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**Treatment and Substance Recovery in
Landfill Leachate Permeates
“An Alternative Sustainable Approach”**



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**Treatment and Substance Recovery
in
Landfill Leachate Permeates
“An Alternative Sustainable Approach”**

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For Crisanto and Delmira

SUMMARY

The objective of this study was to analyze different physicochemical and biological processes at different operating conditions as alternatives for the further treatment and recovery of substances from landfill leachate streams generated in a treatment facility located at a landfill site in Northern Germany. From the analyzed streams, a permeate named in this Doctoral work as landfill leachate permeate (LLP) generated by a NF-stage, which corresponded to the first step during the quantity reduction process of generated concentrate was identified as more extreme than landfill leachate but not as polluted as the evaluated concentrates. The LLP was characterized as relatively salty and very hard water with salinity and hardness values of about 92 dS/m and 5200 mg/L as CaCO_3 respectively at a temperature of $22 \pm 2^\circ\text{C}$. Also, its $\text{NH}_4\text{-N}$ and Ca concentrations of about 2000 and 1300 mg/L respectively were approximately 3 times higher than the values measured in a pretreated landfill leachate, which made of this permeate an acceptable stream for the recovery of Ca and NH_3 from the treatment facility. For the evaluated processes, during the precipitation treatment at pH 12 with $\text{Na}_2\text{CO}_3\text{-NaOH}$ as precipitating agent more than 99% of Ca was removed from the LLP with a recovered solids to permeate ratio of about 5 g/L and based on XRD from the CaCO_3 polymorphs, Calcite was identified as Calcite,-magnesian and Monohydrocalcite in the recovered $\text{CaCO}_3\text{-Rich Solids}$. Moreover, the adsorption treatment of the LLP with a PAC dosage of 10 g/L removed approximately 50% of the initial TOC concentration with values around 1350 mg/L. Furthermore, during the membrane contactor treatment at pH conditions of 12 and 1 in the LLP and acid solution respectively about 80% of the $\text{NH}_3\text{-N}$ was reduced efficiently from the LLP at an estimated $\text{NH}_3\text{-N}$ reduction rate of $0,40 \text{ Kg-N/d}\cdot\text{m}^2$ where only approximately 3% of the 228 L of the treated permeate corresponded to the volume of the recovered Concentrated $(\text{NH}_4)_2\text{SO}_4$ Solution ($\approx 20\%$). The explored reutilization of the recovered materials included as neutralizer agent for the pH correction of acid soil and raw material for $(\text{NH}_4)_2\text{SO}_4$ crystallization. For the case of the $\text{CaCO}_3\text{-Rich Solids}$ with a mass fraction of 0,1, the pH of the acid soil increased from 2,8 to 6,5, which corresponded to a neutralization dosage of about 15 t/ha and based on XRD, $(\text{NH}_4)_2\text{SO}_4$ crystals in the form of Mascagnite and Lecontite were obtained from the recovered Concentrated Amonium Sulfate Solution. Furthermore, in the Nitrifying FBB, pH 8,5 was identified as an optimal pH condition for the treatment of permeates with salinity values up to 50 dS/m at an AOR of 266 mg/L \cdot d and based on salinity, inhibitions in the AOB were observed at values greater than 78 dS/m. Moreover, in the Denitrifying FBB with Methanol as exogenous C-source, pH 6,5 was identified as an optimal pH value for the treatment of the permeates at a DNR of 23,6 mg-N/L \cdot h; where more than 99% of the inorganic-N was removed from the treated permeates through Nitrification/Denitrification in FBBs. The alternative flow diagram proposed for the integration of the evaluated processes with the landfill treatment facility might be beneficial since substances known to be problematic to the environment and/or challenging during operation such as Ca and $\text{NH}_4\text{-N}$ might not only be removed from the permeate but also recovered; hence approaching the landfill leachate treatment towards Sustainability.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
ACC	American Chemistry Council
ACS	American Chemical Society
AIT	Autoignition Temperature
ANC	Acid Neutralizing Capacity
AOB	Ammonia Oxidizing Bacteria
AOR	Ammonium Oxidation Rate
APHA	American Public Health Association
BAT	Best Available Technology
BMJV	Bundesministerium der Justiz und für Verbraucherschutz
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
Conc.	Concentration
Cond.	Conductivity
CU	Color Units
CV	Coefficient of Variation
DE	Germany
Df	Dilution Factor
DIC	Dissolved Inorganic Carbon
DNR	Denitrification Rate
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DSC	Differential Scanning Calorimetry
DW	Deionized Water
EPA	Environmental Protection Agency
EU	European Union
FA	Free Ammonia
FBB	Fixed-Bed Bioreactor
FNA	Free Nitrous Acid
GAC	Granular Activated Carbon
HPRO	High Pressure Reverse Osmosis
HROP	High Pressure Reverse Osmosis Permeate
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
ISE	Ion Selective Electrode
IUPAC	International Union of Pure and Applied Chemistry
LL	Landfill Leachate
LLC	Landfill Leachate Concentrate
LLP	Landfill Leachate Permeate
LN	Natural Logarithm
LOD	Limit of Detection
MBR	Membrane Bioreactor

MLLP	Mixture of Landfill Leachate Permeate
mp	Melting Point
MRWA	Minnesota Rural Water Association
MSWLF	Municipal Solid Waste Landfill
MW	Molecular Weight (Molar Mass)
n.r.	Not Reliable
n.s.	Not Specified
NCHS	Nitrogen Carbon Hydrogen Sulfur-Analyzer
NF	Nanofiltration
NOB	Nitrite Oxidizing Bacteria
P	Pressure
PAC	Powder Activated Carbon
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
p.e.	Population Equivalent
PFD	Process Flow Diagram
PP	Polypropylene
PTE	Potential Toxic Element
RO	Reverse Osmosis
ROP	Reverse Osmosis Permeate
SSA	Specific Surface Area
SSD	Sample Standard Deviation
SI	Saturation Index
t	Time
TC	Total Carbon
TGA	Thermogravimetric Analysis
TIC	Total Inorganic Carbon
TKN	Total Kjeldahl Nitrogen
TMCS	Trans-Membrane-Chemi-Sorption
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
TSS	Total Suspended Solids
US	United States
USDA	United States Department of Agriculture
UWWTP	Urban Wastewater Treatment Plant
VFA	Volatile Fatty Acids
VOCs	Volatile Organic Compounds
WW	Wastewater
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

CHAPTER 1: INTRODUCTION

One of the major hazards involving landfill sites is the generation of landfill leachate considering that the leakage of this wastewater can lead to the pollution of surface and groundwater and the further deterioration of the surrounding environment. Hence, the need of well manage landfill sites and the proper collection and further treatment of the generated leachate. However, a landfill leachate treatment facility might face different challenges not only during the time of landfill gas production but also after the production of gas is low or the landfill is closed. For instance, some of the challenges include the need of high energy demand processes such as membrane technologies and evaporation systems and also more strict environmental regulations might lead to further investment in order to get the BATs. Furthermore, during operation other common challenges include severe scaling in membrane systems due to the high concentration of scaling related substances such as Ca in the treated streams and the need of high pressure RO systems (≈ 120 bars) in order to generate permeates with $\text{NH}_4\text{-N}$ concentrations below the limit value of 70 mg/L as indicated in the German landfill regulation. The mentioned challenges, open also opportunities in order to look for alternatives that might either mitigate or help to lead landfill leachate treatment facilities towards a more sustainable treatment where landfill leachate can not only be seen exclusively as an environmental hazard but also as a potential RESOURCE.

The main body of this Dissertation was divided in three chapters. First, chapter 2 includes a literature review of the main concepts relevant to this Doctoral work follow by chapter 3 where the materials, methods, results and data analysis corresponding to each of the performed experimental work are given and then ending with chapter 4 where the developed and proposed flow diagram is presented. Chapter 3 was divided in five sections. The first section or section 3.1 includes the analysis of the landfill leachate streams generated in a treatment facility located at a landfill site in Northern Germany where the goal was to evaluate the different streams for the potential recovery of substances and their further treatment. After analyzing the different landfill leachate streams, it was seen that the concentration of Ca and $\text{NH}_4\text{-N}$ were relatively high in a permeate generated by a NF-stage, which has a landfill leachate concentrate as the input stream. One of the main characteristics of this permeate called in this work as landfill leachate permeate (LLP) was that compared to a pretreated landfill leachate the concentration of the targeted substances were considerably higher and also with respect to the German landfill regulation the concentration of regulated pollutants such as heavy metals were lower than the indicated limit values. Then, section 3.2 includes the adsorption treatment of the landfill leachate permeate with PAC where the goal was to evaluate different PAC dosages at different treatment times for the removal of TOC, color and heavy metals from the LLP. Furthermore, section 3.3 includes the precipitation treatment, which was divided in two parts. In the first part or section 3.3.2.1, the goal was to evaluate the effect of precipitating agents, pH and organic content on precipitation at different treatment times for the removal of Ca from the permeate and its recovery as CaCO_3 -

Rich solids. Then, in section 3.3.2.2, based on the results obtained from the more control small volume analysis, the aim was to treat larger amount of the LLP in a 10 L designed precipitator for the recovery of CaCO_3 -Rich solids and its further characterization and explored application as pH correction agent for the neutralization of acid soil collected from a lignite mine site located in Eastern Germany. Next, section 3.4 includes the membrane treatment of the LLP, which was mainly divided in two parts. In the first part or section 3.4.2.1, volumes of 8 L of permeate were treated in a designed membrane contactor setup in order to analyze the pH effect during the membrane treatment for the reduction and recovery of NH_3 from the landfill leachate permeate. Then, in section 3.4.2.2, the goal was to reduce more than 80% of the NH_3 -N concentration from the treated permeate and enrich an acid solution until reaching an Ammonium Sulfate Solution with a concentration of about 20%. After the enrichment process, the obtained Ammonium Sulfate Solution ($\approx 20\%$) was used as raw material for the crystallization of $(\text{NH}_4)_2\text{SO}_4$ as described in section 3.4.2.4. The last section of chapter 3 or section 3.5 includes the biological processes where nitrification and denitrification in mixed-permeates were analyzed by using two packed columns, which were conditioned as Nitrifying and Denitrifying FBBs and operated in batch mode for about 2 years and 6 months respectively. The biological removal of inorganic-N were performed at different operating conditions, which included among others salinity values ranging approximately in between 2,5 to 90 dS/m and pH values of 6,5, 7,5 and 8,5. Finally, as described in chapter 4, based on the results obtained throughout the experimental work and data analysis, a flow diagram was developed where the evaluated physicochemical and biological processes were integrated with the landfill leachate treatment facility. The process flow diagram was divided into two sections. The first section or recovery section included the unit operations where the recovery of CaCO_3 -Rich Solids and Concentrated Ammonium Sulfate Solution (20-40%) takes place. Then, the second section included two MBR configurations for the removal of the inorganic-N from mixed-permeates to values below the limit value of 70 mg/L as indicated in the German regulation. In the suggested MBRs configurations, the Nitrifying and/or Denitrifying FBBs were integrated with a RO-stage (≈ 60 bars) and given as alternatives to the high pressure RO-stage (≈ 120 bars) currently used for the treatment of landfill leachate streams including the LLP. Thus, the proposed flow diagram named in this Doctoral work as “An alternative sustainable approach” provides an alternative for the landfill leachate treatment facility where substances known to be not only problematic to the environment but also challenging during operation can not only be removed but also recovered from landfill leachate streams and switching the process towards a more circular or sustainable treatment.

CHAPTER 2: REVIEW OF THE LITERATURE

2.1. LANDFILL AND LANDFILL LEACHATE

According to the European Union (EU) Directive of 1999 “on the landfill of waste” and the United States Environmental Protection Agency (US-EPA) a landfill or modern landfill can be defined as a well-managed site or engineered facility where waste or solid waste is disposed and deposited in land and whose general classification is based on the kind of waste received such as landfills for hazardous waste, for non-hazardous waste and for inert waste (European Commission, 2019) (US-EPA, 2020). Additionally, as indicated in the EU Directive of 2008 “on waste”, waste management encompasses not only the collection, transport, and disposal of waste but also the processes require for its recovery (European Commission, 2019).

Landfills can also be classified not only based on the type of waste they receive but also on their design, some examples include the conventional and bioreactor landfills commonly found in Municipal Solid Waste Landfills (MSWLFs) (US-EPA, 2020). Figure 1 illustrates both types of landfill designs.

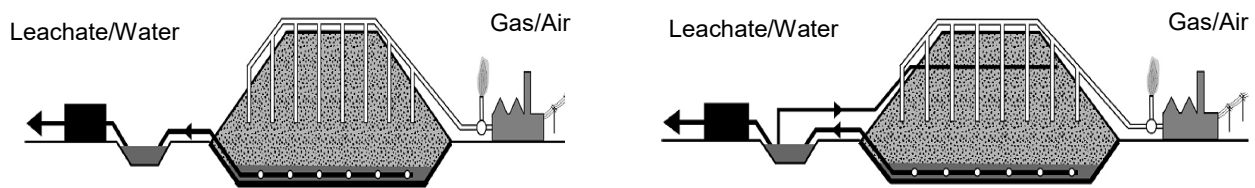


Figure 1. Landfill design; Left: Conventional Landfill; Right: Bioreactor Landfill (Christensen, et al., 2011)

One of the main differences between conventional and bioreactor landfills are the leachate collection system and the recirculation of leachate, which helps to increase the generation of gas (Christensen, et al., 2011). Bioreactor landfills are specifically designed to receive waste from households and other nonhazardous solid waste. One characteristic of this type of MSWLFs is that they operate under control conditions to faster biodegrade the organic content of the waste, which leads to the generation of not only gas rich in methane but also leachate as by-product (EPA, 2020).

Furthermore, as indicated by the European Commission, in terms of waste management options landfills are viewed as the least prefer option (European Commission, 2019) due to the environmental problems that are directly link to them such as groundwater pollution, risk of explosion and damage to vegetation leading to the further deterioration of our major natural resources such as water, air and soil. An overview of the potential environmental problems related to landfills with respect to distance is illustrated in figure 2.

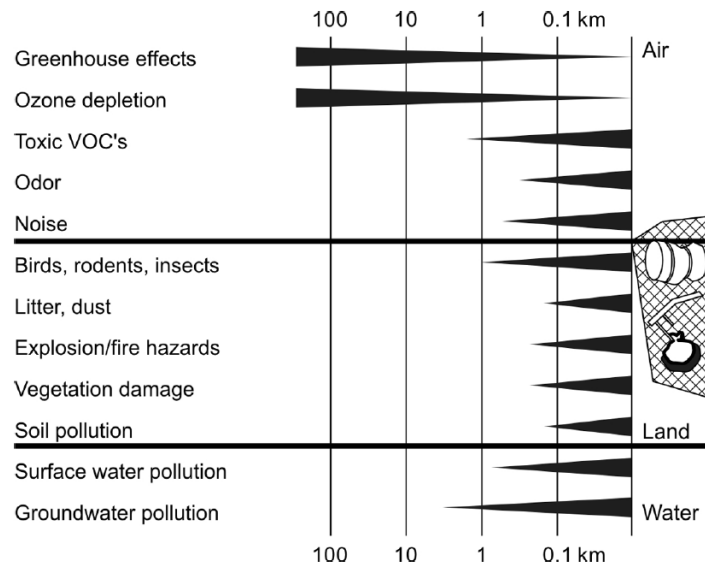


Figure 2. Potential environmental impact of Landfills (Christensen, et al., 2011)

For that reason, in order to better manage and avoid or mitigate the environmental problems related to landfills the current approach is to conceal them as described by the US-EPA and illustrated in figure 3.

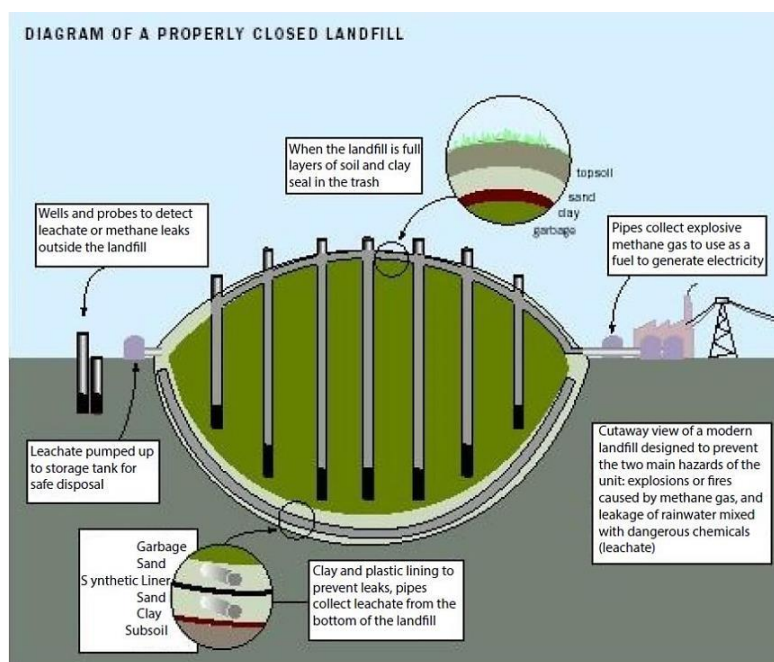


Figure 3. Properly closed municipal solid waste landfill (US-EPA, 2020)

The composition of the gas and leachate generated changes over time and is directly connected with the different biodegradation stages of the organic fraction of the waste occurring within the landfill. In general, for the case of anaerobic landfills the first biodegradation stage is aerobic due to the oxygen trapped within the waste, the duration of this stage depends on several factors including the compaction of the waste. Once the oxygen is being depleted, anaerobic processes start to take place with a second stage known as acidic phase where organic matter such as carbohydrates, fats and proteins are hydrolyzed and fermented by bacteria leading to

the formation of substances such as carbon dioxide, volatile fatty acid (VFA), hydrogen and ammonia. Also, within the acidic phase VFA are transformed into simpler molecules such as acetic acid by acetogenic bacteria. The second phase can last months or even years with a leachate that is characterized by having low pH with relatively high concentration of VFA and inorganic soluble substances such as Na, Cl, Fe, Ca, NH_4 and some heavy metals. Eventually, factors such as the consumption of VFA among others help to improve the pH conditions within the landfill allowing a third and fourth phase to take place. The third phase or initial methanogenic phase as the name suggests is where methane starts to appear as a gas component meaning the emerging of the methanogens, this phase usually last from a few months up to 2 years. Then, the fourth phase or stable methanogenic phase occurs where a more stable equilibrium is reached between the methanogens and the acid producer microorganisms, this balance is reflected in the generated gas where the concentration of methane is slightly higher compare to the carbon dioxide. This stage can last somewhere around 10 to 30 years and it is characterized by having a leachate with a pH slightly higher than the neutral value, a low BOD to COD ratio since a lot of the VFA had already been consumed within the landfill and relatively high concentrations of inorganic substances such as Na, Cl, NH_4 among others. After the fourth phase, the generation of methane is expected to decrease with subsequent phases known as air intrusion, methane oxidation and carbon dioxide. The carbon dioxide phase is characterized by the end of methanogenic activity and a dominant N_2 presence in the gas phase. Additionally, during the last three phases the composition of the leachate is also expected to change with lower concentration of soluble substances including NH_4 , DOC, etc. (Christensen, et al., 2011). The different landfill phases with respect to the gas composition over time are illustrated in figure 4.

