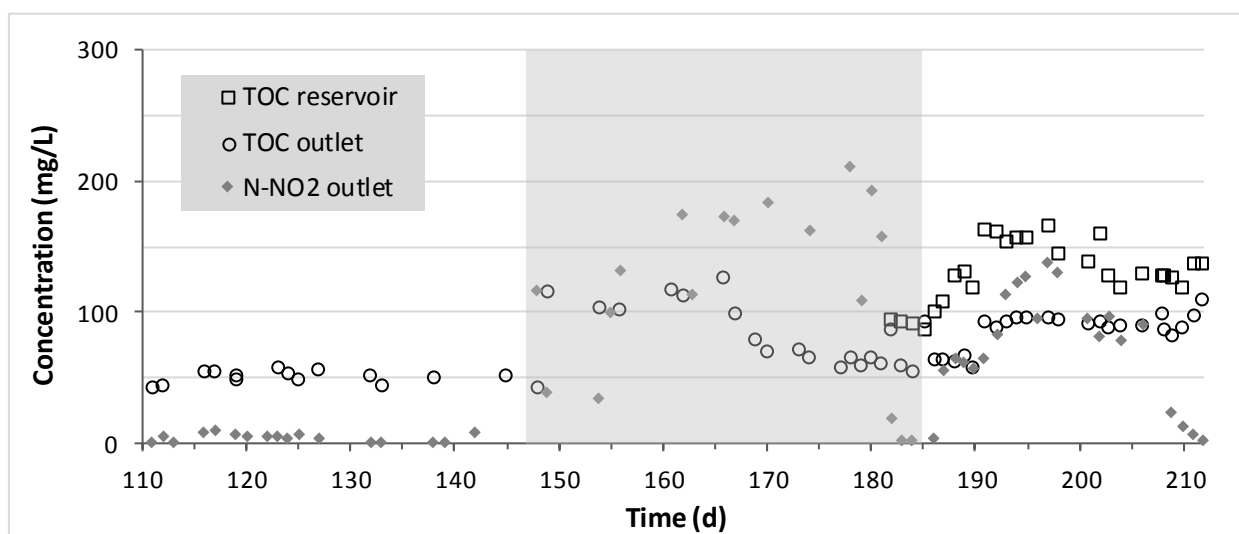
Figure 19. Nitrite accumulation caused by the dissolved organics contained in the NF1'' permeate.

After day 130, the ammonium-nitrogen concentration in the feed reservoir was decreasing slowly (see Figure 18a) resulting in $N-NH_4^+$ concentrations < 5 mg/L in the outlet. From day 135 to 147, feed flow rate was gradually increased in order to have $N-NH_4^+$ concentrations close to 10 mg/L in the effluent and to maintain a constant loading rate. Since the newly collected permeate mix showed a higher $N-NH_4^+$ content, it resulted in a sudden increase in the loading rate after day 147. With increase in loading rate, the removal rate also increased until day 149 to about 1.55 kg $N-NH_4^+ \cdot m^{-3} \cdot d^{-1}$ suggesting that the reactor could be operated at higher loading rates. However, with increasing concentration (accumulation) of permeate organics in the system leading to an apparent inhibition of AOOs, removal and removal percentages started declining. The accumulation of organics and the inception of decrease in nitrification rate from

day 149 (about 2 days after the change of permeate) agrees well with the lag phase of about 2 days calculated from the mathematical model (Section 5.3.2).

The material balance for nitrogen species around the reactor agreed quite well with the expectations, with the sum of $N\text{-}NH_4^+ + N\text{-}NO_2^- + N\text{-}NO_3^-$ concentrations approaching the feed $NH_4^+\text{-}N$ content. An increase of the chloride content in the feed wastewater from 4 g/L (about 16 mS/cm) to 16 g/L (about 43 mS/cm) did not have any marked influence on the nitrification performance.

Figure 20 displays the values of operation parameters (wastewater temperature, pH, DO concentration, air and water up-flow velocities) and the amount of external alkalinity consumed, recorded during this sub-study phase for the PE carrier PBR. On an average, about 7.92 ± 1.67 g Na_2CO_3 (median = 8.15, N = 58) was consumed per g $N\text{-}NH_4^+$ oxidised (see Figure 20a), concurrent with the finding from the batch trials. This value is however slightly (4.6%) higher than the theoretical requirement of 7.57 g/g and is very probably due to the fact that both NF permeates (NF1'' and NF2'') with a pH of about 6.5 were slightly acidic.

Contrary to the notion that the head losses due to biofilm growth would be minimal (since the PE carrier bed has a high voidage), the water flow rate was found to gradually decline during the operation with NF permeate (Figure 20b). The increase in pressure drop was obviously due to the uncontrolled growth of heterotrophic organisms nourished by the organic compounds contained in the NF permeates. Macroscopic brown films could be seen in the Schott bottle and the rotameter (see photographs, Figure 32 in Appendix). The head losses were found to be reversible by performing passive backwashing (as described in 4.3.2), wherein the excess biomass trapped in the inlet zone was removed easily (see photographs of backwash water in Figure 32). The fact that a liquid distribution system was lacking might have supported excessive growth and accumulation of biomass in the inlet zone. This situation is expected not to arise in the practical application with the use of a distributor plate and nozzles for water and air inflows. Although unintentional, the water velocity in this sub-study was about 12 m/h only (against the design up-flow velocity of 18 m/h), which is comparable to the hydraulic loading rate of 10 $m^3/(m^2{\cdot}h)$ recommended for nitrifying biofilters in literature [77,80,82]. Nitrification rates of about 1 kg $N\text{-}NH_4^+{\cdot}m^{-3}{\cdot}d^{-1}$, which were seemingly not the maximum loading potential, could be achieved with water velocities of about 12 m/h. It would be therefore appropriate to hypothesise that much higher nitrification rates (up to about 2 kg $N\text{-}NH_4^+{\cdot}m^{-3}{\cdot}d^{-1}$ or beyond) could be possible with higher water up-flow velocities, as reported by Peladan et al. [83].

To maintain the DO concentration (measured above the packed bed), which had grazed 6.5 mg/L, at about 4.5 mg/L, the air flow rate was slightly reduced after day 130 (see Figure 20b and c). In the presence or with the availability of degradable organic compounds, heterotrophs are known to outcompete nitrifiers for space and oxygen requirements, thereby lowering the nitrification efficiency [114–116]. To check if the accumulation of nitrite in the system could have been due to oxygen limitation caused by heterotrophic organisms, DO concentration was gradually increased to about 6.5 mg/L after day 180 by increasing the air flow rate. Although it

Figure 20. Overview of the operating conditions (temperature, water up-flow and air velocities, pH and dissolved oxygen concentration) and external alkalinity consumption (as g Na$_2$CO$_3$ per g N-NH$_4^+$ removed) monitored in the PE carrier PBR system.

cannot be said conclusively, based on the increased consumption of oxygen (seen as a slow decline in the DO concentration despite the air flow rate maintained constant, Figure 20) and the decrease in nitrite concentration in the effluent (see Figure 19), it seems that the increase in the bulk DO concentration may have relieved the oxygen stress of the NOOs.

5.3.3.2 Results from the Continuously Operated Clay Beads-filled PBR Fed with Synthetic Wastewater

The behaviour and performance of the clay beads-packed reactor over the 100 days period wherein the chloride content in the feed wastewater was gradually increased from 4 to 16 g/L is shown in Figure 21. The reactor was operated with permeate III between days 190 and 197 to validate and confirm that the accumulation of nitrite seen in the PE carrier-filled reactor (when fed with the permeate mix) was due to the organics contained in the NF1'' permeate. From day 190-197, the chloride concentration was about 11 g/L. The sharp decline in $N-NH_4^+$ removal rate from about 650 $g \cdot m^{-3} \cdot d^{-1}$ to almost zero (Figure 21b) and the associated steep increase in reactor inlet and outlet ammonium-nitrogen concentrations (Figure 21a) suggest that the AOOs were strongly inhibited by the organics contained in the permeate. The effect, although of greater impact compared to the PE carrier filled PBR as depicted in Figure 18 (likely because of the fact that the latter was already in operation with NF permeate so that the AOOs therein were partly acclimatised to the permeate-organics), was again only temporary since an increase in percentage removal capacity could be observed from days 194 to 197 when the reactor was still fed with the permeate mix. After the operation was changed to synthetic wastewater on day 197, the VARR returned to about 700 g $N-NH_4^+ \cdot m^{-3} \cdot d^{-1}$ within about 7 days.

Apart from this period, when the reactor was fed with NF permeate, ammonia removal rates achieved by the reactor were 698 ± 78 g $N-NH_4^+ \cdot m^{-3} \cdot d^{-1}$ despite the increase in salinity (NaCl %, w/v) from 0.66% (4 g/L Cl$^-$) to 2.64% (16 g/L Cl$^-$). According to Figure 22, which shows a plot of VARRs and water up-flow rates versus time (for the operation period 80 to 230 days), there wasn't any conclusive influence of wastewater salinity on nitrification efficiency during this period referring to salinity increasing stepwise from the first to the last experimental phase. After the intense washing of the packed bed on day 79, the ammonia removal capacity of the reactor rose up to about 1200 g $N-NH_4^+ \cdot m^{-3} \cdot d^{-1}$, following which it gradually declined and continued to remain fairly constant at about 700 $g \cdot m^{-3} \cdot d^{-1}$ (especially after day 150). It can be seen that the VARR was dependent on the water up-flow velocities. During this period, the reactor bed was subjected to passive backwashing (as described in 4.3.2) which aided in partial remediation of the clogging problem and partly restoring the water flow rates. However, it is also possible that the increase in salinity resulted in some changes in the biofilm structure or distribution controlling the pressure drop across the packed bed, which can be seen from the sustenance of water up-flow rates (Figure 22).

Figure 23 highlights the operating conditions (wastewater temperature, pH, DO concentration, air and water up-flow velocities) and the amount of external alkalinity consumed, for the reactor filled with clay beads. The nitrification process in this reactor operated with synthetic
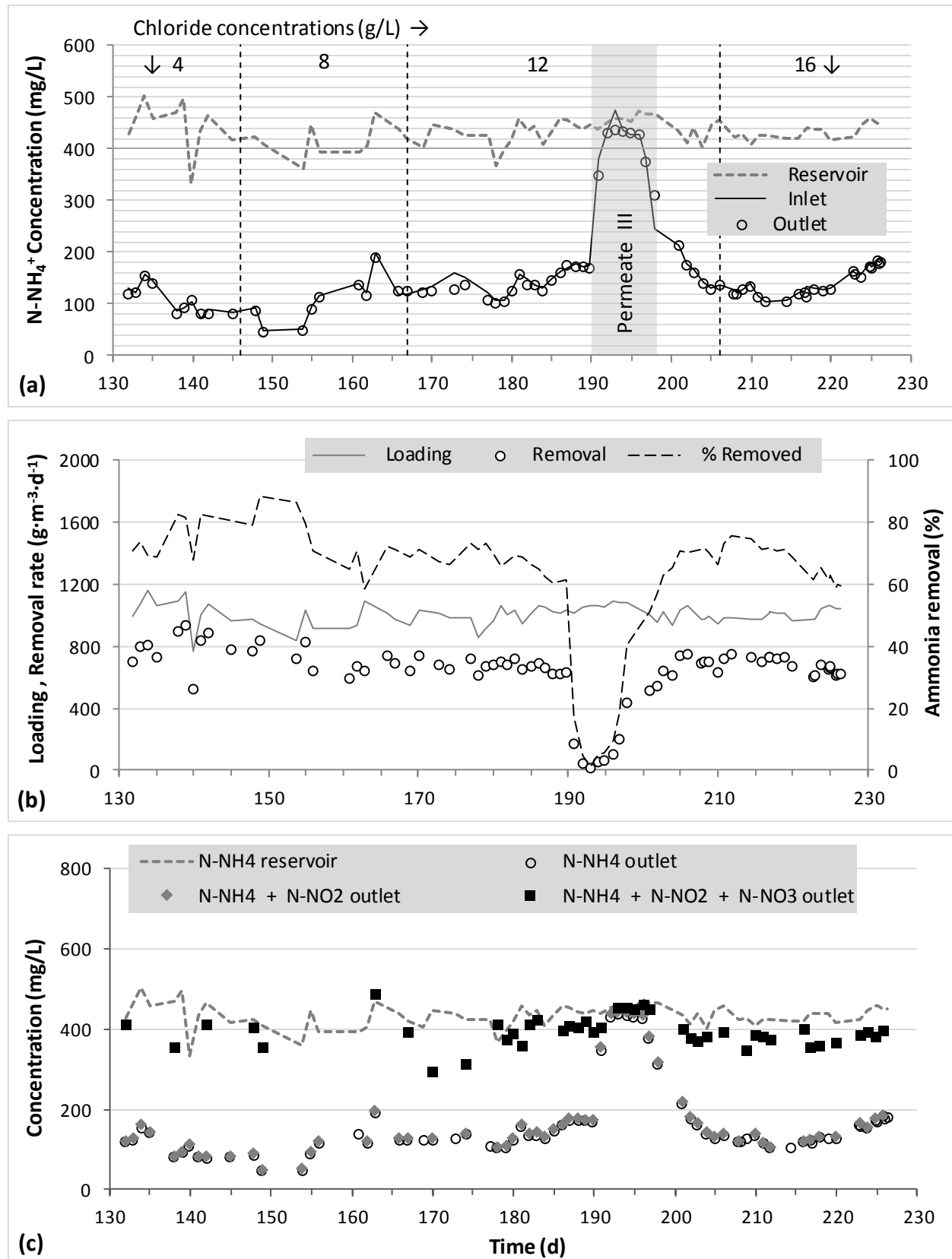
Figure 21. Performance of the clay beads-filled reactor when fed with synthetic wastewater with increasing chloride concentrations and with NF permeate: (a) NH$_4^+$-N concentrations in the feed reservoir, reactor inlet and outlet; (b) Applied NH$_4^+$-N loading rates and obtained removal rates; (c) Nitrogen balance - species in feed reservoir and reactor outlet.

[The step-by-step increment in chloride content in feed water has been depicted using dashed vertical lines. The reactor was fed with permeate III between days 190-197 to verify the influence of organics contained therein.]
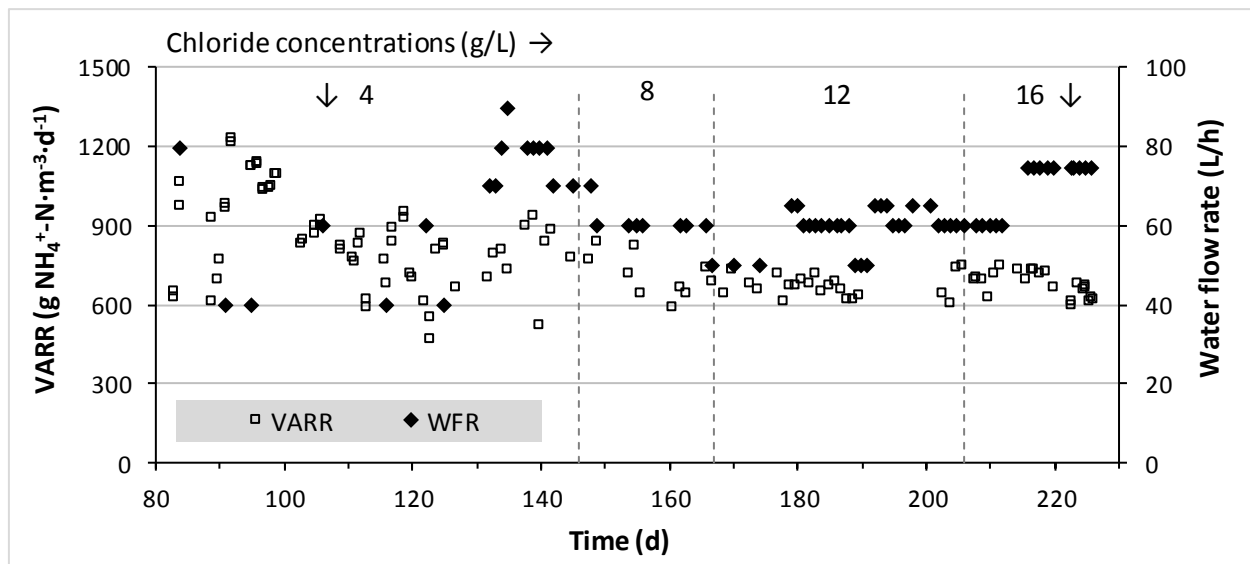
Figure 22. Assessing the influence of salinity and water up-flow rate on nitrification capacity of clay beads-filled PBR.

wastewater consumed an amount of external alkalinity equal to about 7.15 ± 1.33 g Na_2CO_3 per g NH_4^+-N oxidised (median = 7.35, N = 43).

Water up-flow velocities of only about 8 m/h could be achieved (despite practising passive backwashing as described in section 4.3.2) in the clay beads-filled PBR versus about 12 m/h in the reactor packed with PE carrier. Correspondingly, the nitrification rates achieved in this reactor (about 700 g NH_4^+-N·m^{-3}·d^{-1}) were about 30% lower compared to those obtained with the PE carrier-filled PBR. As mentioned earlier, the clay beads medium (due to its low voidage) requires regular intensive backwashing to regulate the pressure losses from the growth of biofilm in order to realise higher nitrification capacities. It must also be noted that the clay beads-filled reactor was operated mostly with synthetic wastewater (which is nearly free from degradable organic compounds) throughout the continuous operation study period. Therefore, the clogging tendencies and subsequently the required backwash frequency when operated with NF permeate (containing dissolved degradable organics) can be expected to be higher.

Air flow rate into this reactor was maintained fairly constant as can be seen in Figure 23b. Thus, the DO concentrations measured above the fixed-bed were mostly about 4 mg/L when operated with synthetic wastewater (Figure 23c). The shoot up of DO concentration to above 8 mg/L (saturation condition) when the reactor was fed with NF permeate mix between days 190-195 was the consequence of the inhibition of ammonia oxidation caused by the organic compounds contained in the permeate.
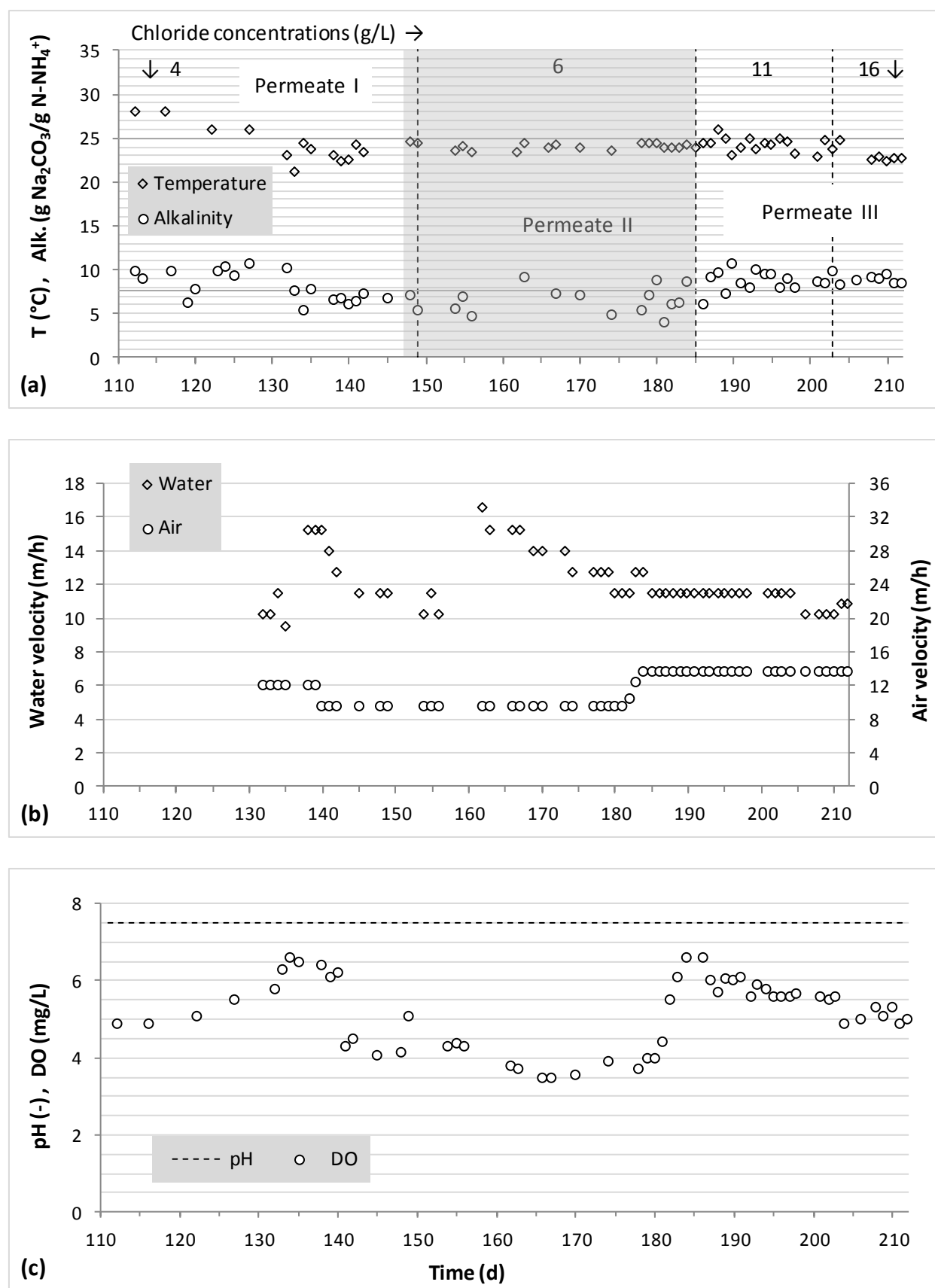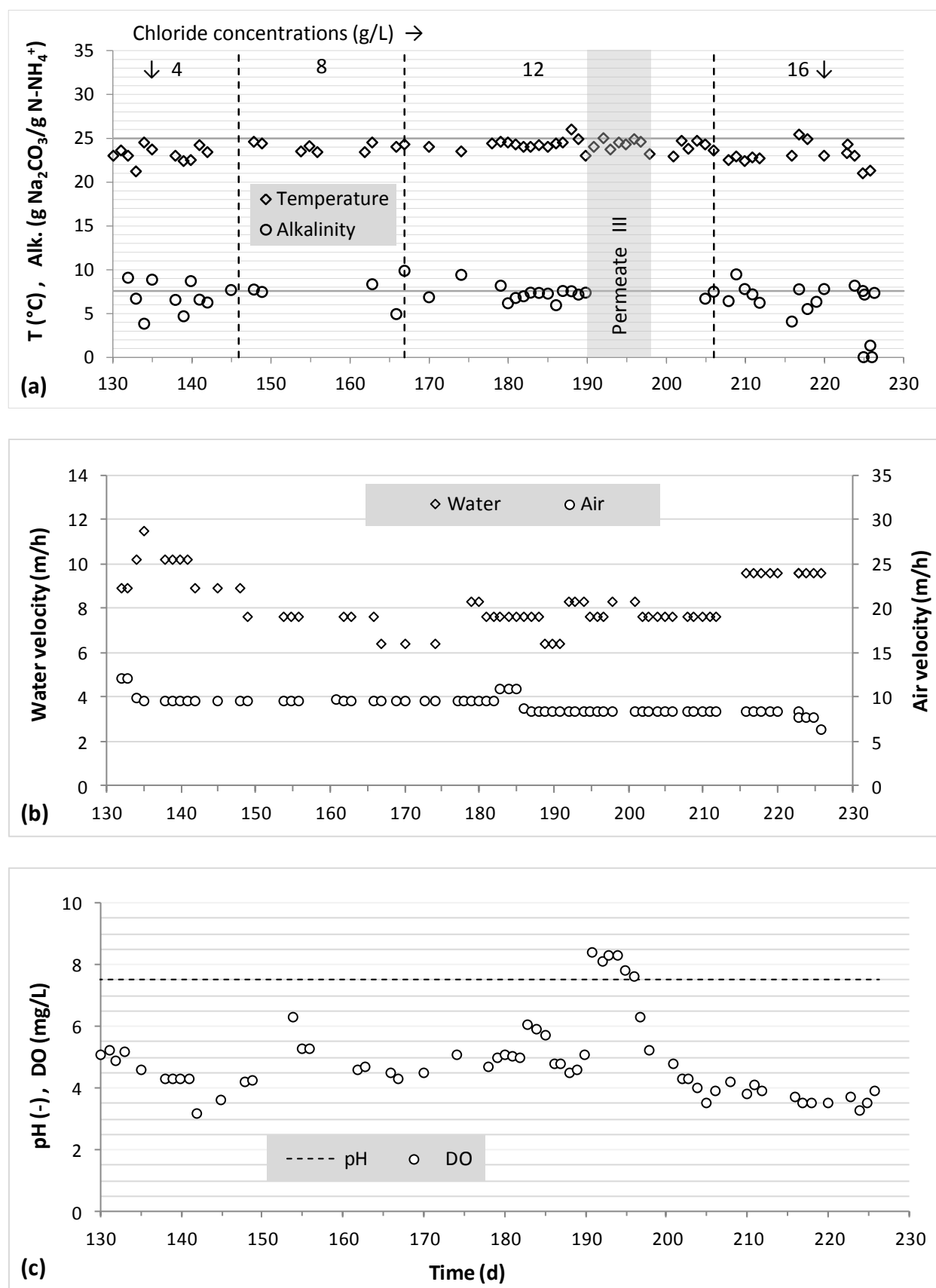
Figure 23. Overview of the operating conditions (temperature, water up-flow and air velocities, pH and dissolved oxygen concentration) and external alkalinity consumption (as g Na₂CO₃ per g N-NH₄⁺ removed) monitored in the clay beads-filled PBR system.

5.4 COMPARISON OF THE PERFORMANCES WITH EXISTING LITERATURE

Table 8 summarises the stable maximum nitrification rates achieved during the different stages of this research project. Jokela et al. [23] reported complete nitrification of a mature leachate at loading rates of 130 g NH_4^+-N$\cdot$m$^{-3}\cdot$d^{-1} using lab scale up-flow biofilters. In this study, nitrification rates of about 570 g$\cdot$m$^{-3}\cdot$d^{-1} NH_4^+-N were achieved with dilutions of a partially stable landfill leachate.

The organics contained in the landfill leachate used in this study caused inhibition of nitrification, which was validated using the SBR trials. At similar initial N-NH_4^+ concentrations (about 500 mg/L), the mass specific nitrification rates achieved with dilutions of RO retentate and NF permeate were 28 and 183 mg/($g_{MLSS}\cdot$d), respectively, with MLSS concentrations of about 6.4 and 3.5 g/L. Ammonium-nitrogen removal rates achieved here with NF permeate dilutions were slightly better than the maximum rate (120 mg$\cdot g_{VSS}^{-1}\cdot$d^{-1}) reported by Yalmaz and Oztürk [117].

Table 8. Stable maximum nitrification rates achieved during various stages of this project

Stage	Section	WW matrix	Media	Nitrification rate (g NH_4^+-N$\cdot$m$^{-3}\cdot$d^{-1})
Batch trials, phase 1	5.2.1.2	RO ret. 1:2	PE	570
		NF per. 1:2	PE	1200
Batch trials, phase 2	5.2.1.4	NF per. 1:4	Clay	900-1300
		NF per. 1:4	PE	800-1200
Continuous flow, initial phase	5.3.1	Syn. WW	Clay	800
		Syn. WW	PE	1000
Continuous flow, final phase	5.3.3	Syn. WW	Clay	700
		NF2'' per.	PE	1000
SBR trials	Appendix D	RO ret. 1:6	-	179
		NF per. 1:4	-	632

Throughout the continuous flow trials, the performance of the reactor packed with PE carrier was consistently better compared to the clay beads medium. Due to the head losses (and the associated decrease in water recirculation flow rates) resulting from clogging, the latter showed nitrification rates of about 700-800 g NH_4^+-N$\cdot$m$^{-3}\cdot$d^{-1}, which seemed to be its maximum if bed washing is not carried out frequently (see Figure 14). On the other hand, even with chloride concentrations as high as 16 g/L (about 2.6% NaCl, 43 mS/cm), the reactor filled with PE carrier (operated with Cl$^-$-spiked NF1''-NF2'' permeate mix) offered removals > 97% for NH_4^+-N loading rates of about 1100 g$\cdot$m$^{-3}\cdot$d^{-1}. It appeared that this reactor can be operated at much higher loading rates still maintaining NH_4^+-N concentrations ≤ 10 mg/L in the effluent, since nitrification rates of up to about 1500 g$\cdot$m$^{-3}\cdot$d^{-1} (see Figure 12 and Figure 18) were achieved.

The nitrification rates achieved in this project were superior in comparison to the rates achieved in recent studies on nitrification of saline wastewaters using packed bed reactors performed by other researchers. Table 9 shows the nitrification rates in saline wastewaters

reported in relevant previous works (viz. using fixed bed reactors and the analogous submerged biofilters). In contrast to these works, increase in chloride content of the wastewater (up to 16 g/L, about 26 g/L NaCl) did not have any detrimental effect on the nitrification efficiencies in this study. This could have resulted from the gradual adaptation of the nitrifiers towards the increasing chloride concentrations [118–121] or due to the proliferation of salt-tolerant nitrifying organisms [122,123].

Table 9. Nitrification efficiencies reported in literature for saline wastewaters treated using fixed bed reactors.