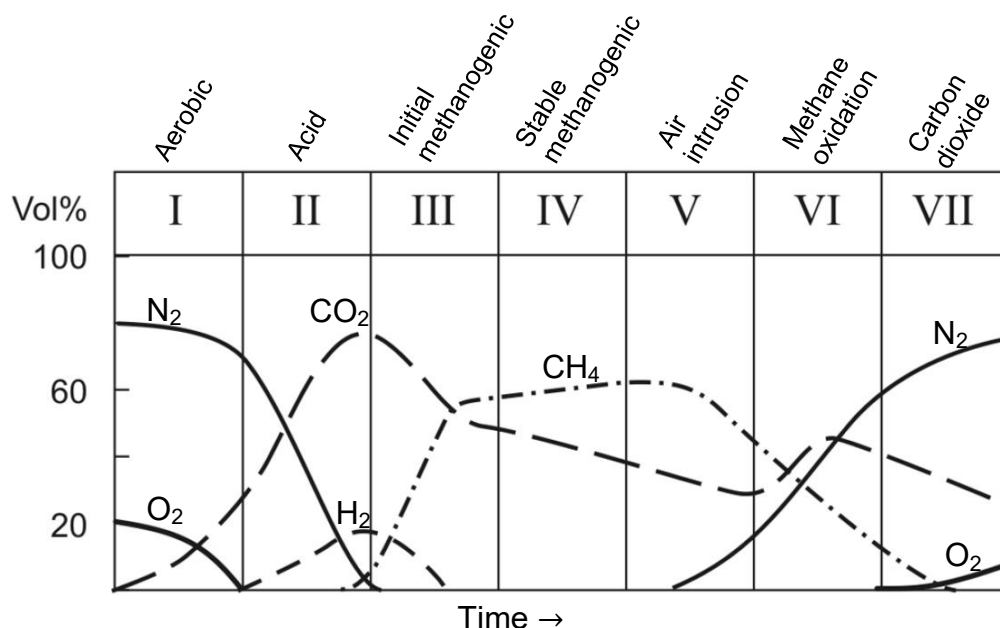


Figure 4. Landfill phases with respect to gas composition; Adapted from (Christensen, et al., 2011)

As indicated by the US-EPA in figure 3, one of the major hazards in landfills is the generated leachate, which is defined as the water that percolates through the waste in a landfill (Ehrig & Robinson, 2011). The main sources of water for this type of wastewater are mainly related to precipitation including rain and snow over the operating landfill, surface infiltration through the covered landfill, groundwater infiltration into the landfill and water either contained within the waste or related to the biodegradation of the organic fraction of the waste (Youcai, 2018) (Robinson, 1986).

The landfill leachate composition depends on several factors including the landfill design, type of waste, climate conditions among others. In general, the leachate composition can be classified in four main groups, which are the bulk organic matter, nitrogenous compounds, inorganic macro-substances and trace compounds either inorganic or organic such as heavy metals and pesticides etc. (Christensen, et al., 2011). Some of the main representative parameters or species related to each of the main groups and their common concentration values are given in table 1 and 2 respectively.

Table 1. Landfill leachate composition main groups; Adapted from (Christensen, et al., 2011)

Main Group		Representative Parameter/Species
Bulk organic matter (Mainly VFA & partly humified substances)		COD, BOD, TOC, DOC
Nitrogenous compounds		TKN: (Organic-N & NH_4^+)
Inorganic macro-substances		Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} & HCO_3^-
Trace compounds	Heavy metals	Cd, Pb, Cu, Ni, Zn, Cr, Hg, As, Sb & Sn
	Organic	Aromatic hydrocarbons e.g. PAH, chlorinated solvents e.g. PCB, pesticides etc.

Table 2. Common concentration values in Landfill leachate; Adapted from (Christensen, et al., 2011)

Conc. range	Acid phase leachate	Methanogenic phase leachate	Old leachate
>10 g/L	COD, BOD	-	-
1 – 10 g/L	Cl^- , $\text{NH}_4\text{-N}$	Cl^- , COD, BOD	-
100 – 1000 mg/L	Na, K, Ca	Na, K, Ca, (BOD), $\text{NH}_4\text{-N}$	Cl^- , Na, Ca, COD, $\text{NH}_4\text{-N}$
1 – 1000 $\mu\text{g/L}$	Cu, Mn, Mo, As, Pb, Cd, Ni, Se, Cr, Hg, Sn	Mn, Mo, As, Cu, Pb, Ni, Se, Cr, Cd, Sn	Zn, Mn, As, Cu, Ni, Cr, Mo, Pb, Cd, Se
< 1 $\mu\text{g/L}$	-	Hg	Hg, Sn

According to the European Commission, many of the substances listed in table 1 and 2 are categorized in wastewater treatment systems as Potential Toxic Elements (PTE) and/or pollutants. The PTEs include cadmium (Cd), chromium (Cr III and Cr VI), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). And some specified pollutants include substances such as arsenic (As), selenium (Se), the platinum group metals, which are composed of iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh), and ruthenium (Ru) and organic substances such as PAH, PCBs, dioxins, furans, pharmaceuticals, etc. (European Commission, 2019). Furthermore, in the EU Directive of 2006 “on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community” substances of environmental concern are given in two list of families, which include the PTEs and other metals such as antimony (Sb), molybdenum (Mo), titanium (Ti), tin (Sn), barium (Ba), beryllium (Be), boron (B), uranium (U), vanadium (V), cobalt (Co), thallium (Tl), tellurium (Te) and silver (Ag). Moreover, substances and/or parameters that negatively influence the oxygen balance such as ammonia, nitrite, BOD, COD and those directly involve in eutrophication including nitrates and phosphates are also included in the same Directive and the Directive of 2000 “on establishing a framework for Community action in the field of water policy” (European Commission, 2006). Additionally, other metals known to be toxic to human health include bismuth (Bi), cerium (Ce), gallium (Ga), gold (Au), iron (Fe), manganese (Mn), and aluminium (Al) (JAISHANKAR, et al., 2014).

Considering the environmental problems related to landfill leachates and their potential deterioration to the quality of groundwater, soil and air, it is worth mentioning the EU efforts to preserve the environment and to prevent and control air, water and soil pollution through the different Directives, some of which are listed below:

- EU Directive of 1986 “on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture”
- EU Directive of 1991 “on concerning urban waste water treatment”
- EU Directive of 1999 “on the landfill of waste”
- EU Directive of 2000 “on establishing a framework for Community action in the field of water policy”
- EU Directive of 2006 “on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community”
- EU Directive of 2008 “on waste”
- EU Directive of 2010 “on industrial emissions (integrated pollution prevention and control)”

In Germany, for the case of landfill leachate treatment facilities the allow limit of substances and/or parameters in their effluents are indicated in the Annex 51 of their landfill regulation (BMJV , 2009). The limit values for different substances and/or parameters of environmental concern indicated in the EU Directives and the German landfill regulation are given in table 3.

Table 3. Limit values indicated in EU Directives and German landfill regulation

	EU Directive		DE Regulation	EU Directive	
Substance/ Parameter	Effluent UWWTP ¹	Effluent Industrial- WW ²	Effluent Landfill ³	Sewage sludge ⁴	Soil ⁴
TN (mg/L)	10 ^a	-	70 ^d	-	-
NO ₂ ⁻ -N (mg/L)	-	-	2	-	-
COD (mg O ₂ /L)	125	-	200	-	-
BOD ₅ (mg O ₂ /L)	25	-	20	-	-
TP (mg/L)	1 ^a	-	3	-	-
Hg (µg/L)	-	30	50	16 – 25 ^b	1 – 1,5 ^b
Cd (µg/L)	-	50	100	20 – 40 ^b	1 – 3 ^b
Tl (µg/L)	-	50	-	-	-
As (µg/L)	-	150	100	-	-
Pb (µg/L)	-	200	500	750 – 1200 ^b	50 – 300 ^b
Cr (µg/L)	-	500	500	1000 – 1750 ^{b,c}	100 – 200 ^{b,c}
Cu (µg/L)	-	500	500	1000 – 1750 ^b	50 – 140 ^b
Ni (µg/L)	-	500	1000	300 – 400 ^b	30 – 75 ^b
Zn (µg/L)	-	1500	2000	2500 – 4000 ^b	150 – 300 ^b
CN ⁻ (µg/L)	-	-	200	-	-

1. EU Directive of 1991 “on concerning urban waste water treatment”

a. TN defined as the sum of Kjeldahl-nitrogen (Organic N+NH₃), NO₃-N and NO₂-N & Limit value for eutrophication sensitive areas & > 100000 p.e.

2. EU Directive of 2010 “on industrial emissions (integrated pollution prevention and control)” - Part 5: “Emission limit values for discharges of waste water from the cleaning of waste gases”

3. DepV - Annex 51

d. TN defined as sum of NH₄-N, NO₂-N and NO₃-N

4. EU Directive of 1986 “on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture”;

b. Units in mg/Kg (ppm)

c. “Proposal for a Council Directive amending in respect of chromium Directive 86/278/EEC on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (88/C 307/10)”

As indicated in table 3, the effluents from landfill sites must comply with the respective environmental regulations; hence the need for landfill leachate treatment processes. The treatment of landfill leachate have had different approaches in different countries; thus, there is no BAT but rather a combination of physical, chemical and/or biological processes, which reflect the local environmental regulations. However, during the last years a general trend has been adopted where not only biodegradable material and nitrogen are the main focus for removal but also the non-biodegradable substances, which have led to the introduction of more sophisticated systems into the treatment of landfill leachate (Ehrig & Robinson, 2011)

An overview of the different processes and possible configurations used for the treatment of landfill leachate are illustrated in figure 5.

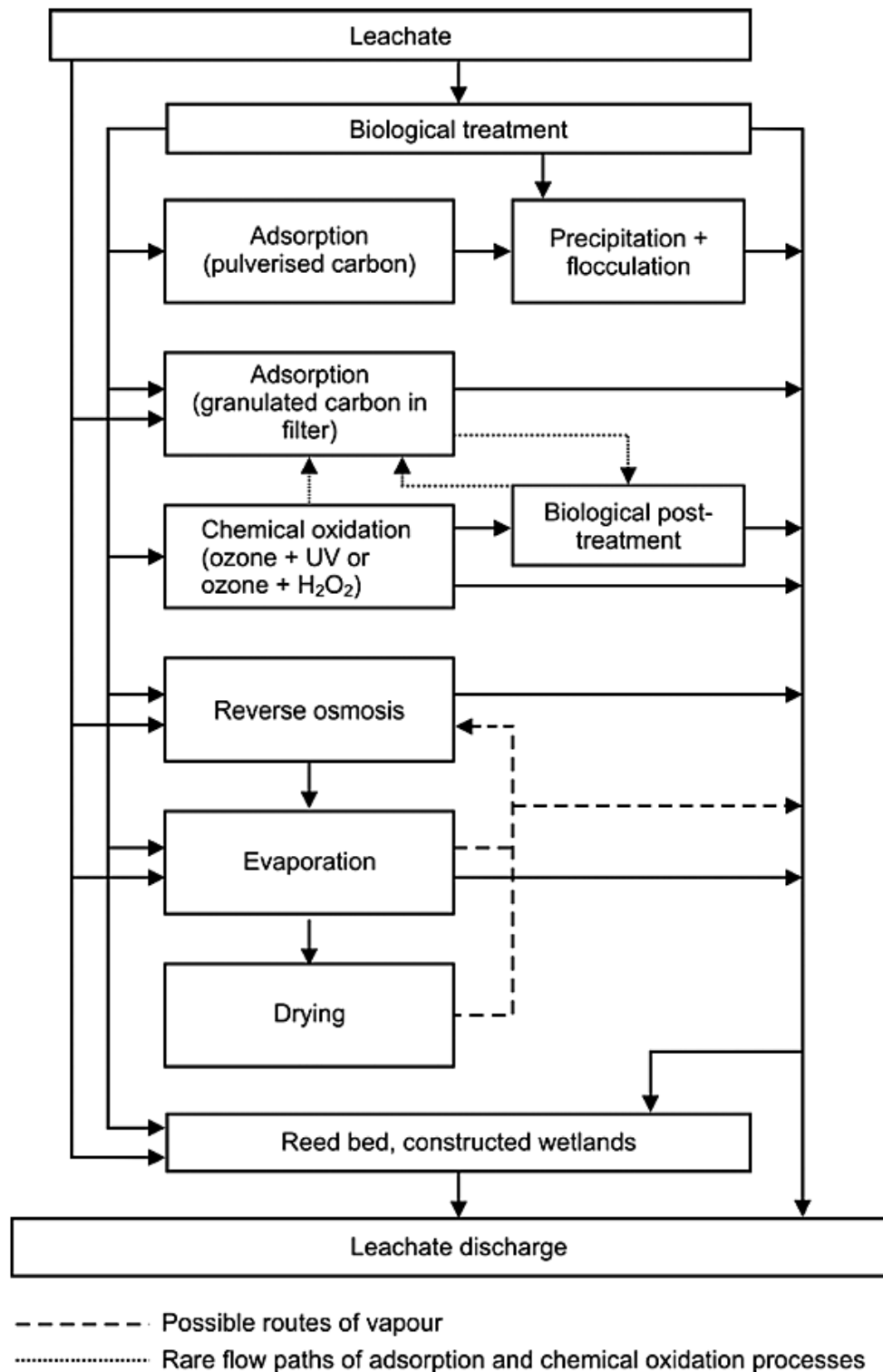


Figure 5. Different processes and possible configurations in the treatment of landfill leachate (Ehrig & Robinson, 2011)

2.2. ADSORPTION

Adsorption is a common mass transfer operation where a substance known as adsorbate is separated from a fluid to a phase usually a solid known as adsorbent. For the case of liquid-solid systems and based on the film theory the mass transfer during adsorption can be described by the following steps. First, the solute or adsorbate travels from the bulk liquid to the liquid stagnant film. Second, the adsorbate goes through the liquid film surrounding the solid to the liquid-solid interface. Third, the adsorbate diffuses into the adsorbent voids where it is finally adsorbed onto the adsorbent surface (Parsons & Jefferson, 2006). Figure 6 illustrates the mass transfer mechanisms in adsorption processes.

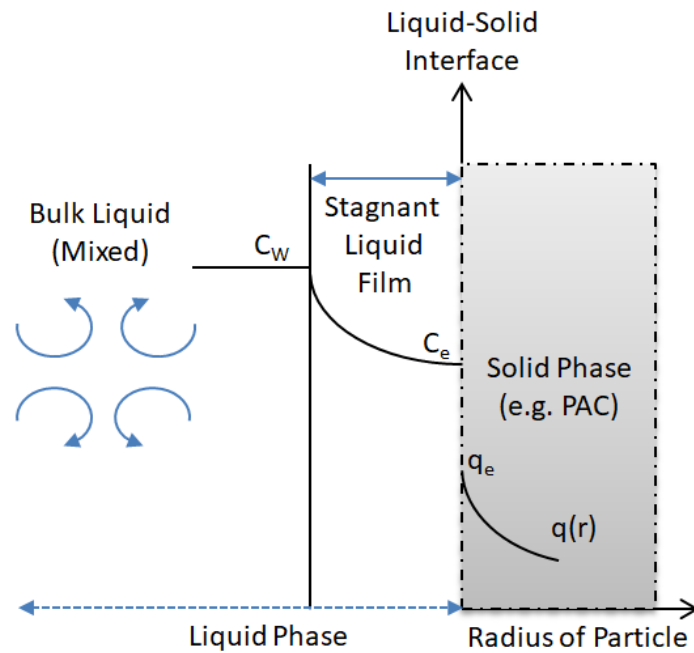


Figure 6. Mass transfer in adsorption processes; Adapted from (Barros, et al., 2012) & (Logan, 2012)

One of the most common inorganic adsorbent material used for the treatment of waste water is activated carbon, properties such as amorphicity, pore structure, stability among others make of this material and excellent adsorbent for a wide range of treatment applications including the removal of color, smell and pollutants such as organic material and heavy metals (Chen, et al., 2018).

Activated carbon can be made out of different initial carbonaceous materials, which include coal, wood, coconut shell among other. The idea of making activated carbon is to increase the internal surface area available for adsorption. For example, a gram of ground coal with an internal surface area of 10 m² can be activated almost 100 times to reach an internal surface area up to 1000 m² (Parsons & Jefferson, 2006).

The initial material from which activated carbon is produced have a direct influence on important adsorbent characteristics such as pore size distribution and regeneration. In general, pore sizes greater than 25 nm are called macropores, those in between 1 and 25 nm are mesopores and those with pore sizes around 1 or less than 1 nm are called micropores and minimicropores respectively. Also, based on the

particle size, activated carbon can be divided as powdered activated carbon (PAC) or granular activated carbon (GAC). Normally, PAC has diameters smaller than 0,074 mm (200 sieve) and GAC diameters are usually larger than 0,1 mm (\approx 140 sieve) (Metcalf & Eddy, et al., 2003). Furthermore, for a particular substance the adsorption efficiency depends not only on the activated carbon characteristics but also it is a function of important operation conditions such as temperature, pH and concentration (Parsons & Jefferson, 2006). Table 4 describes some common PAC and GAC characteristics.

Table 4. Common PAC and GAC characteristics; Adapted from (Metcalf & Eddy, et al., 2003)

Parameter	PAC	GAC
Total Surface Area:	800 – 1800 m ² /g	700 – 1300 m ² /g
Bulk density:	360 – 740 Kg/m ³	400 – 500 Kg/m ³
Particle size range:	5 – 50 μ m	0,1 – 2,36 mm
Mean pore radius:	2,0 – 4,0 nm	1,6 – 3,0 nm

Based on the interaction between the adsorbate and adsorbent, adsorption can be classified as physical or chemical. Physical adsorption or physisorption is characterized by weak van der Waals forces between the adsorbate and adsorbent sites; thus, electron exchange does not take place. On the other hand, chemical adsorption or chemisorption is characterized by exchange of electrons between the adsorbate and specific adsorbent sites leading to chemical bonds with characteristics somewhere in between ionic or covalent in nature. In general, physisorption is stable at temperatures below 150°C while chemisorption can be more stable at relatively higher temperature (Parsons & Jefferson, 2006).

The equilibrium in adsorption systems is normally represented by the equilibrium isotherms where the equilibrium for a particular system is found experimentally at specific conditions. A common experimental procedure known as the bottle-point method is used. This method is performed at constant temperature where a fixed volume of liquid with specific adsorbate concentration is filled to different bottles. Then, different specific amounts of adsorbent are added to each bottle and mixed until an equilibrium point for the particular adsorbate is reached between both phases. In order to find different point of the isotherm the method can be performed by either using different initial adsorbate concentration solutions or by adding different adsorbent masses into the bottles. For activated carbon, one of the parameters affecting the equilibrium time is particle size. This means, the larger the particle size the longer the equilibrium time, which can vary from a few hours to days (Worch, 2019).

In aqueous systems, the equilibrium of the adsorbate between the liquid and the solid phase is usually given as the concentration of the solute in the liquid and the loading of the adsorbate in the adsorbent expressed in units of mass of solute per volume of solution and mass of adsorbate per mass of adsorbent respectively (Seader & Henley, 2006).

Among the most common adsorption isotherm models are the Langmuir, Freundlich and Dubinin–Raduskevish (DR). Other isotherms include the Langmuir–Freundlich, Redlich–Peterson and Sips isotherms (Inglezakis & Pouloupoulos, 2006). Figure 7 shows some typical representative isotherms.

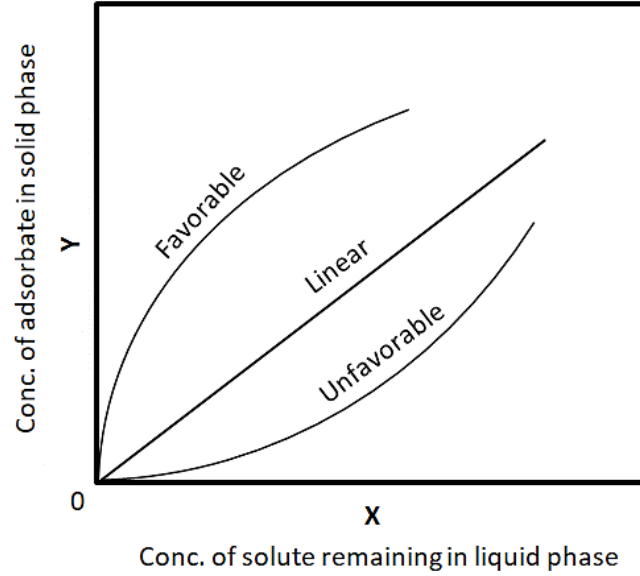


Figure 7. Representative adsorption isotherms; Adapted from (McCabe, et al., 2005)

For the treatment of water and waste water, one of the most frequently used models to describe adsorption equilibrium with activated carbon is the Freundlich isotherm, which has been used to describe not only single-solute but also multi-solute aqueous adsorption systems (Worch, 2019). Adsorbents that follow this type of isotherm are assumed of having heterogeneous surfaces composed of sites with different adsorption potentials (Inglezakis & Pouloupoulos, 2006).