Nitrification of (or ammonia removal from)	Loading rate in 1 - $gm^{-3}d^{-1}$ 2 - $gm^{-2}d^{-1}$	NaCl (%), [EC in mS/cm]	Removal %	Source
model seawater using lab scale packed bed reactors inoculated with halophilic nitrifiers enriched from seawaters	83 [1] 104 130	2.8	>98 >98 85	[85]
synthetic wastewater (without cBOD) using bench scale up-flow submerged aerated biofilters inoculated with acclimatised microflora (T = 28°C)	106 [1]	low 2.5 5.0	94 80 48	[124, 125]
model wastewater (also containing readily degradable cBOD) using bench scale submerged fixed bed biofilm reactors (SFBBR) after DWA guidelines for C-removal without nitrification (T = 25°C)	1.7 [2]	low 2.0	80 43	[126]
primary clarifier effluent (spiked with NaCl) using lab-scale down flow submerged fixed bed bioreactor (T = 20°C)	165 [1] 285 233 249	low [1.5] 0.37 [12] 2.41 [24] 4.41 [48]	98 87 56 41	[127]

cBOD – carbonaceous BOD

Impact of salinity, high chloride concentrations and the resulting osmotic stress on nitrification in suspended growth systems is well investigated [118–120,128,129]. However, research on nitrification of saline wastewaters using PBRs is limited, as also remarked by Sudarno et al. [85] and Cortés-Lorenzo et al. [127].

6 DESIGN, CONSTRUCTION & START-UP OF HALF-TECHNICAL SCALE PLANT AT THE LANDFILL SITE

Within the framework of this PhD project, a plant was planned and commissioned in half-technical scale at the landfill site. Although, taking this plant into operation and presenting the results obtained therefrom were planned to be within the scope of this dissertation, this could not be achieved in time due to some delays from the project partners. This chapter therefore presents the planning and layout of the demonstration-scale plant.

Figure 24 shows the process flow diagram for the plant that was suggested to be implemented at the landfill site. Table 10 lists the various components of the suggested flow diagram and briefly describes their functions or features.

Table 10. Details of various components of the process flow diagram

Line	Component	Function/Feature
Feed line (normal operation)	01 EC	- Measuring electrical conductivity of feed
	02 NF permeate	- 1000 L IBC serving as feed reservoir
	03 Dosing pump	- Controllable pump for dosing NF permeate
	04 Rotameter	- To measure and record feed flow rate
	05 On/off valve	- Operation - open, Backwashing - closed
	06 Static mixer	- To achieve good mixing conditions in the line
	07 Recirculation pump	- Maintains the desired up-flow velocity
	08 Heat exchanger	- To remove any excess heat from pumping
	09 Rotameter	- Measures the recirculation flow rate
	10 Flow controller	- Controls the recirculation pump
	11 Pressure transmitter	- Line pressure measured and transmitted
	12 Powered valve	- On/off valve
	13 Ball valve	- Normally closed, to empty reactor (if needed)
Aeration line	14 Blower/compressor	- Controlled air flow to maintain DO levels
	15 Rotameter	- Measurement of air flow rate
	16 Powered valve	- On/off valve
	17 Check valve	- No return valve
Recirculation line	18 On/off valve	- Operation - open, Backwashing - closed
	19 Line strainer	- To filter out any detached biomass
	20 pH - FC	- pH measurement and control by dosing buffer
	21 Buffer	- Reservoir for 200 g/L Na_2CO_3
	22 DO - FC	- Measurement and control of DO content
	23 EC	- Electrical conductivity measurement
	24 NH_4 - FC	- Analysis of $N-NH_4^+$ and controlling feed pump
Effluent line	25 Line strainer	- To filter out any detached biomass
	26 On/off valve	- Operation - open, Backwashing - closed
Lines for backwash water	27 Powered valves	- Normally closed. Facility to backwash the reactor when the pressure (from PT) or the rotor rpm of recirculation pump exceeds a set value
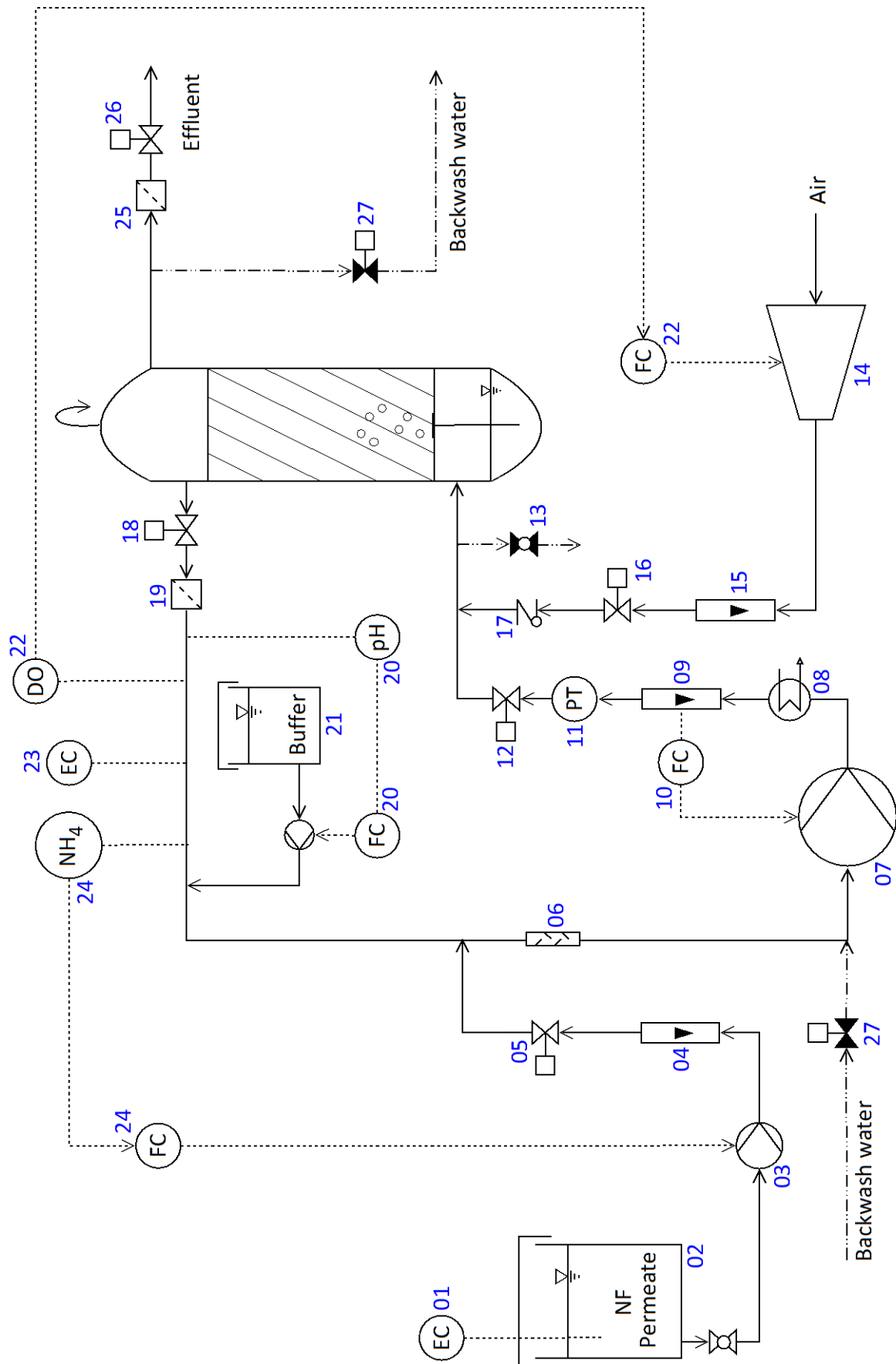
Figure 24. Suggested process flow diagram for the implementation of nitrification using packed bed reactor in half-technical scale at the landfill site for treating the nanofiltration permeate of RO concentrate.

In principle, this setup is very similar to the one used for the continuous mode trials at TUHH (Figure 5). The plant has been designed to be fully automatic, which brings some minor differences. These include (see Figure 24): the feed dosing system which would dose the NF permeate maintaining an NH_4^+-N concentration of about 10 mg/L in the effluent; flow control for air so as to maintain a DO concentration of about 3 mg/L; and a provision to initiate backwashing of the reactor when necessary.

The reactor (made entirely out of PVC) with a volume of 785 L (4 m bed height and 0.5 m ID, see Figure 25) is at the heart of the setup. The packing material Hel-X® HXF13KLL+ (made of recycled HDPE) was purchased from Stöhr GmbH & Co.KG (Marktrodach, Germany). According to the manufacturer, HXF13KLL+ has dimensions of 13 x 12 mm (ϕ x L), a bed density of 0.16 g/cm^3, a specific surface of 955 m^2/m^3 (about 11% larger compared to HXF12KLL, the one used in the studies at TUHH) and a bed porosity of 0.83. For introducing the wastewater and air into the packed bed, 'Typ D' filter nozzles were purchased from KSH GmbH (Herford, Germany). To inoculate the reactor, an inoculum will be obtained from a plant (which treats the blackwater produced from a toilet) at the Hamburg central railway station [96]. The microorganisms in this plant have been acclimatised to salinity concentrations amounting to about 45 mS/cm (Deegener, personal communication).

The demonstration plant will be taken into operation (with an up-flow velocity of 20 m/h) with the permeate from NF2 (see Figure 6), which has lower concentrations of $N-NH_4^+$ and Cl^- than NF1 permeate (Table 6). As mentioned before, the feed pump will be controlled (based on the continuous on-line measurement of NH_4^+-N) to dose NF permeate so as to maintain about 10 mg/L $N-NH_4^+$ in the effluent. Thus, the loading rate (which can be monitored using the feed flow rate) will be progressively increased until stable biofilm conditions are achieved. Table 11 and Figure 26 show the steady state flow conditions and calculated $N-NH_4^+$ concentrations for the plant for a stable biofilm condition, in which an $N-NH_4^+$ oxidation rate of 1 $kg \cdot m^{-3} \cdot d^{-1}$ is assumed. This corresponds to a loading rate of about 1.03 kg $N-NH_4^+ \cdot m^{-3} \cdot d^{-1}$ with an ammonia removal efficiency of about 97.5%.

Another goal of the project is to gradually mix the NF permeates (NF1 and NF2), acclimatising the organisms to higher salinity conditions and validating/investigating the performance. Samples of feed and effluent shall be collected and analysed for other important parameters. Furthermore, the project partners have also been suggested to monitor the energy requirements of the plant.
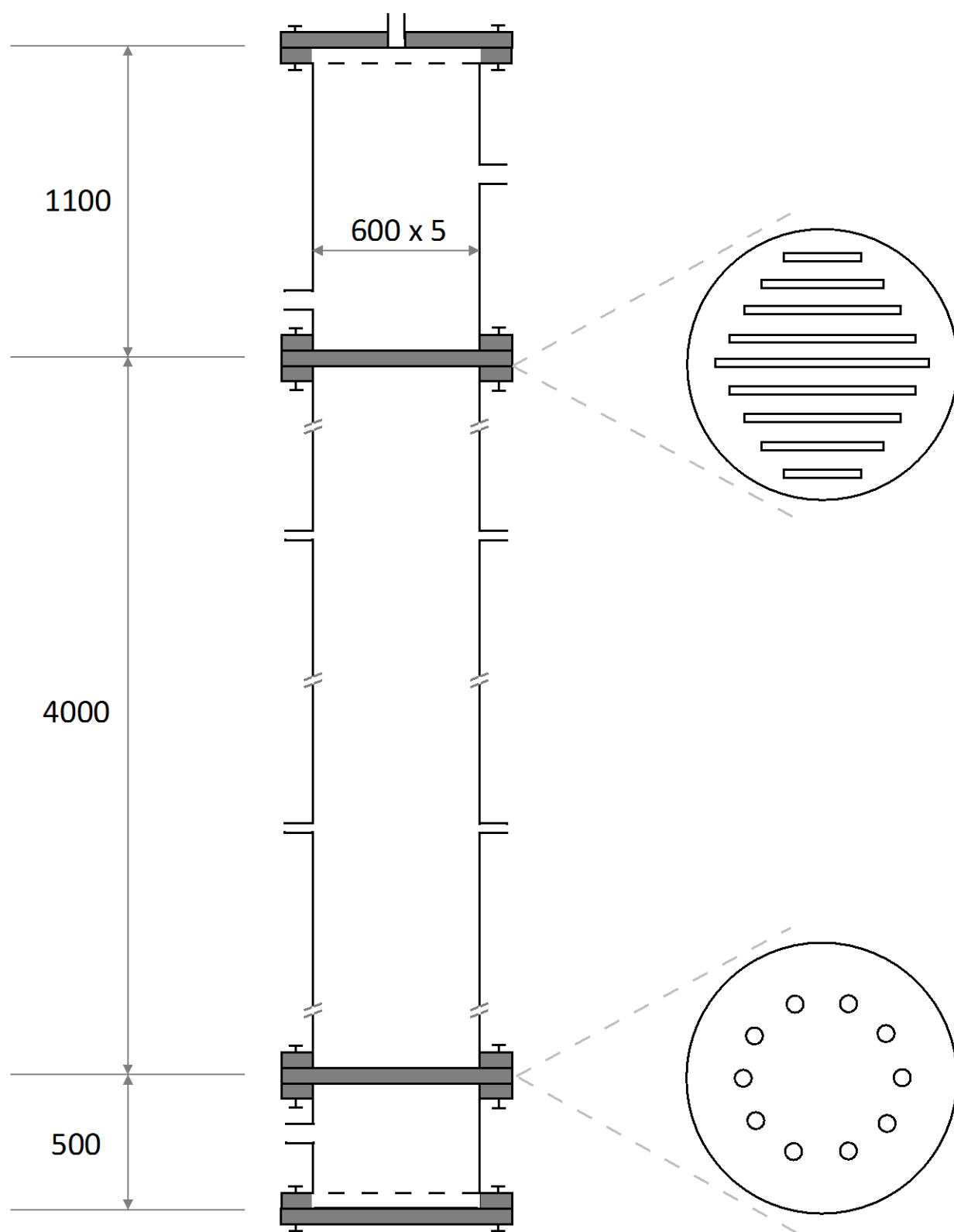
Figure 25. Schematic of the demonstration scale reactor.

Table 11. Estimation of process flow conditions for the half-technical scale plant.

Reactor dimensions	
Height	4 m
Inner diameter	0.5 m
Cross-sectional area	0.20 m^2
Reactor volume	0.79 m^3
N-NH_4^+ oxidation rate	1.00 kg/($m^3 \cdot$d)
Capacity of reactor	0.79 kg/d

NF-Permeate 2	
N-NH_4^+ concentration	0.14 kg/m^3
Volume treatable	6.04 m^3/d
	0.252 m^3/h

pH-control	
Na_2CO_3 required	5.48 kg/d
Concentration	200 kg/m^3
Buffer consumption	0.027 m^3/d

Flow conditions	
Up-flow velocity	20 m/h
Flow rate - inlet	3.927 m^3/h
Flow rate - buffer	0.001 m^3/h
Flow rate - permeate	0.252 m^3/h
Conc N-NH_4^+ inlet	0.018 kg/m^3
Mass of NH_4^+ in	0.072 kg/h
N-NH_4^+ oxidised	0.033 kg/h
Mass N-NH_4^+ out	0.039 kg/h
Conc N-NH_4^+ outlet	0.010 kg/m^3
Flow rate - effluent	0.253 m^3/h
Recirculation flow	3.674 m^3/h
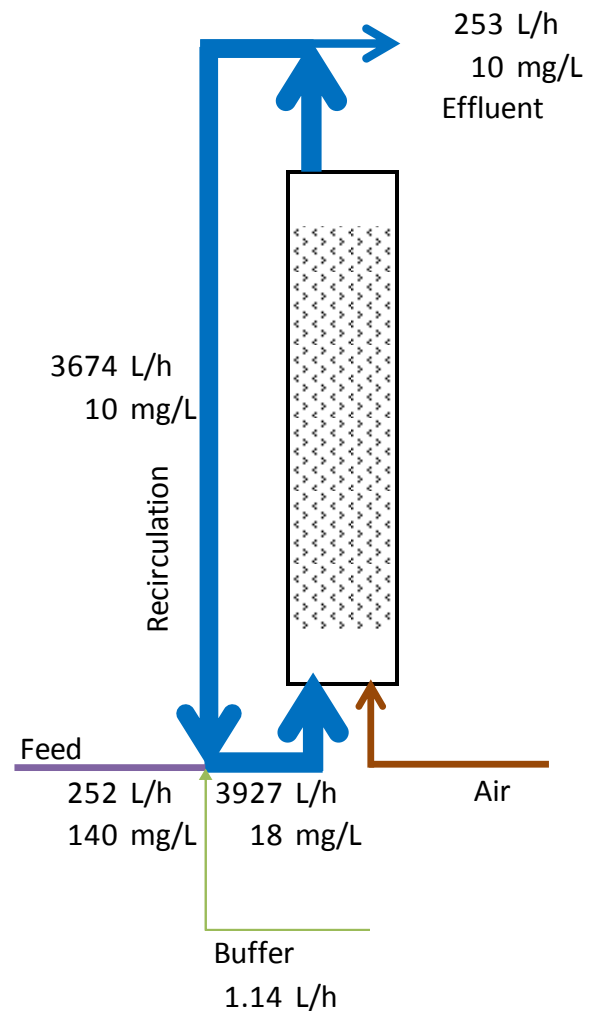
Figure 26. Block diagram of the demonstration scale reactor illustrating the flow rates and N-NH_4^+ concentrations under steady state operation.

7   CONCLUSIONS

Biological nitrification using aerated packed bed reactors was investigated to solve the problem of insufficient ammonia rejection faced by the multi-stage high pressure membrane system treating the leachate at the Ihlenberg landfill site.

From the batch experiments with different dilutions of the RO retentate of raw leachate and the NF permeate of RO concentrate, it was found that the NF permeate is better suited for nitrification than the RO retentate. Under similar operating conditions, the maximum nitrification rate attained in diluted RO retentate was about 570 g NH_4^+-N/(m^3·d) only, whereas with dilutions of NF permeate up to about 1200 g NH_4^+-N/(m^3·d) were achieved. The organic compounds contained in the raw leachate caused nitrification inhibition, which could be verified from the trials conducted in SBRs (in the SBRs, the ammonia removal rates in dilutions of RO concentrate were 30-80 % lower than those in the dilutions of NF permeate, with the difference increasing with increase in organics content). However, it was found that NF permeate lacks alkalinity for efficient nitrification. As a result, an external alkalinity addition of about 6.3 ± 0.6 g $CaCO_3$/g N-NH_4^+ was necessary for complete nitrification in NF permeate dilutions compared to only 3.9 ± 0.8 g $CaCO_3$/g N-NH_4^+ in dilutions of RO retentate. A potential for about 40% TOC removal from raw leachate by aerobic biological treatment could be estimated from the trials with 1:5 dilution of RO retentate conducted in PBRs.

Although coke material, with its beneficial physical characteristics like rugged surface, irregular particle shape and higher specific surface area, supported faster biofilm development during the early stages, it was found to be vulnerable to clogging due to its high adsorptive capacity for organics and subsequent proliferation of heterotrophic organisms. Thus, it also follows that the RO concentrate containing some degradable organic compounds supports the growth of heterotrophs more in comparison to the NF permeate which is organics lean. Furthermore, voidage was found to critically influence the longevity of the reactors. The clay beads packing (having low adsorption capacity) with a porosity of about 0.55 suffered from plugging, whereas the PE carrier bed with a porosity of about 0.85 did not.

During the initial continuous flow trials with synthetic wastewater, the reactor filled with PE carrier demonstrated stable and complete nitrification at the design loading rate of about 925 g NH_4^+-N/(m^3·d). On the other hand, due to low porosity and uncontrolled biofilm growth leading to increased pressure losses and reduction in water up-flow velocity, frequent washing was necessary to be able to maintain the designed nitrification capacity in the clay beads-packed PBR. The OpenModelica model correctly simulated the working of the PBRs as desired. The calculated steady state inlet and outlet concentrations of nitrogen (N-NH_4^+, N-NO_3^- and TN) and inert (Cl^-) species matched well with the experimental values. The code could accurately simulate also the dynamic changes in the concentrations within the system (accumulation and wash out) resulting from a stimulus in the feed.

The plausibility for treating the NF permeate and the effect of high chloride concentrations in the feed (up to 16 g/L) was verified in continuous operation in this study. With the NF permeate mix spiked with NaCl (16 g/L Cl$^-$, about 2.6% NaCl equivalent), the PBR packed with PE carrier gave ammonia removals >97 % at loading rates of about 1100 g NH$_4^+$-N/(m^3·d) achieving N-NH$_4^+$ concentrations <10 mg/L in the effluent. On the contrary, the clay beads filled operated with synthetic wastewater (without backwashing the reactor) showed ammonia removals of about 70% only at loading rates of about 925 g NH$_4^+$-N/(m^3·d) with effluent ammonia concentrations of about 140 mg NH$_4^+$-N/L. A gradual stepwise increase in chloride concentration from 4 to 16 g/L (correspondingly, electrical conductivity increased from about 14 to 45 mS/cm) did not have any detrimental effect on the nitrification efficiencies of the reactors.

Based on the findings from the continuous flow trials, a half-technical scale plant was conceptualised and commissioned at the Ihlenberg landfill site. The planning and layout of the demonstration plant was presented in this work.

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APPENDIX A - TABLES

Table 12. Composition of the raw leachate and its RO concentrate, as measured by the project partner in July 2013.

	Parameter	Method	in raw leachate	in RO retentate	Unit
Cations	Calcium	DIN EN ISO 14911 - E 34	230	1200	mg/L
	Magnesium	DIN EN ISO 14911 - E 34	81	350	
	Sodium	DIN EN ISO 14911 - E 34	3100	15800	
	Potassium	DIN EN ISO 14911 - E 34	1100	5800	
	Iron (total)	DIN EN ISO 11885 - E 22	1.97	4.80	
	Manganese	DIN EN ISO 11885 - E 22	0.66	3.02	
	Barium	DIN EN ISO 11885 - E 22	2.05	1.03	
	Strontium	DIN EN ISO 11885 - E 22	3.38	14.7	
	Aluminium	DIN EN ISO 11885 - E 22	< 0.1	0.58	
	Ammonium-N	DIN EN ISO 14911 - E 34	580	3000	
Anions	Nitrate-N	DIN EN ISO 10304-2 - D 20	< 2	< 2	mg/L
	Nitrite-N	DIN EN 26777 - D 10	< 0.3	1.15	
	Chloride	DIN EN ISO 10304-2 - D 20	5800	30000	
	o-phosphate-P	DIN EN ISO 6878 - D 11	4.50	15.6	
	Total phosphorus	DIN EN ISO 6878 - D 11	12.7	55.5	
	Sulphate	DIN EN ISO 10304-2 - D 20	560	13700	
	Fluoride	DIN 38405 - D 4	2.81	11.3	
	Borate-B	DIN EN ISO 11885 - E 22	36.4	150	
	Sulphide	DIN 38405 - D 27	3.45	0.54	
Sum parameters	pH	DIN 38404 - C 5	8.01	7.45	-
	Electrical conductivity	DIN EN 27888 - C 8	23.5	91.8	mS/cm
	Redox potential	DIN 38404 - C 6	210	190	mV
	Total hardness	DIN 38409 - H 6	9.08	44.4	mmol/L
	Carbonate hardness	DIN 38409 - H 6	9.08	44.4	mmol/L
	$Ks_{4.3}$	DIN 38409-7 - H 7	56.5	131	mmol/L
	$Kb_{8.2}$	DIN 38409-7 - H 7	0.13	7.39	mmol/L
	TOC	DIN EN 1484 - H 3	840	4060	mg/L
	AOX	DIN EN ISO 9562 - H 14	1710	4310	µg/L
	Dry solids	DIN 38414 - S 2	14000	73300	mg/L
	Loss on ignition	DIN 38414 - S 3	1520	12700	mg/L
	COD	DIN 38409 - H 41	1900	11700	mg/L O_2
	BOD_5	DIN EN 1899-1 - H 51	740	960	mg/L O_2
	Filterable solids	DIN 38409 - H 2	570	1200	mg/L
	Total nitrogen	DIN EN 25663 - H 11	588	3120	mg/L

Table 13. Review of existing literature on nitrification of landfill leachates using various reactor types – studies reporting remarkable nitrification rates

System	Type	Reactor features	Operating conditions	Concentrations (mg/L)	Loading ^{L} or removal ^{R} rate in 1 - g/(m^3·d), 2 - mg/(m^2·d), 3 - mg/(g$_{VSS}$·d)	Removal percentages [4] (%), Concentrations in effluent [5] (mg/L)	Source
Attached growth	Fixed bed reactor	Up-flow biofilter, lab scale, media: crushed bricks	T = 25 °C HRT = 1.4 d	BOD$_7$ = 18 COD: 230-510 NH$_4^+$-N: 60-170	NH$_4^+$-N: 110-130 ^{L1}	NH$_4^+$-N: > 90 [4], < 1.0 [5] COD: 26-62 [4]	[23]
		Up-flow biofilter, pilot scale at landfill site, media: crushed bricks (d$_p$ = 16-32 mm)	T = 5-10 °C HRT = 2.1 d	BOD$_7$ = 5 COD: 1300-1600 NH$_4^+$-N: 160-270	NH$_4^+$-N = 50 ^{L1}	NH$_4^+$-N: > 90 [4], < 1.0 [5] COD: < 5 [4]	[23]
		Down-flow biofilter, lab scale, media: wood chips from compost	T = 25 °C HRT = 7.3 d	BOD$_7$ = 18 COD: 230-510 NH$_4^+$-N: 60-170	NH$_4^+$-N: 100-125 ^{L1}	NH$_4^+$-N: > 90 [4], < 1.0 [5] COD: 0 [4]	[23]
	Moving bed biofilm reactor (MBBR)	Suspended carrier biofilm process (SCBP), lab scale, media: Kaldnes PE carrier (40% fill)	T = 25 °C HRT = 1.6 d	BOD$_7$ = 18 COD: 230-510 NH$_4^+$-N: 60-170	NH$_4^+$-N: 100 ^{L1}	NH$_4^+$-N: > 90 [4], < 1.0 [5]	[23]
		Granular activated carbon Biological fluidised bed, two lab-scale reactors in series (overall loading & removal rates presented here)	T = 20 °C Up-flow velocity = 35 m/h	BOD$_5$: 55-160 COD = 2116 NH$_4^+$-N = 535	NH$_4^+$-N = 357 ^{L1} COD = 1410 ^{L1}	NH$_4^+$-N = 93 [4], 37 [5] COD: 55 [4], 958 [5]	[71]
		SCBP (60% fill), lab scale, media: PE tubes (8 x 8 mm, protected surface = 200 m^2/m^3)	T = 20 °C HRT = 2.0 d	BOD$_7$: 30-140 COD: 800-1300 NH$_4^+$-N: 460-600	NH$_4^+$-N = 266 ^{R1}	NH$_4^+$-N = 97 [4], 17 [5]	[70]
		SCBP (60% fill), lab scale, media: PE tubes (8 x 10 mm, protected surface = 390 m^2/m^3)	T = 20 °C HRT = 2.0 d	BOD$_7$: 30-140 COD: 800-1300 NH$_4^+$-N: 460-600	NH$_4^+$-N = 264 ^{R1}	NH$_4^+$-N = 98 [4], 13 [5]	[70]
		Air lift reactor (10% fill), lab scale, media: macro-porous cellulose cubes (3 mm, 170 m^2/m^3)	T = 20 °C HRT = 0.6 d	BOD$_7$: 30-140 COD: 800-1300 NH$_4^+$-N: 460-600	NH$_4^+$-N = 953 ^{R1}	NH$_4^+$-N = 98 [4], 13 [5]	[70]

System	Type	Reactor features	Operating conditions	Concentrations (mg/L)	Loading [L] or removal [R] rate in 1 - g/(m³·d), 2 - mg/(m²·d), 3 - mg/(g$_{VSS}$·d)	Removal percentages [4] (%), Concentrations in effluent [5] (mg/L)	Source
Attached growth	MBBR	SCBP, pilot scale at dumpsite, media: Natrix 6/6C (60% fill, 210 m²/m³ protected surface)	T = 17 °C HRT = 2.5 d	BOD$_7$: 30-140 COD: 800-2000 NH$_4^+$-N: 400-800	NH$_4^+$-N = 288 [R1]	NH$_4^+$-N: < 10 [5]	[73]
		SCBP, pilot scale at dumpsite, media: Natrix 12/12C (60% fill, protected surface 390 m²/m³)	T = 16 °C HRT = 1.2 d	BOD$_7$: 30-140 COD: 800-2000 NH$_4^+$-N: 400-800	NH$_4^+$-N = 576 [R1]	NH$_4^+$-N: < 10 [5]	[73]
	RBC	Two stage RBC, lab scale, 0.68 m² area, operated with diluted leachate	T = 20 °C HRT = 1.0 d Rotation = 7 rpm	BOD$_5$ = 92 COD = 1154 NH$_4^+$-N = 834	NH$_4^+$-N = 244 [L1] = 3580 [L2]	NH$_4^+$-N: > 99 [4], 0.12 [5]	[72]
		Lab scale RBCs with three stages, 0.187 m² per stage (removal% achieved in first stage presented here)	T = 20 °C HRT = 0.36 d Rotn. = 2.3 rpm	BOD$_5$ = 26 COD = 358 NH$_4^+$-N = 154	NH$_4^+$-N = 432 [L1] = 2600 [L2]	NH$_4^+$-N = 94 [4], 10 [5]	[76]
		Pilot scale under field conditions, three stages	T = 18 °C HRT = 0.31 d Rotation = 6 rpm	BOD$_5$: 27-89 COD: 146-532 NH$_4^+$-N: 83-336	NH$_4^+$-N = 890 [L1] = 4600 [L2]	NH$_4^+$-N = 96 [4]	[53]
	TF	Biofilter with effluent recirculation, pilot scale at landfill site, media: Flocor R (A$_{sp}$ = 230 m²/m³)	T: 0-21 °C HRT: 0.62-4.5 d Irrigation rate = 20 m³m⁻²d⁻¹	cBOD: 32-291 COD: 850-1350 NH$_4^+$-N: 184-520 EC: 11.2-14.0	NH$_4^+$-N: 8.2-70.8 [R1] : 36-309 [R2]	NH$_4^+$-N: 1.0-34 [5]	[50]
Suspended	AS	Aerobic tank and clarifier, pilot scale at the landfill site	T: 0-24 °C HRT: 0.5-8 d MLVSS: 1.4-4.2 g/L	cBOD: 56-290 COD: 850-1350 NH$_4^+$-N: 184-487 EC: 11.2-14.0	NH$_4^+$-N: 17-508 [R1] : 8-131 [R3]	NH$_4^+$-N: < 1.0-19 [5]	[50]