The Freundlich isotherm model is represented by equation 1 (Metcalf & Eddy, et al., 2003).

$$q_e = K_f C_e^{1/n} \quad (\text{Eq. 1})$$

Where,

q_e (mg/g) = Adsorbate equilibrium concentration in the solid phase or adsorbent

K_f = Freundlich capacity factor

C_e (mg/L) = Adsorbate equilibrium concentration in aqueous solution

$1/n$ = Freundlich intensity parameter

Equation 1 can be rewritten in its linearized form as shown by equation 2

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (\text{Eq. 2})$$

K_f and n are the Freundlich isotherm parameters and they are unique to a particular adsorbate-adsorbent equilibrium. As seen in equation 2 by plotting the experimental data the parameters K_f and $1/n$ can be estimated by using a linear regression that best fit the data where the intercept and slope are K_f and $1/n$ respectively (Hendricks,

2011). Furthermore, when $1/n$ is smaller than 1 adsorption is favorable or it usually indicates a better fit especially for the case of adsorption from liquids (McCabe, et al., 2005) and the isotherm is of the concave shape with respect to the X axis as indicated in figure 7 (Worch, 2019).

In contrast to the Freundlich isotherm, the Langmuir isotherm assumes an adsorbent with uniform surface composed by fixed individual sites that can take one adsorbate molecule per site and forming a monolayer in the process. Thus, saturation is reached when the adsorbent is covered with a monolayer of adsorbate (Inglezakis & Pouloupoulos, 2006).

The Langmuir isotherm model is represented by equation 3 (Metcalf & Eddy, et al., 2003).

$$q_e = \frac{QbC_e}{1 + bC_e} \quad (Eq. 3)$$

Where,

q_e (mg/g) = Adsorbate equilibrium concentration in the solid phase or adsorbent
 Q (mg/g) = Saturation capacity of adsorbent for adsorbate
 b (L/mg) = Equilibrium constant
 C_e (mg/L) = Adsorbate equilibrium concentration in aqueous solution

The Q and b empirical constant from Langmuir equation can be determined from the experimental data by plotting C_e/q_e versus C_e and by rewriting equation 3 in the form shown by equation 4 (Metcalf & Eddy, et al., 2003).

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{1}{Q}C_e \quad (Eq. 4)$$

For the Langmuir case an equilibrium parameter (R_L) also known as separation factor is defined by equation 5. This parameter is used to indicate the adsorption favorability case as illustrated in figure 7. Adsorption is favorable when R_L is smaller than 1 (Inglezakis & Pouloupoulos, 2006).

$$R_L = \frac{1}{1 + bC_0} \quad (Eq. 5)$$

Where,

R_L = Equilibrium parameter or Separation factor
 C_0 (mg/L) = Adsorbate initial concentration in aqueous solution

Additionally, regeneration includes all of the processes that lead to the restoration of the spent carbon to its original adsorptive state. In general, regeneration can be achieved through thermal, chemical and biological means; some examples include the desorption of substances by means of steam and solvents. During the regeneration process about 4 to 10 percent of the carbon adsorptive capacity is lost (Metcalf & Eddy, et al., 2003).

2.3. CRYSTALLIZATION AND CHEMICAL PRECIPITATION

Crystallization is known as the one of the oldest separation processes in which solids in the form of crystals are separated from homogenous fluid phases. The application of crystallization dates back to antiquity where sodium chloride crystals were recovered through the evaporation of water (Seader & Henley, 2006). The discovery of X-Rays in the year of 1895 led to its application and allowed the crystalline structure of solids to be determined through a technique known as X-ray powder diffraction (XRD) (SERC, 2020). Some examples of inorganic salts recovered from aqueous solutions are described in table 5.

Table 5. Inorganic salts recovered from aqueous solutions; Adapted from (Seader & Henley, 2006)

Chemical Name	Formula	Common Name	Crystal System
Calcium carbonate	CaCO_3	Calcite	Rhombohedral
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	Muscagnite	Orthorhombic
Magnesium sulfate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Epsom salt	Orthorhombic
Sodium chloride	NaCl	Salt, halite	Cubic
Silver nitrate	AgNO_3	Lunar caustic	Orthorhombic

According to the IUPAC, the solubility of a solute in the respective solvent can be defined as the analytical composition of a saturated solution normally expressed as a concentration (IUPAC, 2020). Solubility often increases with the increase of the solution temperature. However, in some cases the opposite is observed such as the case of CaCO_3 in water where solubility increases with the decrease of temperature as indicated in figure 8.

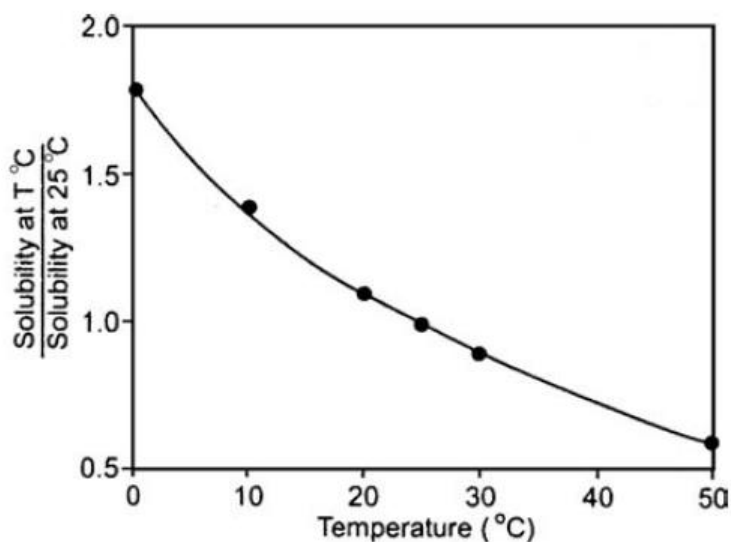


Figure 8. Solubility of CaCO_3 in water as function of temperature (Randall & Sharon, 2005)

The process of crystallization is usually explained with the help of an equilibrium phase diagram or solubility-supersolubility diagram. This phase diagram is divided in three zones known as undersaturated, metastable and labile. The undersaturated zone is a region where the crystals present will dissolve, the metastable zone is a

supersaturated region in which crystals will grow and the labile zone is a region in which nucleation will occur spontaneously (Jones, 2002). The described solubility-supersolubility diagram is illustrated in figure 9.

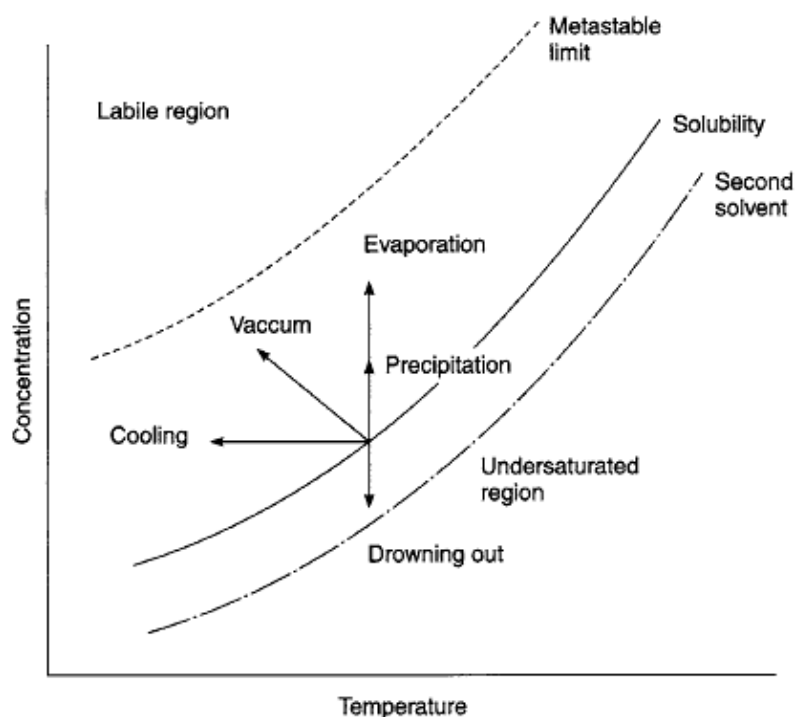


Figure 9. Solubility-supersolubility diagram (Jones, 2002)

As indicated in figure 9, crystallization can be performed by achieving supersaturation either by cooling and/or evaporation or also by reducing the solubility of a solute with the addition of a second solvent. In the last case, fast crystallization or precipitation can occur, which is characterized by the formation of many very small crystals. Also, precipitation can be formed after the addition of a third component for the initiation of a chemical reaction yielding a product or solid with low solubility. The generation of low solubility solids usually involves fast reactions; hence precipitation in the form of very fine crystals is produced rather than the desire large crystals. Thus, solubility is considered as one of the most important properties in order to determine the best method for crystallization (Seader & Henley, 2006). Furthermore, the presence of impurities and the pH of the solution have strong influence in crystal growth (Schmidt, et al., 2013). For instance, the presence of colloidal organic substances in aqueous solutions such as gelatin can inhibit the nucleation process during crystallization and inorganic substances including Cr^{3+} and Fe^{3+} can have a similar effect on inorganic salts like in the case of $(\text{NH}_4)_2\text{SO}_4$ crystallization. In a system, the inhibition effect of impurities is difficult to evaluate. However, a trend with respect to cation charge had been observed where the higher the positive charge the higher the inhibition effect, for example $\text{Cr}^{3+} > \text{Fe}^{3+} > \text{Al}^{3+} > \text{Ni}^{2+} > \text{Na}^+$ (Mullin, 2001). The solubilities of some inorganic compounds in water at different temperature conditions are given in table 6.

Table 6. Solubility of inorganic compounds in water at different temperatures; Adapted from (Seader & Henley, 2006)

T (°C)	Solubility [‡] (g/100 g H ₂ O)				
	NaCl	(NH ₄) ₂ SO ₄	Na ₂ SO ₄	K ₂ SO ₄	MgSO ₄
0	35,6	71,0	4,8	7,4	22,3
10	35,7	73,0	9,0	9,3	27,8
20	35,8	75,4	19,4	11,1	33,5
30	36,1	78,0	40,8	13,1	39,6
40	36,4	81,0	48,8	14,9	44,8
60	37,1	88,0	45,3	18,3	55,3
80	38,1	95,3	43,7	21,4	56,0
100	39,8	103,3	42,5	24,2	50,0

‡ Stable hydrate at room temperature: NaCl= 0; (NH₄)₂SO₄ = 0; : Na₂SO₄= 10; K₂SO₄= 0; MgSO₄= 7

As indicated in table 6, cooling crystallization is perhaps not the best alternative for the crystallization of substances such as NaCl considering that its solubility only decreases about 10% from 100 to 0°C. On the other hand, for the case of (NH₄)₂SO₄ for the same temperature range the decrease in solubility is higher than NaCl with a value around 30%. However, evaporative crystallization is the popular technique use for the crystallization of most of the soluble inorganic compounds such as Epsom salt (MgSO₄·7H₂O) (Seader & Henley, 2006). In contrast to cooling crystallization, evaporative crystallization is usually performed at isothermal conditions and one of the main advantages of cooling crystallization is the larger uniformity of crystal size (ThermalKinetics, 2020). Furthermore, in a supersaturated solution one common way to stimulate crystal growth without having to rely entirely in nucleation is the addition of a seed material. The seed material provides surface area for crystal growth, which defines not only the growth rate but also the quality of the formed crystals (Ulrich & Jones, 2011). The solubility values for other inorganic compounds in water are given in table 7.

Table 7. Solubility of inorganic compounds in water (PubChem, 2020)

Chemical Name	Formula	Solubility at 20°C (g/100 g)	Degree of Solubility
Calcium carbonate	CaCO ₃	0,0014	Practically insoluble
Magnesium carbonate*	MgCO ₃ ·nH ₂ O	0,01	
Magnesium hydroxide	Mg(OH) ₂	0,0009**	
Calcium hydroxide	Ca(OH) ₂	0,16	Slightly soluble
Sodium carbonate	Na ₂ CO ₃	30	Freely soluble
Sodium hydroxide	NaOH	109	Very soluble

* n-Hydrated

**At 18°C

In landfill leachate treatment processes precipitation had been used to reduce the concentration of relatively large organic molecules such as humic- related substances. Usually, this is performed by using precipitation agents including iron

and aluminium sulfates or chlorides at low pH values ranging from 4,5 to 5,0 and 5,0 to 5,5 for iron and aluminium respectively. The removal of organic substances from landfill leachate by the use of both biological and the mentioned precipitation treatment can reduce the COD content up to 60 or 70%. However, this treatment increases the amount of sludge generated and also the salt content in the treated landfill leachate. Additionally, considering the relatively low concentration of heavy metals in landfill leachates, precipitation is not a common practice for the removal of these substances from landfill leachates (Ehrig & Robinson, 2011).

One important application of chemical precipitation is the reduction of hardness from water known as water softening. The hardness in water is mainly attributed to the presence of Ca^{2+} and Mg^{2+} salts and the higher the hardness the higher the potential for scale formation in processes including membrane systems. As a general rule, in order to prevent scaling the used water should have a total hardness of less than 75 mg/L as CaCO_3 . Precipitation softening is usually performed by the use of lime (CaO) or a mixture between lime and soda ash (Na_2CO_3), where the added chemicals react with the hardness and alkalinity of the water yielding insoluble compounds. The formed precipitation is then removed from the liquid by conventional separation processes such as coagulation/flocculation, sedimentation, and filtration (MRWA, 2020). Table 8 provides an indication of water hardness commonly used in the industry.

Table 8. Indication of water hardness as calcium carbonate (Lenntech, 2020)

Water indicator	Hardness as CaCO_3 (mg/L)
Soft water	0 - 60
Moderately hard water	60 - 120
Hard water	120 - 180
Very hard water	>180

In scaling prevention it is common to calculate the CaCO_3 saturation index (SI) in order to evaluate the scaling forming in the particular system such as piping, heat exchangers, evaporators and filtration systems etc. In a nutshell, the CaCO_3 SI represents the line in between the tendency of the water to precipitate CaCO_3 (Oversaturated) or to dissolve CaCO_3 (Undersaturated). If the calculated SI yields a negative value it indicates that the water is undersaturated with respect to CaCO_3 but if the value is positive it means that the water is oversaturated with respect to CaCO_3 and precipitation might take place. Furthermore, a SI with a value of zero indicates that the water is in equilibrium with CaCO_3 (APHA, 2005)

Additionally, the strong base sodium hydroxide (NaOH) also known as caustic soda (NaOH) besides being used in the manufacturing of everyday products including soap, paper, disinfectants, etc. (PubChem, 2020) has also found its applications in other sectors including wastewater treatment plants. In WWTP, caustic soda has been used for adjustment and/or control of the pH in the treated streams and also for the removal of pollutants such as heavy metals (ACC, 2020).

2.4. MEMBRANE TECHNOLOGIES

As already indicated in figure 5, membrane systems such as RO have been used in the treatment of landfill leachate. These physical systems generate two output streams, which are known as permeate and concentrate. The permeate is the treated stream and the concentrate also known as brine is the residual stream that requires further treatment. A common way to further treat the generated concentrate is by turning the residual stream into a solid material through evaporation and/or drying processes. Furthermore, in the treatment of landfill leachate, reverse osmosis (RO) has been the most used membrane process due to the high quality of the generated permeates but also other common membrane processes include nanofiltration and ultrafiltration. Ultrafiltration has been used for the separation of solids in processes such as in between biological stages and nanofiltration has not been used largely in the treatment of landfill leachate mostly due to its low rejection for small molecules such as chloride (Ehrig & Robinson, 2011). Based, on the dimension of the substances to be separated, membrane processes can be classified as indicated in table 9.

Table 9. Classification of membrane processes base on dimension of component to be separated; Adapted from (Ehrig & Robinson, 2011)

Membrane Process	Range dimension of component (μm)	Range Description
Microfiltration	0,05 – 2,0	Macromolecular to microparticle
Ultrafiltration	0,005 – 0,2	Molecular to macromolecular
Nanofiltration	0,001 – 0,01	Molecular
Reverse osmosis	<0,002	Ionic

For the case of RO, when two liquids with different concentration are separated by a semipermeable membrane, water will flow from the less concentrated to the more concentrated side until the concentration on both sides is equal, at this point the liquid elevation on the concentrated side had increased and the water level difference is called osmotic pressure ($\Delta\pi$). RO operates in the opposite direction, concentrating the already concentrated side; thus, a pressure greater than the osmotic pressure ($\Delta\pi + \Delta P$) needs to be applied. Furthermore, the usual operation mode in membrane processes is cross flow with high flow rate recirculation of the concentrate and typical modules for RO systems include tubular, spiral wound, hollow fiber and disc tube. For the treatment of landfill leachate the spiral wound and especially the hollow fiber modules are not commonly used due to their high sensitivity for the presence of solids. Instead, the disc tube or circular disc (plate and frame) modules are the choice of preference and common RO operating pressures can be found up to 70 bars or high pressure RO up to 150 bars (Ehrig & Robinson, 2011). The reverse osmosis principle and the common operating mode are illustrated in figure 10.

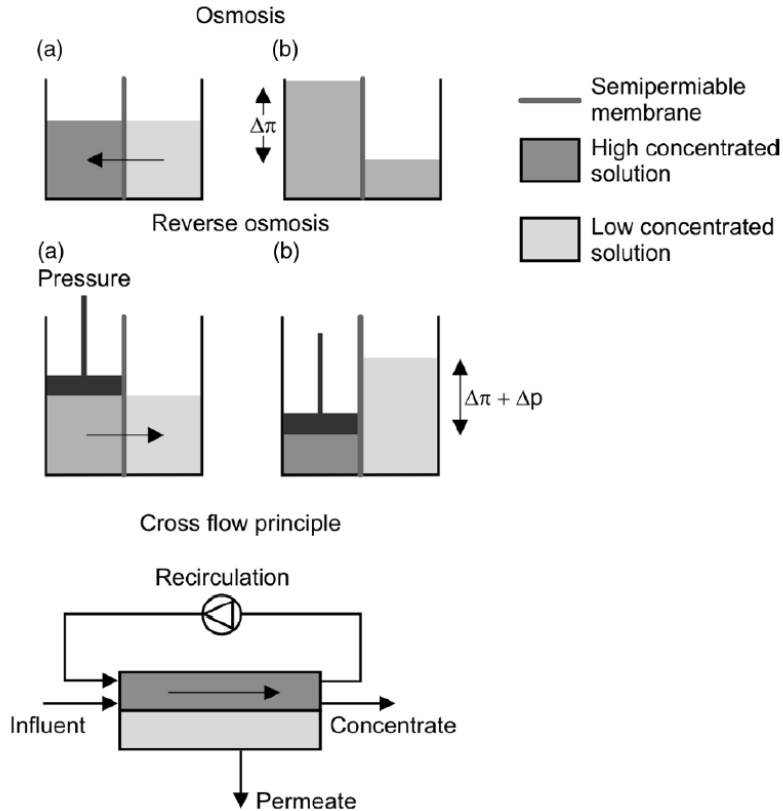


Figure 10. Reverse osmosis principle and common operation mode (Ehrig & Robinson, 2011)

RO membranes were developed with the objective of seawater desalination and over time their performance has improved where required operating pressures conditions of 100 bars had decreased to 50 to 60 bars for the same salt rejection of about 98 to 99%. Some common membrane materials include cellulosic membranes such as cellulose acetate, non-cellulosic membranes such as polyamide membranes and the interfacial composite membranes, which are made by the method of interfacial polymerization such as the thin film composite membranes, this method became the industry standard. Furthermore, based on the operating pressure, RO membranes can be further categorized as low-pressure nanofiltration (NF) with typical operating pressures ranging in between 5 to 10 bars. Nanofiltration membranes have lower salinity rejections, which can range in between 20 to 80% but they possess higher water permeability. In nanofiltration systems the rejection of salts can depend on molecular size and also Donnan exclusion effects or charged particle interactions that can exist in between the membrane and the particular substance. For example, for the case of neutral nanofiltration membranes the rejection of salts can be proportional to the molecular size in the following order $\text{Na}_2\text{SO}_4 > \text{CaCl}_2 > \text{NaCl}$ (BAKER, 2012). A typical solute rejection as a function of the solute molecular weight found in NF systems is illustrated in figure 11.