System	Type	Reactor features	Operating conditions	Concentrations (mg/L)	Loading ^{L} or removal ^{R} rate in 1 - g/(m^3·d), 2 - mg/(m^2·d), 3 - mg/(g$_{VSS}$·d)	Removal percentages [4] (%), Concentrations in effluent [5] (mg/L)	Source
Suspended growth	AS	Anaerobic (up-flow biofilm reactor)-aerobic (activated sludge) system, lab-scale	T = 23 ± 2 °C HRT = 4 d	BOD$_5$: 9250-11650 COD: 21300-26940 NH$_4^+$-N: 680-1100	NH$_4^+$-N = 750 ^{L1} = 500 ^{R1}	NH$_4^+$-N = 67 [4]	[51]
		Continuous activated sludge system with clarifier, lab-scale	HRT = 0.53 d SRT = 50 d TSS = 20 g/L	BOD$_5$: 107-480 COD: 3225-5925 NH$_4^+$-N: 1080-2350 Cl$^-$: 2870-3850	NH$_4^+$-N = 2560 ^{L1} = 229 ^{R3} BOD = 590 ^{L1}	NH$_4^+$-N: 99 [4], < 10 [5] BOD$_5$: 85-95 [4], 6-36 [5]	[52]
	Sequencing batch reactor	Pilot scale under field conditions	T = 20 °C HRT = 0.7 d MLSS = 1.1 g/L	BOD$_5$: 27-89 COD: 146-532 NH$_4^+$-N: 83-336	NH$_4^+$-N = 343 ^{L1} = 510 ^{L3}	NH$_4^+$-N = 93 [4]	[53]
		Lab scale single sludge nitrification-denitrification reactor without intentional sludge wastage	T = 20 ± 2 °C HRT = 1.82 d MLVSS = 8 g/L	BOD$_5$: 50-240 COD: 850-1600 NH$_4^+$-N: 1635-1810 Cl$^-$: 2600-4200	NH$_4^+$-N = 120 ^{L3}	NH$_4^+$-N: > 95 [4], < 5 [5]	[117]
		Bench scale reactors operated over 2 years without sludge wastage	T = 22 ± 2 °C HRT = 0.21 d MLSS = 9.6 g/L	BOD$_5$ = 60 COD = 1100 NH$_4^+$-N = 880	NH$_4^+$-N = 5910 ^{R1} = 880 ^{R3}	-	[54]

T - temperature
TF - trickling filter
AS - activated sludge
TSS - total suspended solids
HRT - hydraulic retention time
GAC - granular activated carbon
RBC - rotating biological contactor
EC - electrical conductivity (mS/cm)
MLVSS - mixed liquor volatile suspended solids

Table 14. Raw data – concentrations of nitrogen species (as mg N/L) in the feed reservoir and reactor effluent from the initial trials during continuous operation [Clay beads packing (left) and PE carrier media (right)].

Time (d)	$N-NH_4^+$ feed	$N-NO_3^-$ effl.	$N-NO_2^-$ effl.	$N-NH_4^+$ effl.	Time (d)	$N-NH_4^+$ effl.	$N-NO_3^-$ effl.	$N-NO_2^-$ effl.	$N-NH_4^+$ effl.
0.00	345			11	0.00	345			49.6
0.09	301			11	0.09	326			47.7
1.05	414			19	1.05	438			167
3.99	417			35	3.99	285			102
5.07	320			49	5.07	153			65.2
5.16	320			33	5.16	153			46.5
7.08	434			29	7.08	227			56.1
7.16	434			29	7.16	227			44.1
7.99	406			56	7.99	294			47.3
8.11	406			55	8.11	294			39.2
11.07	457			115	11.07	216			46.3
11.99	442			15	11.99	219			94.8
12.11	442			9	12.11	219			159
12.99	427	91		141	12.99	226	155		77.0
13.11	427	156		143	13.11	226	121		56.2
19.97	513			148	19.97	252			60.2
20.05	513			160	20.05	252			54.3
20.99	419			78	20.99	213			35.6
21.06	419			77	21.06	213			41.2
22.09	399			46	22.09	219			30.9
24.99	378	193		163	24.99	404	215		76.8
25.14	378	206		153	25.14	404	218		149
25.99	461	179		182	25.99	427	183		202
26.10	461			205	26.10	427			216
26.99	403			172	26.99	424			215
27.10	512			159	27.10	424			190
28.08	381			104	28.08	438			216
28.98	426			124	28.98	449			210
29.09	426			119	29.09	449			217
35.02	446			23	35.02	506			362
35.99	399			20	35.99	534			421
42.97	527			53	42.97	530			461
46.08	477	86		30	46.08	495	96		298
46.97	447	210		14	46.97	442	187		213
47.07	447			12	47.07	442			193
47.97	364	214		5	47.97	430	260		133
48.95	366			5	48.95	549			135
49.08	366			2	49.08	549			172
49.99	380			3	49.99	415			240
53.10	429	132		29	53.10	433	111		132
55.99	534			89	55.99	406			81.0
56.99	403			98	56.99	432			196

Time (d)	N-NH$_4^+$ feed	N-NO$_3^-$ effl.	N-NO$_2^-$ effl.	N-NH$_4^+$ effl.
60.97	438			26
61.98	447			48
62.09	447			39
66.98	428			51
67.97	402			82
68.07	402			70
69.00	435			99
69.14	435			82
69.99	441			111
70.09	441			111
70.98	399			53
74.02	391			110
74.08	391			115
74.96	414			102
75.02	414			124
75.96	470			221
82.00	419			199
82.97	518			233
83.11	518			227
83.98	518			72
84.09	518			56
88.97	439	460		40
89.08	439			167
89.96	488	420		176
90.03	488			155
90.97	451		126	35
91.09	451		94.1	27
91.97	550	468	29.9	15
92.08	550			25
94.98	506		431	15
95.07	506			19
95.99	505			11
96.08	505			11
96.97	471			20
97.09	471			19
97.97	475			23
98.08	475			19
98.97	495	452		17
99.09	495			19
102.94	387		35.9	22
103.03	387			21
104.99	438			35
105.09	438			38
105.96	436	429		43

Time (d)	N-NH$_4^+$ effl.	N-NO$_3^-$ effl.	N-NO$_2^-$ effl.	N-NH$_4^+$ effl.
60.97	443			14.0
61.98	413			8.0
62.09	413			6.5
66.98	427			4.8
67.97	443			5.1
68.07	443			8.6
69.00	522			10.3
69.14	522			8.1
69.99	340			3.5
70.03	340			3.9
70.09	340			5.0
70.14	340	264		2.9
70.18	374	264		3.2
70.98	374	406	8.0	4.8
71.03	374	398	9.5	4.3
71.09	374	419	9.1	6.1
71.14	374	418	12.2	6.5
71.18	388	430		5.5
71.26	388			6.0
71.90	388			15.4
71.99	358			15.7
72.08	358	420		12.5
72.24	358	420		11.4
72.49	357	386		8.9
72.90	357	363		10.1
73.16	357			5.3
73.26	415	332		5.5
73.39	415			4.2
74.02	415	320		6.0
74.08	415	332		6.3
74.96	415			1.4
75.02	415			2.0
75.96	404			2.0
81.91	404	395		2.2
82.00	404			2.2
82.97	404	349		1.9
83.11	404			2.7
83.98	428	368		1.2
84.09	428			3.0
88.97	923	334		45.6
89.08	923			56.5
89.96	888	353		49.3
90.03	888			45.4
90.97	871		136	57.8

Time (d)	N-NH$_4^+$ feed	N-NO$_3^-$ effl.	N-NO$_2^-$ effl.	N-NH$_4^+$ effl.
106.08	436			34
108.95	379		33.5	22
109.07	379			21
110.96	372	460	31.9	35
111.07	372			43
111.96	469		4.3	82
112.08	469			87
113.00	364		6.9	83
113.10	364			78
115.94	443	307	5.4	90
116.02	443			142
116.95	558		7.1	159
117.08	558			186
118.96	633	276	4.8	162
119.07	633			231
119.99	587		4.9	260
120.07	587			258
122.07	593		2.2	326
122.98	588	296	2.4	380
123.08	588			339
123.98	729		2.0	360
124.98	787	279	3.2	401
125.09	787			429
126.98	757	261	2.8	446

Time (d)	N-NH$_4^+$ effl.	N-NO$_3^-$ effl.	N-NO$_2^-$ effl.	N-NH$_4^+$ effl.
91.09	871		533	82.4
91.97	910	221	557	127
92.08	910			168
94.98	848		437	344
95.07	848			403
95.99	852	184	557	155
96.08	852			140
96.97	946			174
97.09	946			193
97.97	401		304	28.8
98.08	401			18.0
98.97	571	451		19.1
99.09	571			14.9
102.94	474	486	17.3	12.1
103.03	474			10.8
104.99	433		11.8	16.4
105.09	433		10.9	13.0
105.96	411	469	10.7	19.7
106.08	411			16.0
108.95	383		4.3	11.8
109.07	383			11.9
110.96	367		1.7	11.3
111.07	350			10.9
111.96	396		5.3	18.8
112.08	367			14.2
113.00	387		1.3	9.7
113.10	387			5.5
115.94	363	401	7.9	25.1
116.02	363			49.6
116.95	359		9.3	37.4
117.08	359			34.4
118.96	406	415	6.8	19.1
119.07	406			15.5
119.99	356		5.6	14.0
120.07	356			10.4
122.07	362		6.2	7.0
122.98	363	429	6.1	6.8
123.08	363			6.2
123.98	367		3.4	7.4
124.98	383	408	7.0	6.0
125.09	383			6.6
126.98	356	424	4.1	9.4

Table 15. Raw data – concentrations of nitrogen species (as mg N/L) and TOC (mg/L) in the feed reservoir and reactor effluent during the continuous flow trials for studying the effect of chloride content.

Time (d)	Clay beads PBR						PE carrier PBR					
	NH_4^+ res	NO_3^- out	NO_2^- out	NH_4^+ out	TOC res	TOC out	NH_4^+ res	NO_3^- out	NO_2^- out	NH_4^+ out	TOC res	TOC out
131.93	428	291	4.9	118		25	390	321	1.5	23		52
132.93	464		5.2	121		19	414		0.8	2.4		45
133.97	502		7.9	154			381			3.7		
134.98	459		4.6	141			388			1.8		
137.93	471	271	4.3	79		21	369	329	1.3	3.9		50
138.95	497		4.3	91			338		0.7	4.2		
139.88	332		4.3	108			366			4.8		
140.97	435		4.3	79		36	356			4.5		
141.97	465	329	3.2	79			356	313	8.7	4.9		
144.95	418		3.6	80		29	318			4.8		53
147.86	423	313	4.2	86		26	341	200	117	14		43
148.88	408	307	4.2	45		30	482	268	39	40		116
153.80	360		6.3	47		24	519		35	216		103
154.86	447		5.3	88			502		100	201		945
155.88	393		5.3	114		30	494		132	181		103
160.85				136		37				103		117
161.86	406		4.6	115		26	495		174	72		113
162.07										63		
162.82	471	295	4.7	191			475	305	114	13		
165.86	439		4.5	123		32	508		173	12		127
166.88	419	266	4.3	124		11	476	274	170	10		99
168.83	403			123			448			7.8		79
170.01	446	167	4.5	124			465	258	183	8.8		70
172.91	438			128			452			6.2		72
174.07	425	171	5.1	136			468	187	162	6.4		66
177.07				108						6.4		58
177.97	369	305	4.7	102			388		210	9.1		66
179.05	397	265	5.0	105			440	215	109	5.2		59
179.97	417	260	5.1	123			462	267	193	5.0		66
180.96	458	199	5.0	158			511	301	158	3.9		61
181.94	435	273	5.0	135	0.0	33	514	438	19	2.3	94	87
182.83	445	283	6.0	136			503	453	3.1	1.9	93	59
183.89	408		5.9	125			362		1.8	1.9	92	55
185.03	436		5.7	146			401				87	93
186.07	458	233	4.8	159			440	369	4.5	3.0	100	64
186.92	454	230	4.8	173			428	305	56	6.2	108	64
188.02	442	229	4.5	173			405	294	65	3.4	128	63
188.88	438	246	4.6	170			444	289	62	4.2	131	67
189.79	446	221	5.1	169			447	399	57	9.2	119	57
190.84	439	49	8.4	347	158	143	450	268	65	9.3	163	93