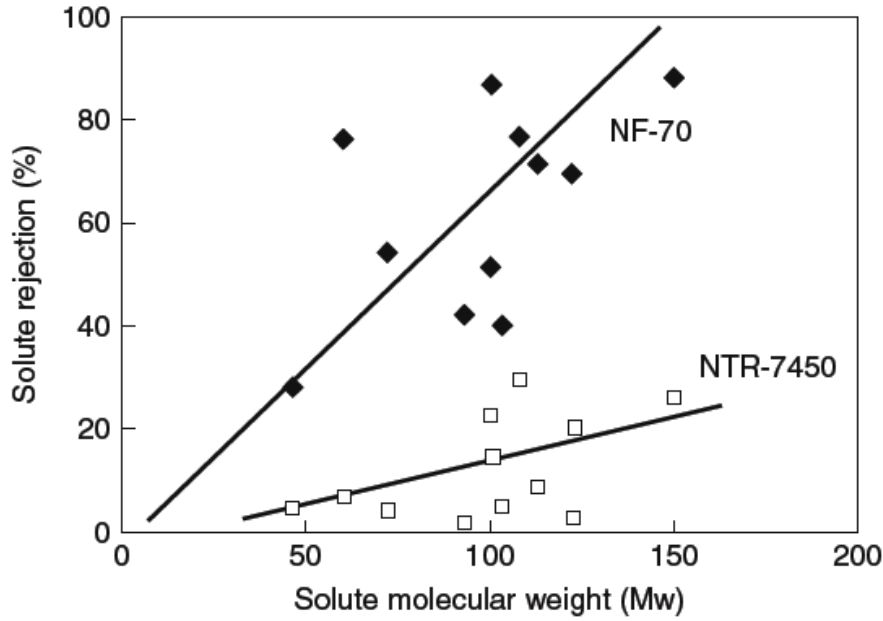


Figure 11. Common Solute rejection vs. Solute MW diagram (BAKER, 2012).

In membrane systems such as RO, the degree of membrane selectivity for the separation of the particular substance can be evaluated through a coefficient known as the rejection coefficient “R” and it can be calculated as indicated in equation 6.

$$R = \left(1 - \frac{C_{pi}}{C_{fi}}\right) * 100\% \quad (Eq. 6)$$

Where,

C_{pi} (mg/L) = Concentration of species “i” in permeate

C_{fi} (mg/L) = Concentration of species “i” in feed

Based on the rejection equation, two extreme cases can be found, which include the perfectly selective and unselective membranes. For a completely unselective membrane the rejection coefficient is equal to 0%, which means that the concentration of the species is equal in both the feed and the permeate streams. On the other hand, perfectly selective membranes have rejection coefficient equal to 100% in which the concentration of the species in the permeate is equal to zero (BAKER, 2012).

2.4.1. Membrane contactor:

As is the case of any other membrane process, the membrane act as a selective barrier where substances are either retained or can pass through the physical barrier (BAKER, 2012). But, what makes membrane contactors important is that they can achieve the same degree of separation as other well-known processes such as gas absorption and liquid-liquid extraction and with the advantage of considerably reducing the volume of equipment needed, which can be more than 20 or even 500 times smaller than the volume required by the conventional separation processes. For that reason, usually membrane contactors are hollow fiber modules with

microporous membranes and large surface area per volume. The selection of the membrane can be particular for the application but in general two heuristics are followed. The first is to choose a membrane that can be wetted by the fluid that has the higher partition for the solute of interest and the second is that the selected membrane promotes solute diffusion. Applications of membrane contactor are found in drug recovery, ammonia stripping, oxygen transfer and extraction of solvents and VOCs (Reed, et al., 1995).

Membrane contactors have been used in the removal and recovery of ammonia from industrial wastewaters in a process known as Trans-Membrane-Chemi-Sorption (TMCS). The process relies in the shift of equilibrium in between NH_4^+ and NH_3 when pH conditions are changed, favoring the formation of either one of the N species (3M, 2018). The composition of NH_3 as a function of pH and T are illustrated in figure 12.

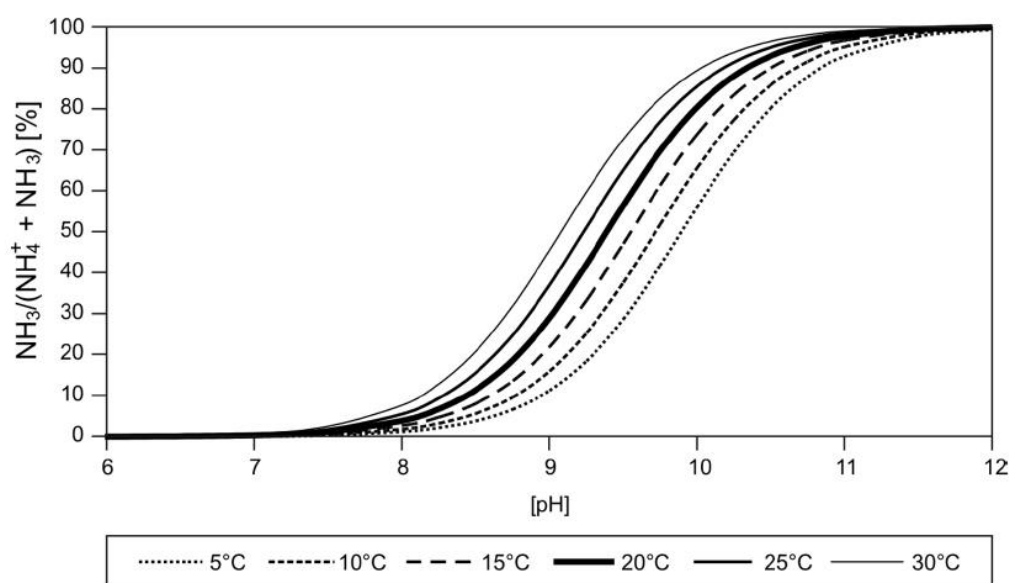
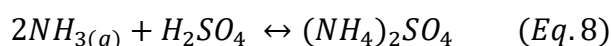
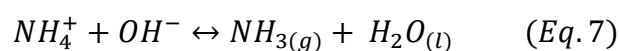


Figure 12. Composition of NH_3 in the NH_4 - NH_3 equilibrium at different pH and T conditions (Ehrig & Robinson, 2011)

Figure 12 indicates that as the pH and T increases so does the formation of NH_3 gas. Hence, in the TMCS the formed NH_3 gas diffuses through the air that fills the microporous material of a hydrophobic hollow fiber membrane and then it is recovered by the reaction in between NH_3 and H_2SO_4 and the formation of $(\text{NH}_4)_2\text{SO}_4$. The process relies in the hydrophobicity and the small pores of the membrane to prevent the aqueous phases to go across and get in contact with each other. The reactions that take place during the process, when NH_3 formation is being favor due to the increase in pH and when ammonium sulfate is being produced are indicated in equations 7 and 8 respectively (3M, 2018).



Furthermore, during operation the wastewater runs through the shellside, which is the outside of the membrane and the sulfuric acid solution flows through the lumen side of the membrane contactor. The reactions and the TMCS operation mode are illustrated in figure 13.

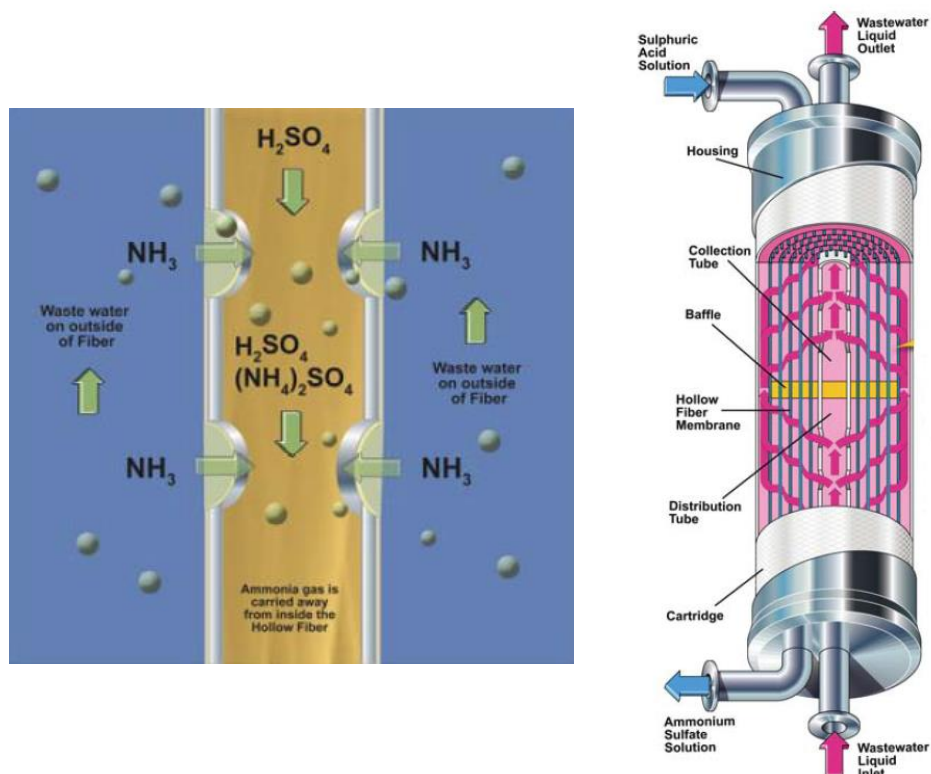


Figure 13. TMCS process for the removal of NH_3 from wastewater (3M, 2018)

Some of the advantages of the TMCS process for the removal of ammonia include very compact modules compare to the conventional alternatives such as air stripping, also up to 95% of ammonia can be removed and recovered as ammonium sulfate solutions with concentrations up to 30%, which can be further use as a fertilizer (3M, 2018). A description of commercial membrane contactors are given in table 10.

Table 10. Description of Liqui-Cel[®] hollow fiber membrane contactor; Adapted from (BAKER, 2012)

Module dimensions		No. of fibers (*1000)	Membrane Area (m^2)	Area/Volume (cm^2/cm^3)
Diameter (cm)	Length (cm)			
8	28	8	1,4	29
10	71	45	19	36
25	71	300	130	39

2.5. BIOLOGICAL NITROGEN REMOVAL

The processes involved in the different technologies used for the biological removal of nitrogen generally include Nitrification/Denitrification, Nitritation/Denitrification or Deammonification. The main steps of the mentioned processes and some of their characteristics are given in figure 14.

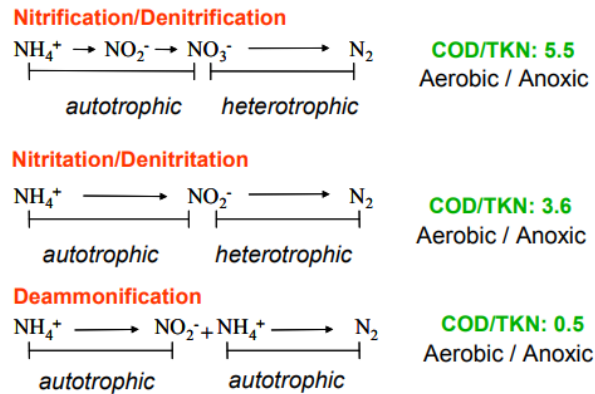


Figure 14. Processes involved in the biological removal of nitrogen (Jardin, et al., 2006)

Nitrification/Denitrification is regarded as the conventional method for the removal of N where the main forms of N with respect to their oxidation state are ammonia (NH_3) and ammonium (NH_4^+) with oxidation number of minus three (-3), nitrogen gas (N_2) with oxidation number of zero (0) and nitrite (NO_2^-) and nitrate (NO_3^-) with oxidation numbers of plus three (+3) and plus five (+5) respectively. The conventional pathways followed by N in biological treatment processes are shown in figure 15.

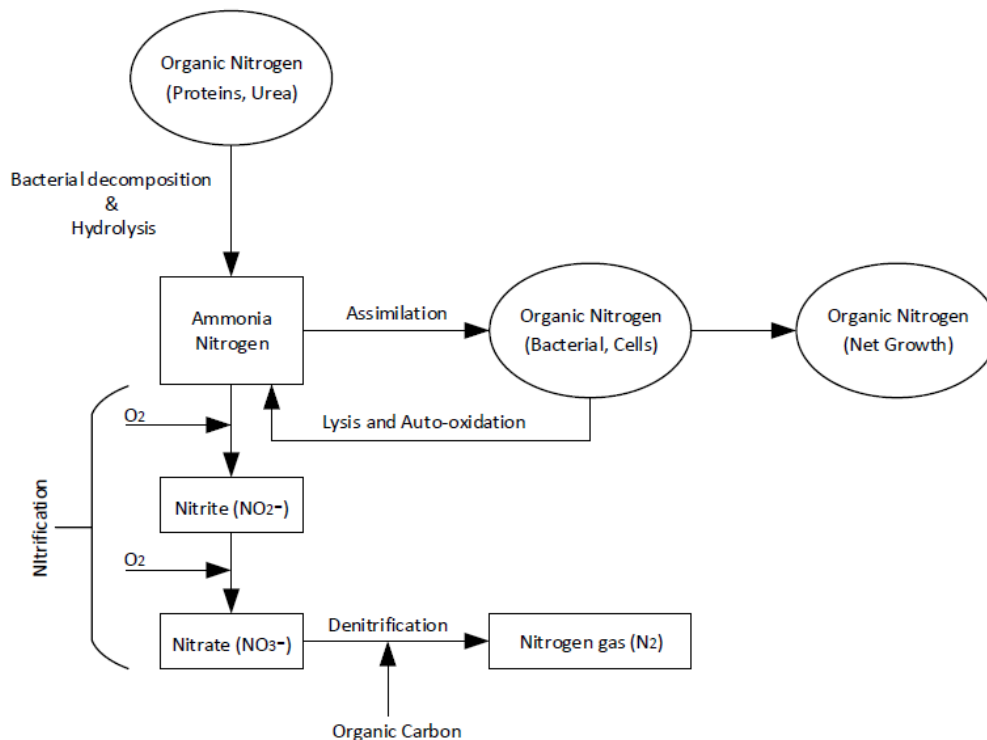
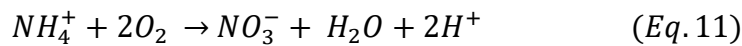
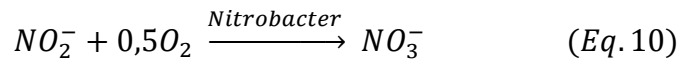
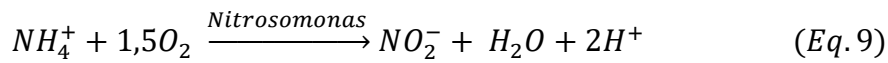


Figure 15. Conventional N transformation in biological treatment processes; Adapted from (Sedlak, 1991)

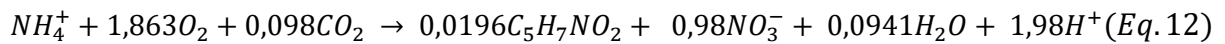
As illustrated in figure 15, biological decomposition and hydrolysis of organic-N compounds like urea leads to the formation of ammonia. The ammonia nitrogen will eventually be assimilated by microorganisms for the formation of new cells where approximately 12 to 13 % of the cell dry mass corresponds to nitrogen. Some of the assimilated nitrogen will return to the system due to cell lysis either caused by process conditions or other biological factors. Furthermore, ammonia nitrogen in the presence of oxygen can be further oxidized to nitrite and nitrate in a process known as nitrification by the group of microorganisms commonly known as nitrifiers. Finally, nitrate in the absence of oxygen but with the presence of carbon source can be transformed to nitrogen gas through a process known as denitrification (Sedlak, 1991).

2.5.1. Nitrification

Nitrification can be described as a two-step process in which aerobic, autotrophic nitrifying bacteria oxidizes ammonia to nitrate. In activated sludge processes the main genera of nitrifying bacteria are the *Nitrosomonas* and *Nitrobacter*. In the first step, the *Nitrosomonas* or ammonia oxidizing bacteria (AOB) oxidizes ammonium to nitrite and in the second step the *Nitrobacter* or nitrite oxidizing bacteria (NOB) oxidizes the nitrite produced by the AOB to nitrate. The reactions for AOB, NOB and the total oxidation reaction are shown in equations 9, 10 and 11 respectively (Wiesmann, et al., 2007).



Furthermore, the overall reaction that includes both oxidation and synthesis is given by equation 12, where the bacteria cells are represented by the formula $C_5H_7NO_2$ (Sudarno, 2011).



As indicated in equations 9 through 12, some of the main characteristics of nitrifiers can be described as high oxygen demanders, generate small amounts of biomass when compared to the oxygen they take and they affect the alkalinity of the system by the generation of hydrogen ions (H^+) and consumption of CO_2 . For example, for each gram of NH_3-N they convert to NO_3^- , approximately 4,25 g of O_2 and 0,30 g of CO_2 are consumed for the formation of about 0,16 g of new biomass. Another important characteristic is that they grow slower than heterotrophic bacteria whose maximum specific growth rate is approximately 10 to 20 times larger compare to nitrifying bacteria. The slow growth of nitrifiers is explained by the low amount of energy obtained by the oxidation of inorganic matter and the high energy that is required to assimilate the inorganic carbon as the carbon source. For instance,

typical doubling time for nitrifiers and heterotrophic bacteria at 20°C can be found in between 24 to 48 h and in between 20 to 30 min respectively (AQUAFIX, 2020). A comparison between the auto-chemolithotrophic process corresponding to nitrifiers and the hetero-chemoorganotrophic process is shown in figure 16.

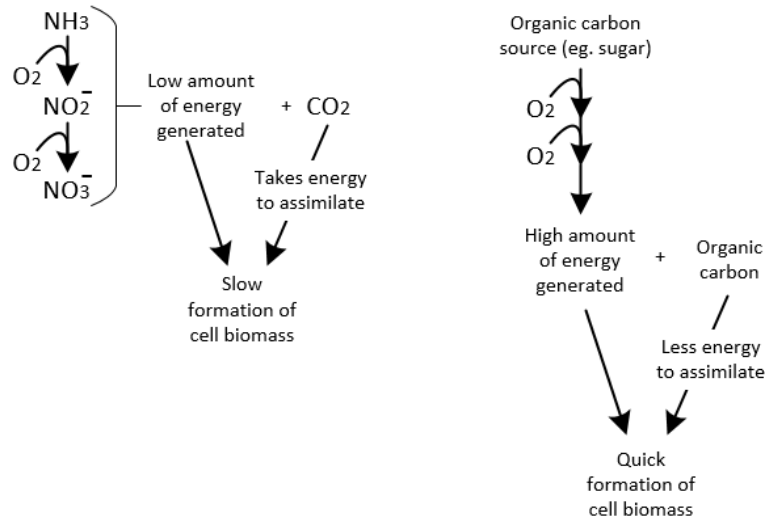
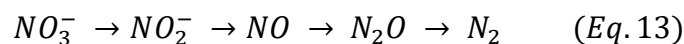


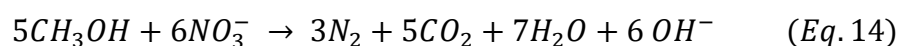
Figure 16. Auto-chemolithotrophic vs. hetero-chemoorganotrophic process; Adapted from (AQUAFIX, 2020)

2.5.2. Denitrification

Denitrification is known as the reduction of nitrate or nitrite to different reduced forms such as nitrous oxide (N_2O), nitrogen monoxide (NO) and Nitrogen (N_2). The biological reduction is performed by a diverse group of facultative heterotrophic microorganisms that are able to use nitrate or nitrite as the final electron acceptor instead of molecular oxygen (O_2). The general denitrification reaction is given by equation 13.



As described in equation 13, the reduction of nitrate or nitrite during the denitrification process is a chain of different intermediate products owed to the activity of specific reductase enzymes, which are promoted by the lack of molecular oxygen (O_2) in the system. The term anoxic has been used to distinguish anaerobic conditions in biological systems where nitrate and/or nitrite are the main electron acceptor (USA-EPA, 2009). Furthermore, if the organic substrate in the system is methanol its oxidation reaction for the formation of N_2 can be represented by equation 14 (Metcalf & Eddy, et al., 2003).



A comparison between nitrifying and denitrifying bacteria is given in table 11.

Table 11. Nitrifying vs. denitrifying bacteria; Adapted from (Wiesmann, et al., 2007)

Characteristic	Nitrifiers		Denitrifiers
	AOB	NOB	
C-source:	Inorganic (CO ₂)	Inorganic (CO ₂)	Organic carbon
Cell shape:	Coccus (spherical)	Bacillus (rod-shaped)	-
Cell size: (µm)	1,0 – 1,5	0,5 – 1,0	-
O ₂ demand:	Obligate aerobic	Obligate aerobic	Facultative aerobic
pH range:	5,8 – 8,5	6,5 – 8,5	6,5 – 8,5
t _{Growth} : (h)	8 - 36	12 - 60	0,25 – 0,5
T _{Growth} range: (°C)	5 – 30	5 - 40	

2.5.3. Environmental factors affecting nitrification

In general, nitrifiers are more sensitive to changes in environmental conditions than heterotrophic microorganisms. The main environmental factors affecting nitrification processes are substrate availability, pH, temperature and the presence of toxic substances (Wang, et al., 2009).