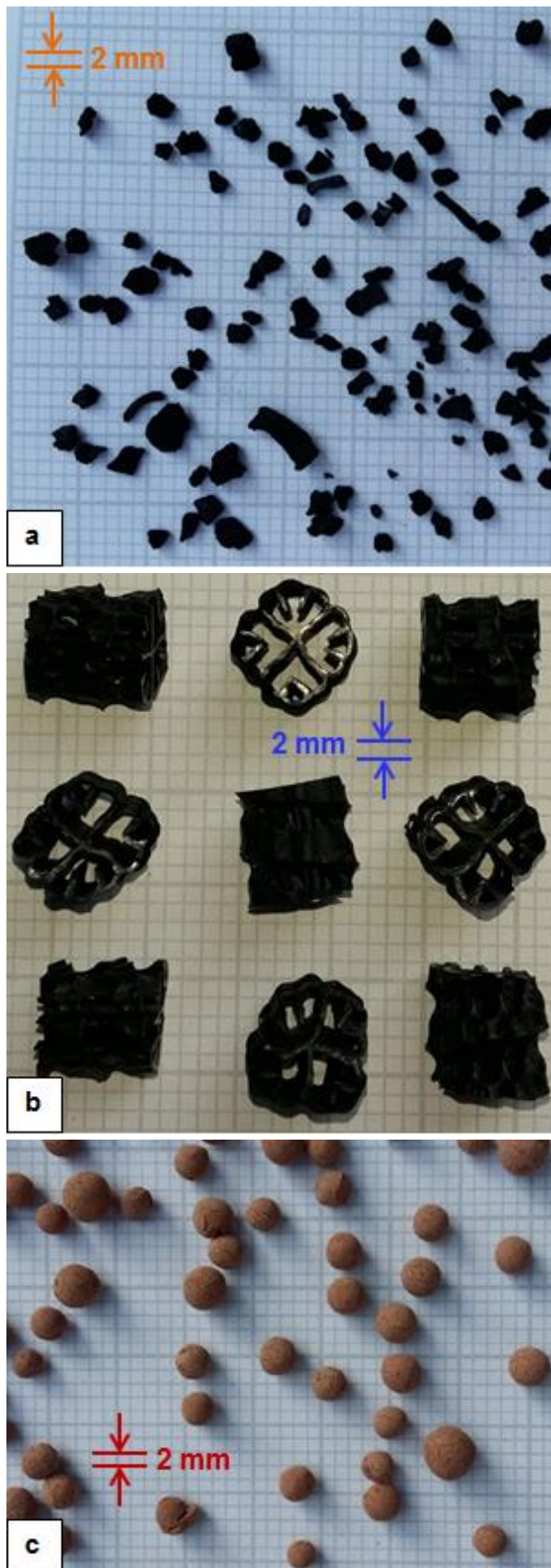| Time (d)	Clay beads PBR						PE carrier PBR					
	NH_4^+ res	NO_3^- out	NO_2^- out	NH_4^+ out	TOC res	TOC out	NH_4^+ res	NO_3^- out	NO_2^- out	NH_4^+ out	TOC res	TOC out
192.05	453		8.1	430	150	126	449		83	15	161	88
192.92	459	10	8.3	435	155	123	451	254	114	7.7	153	94
194.00	424	11	8.3	433	157	124	423	243	123	6.9	158	96
194.88	454	15	7.8	429	161	133	450	240	128	7.1	157	95
195.96	472	28	7.6	426	152	118	458	265	96	10		
196.76	466	66	6.3	376	165	97				11		
196.96							459	216	137	6.2	167	96
197.90	466		5.2	311	13	36	497		130	7.5	145	94
200.82	435	183	4.8	214	8.2	25	464	270	95	7.1	138	91
201.95	411	200	4.3	176	3.0	25	451	268	82	6.6	160	92
202.79	440	205	4.3	161	6.0	24	428	254	96	11	127	88
203.90	402	242	4.0	138	14	30	469	275	79	11	119	90
204.93	448		3.5	128	16	29						
206.00	457	255	3.9	135	8.3	21	464	264	90	12	130	89
207.86	422		4.2	118	13	29	434			8.8	127	100
208.08				118	13	44				7.9	127	88
208.85	428	223		126	17	29	410	323	24	7.2	127	82
209.90	407	248	3.8	134	21	29	432	379	13	6.0	118	88
210.88	425	266	4.1	114	17	37	448	359	6.6	4.3	137	97
211.80	425	267	3.9	103	34	80	429	376	2.9	4.2	137	110
214.38	421			105								
215.88	421	281	3.7	118	33	53						
216.78	439	228	3.5	122	18	20						
216.95	440			114	18	22						
217.86	439	229	3.5	128		21						
218.97				125		24						
219.95	417	238	3.5	127	19	23						
222.83	422	218	3.7	162	12	30						
222.95				158		27						
223.82	448	239	3.3	152	4.8	21						
224.85	459	206	3.5	173	6.9	17						
224.94				172		25						
225.06				169		19						
225.79	448	212	3.9	183	32	32						
226.01				177		23						
226.30				180		26						

APPENDIX B - FIGURES

Figure 27. Photographs of virgin packing materials: (a) coke, (b) PE carrier and (c) clay.

Courtesy:
a - Sruthi Kalyanasundaram
b - Mohamad S. Mahmood
c - Imke Hollander

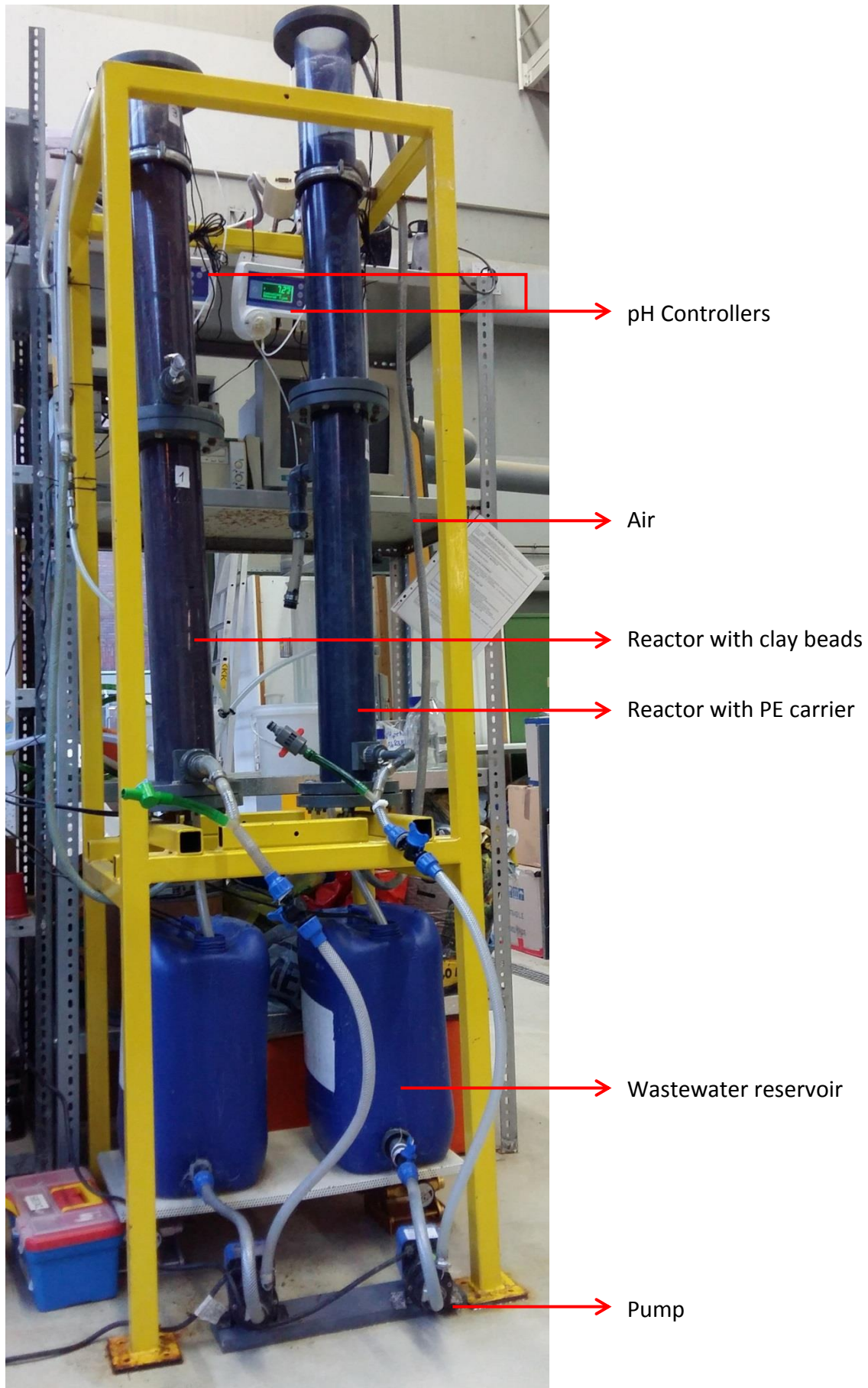**Figure 28. Photographs of the reactor setup used for the lab-scale batch trials.**

Figure 29. Photograph of the setup used for validation of nitrification rates (before transiting to continuous mode).
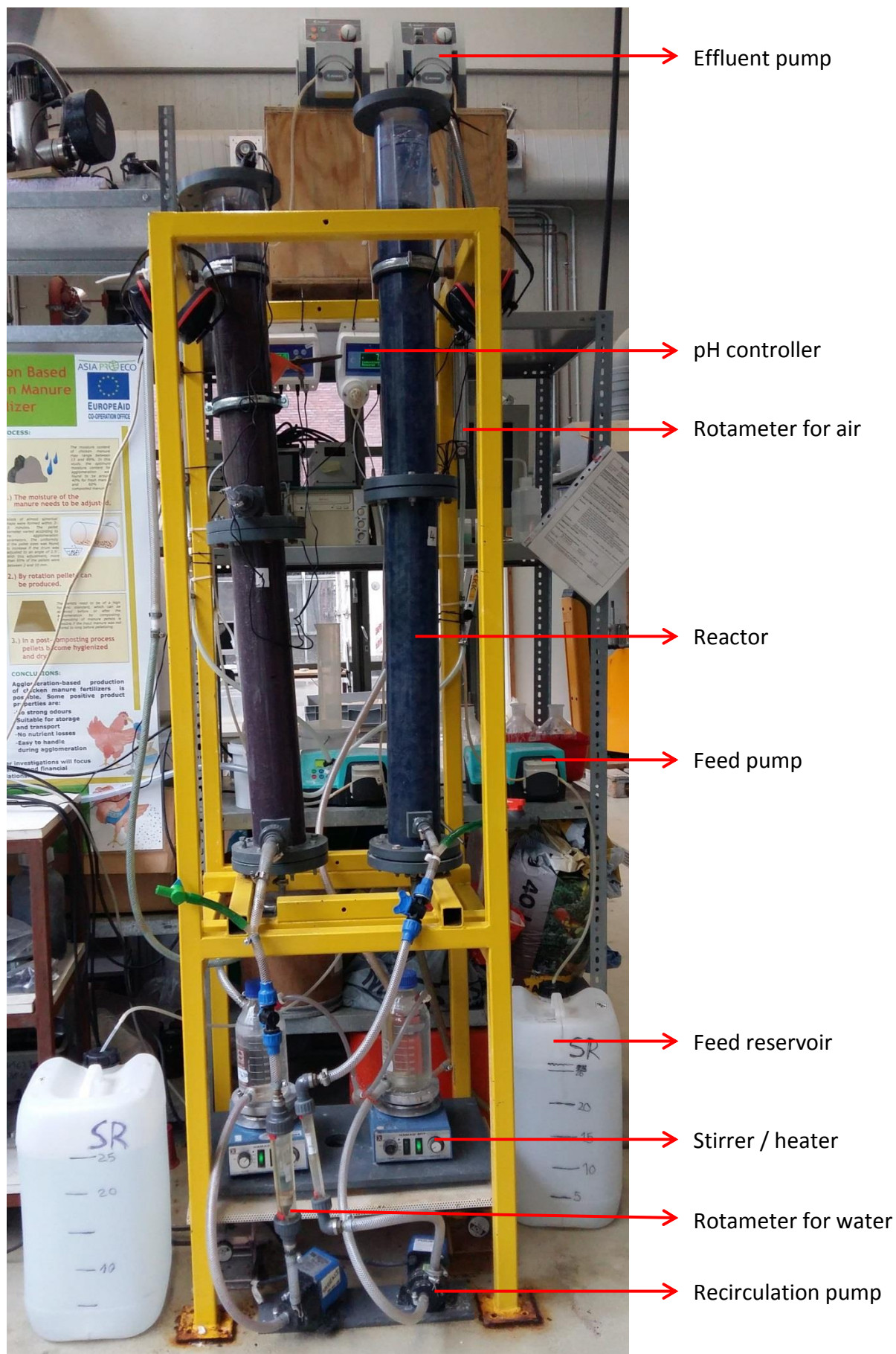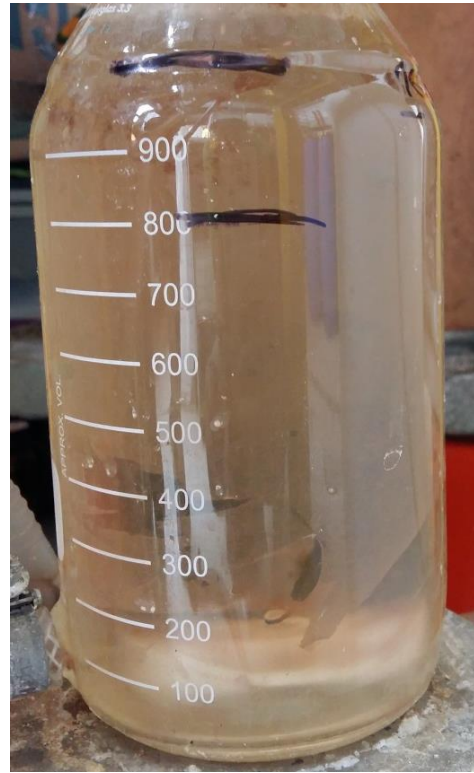
Figure 30. Photograph of the continuous flow experimental setup.

Figure 31. Photograph of rubber air diffusers introduced into the reactors.

Schott bottle - on day 117

Schott bottle - on day 19 0

Backwash water - on day 117

Backwash water - on day 210

Water rotameter - on day 210

Figure 32. Photographs from the PE carrier-filled PBR system portraying the proliferation of heterotrophic organisms.

APPENDIX C - UNDERSTANDING THE EFFECT OF UP-FLOW VELOCITY

This section explains the influence of water velocity on the nitrification efficiency of packed bed reactors. As a part of a sub-study of the research project, nitrification experiments were carried out using a set of 10 PBRs in series (see experimental setup in Figure 33) inspired from a previous work at TUHH [89]. The goals behind this sub-study were: to characterise the change in $N-NH_4^+$ concentration per unit reactor length; to investigate the effect of parameters: pH and up flow velocity; and to gather more experimental data with NF permeate (thereby enhancing reproducibility). Only the results from the trials aimed at studying the effect of water flow rate will be presented here.
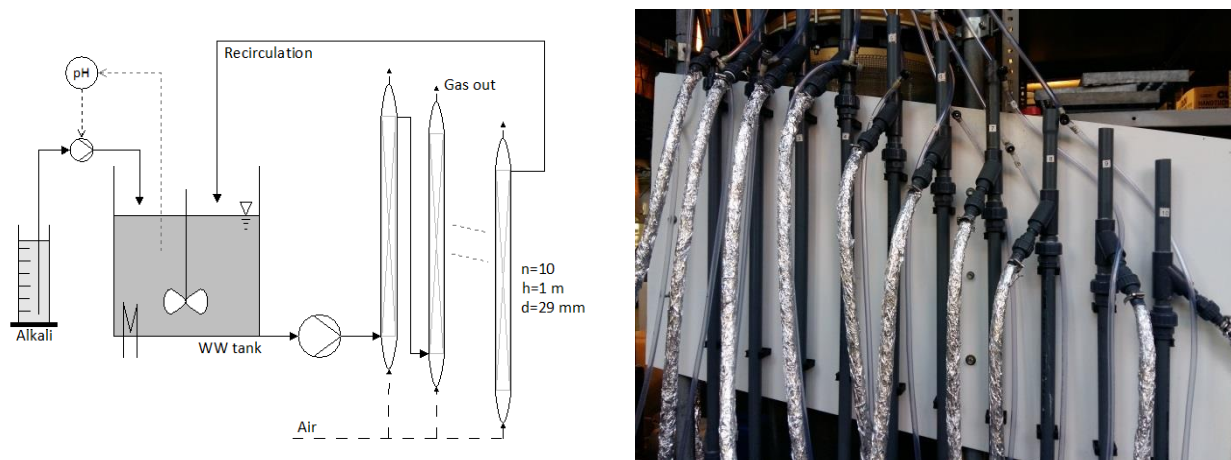

Figure 33. Schematic of the experimental setup used (left) and photograph of the reactor cascades (right).