The effect of substrate concentration on the kinetics of nitrification processes can be explained by Monod equation. In its standard form, the Monod equation describes the growth rate of bacteria as a function of the dissolve limiting substrate concentration available for the microorganisms. The standard Monod equation is given by equation 15 (Sudarno, 2011).

$$\mu = \mu_{max} \frac{S}{K_s + S} \quad (Eq. 15)$$

Where,

μ (mg new cells/mg cells·h⁻¹) = Specific growth rate

μ_{max} (h⁻¹) = Maximum specific growth rate

S (mg/L) = Concentration of limiting substrate

K_s (mg/L) = Saturation coefficient or Monod constant

The specific growth rate can be defined as the ratio between the rate of biomass produced and the original biomass present in the system and the saturation coefficient is the substrate concentration corresponding to one half the maximum specific growth rate (Metcalf & Eddy, et al., 2003). Figure 17 describes the relation between specific growth rate and substrate concentration given by the Monod equation.

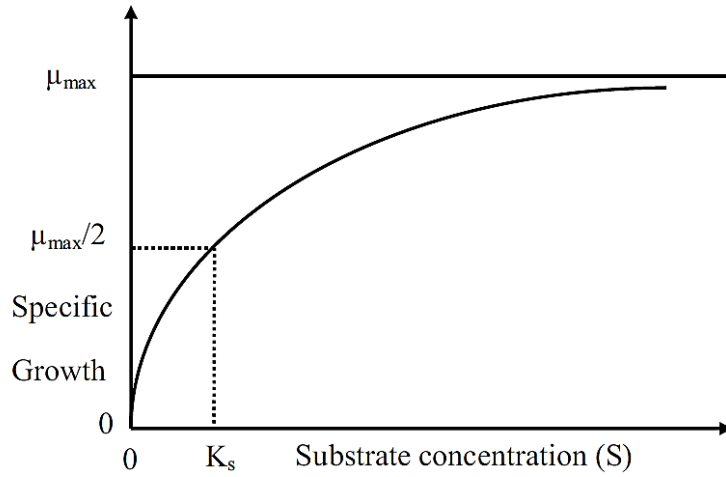


Figure 17. Monod model for bacterial growth (Sudarno, 2011)

As seen in the Monod model, bacteria grow at its maximum rate when the substrate concentration is readily available. Thus, for the case of nitrifying bacteria, parameters such as dissolve oxygen (DO) concentration need to be monitored during the biological processes. Also, as indicated in equation 12, inorganic carbon is an important substrate that needs to be considered during nitrification processes. However, the equilibrium of the different forms of inorganic carbon depends on the pH conditions of the system as indicated in figure 18.

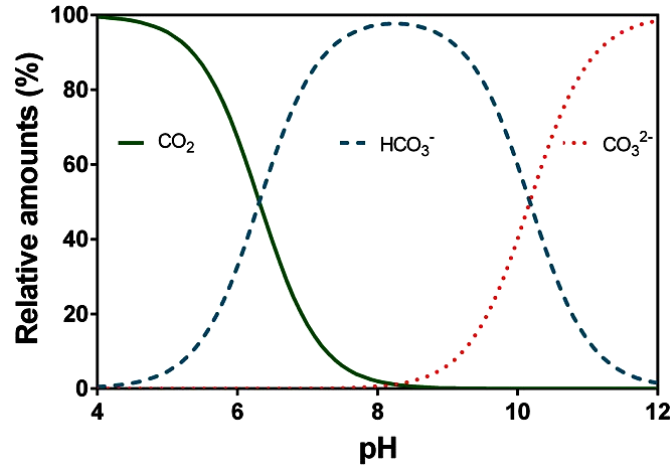


Figure 18. Equilibrium of inorganic carbon with respect to pH (Pedersen, et al., 2013)

Furthermore, the effect of temperature in nitrification systems is mainly reflected in the growth rate of the microorganisms. Expressions describing the specific growth rate constant (μ) of *Nitrosomonas* (AOB) and *Nitrobacter* (NOB) in suspension systems as a function of temperature have already been published and are given in equations 16 and 17 for the AOB and NOB respectively (Knowles, et al., 1965).

$$\log_{10}\mu_{NS}(d^{-1}) = 0,0413T(^{\circ}C) - 0,944 \quad (Eq. 16)$$

$$\log_{10}\mu_{NB}(d^{-1}) = 0,0255T(^{\circ}C) - 0,492 \quad (Eq. 17)$$

The application range of the given expressions is approximately in between 8 to 30°C. These equations suggest an increase in the AOB and NOB growth rate

constant of approximately 10 and 6% per increase in degree Celsius respectively and for a given temperature the growth rate of AOB is almost 50% greater than the one from NOB (Knowles, et al., 1965). In general, nitrification critical temperatures are found to be below 5°C and over 40°C and for a pH value of 7,5 the optimal nitrification temperature can be found in between 30 to 37,5 °C (Wiesmann, et al., 2007). However, for the case of biofilm systems the effect of temperature on nitrification growth rates could be more complex to quantify than for the case of suspended systems considering the effects of other external factors such as oxygen limitations due to mass transfer mechanisms (Sudarno, 2011).

Moreover, with respect to toxic substances in nitrification processes, free ammonia (FA) and free nitrous acid (FNA) are known to inhibit nitrification. In general, FA can affect both AOB and NOB where NOB is more sensitive than AOB to FA concentrations. Free ammonia can start to inhibit AOB and NOB at concentrations around 10 to 150 mg/L and 0,1 to 4,0 mg/L respectively. The FA inhibition may lead to accumulation of nitrite in the system, which may promote the formation of nitrous acid. Hence, further affecting the NOB whose nitrous acid inhibition can take place at concentrations starting from 0,2 or 2,8 mg/L (Wang, et al., 2009). Besides the inhibitory effects caused by FA and FNA, other organic and inorganic compounds have been reported to inhibit nitrification rates at concentration levels so much lower compared to the ones that normally affect aerobic heterotrophic microorganisms. Many organic compounds include amines, proteins, tannins, phenolic compounds, alcohols, cyanates, ethers, carbamates and benzene. For that reason, in wastewater treatment plants it is difficult to find the source of nitrification toxicity considering the complexity of wastewater composition and the large amount of organic substance that may interfere with the nitrification process (Metcalf & Eddy, et al., 2003). Some examples of organic compounds include thiourea and 2-chloro-6-(trichloromethyl) pyridine (TCMP), which have been used to inhibit nitrification during BOD tests (Orhon & Artan, 1994). Furthermore, some metals such as nickel (Ni), chromium (Cr) and copper (Cu) have been reported to inhibit ammonia oxidation at concentrations levels of 0,25, 0,25 and 0,10 mg/L respectively (Metcalf & Eddy, et al., 2003). Other metals include cadmium (Cd), zinc (Zn) and lead (Pb). Their general inhibitory effect in nitrification systems increases in the following order $Cd > Cu > Zn$ and $Pb > Cr$ (Wang, et al., 2009).

CHAPTER 3: COMPOSITION ANALYSIS AND EVALUATED PROCESSES

3.1.COMPOSITION AND SELECTIVITY ANALYSIS IN MEMBRANE SYSTEMS FROM A LANDFILL LEACHATE TREATMENT FACILITY

3.1.1. Materials and Methods

The composition and selectivity analysis were performed on the streams corresponding to a RO system and NF and RO stages, which are part of the landfill leachate treatment process located at a landfill site in northern Germany. In general, the landfill leachate treatment is composed of different pretreatment steps, which include among others pH adjustment and sand filtration units follow by a RO system and a series of concentrate volume reduction steps.

The pretreated landfill leachate (LL) is fed to a RO system, which consisted of a RO and high pressure RO stages with pressures around 75 and 120 bars respectively where the first generated landfill leachate concentrate (LLC-1) is fed to a NF-stage for further treatment and the high pressure RO permeate (HROP) is directed to a series of adaption ponds before its final release to the environment. The operating pressure in the NF-stage ranged in between 10 to 20 bars.

After the NF-stage the generated landfill leachate permeate (LLP) is fed to a high pressure RO (HPRO) stage and the second generated landfill leachate concentrate (LLC-2) is fed to a RO stage with pressures around 70 bars. The permeate generated in the RO stage (ROP) is mixed with the HROPs and the generated concentrates from the membrane stages are mixed and further treated in an evaporation system.

Additionally, each of the membrane stages are made up of different number of plate and frame modules having thin film composite polyamide as the membrane material and the temperature in the membrane processes can be found in between 30 to 35°C. The overview of the landfill leachate treatment facility and the sampling points are illustrated in figure 19.

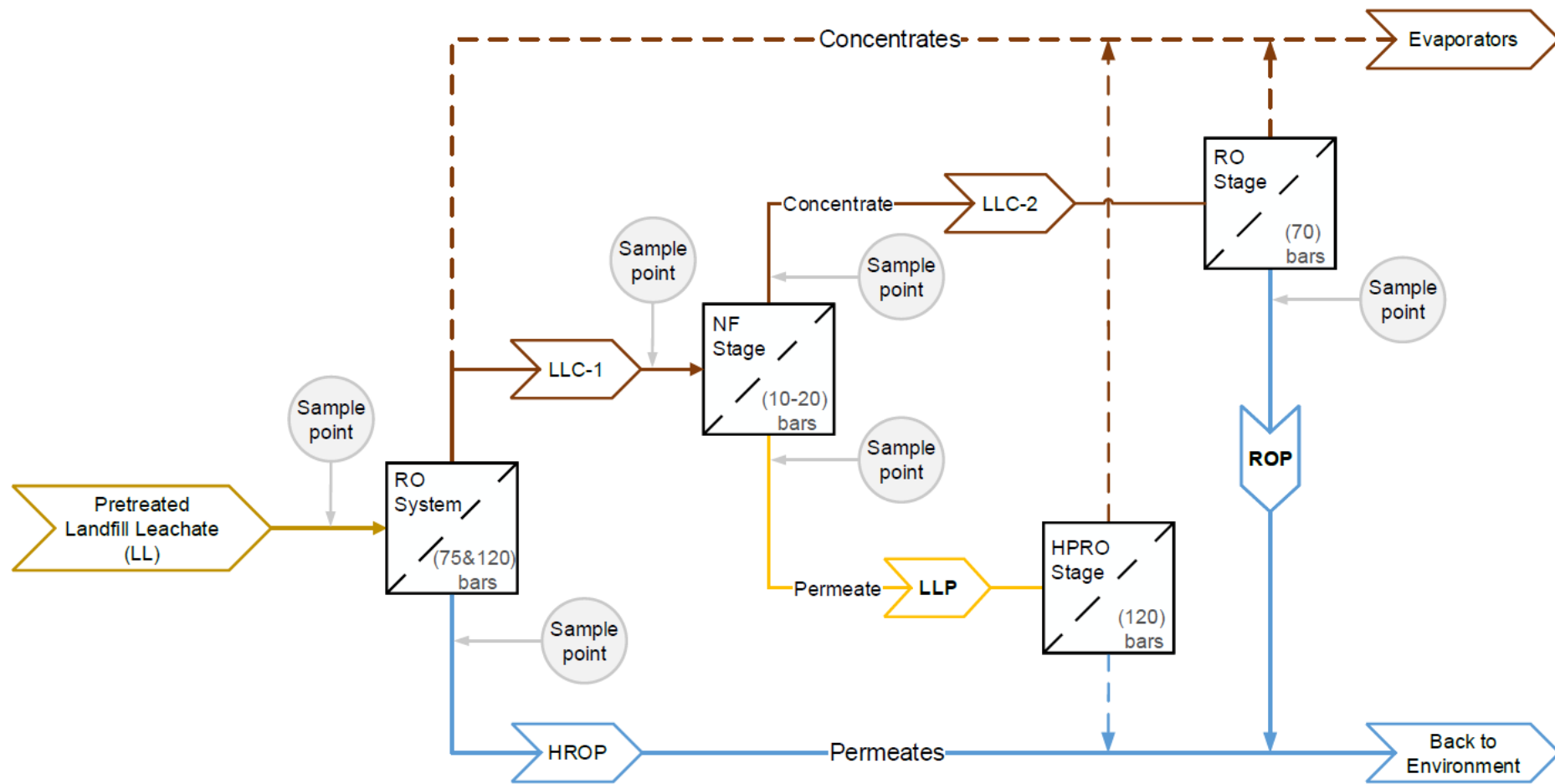


Figure 19. Overview of the landfill leachate treatment facility and sampling points

The composition analysis in each of the streams were performed by using different analytical methods, which include among others Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Spectrophotometry. For the elemental analysis the samples were pretreated with aqua regia and parameters such as pH, conductivity and TSS were measured off-site. Furthermore, some characteristics of the analyzed streams such as high salinity, color and complex matrix might have influenced or interfered with the different analytical methods; hence generating uncertainties in the results. Thus, based on previous composition analysis performed on the same streams and the comments given by the University's central lab for chemical analysis most of the results' uncertainties were within 5%. However, some substances such as Si yielded high scattered results as well as Pb, Mo, Zn and As whose uncertainties in the results might had been around 10%.

The TSS was analyzed in the landfill leachate and concentrates as described in the Standard Method 2540D for Total Suspended Solids Dried at 103-105°C. The analytical methods used for each of the analyzed substances, the corresponding equipment and the raw data are given in appendixes A, B and C respectively.

3.1.1.1. Analytical Methods







ICP-MS and ICP-OES are techniques used to determine the elemental composition of aqueous samples such as wastewater. The ICP is based on the use of a very hot argon plasma at about 8000 K for the ionization of the analyze elements; the sample to be analyzed is first converted into an aerosol and then introduce into the plasma flame where it is ionized. In the case of ICP-MS, the resulting ions are transferred to the mass spectrometer where they are separated based on the mass-to-charge ratio, then detected and quantified with the help of an external calibration solution (Cöllen & Frerichs, 2018). For the case of ICP-OES, the emission intensity of the light produced by the excited matter is detected in a wavelength range of 170 to 900 nm and quantified through the use of a calibration solution. The elements are detected based on the wavelength of the spectral line and their quantification is based on the linear relation that exists in between the signal intensity of the emitted light and the concentration of a substance (Fütterer, 2018). Furthermore, spectrophotometry as the OES is a spectroscopy technique in which the interaction of light with matter is analyzed for the determination of properties in a substance such as concentration. For the case of spectrophotometry, the absorbed light is of importance, which differs from the OES in which the emitted light is the one being analyzed. In general, a spectrophotometer can be divided in two main sections. The first part or spectrometer section is composed of a light source, a collimator (lenses), a monochromator (prism) and a wavelength selector. In this first section, the light emitted by the source is transmitted by the collimator into the monochromator as straight beam where it is separated into its different components and then manipulated by the wavelength selector in order to get the desire wavelength. The second part is the photometer, which is the section that follows the absorption process and where the amounts of photons absorbed by the analyte are estimated by a detector (photocell)

(Chem.LibreTexts, 2020). The amount of analyte present in the sample is estimated based on the linear relation between absorbance and the analyte concentration, which is described by Beer-Lambert law or just Beer's law. (Holler, et al., 2013).

3.1.2. Results and Discussion

The parameters measured in the analyzed samples corresponding to the different streams collected from the landfill leachate treatment facility are given in table 12. The pH and conductivity were measured in the collected samples at a temperature of $22\pm 2^{\circ}\text{C}$ with an average pH value equal to $6,5\pm 0,2$.

Table 12. Parameters in streams generated at the landfill leachate treatment facility

Membrane Processes	Stream	Cond. (mS/cm)	Hardness [‡]		TSS (mg/L)
			(°dH)	as CaCO ₃ (mg/L)	
RO System	LL-Input 	30,9±0,6	101±5	1800	7,2±0,5
	HROP 	0,0874 ±0,0016	<1	<18	-
NF Stage	LLC-1 _{Input} 	96,1±1,8	344±17	6120	44,4±3,0
	LLP 	91,9±1,7	292±15	5200	-
RO Stage	LLC-2 _{Input} 	102,5±1,9	428±21	7620	755±50
	ROP 	2,22±0,04	2,1±0,1	37,5	-
-	Tap Water	0,264 ±0,005	6,8±0,3	121	-

[‡]Lenntech hardness calculator for CaCO₃ conversion (Lenntech, 2020)

As seen in table 12, one of the main characteristics of the landfill leachate treatment facility is the wide range in conductivity and hardness among the analyzed streams where the only stream whose conductivity was below the value of 264 $\mu\text{S/cm}$ corresponding to the local tap water was the HROP with a value of about 87,4 $\mu\text{S/cm}$, which was very close to the range of 1 to 80 $\mu\text{S/cm}$ characteristic of demineralized water at 25°C (Van London Co., 2019). In contrast, the conductivities of the LLP and LLC-1 were very close to each other with values around 95 mS/cm and the highest conductivity corresponded to the LLC-2 with a value of 102,5 mS/cm.

These values were almost twice the value of 53 mS/cm characteristic of ocean waters and are within the range of industrial process water, which can be found in between 7 to 140 mS/cm at 25°C (Van London Co., 2019). Additionally, the conductivity values for both the HROP and the ROP are below the limit value of 2,5 mS/cm at 20°C indicated on the EU directive of 1998 “on the quality of water intended for human consumption” (European Commission, 1998)

Furthermore, the hardness values in the HROP and ROP were below the local tap water value of 121 mg/L as CaCO₃ and as indicated in table 8 these two permeates were the only streams that could be categorized as soft water considering that their hardness were below 60 mg/L as CaCO₃. On the other hand, the conductivity of the other analyzed streams had values considerably greater than 180 mg/L as CaCO₃, which not only categorized them as very hard water but also indicated the highly likelihood of aggressive scaling during the treatment of these streams within the membrane processes.

The reduction of hardness and conductivity in each of the evaluated membrane systems are illustrated in figure 20.

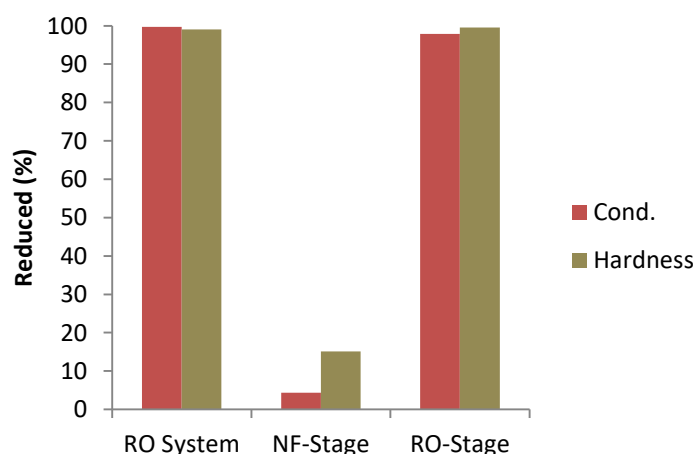


Figure 20. Reduction of hardness & conductivity in membrane systems

As seen in figure 20, the reduction of hardness and conductivity in the high pressure RO system and the RO stage were greater than 98%, which as indicated in chapter 2.4 the results were within the typical salt rejection values found in RO membranes of about 98 to 99%. However, for the low pressure NF-stage the reduction of hardness and conductivity were only of about 15 and 4% respectively, which indicated low rejection of salinity and as discussed in chapter 2.4 the rejection of salinity in NF systems can be found around 20% where substances such as NaCl might have the lowest rejections.

Based on the LL composition, the results obtained for the analyzed substances in the evaluated streams were divided into three groups. The first group included substances whose concentrations in the landfill leachate were found to be in the range of 1 to 10 g/L. The second group included substances whose concentrations were within 1 to 1000 mg/L and the third group included those whose concentrations were less than 1000 µg/L. The results obtained for the composition analysis

corresponding to the each of the described groups are given in tables 13 through 15. Additionally, a comparative matrix for the evaluated streams with respect to the landfill German regulation is given in appendix C.

Table 13. Group 1: Macro-substances; based on landfill leachate composition (Range: 1 – 10 g/L)

Membrane Processes:		RO System		NF Stage		RO Stage	
Substance	Units	LL-In	HROP	LLC-1-In	LLP	LLC-2-In	ROP
Cl ⁻	(g/L)	9,3	0,008	33	33	30	0,44
Na	(g/L)	4,46	0,088	17,0	15,6	18,4	0,22
COD	(g/L)	2,38	<0,10	8,9	6,06	12,9	0,11
SO ₄ ²⁻	(g/L)	1,69	<0,15	10,46	9,26	20,8	<0,15
K	(g/L)	1,015	<0,08	1,61	1,66	1,63	0,12

Red: Substances whose limit values are stated in the EU Directive and/or German landfill regulation, see table 3

As indicated in table 13, from the analyzed substances five had concentration values in the landfill leachate located within the 1 to 10 g/L range and as described in table 1 all of these substances are considered in landfill leachate as macro-substances. The three substances with the highest concentration in the LL were Cl⁻, Na and COD. This was almost the case for the LLC-1, LLP and LLC-2 where only SO₄²⁻ replaced COD as the third highest in concentration, which might be linked directly to the use of H₂SO₄ acid during the treatment process for the adjustment of pH. Also, based on table 2, the concentration values of Cl⁻ and COD in the landfill leachate were within a range of 1 to 10 g/L, which are characteristic of a methanogenic phase leachate. Furthermore, based on table 3, the COD concentration in the HROP and ROP were below the limit values of 200 and 125 mg/L indicated in the German landfill regulation and EU Directive respectively. Additionally, the COD in the LLP was about 2,5 times higher than the COD in the LL but about 30 and 50% less than the COD values corresponding to the LLC-1 and LLC-2 respectively.

Table 14. Group 2: Macro-substances; based on landfill leachate composition (Range: 1 – 1000 mg/L)

Membrane Processes:		RO System		NF Stage		RO Stage	
Substance	Units	LL-In	HROP	LLC-1-In	LLP	LLC-2-In	ROP
TOC	(mg/L)	662	2,7	2106	1348	3937	18,7
TN	(mg/L)	657	3,8	2322	2032	2547	89,9
NH₄⁺-N	(mg/L)	598	3,5	1942	1920	2120	80,5
TIC	(mg/L)	561	18,1	615	284	336	48,7
Ca	(mg/L)	443	<5	1470	1278	1875	9,44
Mg	(mg/L)	169	<3	595	488	715	3,24
Br ⁻	(mg/L)	110	<40	430	420	380	8
NO₃⁻-N	(mg/L)	5,6	<0,23	19,2	<0,23	56,0	<0,23

Red: Substances whose limit values are stated in the EU Directive and/or German landfill regulation, see table 3

As seen in table 14, and as indicated in table 1, from these substances $\text{NH}_4\text{-N}$, Ca, Mg, TIC and TOC are considered in landfill leachates as representative species of either the main inorganic or bulk organic matter groups. Also as indicated in table 2 the concentrations of Ca and $\text{NH}_4\text{-N}$ within this range are characteristic of a methanogenic phase leachate. Furthermore, as described in table 3 for the German landfill regulation, the limit value of TN is 70 mg/L, from the analyzed streams the only permeate whose TN was considerably below this limit value was the HROP with a concentration of about 3,8 mg/L. Even though the TN concentration in the ROP was considerably lower compared to the other analyzed streams including the LLP, its concentration of about 89,9 mg/L was still slightly higher than the limit value indicated in the German regulation. Furthermore, the concentration of $\text{NH}_4\text{-N}$ and Ca in the LLP were about 3 times higher than the concentration of these substances in the landfill leachate and compare to the concentrates, the $\text{NH}_4\text{-N}$ concentration in the LLP was only about 1 and 9% less than the values in the LLC-1 and LLC-2 respectively and for the case of Ca the concentration in the LLP was only about 13 and 30% less than the values in the LLC-1 and LLC-2 respectively. Moreover, the tendency for TOC was very similar to COD, for instance the TOC concentration in the LLP with value of 1348 mg/L was almost 2 times higher than the one from the LL but almost less than 35 and 65% the TOC values corresponding to the LLC-1 and LLC-2 respectively. Additionally, the concentration of $\text{NO}_3\text{-N}$ in all of the evaluated streams were in between 1 to 100 mg/L, which based on the concentration range is located in between the macro- and trace- substances. The removal of $\text{NO}_3\text{-N}$ from effluents is of environmental and human health importance since it is not only responsible for eutrophication but also its presence in drinking water is linked to a blood disorder known as blue baby syndrome, which mainly affects children under the age of 4 months (WEF, 2008).

Table 15. Group 4: Trace-substances indicated in German landfill regulation; based on landfill leachate composition (Range: <1000 µg/L)

Membrane Processes:		RO System		NF Stage		RO Stage	
Substance	Units	LL _{-In}	HROP	LLC-1 _{-In}	LLP	LLC-2 _{-In}	ROP
$\text{NO}_2\text{-N}$	(µg/L)	<600	<600	<600	<600	<600	<600
Ni	(µg/L)	400	<40	1500	680	2800	<40
Cu	(µg/L)	240	<80	740	<80	1910	<80
Zn	(µg/L)	210	-	610	90	1330	<80
CN ⁻	(µg/L)	210	<5	890	290	1490	10
Cr	(µg/L)	180	<40	610	<200	1500	<40
As	(µg/L)	150	<40	320	290	570	<40
Pb	(µg/L)	50	<40	<200	<200	360	<40
Cd	(µg/L)	<40	<40	<200	<200	<200	<40
Tl ⁺	(µg/L)	<40	<40	<200	<200	<200	<40
Hg	(µg/L)	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25

*Not regulated in German landfill regulation

As seen in table 15, most of the analyzed substances with concentrations below 1000 µg/L were heavy metals and as described in table 1 and 2, based on the concentration range they are considered trace compounds in landfill leachates whose common concentrations in methanogenic phase leachates are found below 1000 µg/L or even lower than 1 µg/L, which is the case of Hg. Additionally, based on table 3 for the German landfill regulation, in all of the analyzed streams the concentration of NO₂-N, Zn, Pb and Hg were below the limit values of 2000, 2000, 500 and 50 µg/L respectively. And, with respect to the permeates the concentration of Ni, Cu and Cr in the LLP were also below the limit values and for the HROP and ROP the concentration of all of the analyzed trace substances were below the limit values indicated in the landfill German regulation.

Furthermore, based on the results obtained in the composition analysis some relevant ratios were calculated for each of the streams as indicated in table 16.

Table 16. Relevant substances ratios in membrane systems

Membrane Processes	Stream	Relevant ratios		
		TOC/COD	NH ₄ -N/TN	Ca/Mg
RO System	LL-In	0,28	0,91	2,7
	HROP	-	0,90	-
NF Stage	LLC-1-In	0,24	0,84	2,9
	LLP	0,22	0,94	2,9
RO Stage	LLC-2-In	0,31	0,83	3,0
	ROP	0,17	0,90	-

Table 16 shows that the TOC to COD ratio in the landfill leachate was closed to 0,3, which was also the case for the LLC-2. However, for the LLC-1, LLP and ROP this ratio was closer to 0,2 being a little lower in the ROP with a value of 0,17. Furthermore, in general the NH₄-N to TN ratios in the LL and analyzed permeates were near to 0,9 and for the concentrates it was close to 0,85. Finally, due to their low concentration the Ca to Mg ratio could not be determined in the HROP and ROP but for the other streams this ratio had a value close to 3.

Based on the composition analysis, the selectivity of the membrane systems for each of the analyzed substances was evaluated by using the rejection coefficient given by equation 6. However, due to the nature of the data many of the estimated rejections were obtained in terms of greater than ranges rather than specific values. The evaluated substances were classified in groups, which included among others the alkali and alkaline earth metals, transition metals, anions and nitrogen and carbon species. The results obtained in the selectivity analysis for each of the membrane system are given in table 17.

Table 17. Selectivity analysis for evaluated membrane systems

Group	Substance	Rejection (%)		
		RO System (RO & HPRO) (75 & 120 bars)	RO Stage (70 bars)	NF Stage (10 – 20 bars)
Alkali Metals	Na	98	99	8
	K	>92	93	0
Alkaline Earth Metals	Mg	>98	99	18
	Ca	>99	99	13
Transition Metals	Cr	>78	>97	>67
	Ni	>90	>99	55
	Cu	>67	>96	>89
	Zn	-	>94	85
Metal	Pb	>20	>89	-
Semimetal	As	>73	>93	9
Anions	Cl ⁻	99	99	0
	Br ⁻	>64	98	2
	CN ⁻	>98	99	67
	SO ₄ ²⁻	>91	>99	11
Nitrogen Species	NH ₄ ⁺ -N	99	96	1
	NO ₃ ⁻ -N	>96	>99	>99
	TN	99	96	12
Carbon Species	TOC	99	99	36
	COD	>96	99	32

Red: Substances whose limit values are stated in the EU Directive and/or German landfill regulation, see table 3

As described in table 17, the selectivity of the membranes in the high pressure RO systems for most of the evaluated substances approached the ideal case of perfectly selective membranes whose rejection coefficient as stated in chapter 2.4 is equal to 100%. On the other hand, some of the evaluated substances in the low pressure NF-stage yielded rejection values that were below 10% or even equal to zero, which as indicated in chapter 2.4 this corresponded to the case of unselective membranes. For instance, in the RO system and the RO stage for most of the analyzed substances it was possible to determine the selectivity of the analyzed substances with rejections values greater than 90% as indicated by the blue color. Also, the concentration of ions including Na⁺, Cl⁻ and SO₄²⁻ were the highest in the treated LL and LLC-2 and their rejections in their respective RO systems were also high with values greater than 98%, which correlated with figure 20 where the percentage reduction of conductivity within these membrane systems was also greater than 98%. On the other hand, the membrane selectivity for the alkali and alkaline earth metals in the low pressure NF-stage was very low, with many rejection values less than 20% as indicated by the orange color, which included the alkali and alkaline earth metals and most of the anions. For instance, the rejections for the alkali and alkaline earth metals were below 10% and only around 15% respectively and even no rejection was observed for substances such as K and Cl⁻, which correlated well with the low

reduction in conductivity of only about 4% illustrated in figure 20. Furthermore, in contrast to the alkali metals, the membrane selectivity in the NF-stage for the analyzed transition metals was considerable and in some cases relatively large such as Cu and Zn, which had rejection values estimated as >89 and 85% respectively. Moreover, with respect to the organic C parameters and N species, in general the membrane selectivity in the high pressure RO systems was very high with rejections greater than 95%. On the other hand, in the NF-stage the carbon species had rejections around 35% and the N-species with the exception of $\text{NO}_3\text{-N}$ had rejections around or below 10%. Additionally, $\text{NO}_3\text{-N}$ was the only analyzed substance whose rejection was possible to be estimated as greater than 96% in all of the membrane systems.

In order to evaluate the selectivity in the NF-stage with respect to the solute molecular weight, a rejection curve was obtained based on the estimated rejection percentages plotted as a function of the MW corresponding to the analyzed substances as illustrated in figure 21.

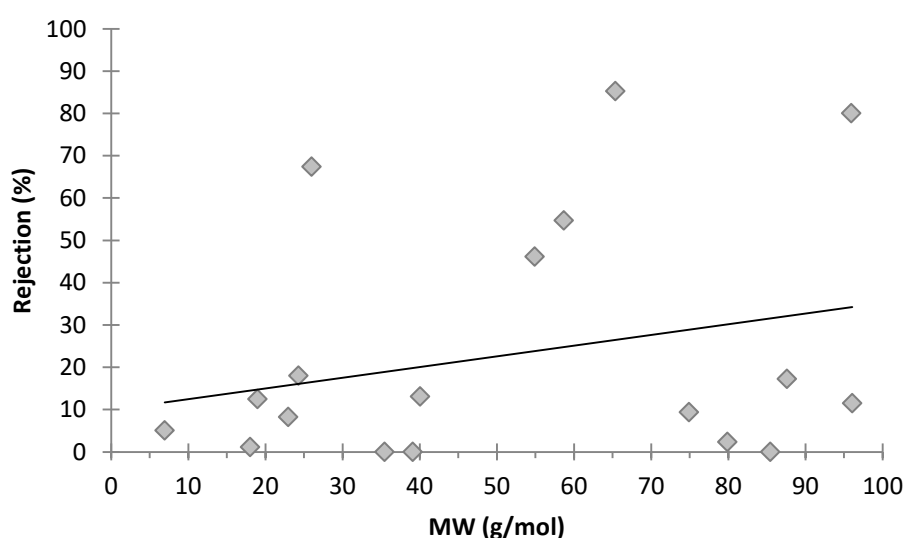


Figure 21. Rejection curve in NF-stage (P: 10 - 20 bars)

As seen in figure 21, the rejection curve obtained for the NF-stage was very similar to the one discussed in chapter 2.4 corresponding to the case of neutral nanofiltration membranes for the rejection of various salts based on their molecular weight. Furthermore, the trend line calculated by the use of the linear regression option in MS Office Excel 2010 indicated an increase of solute rejection based on the MW. This result might provide a good indication of better membrane selectivity for N-species such as NO_3 and NO_2 compared to NH_4 . For instance, the MW of NO_3 and NO_2 are 62 and 46 g/mol respectively, which are larger than the MW of NH_4 with value of 18 g/mol. Thus, the membrane selectivity in a NF system based on MW might be advantageous for the removal of N-species from landfill leachate streams but in the form of NO_3 and/or NO_2 rather than the typical form of inorganic-N found in wastewater such as NH_4 .

3.2.ADSORPTION TREATMENT FOR THE REMOVAL OF COLOR AND HEAVY METALS WITH PAC

3.2.1. Materials and Methods

Volumes of 500 mL of the collected landfill leachate permeate (LLP) were treated with powdered activated carbon (PAC) by using a jar test apparatus. The removal of color and TOC were analyzed at PAC dosages of 5, 10, 15 and 20 g/L and contact times of 10, 20, 30, 60 and 120 min. The removal of heavy metals and halogens were analyzed with adsorbent dosages of 5, 10, 20 and 40 g/L at a treatment time of 4 h. The jar test apparatus and the characteristics of the activated carbon used during the adsorption treatment are shown in figure 22 and table 18 respectively.

Table 18. Characteristics of powdered activated carbon (Sigma-Aldrich, 2020)

Particle size:	< 149 μm (-100 mesh)
Application:	Decolorizing
AIT:	450 $^{\circ}\text{C}$
mp:	3550 $^{\circ}\text{C}$
Brand:	Sigma Aldrich



Figure 22. Jar test apparatus used during PAC treatment

During the adsorption treatment the stirring was fixed at 300 rpm and conditions such as pH, temperature and conductivity were monitored during the treatment by the used of the portable multimeters specified in appendix B. After adsorption, for analysis, the activated carbon was separated from the treated permeate by using a vacuum filtration system and 0,45 μm nylon membrane filters as illustrated in figure 23.



Figure 23. Vacuum filtration system for PAC treatment

The TOC and TN concentrations were determined by using a Multi N/C 3000 analyzer and the color of the treated permeate was analyzed as described in the Standard Method 2120C for spectrophotometric single wavelength method.

For color determination, the standard stock solution with 500 CU was prepared as indicated in the Standard Method 2120B for visual comparison method section 4. The reagents used for its preparation were of analytical grade and are listed in appendix B. The color calibration curve and color analysis were determined by the use of the Spectrophotometer V-550 from JASCO at a wavelength of 456 nm as indicated in the standard method.

The concentration of the heavy metals and other elements were determined by using ICP-MS, ICP-OES, AAS and IC techniques as specify in appendix A and the name of the equipment used are given in appendix B.

The experimental procedure and operation conditions used during the adsorption treatment of the LLP with PAC are illustrated in figure 24.

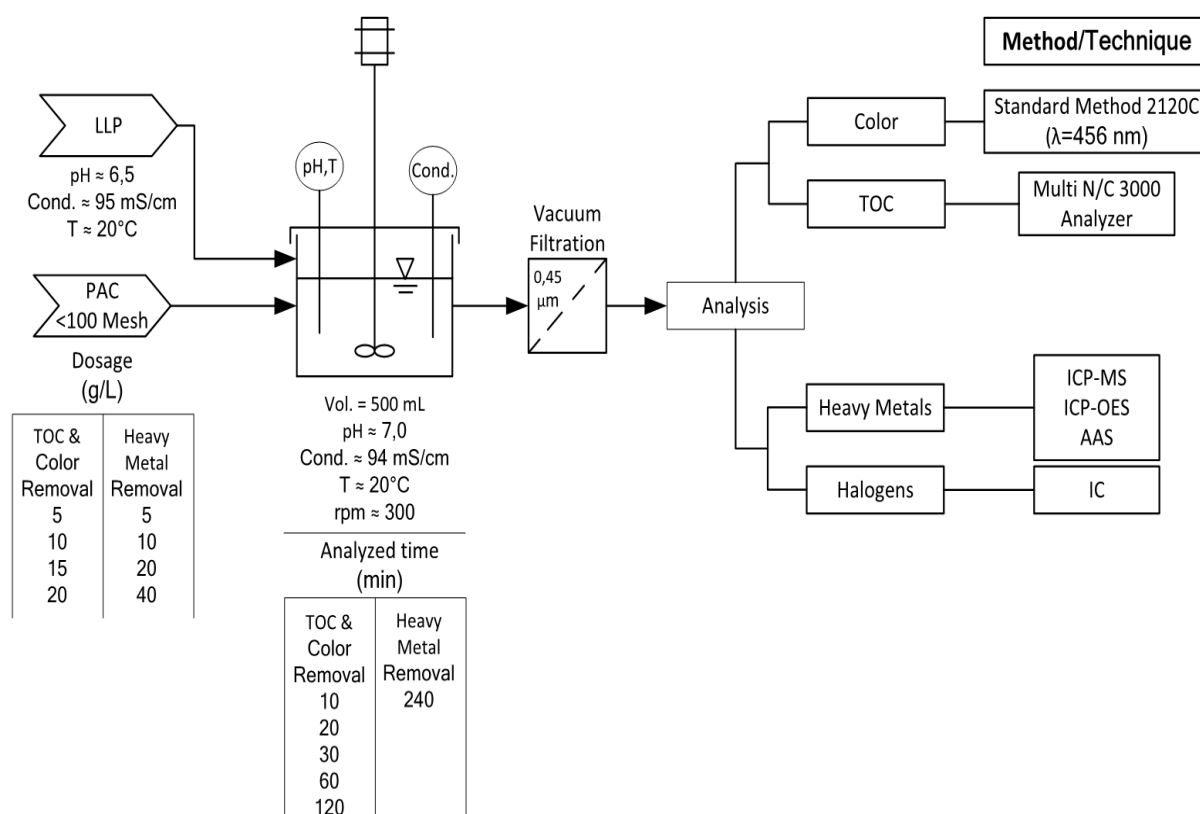


Figure 24. Experimental procedure for the treatment of LLP with PAC

3.2.2. Results and Discussion

3.2.2.1. Removal of Color and TOC

The color calibration curve and the raw data are given in appendix D. The characteristics of the untreated landfill leachate permeate (LLP) for the color and TOC removal are given in table 19.

Table 19. Permeate characteristics before adsorption

Parameter	Average value
TOC (mg/L)	1490,2 ± 103,8
TIC (mg/L)	226,3 ± 24,2
TC (mg/L)	1717,4 ± 107,8
TN (mg/L)	2095,8 ± 185,4
Color (CU)	1244,7 ± 196,9
Conductivity (mS/cm)	94,8 ± 0,2
pH	6,5 ± 0,2
T (°C)	20,1 ± 0,4

During the PAC treatment for the different evaluated PAC dosages the parameters pH, conductivity and temperature were relatively constant with average values of 7,0 ± 0,2, 93,7 ± 2,4 mS/cm and 19,9 ± 0,2 °C respectively. The TOC and CU values analyzed during the PAC treatment corresponding to each of the PAC dosages are indicated in figure 25.