The setup consisted of: a 50 L tank (equipped with an overhead mixer, an aquarium heater to maintain a temperature of 25 ± 1°C and a Bluelab pH controller maintaining the pH at 7.8 ± 0.1); an adjustable peristaltic pump; ten PBRs (made out of 32 x 1.6 mm PVC pipes, each 1 m long and filled with PE carrier, offering a reactor volume of 6.5 L in total); and provision for aeration (DO was maintained at 3.0 ± 0.2 mg/L). The PVC hose directing the wastewater from one column to the next were wrapped in aluminium foil (photograph, Figure 33) to prevent the growth of algae inside them. Duplicate trials were conducted in batch mode with dilutions of NF permeate (50 L wastewater having initial concentrations of about 170 mg NH_4^+-N/L) at up-flow velocities of 5, 12, 20 and 25 m/h (keeping all other parameters constant). Samples were taken from the reservoir and analysed for $N-NH_4^+$ concentration.

Figure 34 shows the calculated average values (n=2) for ammonia removal or nitrification rates plotted against the up-flow velocities (used in the respective trials). Although the biofilm was not yet mature[§], a positive relationship between ammonia removal rate and water velocity becomes obvious from the plot.

[§] Nevertheless, these trials were conducted within a short span of time (with each batch lasting less than 4 days) making the obtained results comparable.
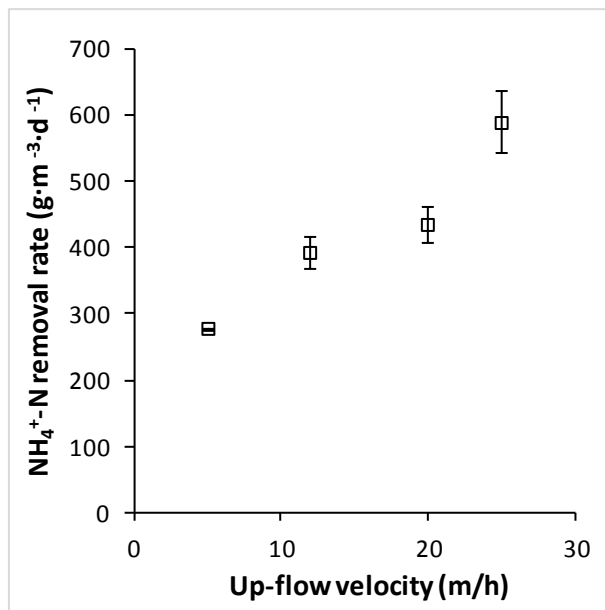
Figure 34. Dependence of volumetric nitrification rate on up-flow velocity.

Bédard [80] reviewed the enhancements achieved in the maximum loading rates (for carbon, nitrogen and suspended removals) with increase in water velocity in biological aerated filters. Particularly, Peladan et al. [83] demonstrated the possibility to achieve nitrification rates as high as 2.7 $kg \cdot m^{-3} d^{-1}$ (compared to conventional eliminated loads of up to 1.2 $kg \cdot m^{-3} d^{-1}$ with hydraulic loads ranging between 1 and 10 $m^3 \cdot m^{-2} \cdot h^{-1}$ [80]) when higher water velocities (from 15 to 30 m/h) were used. Previous research ([130,131] according to [80,83]) showed an improvement in transfer of substrate and oxygen from the bulk liquid to the biofilm as well as a more even distribution of biomass in the bed with increase in water up-flow velocity.

APPENDIX D - TRIALS WITH SEQUENCING BATCH REACTORS

To validate the nitrification inhibition caused by the organic compounds contained in the RO concentrate, batch experiments were conducted parallelly using two identical sequencing batch reactor (SBR) setups (see Figure 35). Reactors R1 and R2 were operated with dilutions of RO retentate and NF permeate (composition in Table 3), respectively. A series of experiments (at different initial N-NH$_4^+$ concentrations, with each trial performed in duplicate) were conducted (over a period of 4 weeks) in SBR fashion (Figure 36 illustrates SBR operation).
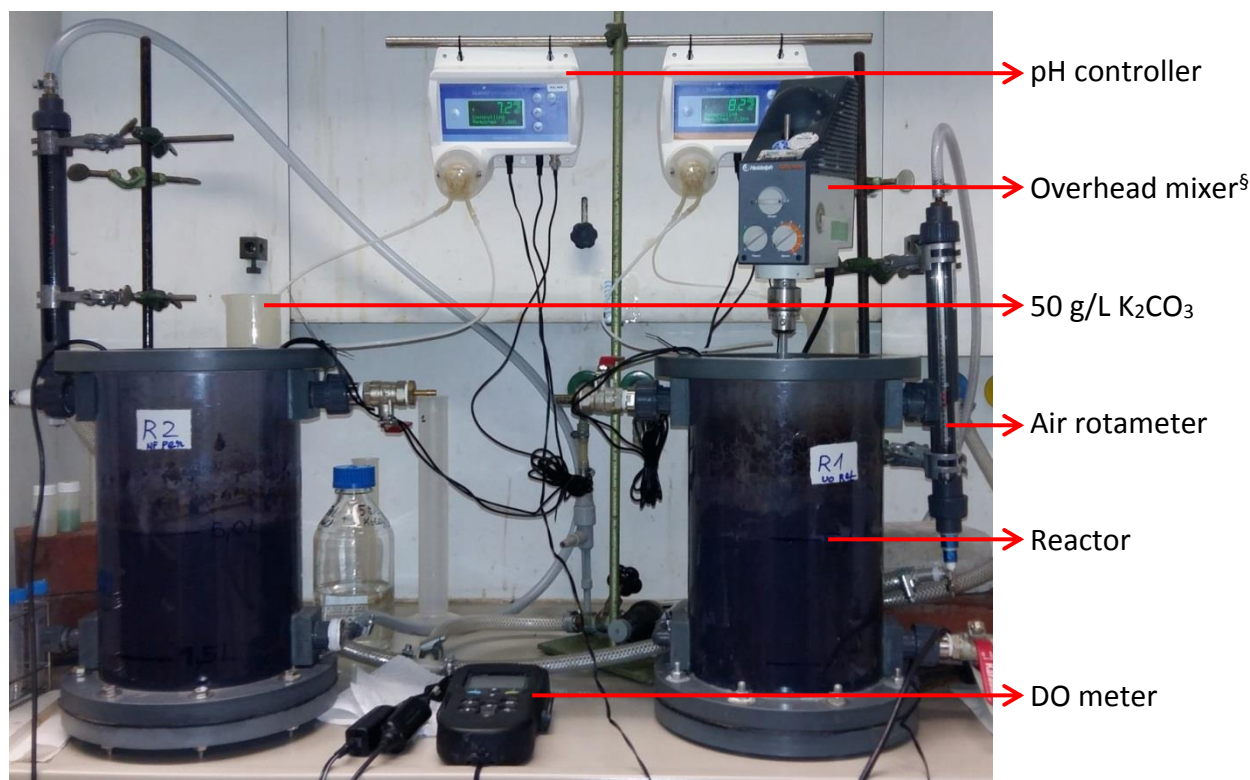

Figure 35. Photograph of experimental setup used for sequencing batch reactor studies.

The start N-NH$_4^+$ concentration was increased from about 50 mg/L to 600 mg/L in small steps, in which the organic load in reactor R1 also increased gradually. This was achieved (at the start of each batch) by adding calculated volumes of RO concentrate or NF permeate, respectively and deionised water into the reactors containing residual sludge (after pump out phase performed every weekday morning).

During nights and weekends, reactor R2 was left with the residual mixture from the respective weekday and the solution of pH controller was changed from 50 g/L K$_2$CO$_3$ solution to a feed solution (a solution of 2.5 g/L NH$_4$Cl and 15 g/L K$_2$CO$_3$ in deionised water), thereby maintaining the pH and ensuring the availability of substrate all the time. This change of pH controller solution was (mostly) not practised for reactor R1 (except for initial batches where start N-NH$_4^+$ concentrations were low) since it was assumed that the reactor could sustain itself

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§ To counter the foaming caused due to the organics in RO concentrate and subsequent floating of biomass.

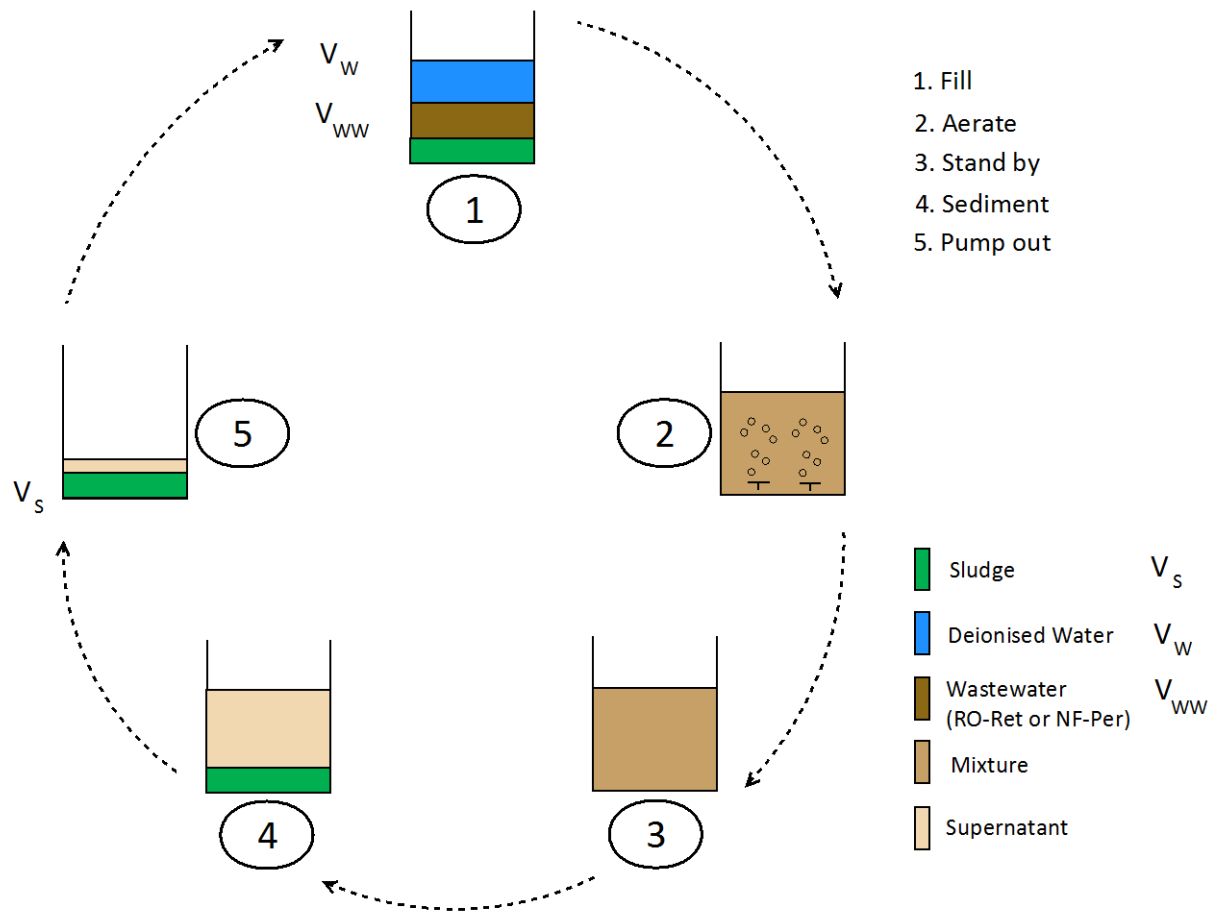with the residual mixture until next weekday morning (due to its observed lower ammonia oxidation rates).

V_w

V_{ww}

1. Fill
2. Aerate
3. Stand by
4. Sediment
5. Pump out

5

V_s

2

	Sludge	V_s
	Deionised Water	V_w
	Wastewater (RO-Ret or NF-Per)	V_{ww}
	Mixture	
	Supernatant	

4

3

Figure 36. Illustration of sequencing batch reactor operation.

Operating conditions such as mixed liquor suspended solids (about 3 to 4 g/L) and DO concentration (about 3 mg/L), pH (controlled at 7.2) and temperature (ambient ≈ 22°C) were maintained alike in both setups. To estimate the ammonia oxidation rates, samples were taken regularly throughout the day from each reactor and analysed for $N-NH_4^+$ concentration. Selected samples from some trials were also analysed for TN concentration to confirm that ammonia was not getting stripped.

Figure 37 compares the observed trends for ammonia removal (for selected batches) in dilutions of NF permeate and RO retentate at similar NH_4^+-N initial concentrations. The desired start concentrations for these trials were 50, 200 and 300 mg/L (Figure 37a), and 400 and 600 mg/L (depicted in Figure 37b). It can be readily seen that nitrification in RO retentate medium was slower compared to that in NF permeate. From batch to batch, there was an accumulation of $N-NH_4^+$ in reactor R1 (fed with RO retentate), since its ammonium removal rates were lower in comparison to R2. As a result, the actual starting concentrations in R1 were steadily positively deviating from the desired values, which were matching very well with the material balance calculations (based on the residual $N-NH_4^+$ concentration, mixture volume after pumping out, and the amount of freshly added RO retentate).
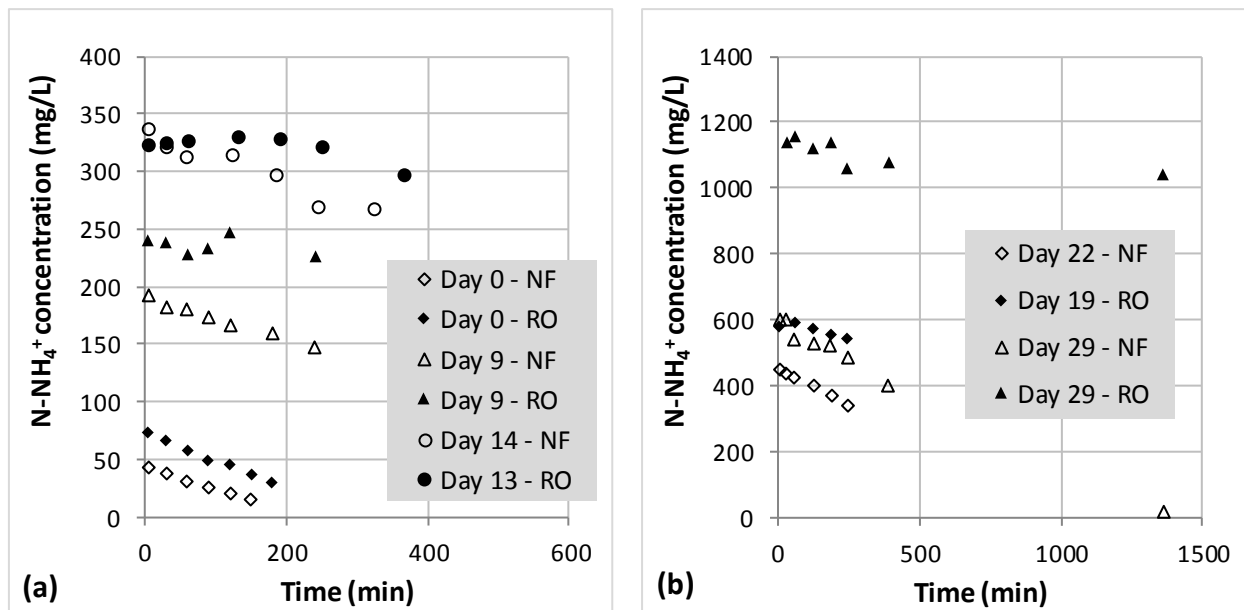
Figure 37. Comparison of ammonia removal using SBRs in different dilutions of NF permeate and RO concentrate at similar N-NH$_4^+$ start concentrations.