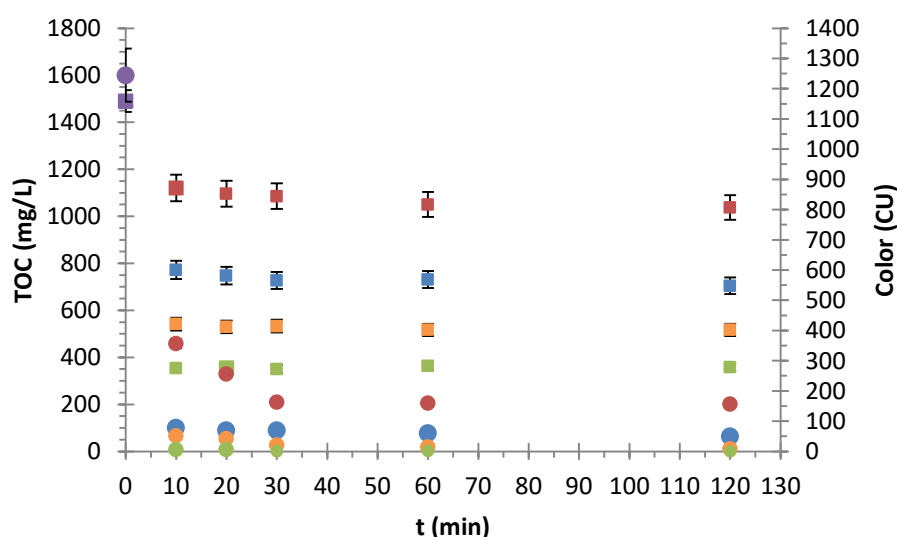


Figure 25. TOC and color removal during PAC treatment; TOC: ■; Color: ●; Purple: Untreated LLP; PAC dosage: Red: 5 g/L; Blue: 10 g/L; Orange: 15 g/L; Green: 20 g/L

As seen in figure 25, for all the PAC dosages the TOC adsorption equilibrium was reached within the first hour of treatment since the values stayed relatively constant after the treatment time of 30 min. At the end of the PAC treatment, the TOC values for the PAC dosages 5, 10, 15 and 20 g/L were $1037,6 \pm 51,9$, $704,4 \pm 35,2$, $517,0 \pm 25,9$ and $358,4 \pm 17,9$ mg/L respectively. In general, for the color removal case, relatively constant color unit values were reached after 30 min and by the end of the treatment the color values were $156,7 \pm 6,3$, $50,2 \pm 2,0$, $8,3 \pm 0,3$ and $0,0$ CU for the PAC dosages 5, 10, 15 and 20 respectively. The TOC and color percentage removals as a function of time for each of the PAC dosages are given in figures 26 and 27 respectively.

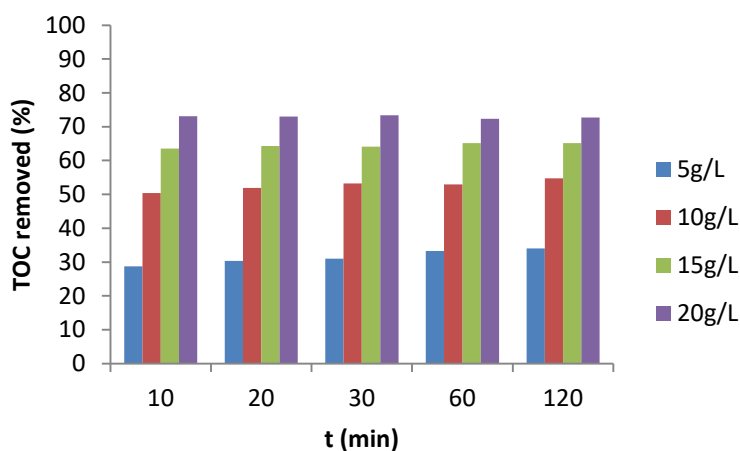


Figure 26. TOC percentage removal vs. time in LLP during adsorption treatment

In general, figure 26 showed that the removal of TOC did not change considerably within the treatment time interval of 10 to 120 min where the removal of TOC was higher with the higher PAC dosage concentration and by the end of the PAC treatment the TOC removal percentage values were 34, 55, 65 and 73% for the 5, 10, 15 and 20 g/L dosages respectively.

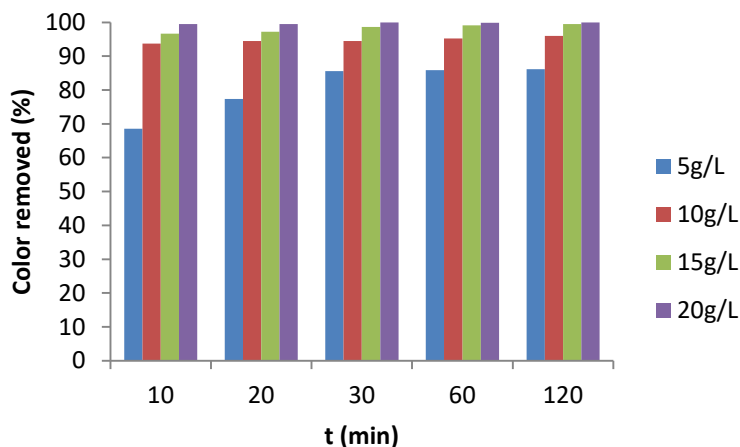


Figure 27. Color percentage removal vs. time in LLP during adsorption treatment

Figure 27 showed that by the end of the 2 h treatment color removals of 96, 99 and 100 % were achieved with the PAC dosage of 10, 15 and 20 g/L respectively and a maximum color removal of 86% was obtained for the 5 g/L dosage. Furthermore, for the PAC dosage 10, 15 and 20 g/L most of their respective removed color took place within the first 10 min of treatment while for the 5 g/L dosage it took place within the 30 min of treatment until reaching a relatively stable removal percentage value of 86%.

A correlation between the removal of color and TOC can be better observed by plotting the TOC and color removed versus their corresponding CU to TOC ratios calculated for all of the analyzed treatment times at their respective PAC dosage. The treated data is given in appendix D. For instance, The CU/TOC ratio for the untreated permeate had an average value of $0,84 \pm 0,16$ and this ratio approaches to zero as the color is being removed. The plotted values are given in figure 28.

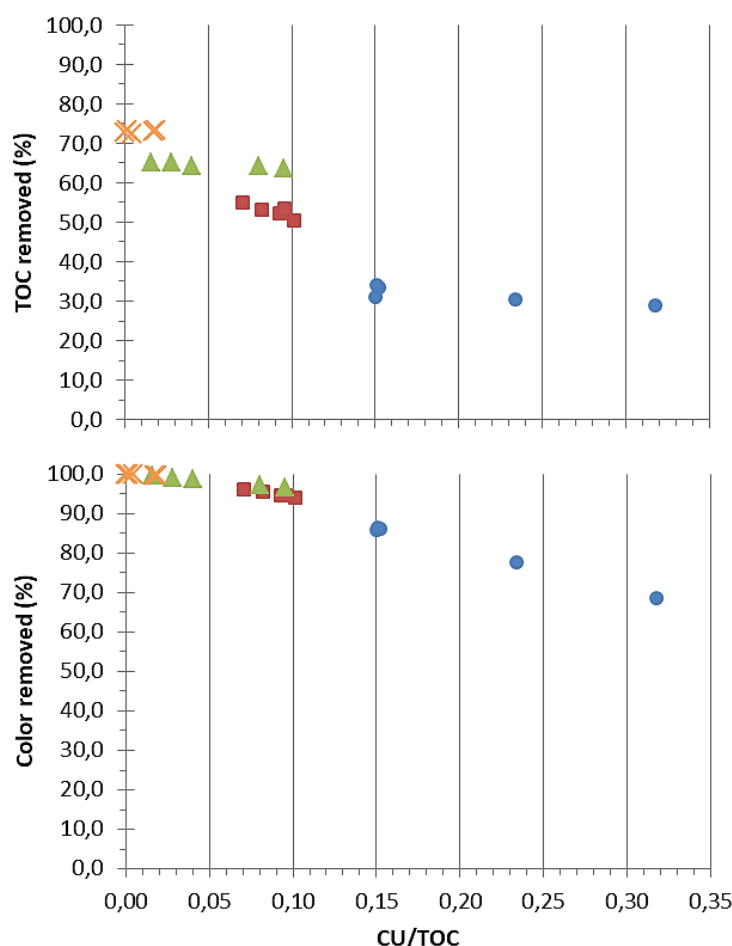


Figure 28. Color and TOC percentage removal correlation from LLP with PAC

As seen in figure 28, for a CU/TOC ratio of 0,1 the removal of color was around 95% and for the same CU/TOC ratio the removal of TOC was around 55%. Furthermore, by looking at the plotted points corresponding to the PAC dosage of 15 g/L it can be seen that in between the CU/TOC ratio of 0 to 0,05 as the color removal approached 100% the TOC removed percentage approached the 65% value. Thus, the fraction of

TOC related to the color of the landfill leachate permeate could be located in between 55 to 65% of TOC removed from the initial concentration. Hence, the TOC value related to color in the permeate was estimated as 894 mg/L, which corresponded to about 60% of the initial TOC concentration.

Finally, at the 2 h treatment and for all the PAC dosages the average concentration of TIC and TN were $183,7 \pm 11,6$ mg/L and $1898,3 \pm 171,3$ mg/L, which corresponded to an average percentage removal of 19 and 9 % for TIC and TN respectively.

3.2.2.2. Removal of Heavy Metals and Halogens

The raw data corresponding to the elemental analysis of heavy metals and halogens for the PAC treatment are given in appendix D. The analyzed heavy metals were chosen based on the heavy metals of concern and PTE already discussed in chapter 2.1. Based on the information provided by the University's central lab for chemical analysis, the elemental analysis was at some degree challenging especially due to the high salinity of the permeate, which interfered with the analysis methods. Thus, some of the results obtained for the analyzed elements might have uncertainties around or greater than 10%. For example, Zink and Selenium yielded high uncertainties with unreliable results; hence they were not included in this discussion. For that reason, the concentrations of the analyzed elements were estimated after evaluating, selecting and/or treating the collected data that led to the best fit. The results obtained for each of the analyzed elements corresponding to each of the PAC dosages and the LLP are given in table 20 and table 21 for the analyzed heavy metals and halogens respectively.

Table 20. Heavy metal analysis for PAC treatment in LLP

Substance	Unit	LLP	5 g-PAC/L	10 g-PAC/L	20 g-PAC/L	40 g-PAC/L
V	µg/L	< 200	< 100	< 100	< 10	< 10
Cr	µg/L	97	35	30	16	< 10
Mo	µg/L	150	< 100	< 100	< 100	< 100
Mn	µg/L	1110*	1100	1100	1000	-
Fe	µg/L	810	580	430	230*	81
Co	µg/L	24	19	16	< 10	< 10
Ni	µg/L	680	510	440	270*	130
Pb	µg/L	< 200	< 10	< 10	< 10	< 10
Cu	µg/L	38	14	8,8	< 10	< 10
Cd	µg/L	< 200	< 10	< 10	< 10	-
Hg	µg/L	< 0,25	< 0,2	< 0,2	< 0,2	-
Al	µg/L	< 4000	404*	373*	391*	-
Tl	µg/L	< 200	< 10	< 10	< 10	< 10
As	µg/L	255*	215*	230*	225*	260
Sb	µg/L	< 80	< 100	< 100	< 100	< 100

* Calculated average

Table 21. Halogen analysis for PAC treatment in LLP

Substance	Unit	LLP	5 g-PAC/L	10 g-PAC/L	20 g-PAC/L	40 g-PAC/L
Fluoride	mg/L	17*	20*	18*	15*	15
Chloride	g/L	31*	31*	31*	31*	34
Bromide	mg/L	425*	455*	450*	455*	490

* Calculated average

As seen in table 20 many of the given concentrations were found within a range or below a value; thus, for many of the analyzed elements an approximate concentration value could not be determined. Therefore, based on the results and considering their possible large uncertainties, the analyzed substances were divided into four groups. The first group or clear removed group included those substances whose removals were consistent and also greater than 20%. The second group or unclear removed group included those substances that as the name imply the removal percentage could not be determined due to the nature of the data. The third group included those substances that in general showed not removal or it was smaller than 20%. And, the last group or low concentration group included those substances whose concentrations in the permeate were found to be below the lower limit of detection for the corresponding method at the analyzed conditions. The groups and their respective substances are described in table 22.

Table 22. Removal groups for analyzed elements with PAC treatment

Clear Removed	Unclear Removed	Not Removed	Low conc.
Cr	V	Mn	Pb
Fe	Mo	As	Cd
Co	Al	Cl ⁻	Hg
Ni	Sb	Br ⁻	Tl
Cu		F ⁻	

Table 22 shows that from the eighteen evaluated substances only for ten of them it was possible to determine if removal took place or not. For the substances listed in the clear removed group it can be seen that their concentration in the treated permeate decreased as the PAC dosage increased. Furthermore, some substances and specifically those not removed by the PAC treatment including Arsenic and the halogens showed a slightly increase in concentration after treatment with certain PAC dosages. The increase in concentration could possibly be attributed to the higher removal of substances that might interfered with the analytical method and were removed by the PAC treatment and possibly yielded to more accurate concentration values for the particular analyzed substances.

The percentage removals for the heavy metals listed within the clear removed group are given in figure 29.

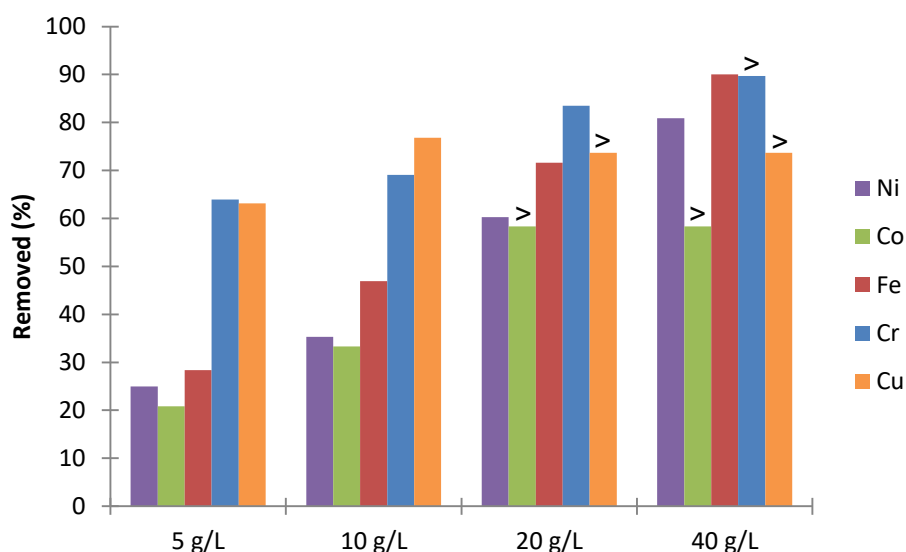


Figure 29. Heavy metals percentage removed from LLP with PAC treatment (>: greater than)

Figure 29 shows that the percentage removals of the heavy metals increased with the increased of PAC dosage. For instance, Iron presented removals of 28, 47, 72 and 90% with the PAC dosages of 5, 10, 20 and 40 g/L respectively. Furthermore, Chromium and Copper were the only two heavy metals whose removals were higher than 50% at all the PAC dosages while for Nickel and Cobalt removals higher than 50% were only possible with PAC dosages of 20 and 40 g/L. However, with all the PAC dosages the removals of the analyzed heavy metals from the permeate were higher than 20%. Finally, from the analyzed halogens, none of them showed a clear removal.

3.2.2.3. Adsorption Isotherms for Cr, Fe, Ni and TOC

The Freundlich and Langmuir isotherms for Cr, Fe, Ni and TOC with the PAC were estimated based on the analyzed data and the models' equations already discussed in chapter 2.2. The calculated values are given in appendix D.

Even though, Cobalt and Copper were removed with the PAC treatment the isotherms were not able to be estimated since only two value points were obtained from the analyzed data. The equilibrium concentrations of Cr, Fe, Ni and TOC in the PAC versus their equilibrium concentrations in the permeate are shown in figure 30.

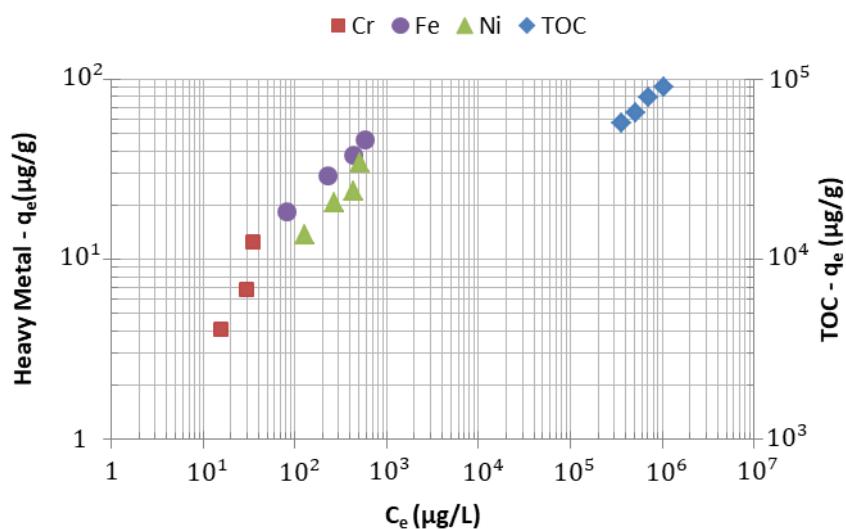


Figure 30. Cr, Fe, Ni and TOC equilibrium concentration in solid and aqueous phases

Figure 30 indicates that the adsorption equilibrium with PAC for the evaluated adsorbates might follow the Freundlich model due to their linear tendencies. The results obtained for the Freundlich and Langmuir adsorption isotherms for Chromium, Iron, Nickel and TOC are given in figures 31, 32, 33 and 34 respectively.

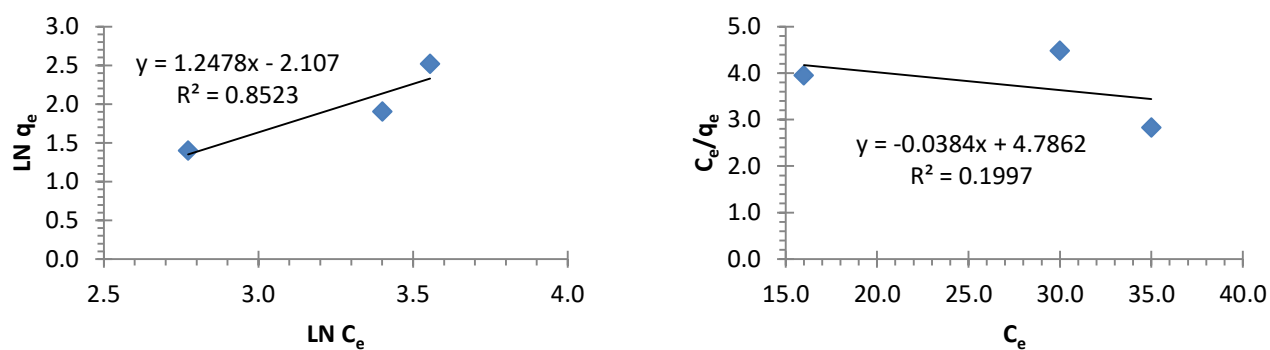


Figure 31. Freundlich & Langmuir adsorption isotherms for Chromium; Left: Freundlich; Right: Langmuir

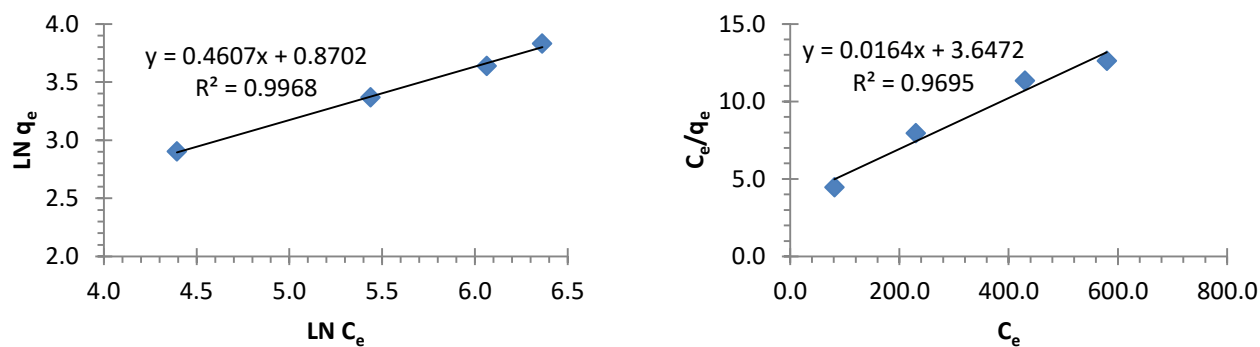


Figure 32. Freundlich & Langmuir adsorption isotherms for Iron; Left: Freundlich; Right: Langmuir