Figure 38a and b show the ammonium-nitrogen removal rates from all batches plotted against time and initial concentration, respectively. From the values of TN concentrations measured for selected trials, which stayed nearly constant during the batches, it was confirmed that ammonia was not getting stripped. Initially, both systems showed a decline in oxidation rates with decrease in dilution factors, which could likely have been due to the stress resulting from the differences in feed composition (i.e. leachate matrix compared to municipal wastewater). Nijhof and Bovendeur [121] reported an initial decline followed by an acclimatisation when nitrifying biofilter treating freshwater was exposed to seawater. The salinity in both SBRs increased gradually from about 1.5 mS/cm in the beginning (compared to typically less than 1 mS/cm in municipal wastewaters [132,133]) to about 20 mS/cm by day 30.

It can be seen that the nitrifiers were able to acclimatise to the higher salinity content of the feed waters, since the ammonia removal rates started to increase after a period of about 7 days (Figure 38a). Especially in reactor R2 (operated with dilutions of NF permeate), the nitrifying organisms thrived with time; leading to a steady increase in ammonia removal rates. Stepwise multiple regression analyses (using SPSS software with removal rate as dependent variable, and initial concentration and time as predictors) for both reactors revealed that: (1) the removal rate in reactor R2 was only time dependent (the non-dependence on concentration, also visible from the scattering in Figure 38b and reported in literature [108,109]), and (2) the removal rate in reactor R1 was not significantly correlated to time or initial NH$_4^+$-N concentration.

The nitrification rates in dilutions of RO concentrate were significantly lower than that in dilutions of NF permeate. The rates in the former were about 34 to 83% smaller compared to the latter, with the difference gradually becoming larger with increase in organic load (which increased with increase in N-NH$_4^+$ concentration). The inhibition due to organics contained in RO retentate thus becomes evident without doubt. Other operating problems in the reactor

operated with RO retentate included: intensive foaming, rise in pH during operation (up to about 8.5) and sludge bulking. In contrast, the sludge in the reactor fed with NF permeate was well settleable.
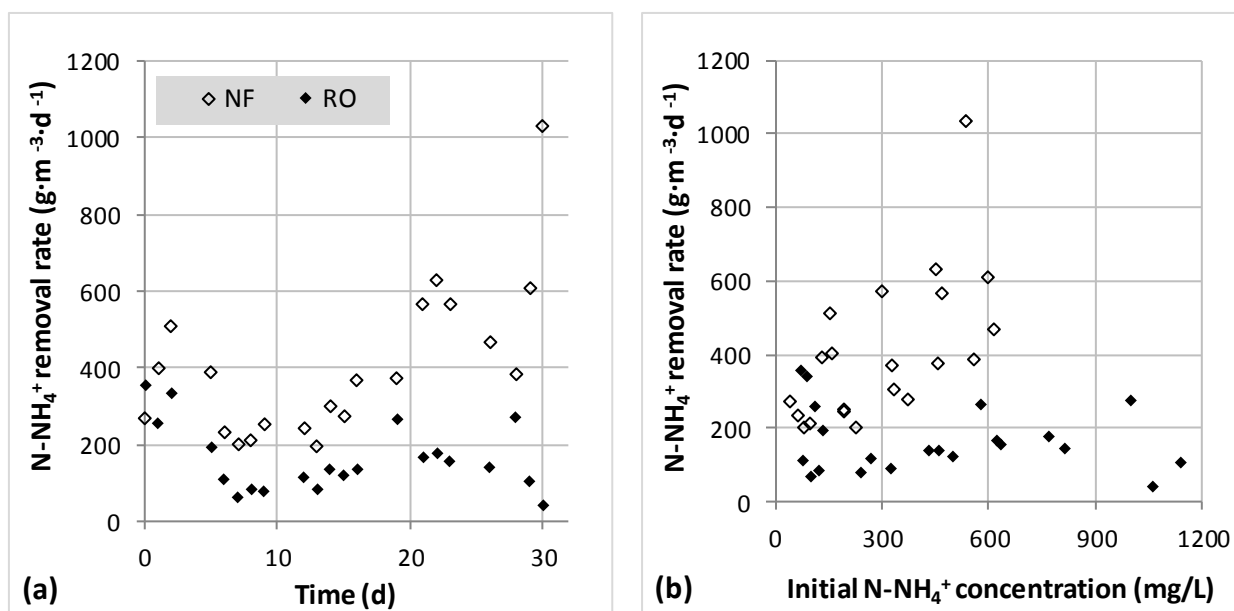

Figure 38. Comparison of ammonia removal rates in dilutions of NF permeate and RO retentate using SBRs.

To see if the nitrifying organisms in reactor R1 could recover when the stress due to organics is removed; the sub-study was concluded by performing five more batches (totalling to 37 days of operation from the beginning) with the setups, wherein both reactors were fed with NF permeate to obtain start $N-NH_4^+$ concentrations of about 100 mg/L. Prior to conducting these trials, reactor R1 was flushed multiple times (by filling with deionised water, mixing shortly, sedimenting and pumping out) to lower the organics content. Nevertheless, the ammonia removals rates in R1 did not improve and were found to be 41 ± 32 $g \cdot m^{-3} \cdot d^{-1}$ (which also matches the observed declining trend in removal rate during the last batches, to be seen in Figure 38a). On the other hand, the ammonia oxidation rates in reactor R2 during these trials were 441 ± 54 $g \cdot m^{-3} \cdot d^{-1}$ (n=5). These relatively high rates in reactor R2 (after 37 days of operation) when compared with the rate of about 208 $g \cdot m^{-3} \cdot d^{-1}$ observed on 7th and 8th days of operation (conducted also with about 100 mg NH_4^+-N/L batch concentrations) confirms the acclimatisation of the biomass during the study period (in other words, the dependence of removal rate on adaptation time and the non-dependence on initial NH_4^+-N concentration).

APPENDIX E - OPENMODELICA CODE FOR CONTINUOUS OPERATION

```
package Continuous_Mode
 class Nitrogen
   Real NH4, NO3, TN;    /* all in mg N/L */
 end Nitrogen;

 class Inert
   Real Na, Cl;     /* all in mg/L */
 end Inert;

 connector FlowInfo
   input Real Q;
 end FlowInfo;

 connector Pipe
   Real T;
   flow Real Q "L/h";
   input Nitrogen N;
   input Inert I;
 end Pipe;

 model Feed
   Nitrogen N;
   Inert I;
   parameter Real Q = 0.907 "L/h";
   Pipe Out1;
   FlowInfo FI;
 equation
   N.NH4 = 400;
   N.NO3 = 0;
   N.TN = N.NH4 + N.NO3;
   I.Na = 1934;
   I.Cl = 4000;
   Out1.Q + Q = 0;
   Out1.T = 20;
   Out1.N = N;
   Out1.I = I;
   FI.Q = Q;
 end Feed;
```

```
model Buffer "200 g/L Na2CO3 solution"
 Nitrogen N;
 Inert I;
 parameter Real Q = 0.013 "L/h";
 Pipe Out1;
 FlowInfo FI;
equation
 N.NH4 = 0;
 N.NO3 = 0;
 N.TN = 0;
 I.Na = 86792;
 I.Cl = 0;
 Out1.Q + Q = 0;
 Out1.T = 20;
 Out1.N = N;
 Out1.I = I;
 FI.Q = Q;
end Buffer;

model Mixer
 Pipe In1, In2 "buffer", In3 "recirculation", Out1;
 parameter Real u = 18 "up flow velocity in m/h";
 parameter Real A = 3.14159 * 0.1 * 0.1 / 4 "cross sectional area of reactor in m2";
equation
 Out1.T = In1.T;
 Out1.Q + u * A * 1000 = 0;
 Out1.Q * Out1.N.NH4 + In1.Q * In1.N.NH4 + In2.Q * In2.N.NH4 + In3.Q * In3.N.NH4 = 0;
 Out1.Q * Out1.N.NO3 + In1.Q * In1.N.NO3 + In2.Q * In2.N.NO3 + In3.Q * In3.N.NO3 = 0;
 Out1.Q * Out1.N.TN + In1.Q * In1.N.TN + In2.Q * In2.N.TN + In3.Q * In3.N.TN = 0;
 Out1.Q * Out1.I.Na + In1.Q * In1.I.Na + In2.Q * In2.I.Na + In3.Q * In3.I.Na = 0;
 Out1.Q * Out1.I.Cl + In1.Q * In1.I.Cl + In2.Q * In2.I.Cl + In3.Q * In3.I.Cl = 0;
end Mixer;

model Splitter
 FlowInfo feed, buffer;
 Pipe In1, Out1, Out2 "recirculation";
equation
 Out1.T = In1.T;
 Out2.T = In1.T;
 Out1.Q + feed.Q + buffer.Q = 0;
 In1.Q + Out1.Q + Out2.Q = 0;
 Out1.N.NH4 = In1.N.NH4;
```

```
  Out1.N.NO3 = In1.N.NO3;
  Out1.N.TN = In1.N.TN;
  Out1.I.Na = In1.I.Na;
  Out1.I.Cl = In1.I.Cl;
  Out2.N.NH4 = In1.N.NH4;
  Out2.N.NO3 = In1.N.NO3;
  Out2.N.TN = In1.N.TN;
  Out2.I.Na = In1.I.Na;
  Out2.I.Cl = In1.I.Cl;
end Splitter;

model Reactor
  Pipe In1, Out1;
  parameter Real A = 3.14159 * 0.1 * 0.1 / 4 "cross sectional area in m2";
  parameter Real z = 1.2 "height of the reactor in m";
  Real V;
  parameter Real ARR = 900 / 24 "nitrification rate in mg/(L.h)";
  Nitrogen N;
  Inert I;
initial equation
  N.NH4 = 10;
  N.TN = 10;
  N.NO3 = 0;
  I.Na = 0;
  I.Cl = 25;
equation
  V = A * z * 1000 "in L";
  V * der(N.NH4) = In1.Q * (In1.N.NH4 - N.NH4) - ARR * V;
  V * der(N.NO3) = In1.Q * (In1.N.NO3 - N.NO3) + ARR * V;
  N.TN = N.NH4 + N.NO3;
  V * der(I.Na) = In1.Q * (In1.I.Na - I.Na);
  V * der(I.Cl) = In1.Q * (In1.I.Cl - I.Cl);
  In1.Q + Out1.Q = 0;
  Out1.T = In1.T;
  Out1.N = N;
  Out1.I = I;
end Reactor;

model Sink
  Pipe In1;
end Sink;
```

```
   model Main
    Feed feed;
    Buffer buffer;
    Mixer mixer;
    Reactor reactor;
    Splitter splitter;
    Sink sink;
   equation
    connect(feed.Out1, mixer.In1);
    connect(buffer.Out1, mixer.In2);
    connect(splitter.Out2, mixer.In3);
    connect(mixer.Out1, reactor.In1);
    connect(reactor.Out1, splitter.In1);
    connect(splitter.Out1, sink.In1);
    connect(feed.FI, splitter.feed);
    connect(buffer.FI, splitter.buffer);
   end Main;

end Continuous_Mode;
```

LIST OF PUBLICATIONS

From the Dissertation:

1. Ramaswami S, Behrendt J, Kalyanasundaram S, Eggers S, Otterpohl R, 2018. Experiences from an investigation on the potential of packed bed reactors for high rate nitrification of mature landfill leachates. Journal of Water Process Engineering 22, 59–65. doi:10.1016/j.jwpe.2018.01.006

2. Ramaswami S, Jalal Uddin F.M, Behrendt J, Otterpohl R. High-rate nitrification of saline wastewaters using fixed-bed reactors. (awaited)

From the Research Project:

1. Ramaswami S, Behrendt J, Otterpohl R, 2018. Comparison of NF-RO and RO-NF for the Treatment of Mature Landfill Leachates: A Guide for Landfill Operators. Membranes 8, 17. doi:10.3390/membranes8020017

2. Ramaswami S, Gulyas H, Behrendt J, Otterpohl R, 2017. Measuring nitrate concentration in wastewaters with high chloride content. International Journal of Environmental Analytical Chemistry 97, 56–70. doi:10.1080/03067319.2016.1277215

3. Shah T.M, Ramaswami S, Behrendt J, Otterpohl R, 2017. Simultaneous removal of organics and ammonium-nitrogen from reverse osmosis concentrate of mature landfill leachate. Journal of Water Process Engineering 19, 126–132. doi:10.1016/j.jwpe.2017.07.024

4. Ramaswami S, Behrendt J, Wang G, Eggers S, Otterpohl R, 2016. Combining magnesium ammonium phosphate precipitation with membrane processes for ammonia removal from methanogenic leachates. Water and Environment Journal 30, 218–226. doi:10.1111/wej.12210

Lebenslauf

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Landfill leachates containing high ammonia concentrations cannot be treated satisfactorily using reverse osmosis (RO) systems alone. In this work, leachate nitrification using aerated packed bed reactors was investigated to solve the problem of insufficient ammonia rejection faced by the multi-stage high pressure membrane system (comprising of RO and nanofiltration (NF) operations) treating the leachate at the Ihlenberg landfill site. Ammonia removal efficiencies greater than 97% were achieved with the NF permeate of RO retentate of raw leachate (having 16 g/L Cl⁻, 45 mS/cm) at loading rates of about 1100 g NH_4^+-N/(m³·d) at 25°C. Based on the findings, a half-technical scale plant was conceptualised and commissioned at the Ihlenberg landfill site.