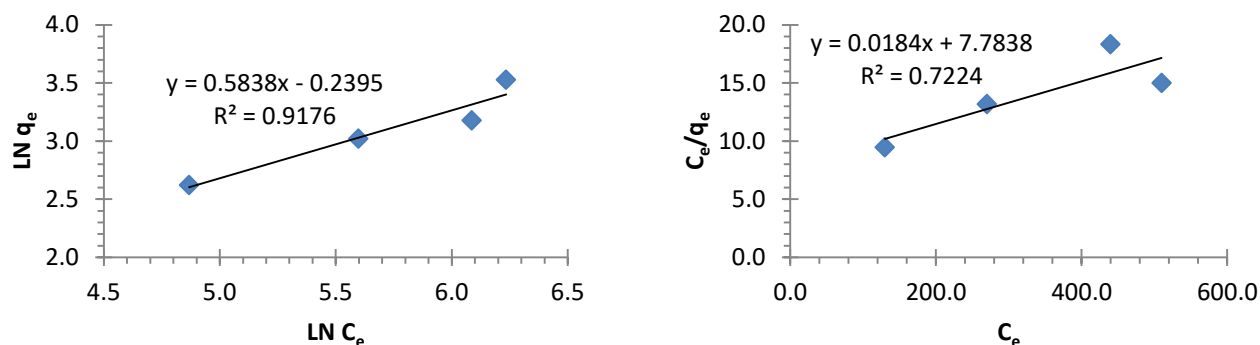


Figure 33. Freundlich & Langmuir adsorption isotherms for Nickel; Left: Freundlich; Right: Langmuir

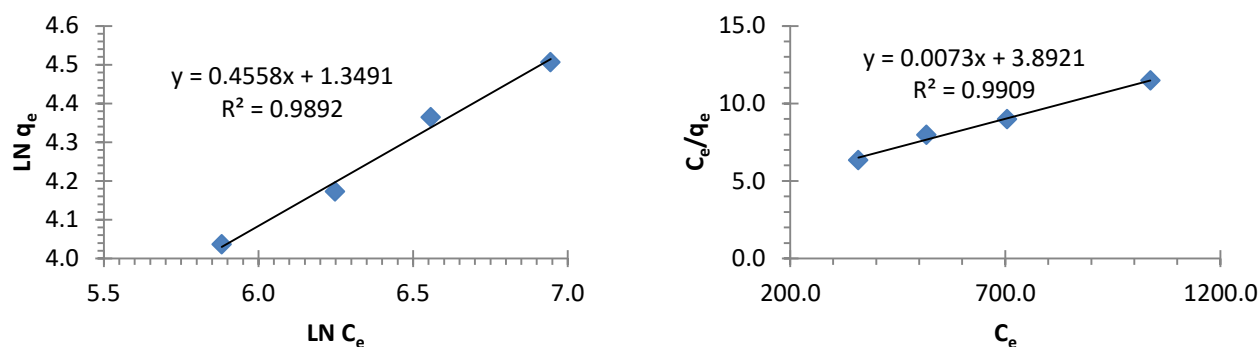


Figure 34. Freundlich & Langmuir adsorption isotherms for TOC; Left: Freundlich; Right: Langmuir

As seen in figures 31 and 33 the Langmuir isotherms for Cr and Ni had the lowest R-squared values of 0,20 and 0,72 respectively. On the other hand, the adsorption data of Iron and TOC fitted well the Langmuir isotherm with R-squared values of 0,97 and 0,99 respectively. Furthermore, the adsorption data for all of the analyzed adsorbates fitted relatively well the Freundlich isotherm having the lowest R-squared value of 0,85 for Chromium followed by the values of 0,92, 0,99 and 0,99 for Nickel, Iron and TOC respectively and as mentioned in chapter 2.2 the Freundlich Isotherm is one of the most used models to describe adsorption equilibrium of wastewater with PAC

The equilibrium constants corresponding to the Freundlich and Langmuir isotherms for each of the analyzed substances are summarized in table 23.

Table 23. Freundlich and Langmuir isotherms equilibrium constants for TOC, Cr, Fe and Ni with PAC

Substance	Freundlich			Langmuir			
	K_f^*	$1/n$	R^2	Q^{**}	b^{***}	R_L	R^2
Cr	0,12	1,2	0,85	-26	$-8,0 \cdot 10^{-3}$	4,5	0,20
Fe	2,4	0,46	0,99	61	$4,5 \cdot 10^{-3}$	0,22	0,97
Ni	0,79	0,58	0,92	54	$2,4 \cdot 10^{-3}$	0,38	0,72
TOC	3,9	0,46	0,99	137	$1,9 \cdot 10^{-3}$	0,26	0,99

* For Cr, Fe and Ni: $(\mu\text{g/g})/(\mu\text{g/L})^{1/n}$ and TOC: $(\text{mg/g})/(\text{mg/L})^{1/n}$

** For Cr, Fe and Ni: $(\mu\text{g/g})$ and TOC: (mg/g)

*** For Cr, Fe and Ni: $(\text{L}/\mu\text{g})$ and TOC: (L/mg)

Table 23 shows that the Freundlich intensity parameters with the exception of Cr were smaller than 1 for Fe, Ni and TOC with values of 0,46, 0,58 and 0,46 respectively. Even though, the R-squared value of Chromium could be an indication of an acceptable fit its Freundlich intensity parameter value of 1,2 was slightly greater than 1, which could indicate that the Freundlich model was not the best fit for its adsorption equilibrium. Furthermore, the maximum adsorption capacity for the analyzed adsorbates was 137 mg/g for TOC followed by 61 and 54 µg/g for Iron and Nickel respectively.

The Freundlich and Langmuir isotherm models for all of the adsorbates and their validation with respect to their experimental data and estimated based on the mean absolute percent error are given in table 24. For the case of Chromium the Langmuir isotherm model was not shown considering that its constants contained negative values. The numerical values for the validation are given in appendix D.

Table 24. Validation of Freundlich & Langmuir Isotherm Models

Adsorbate	Freundlich Isotherm		Langmuir Isotherm	
	Model	Error (%)	Model	Error (%)
Cr	$q_e = 0,12 C_e^{1/0,8}$	16	-	-
Fe	$q_e = 2,4 C_e^{1/2,2}$	3	$q_e = \frac{0,27C_e}{1 + 4,5 * 10^{-3}C_e}$	7
Ni	$q_e = 0,79 C_e^{1/1,7}$	8	$q_e = \frac{0,13C_e}{1 + 2,4 * 10^{-3}C_e}$	10
TOC	$q_e = 3,9 C_e^{1/2,2}$	2	$q_e = \frac{0,26C_e}{1 + 1,9 * 10^{-3}C_e}$	2

Table 24 shows that the higher average percentage error for the Freundlich model with respect to the experimental data were for Chromium and Nickel with values of 16% and 8% respectively. For the case of Nickel the Freundlich isotherm might still be an acceptable fit for its adsorption equilibrium with PAC considering the uncertainties of about 10% in the concentration values obtained for the treated permeate at the different PAC dosages. Furthermore, the low percentage error for Iron and TOC with values of 3 and 2% respectively reinforced the acceptable fit of the Freundlich model for their adsorption equilibrium with PAC. Moreover, the only adsorbate that yielded a low percentage error for the Langmuir isotherm was TOC with a value of 2% and for the case of heavy metals the Langmuir isotherm had errors of 7 and 10% for Iron and Nickel respectively.

3.3.PRECIPITATION TREATMENT AND RECOVERY OF CALCIUM CARBONATE-RICH SOLIDS

As discussed in section 3.1, the results obtained in the composition analysis indicated that the relatively low concentration of pollutants such as heavy metals but the higher concentration of Ca^{2+} in the LLP with respect to LL made of the permeate a suitable stream for the precipitation and recovery of CaCO_3 from the landfill leachate treatment facility. Also, considering the downstream high pressure membrane system labeled in figure 19 as HPRO used for the further treatment of the LLP, the removal of scaling related substances from the permeate might be beneficial from the operating point of view. For example, less scale formation can lead to less needed frequently cleaning, used of pre-filters and addition of anti-scaling chemicals and also might preserve the membranes longer; hence extending their replacement time and yielding to a better performance and potentially reducing the overall operating cost of the treatment process.

3.3.1. Materials and Methods

The effect of treatment time, precipitating agent, organic content and different volumes of treated permeate were analyzed during the precipitation treatment of the landfill leachate permeate (LLP) at different pH conditions. The raw data can be found in appendix E and the analytical methods and material used are listed in appendix A and B.

3.3.1.1. Sampling of landfill leachate permeate

The landfill leachate permeate (LLP) used during this experimental work was collected from the landfill leachate treatment facility as indicated in figure 19 during the seasons of spring, summer and fall. The LLPs collected during the spring and summer seasons were used for the evaluation of NaOH and the mixed Na_2CO_3 -NaOH reagents respectively as precipitating agents with permeate volumes of 0,5 L; and the LLP collected in the fall season was used during the 10 L precipitation treatment of the permeate with the mixed Na_2CO_3 -NaOH reagents.

3.3.1.2. Saturation index

The saturation index for the LLP was estimated as described in the Standard Method 2330B for Indices Indicating Tendency of Water to Precipitate CaCO_3 or Dissolve CaCO_3 – Section 2: Saturation Index by Calculation. The concentration of the macro-substances analyzed in the LLP given in tables 13 and 14 of section 3.1.2 whose concentrations were greater than 100 mg/L and the average acid neutralizing capacity (ANC) or alkalinity estimated for the LLP were used for the determination of the SI. The calculations were performed with the help of Spyder-Python 2.7. The values used and the assumptions made for the SI determination are described in appendix E.

3.3.1.3. Adsorption

The characteristics of the powdered activated carbon used during the adsorption pretreatment of the LLP are indicated in table 18. Volumes of 1500 mL of the LLP were treated with 15 g of PAC (-100 mesh) during 1h at room temperature ($T \approx 22^\circ\text{C}$). During the treatment, the PAC was kept suspended by the use of a magnetic stirrer set at 350 ± 30 rpm. After the PAC treatment the system was centrifuged at 4000 rpm for 10 min and then the PAC treated permeate (PAC-LLP) was separated from the used carbon by vacuum filtrating first through a 20-25 μm paper filter and then through a 1,5 μm glass fiber filter as indicated in figure 35.



Figure 35. Adsorption treatment of LLP for effect of organic content during precipitation

3.3.1.4. 0,5 L Precipitation

Caustic soda (NaOH) and a mixture of caustic soda and soda ash (Na_2CO_3) were evaluated as precipitating agents at different treatment times by adding their respective amounts to the 0,5L permeate at the working pH condition. The pH values were reached as followed, for the case of sodium hydroxide the respective volume of a 12 M NaOH solution was added by the use of a micropipette and for the case of the mixed Na_2CO_3 -NaOH reagents their respective amounts were weighted and added in solid form to the treated permeate in order to reach the desire pH condition. During the treatment, the mixing was performed by using the jar test apparatus set at 300 rpm as illustrated in figure 36. The different procedures followed during the 0,5L precipitation treatment are described in figure 37.

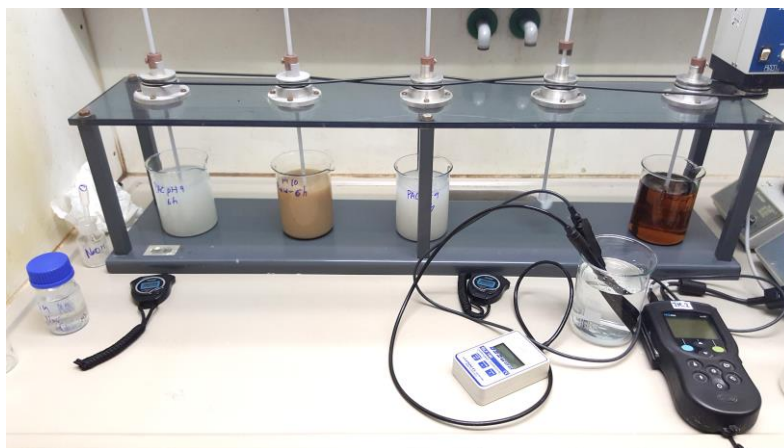


Figure 36. Precipitation treatment of LLP and PAC-LLP with mixed Na_2CO_3 -NaOH as precipitant. Right side: Untreated LLP; Left side: Precipitation treatment of PAC-LLP (Whiter) and LLP

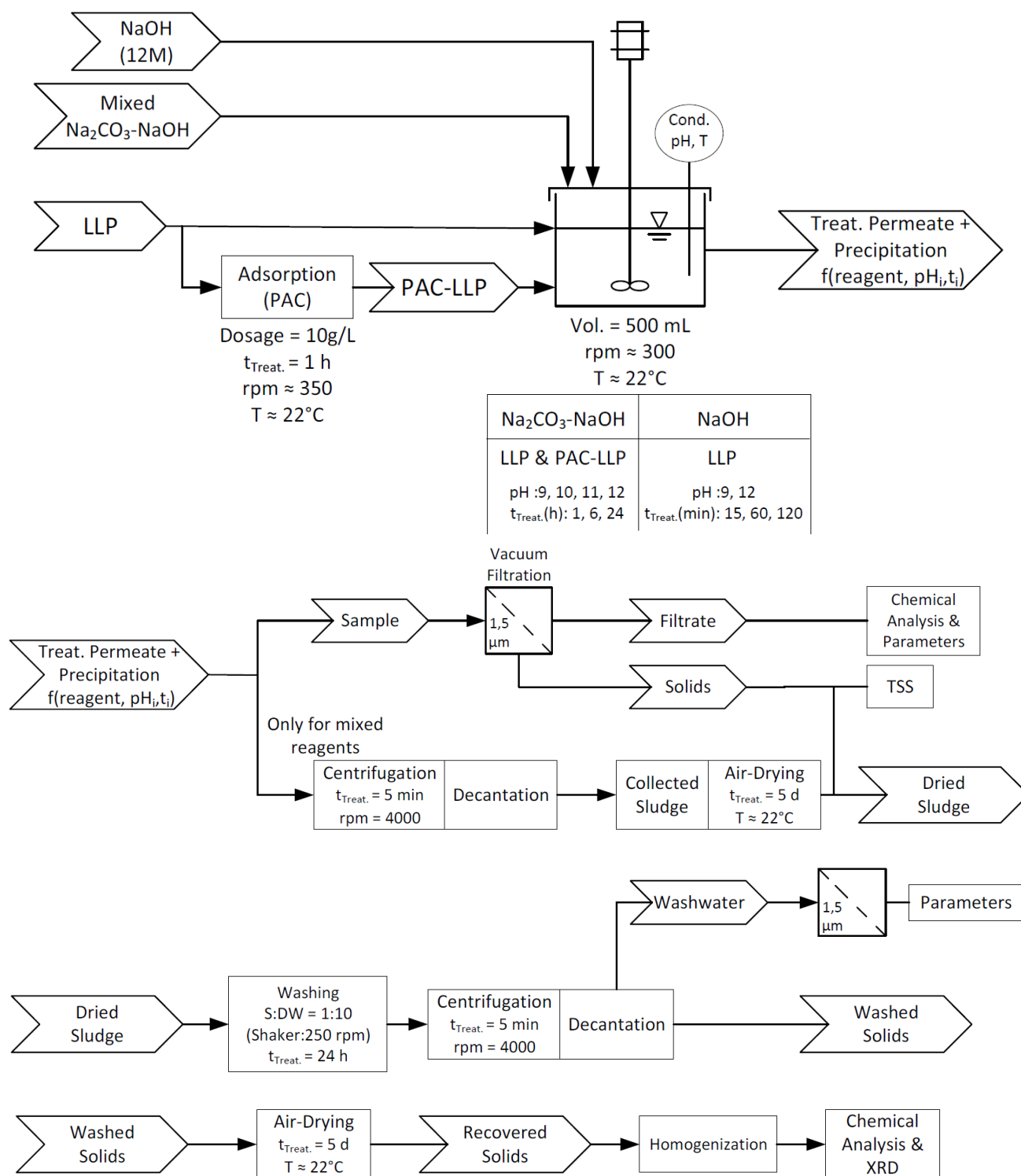


Figure 37. Overview of the procedures followed during the 0,5 L precipitation treatment of the permeates

3.3.1.5. TSS

The determination of TSS was performed as indicated in the Standard Method 2540D for Total Suspended Solids Dried at 103-105°C where each of the precipitating agents in solid form were used to treat 100 mL of the LLP during 4 h and evaluated at pH values of 9, 10, 11 and 12; the mixing was performed by using a magnetic stirrer set at 250 rpm.

3.3.1.6. 10 L Precipitation

Volumes of 10 L of permeate were treated at the pH conditions of 10, 11 and 12 by adding the mixed Na_2CO_3 - NaOH reagents in solid state as precipitant as illustrated in figure 38.

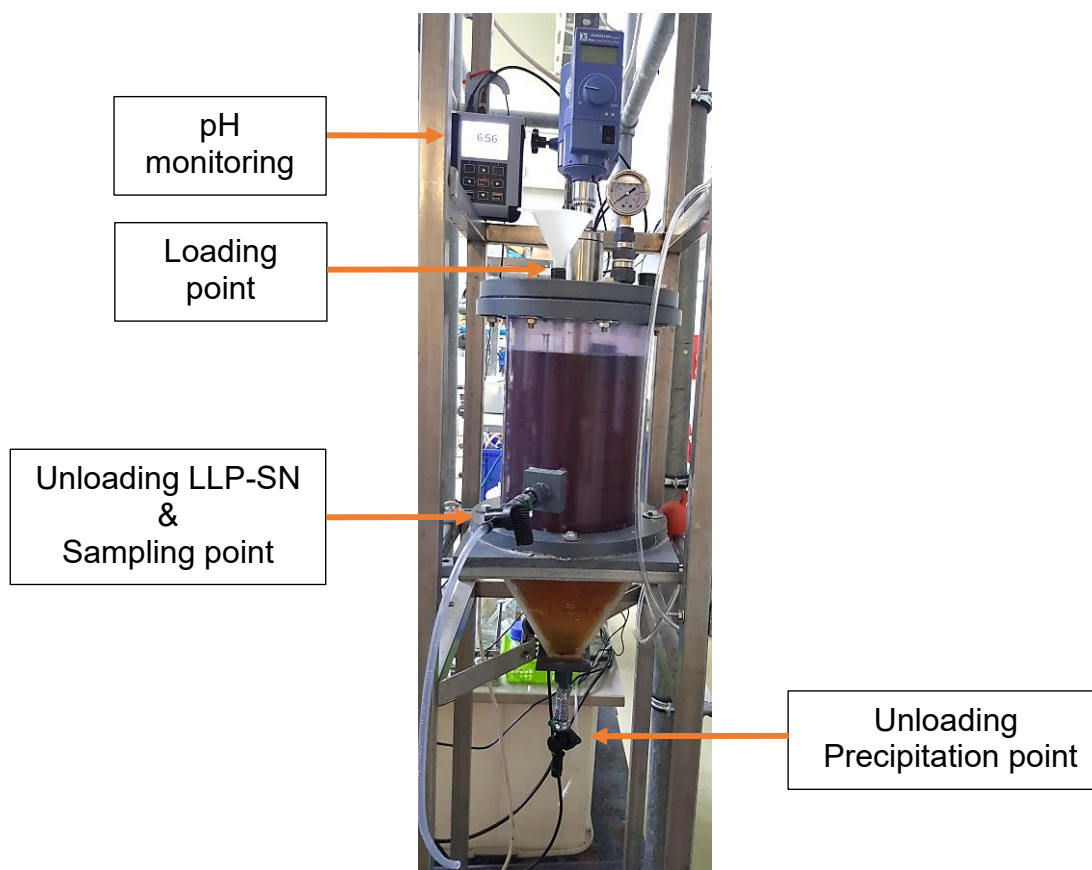


Figure 38. Starting of precipitation treatment in 10 L precipitator

The methodology followed for the 10 L precipitator was very similar to the one followed for the 0,5 L precipitation. However, due to the larger amount of treated permeate sedimentation-decantation was used in order to separate the treated permeate from the generated precipitation. After the sedimentation-decantation step the precipitation in the form of sludge collected from the 10 L precipitator was further dewatered by the use of the centrifuge. The procedures performed during the 10 L precipitation treatment for the recovery and further analysis of the CaCO_3 -rich solids are described in figure 39.

3.3.1.7. Acid Soil samples

The samples of acid soil used in the explore application of the recovered CaCO_3 -rich solids came from a lignite mine site located on the east side of Germany and they were sieved through a 2,8 mm mesh before the experimental procedures.

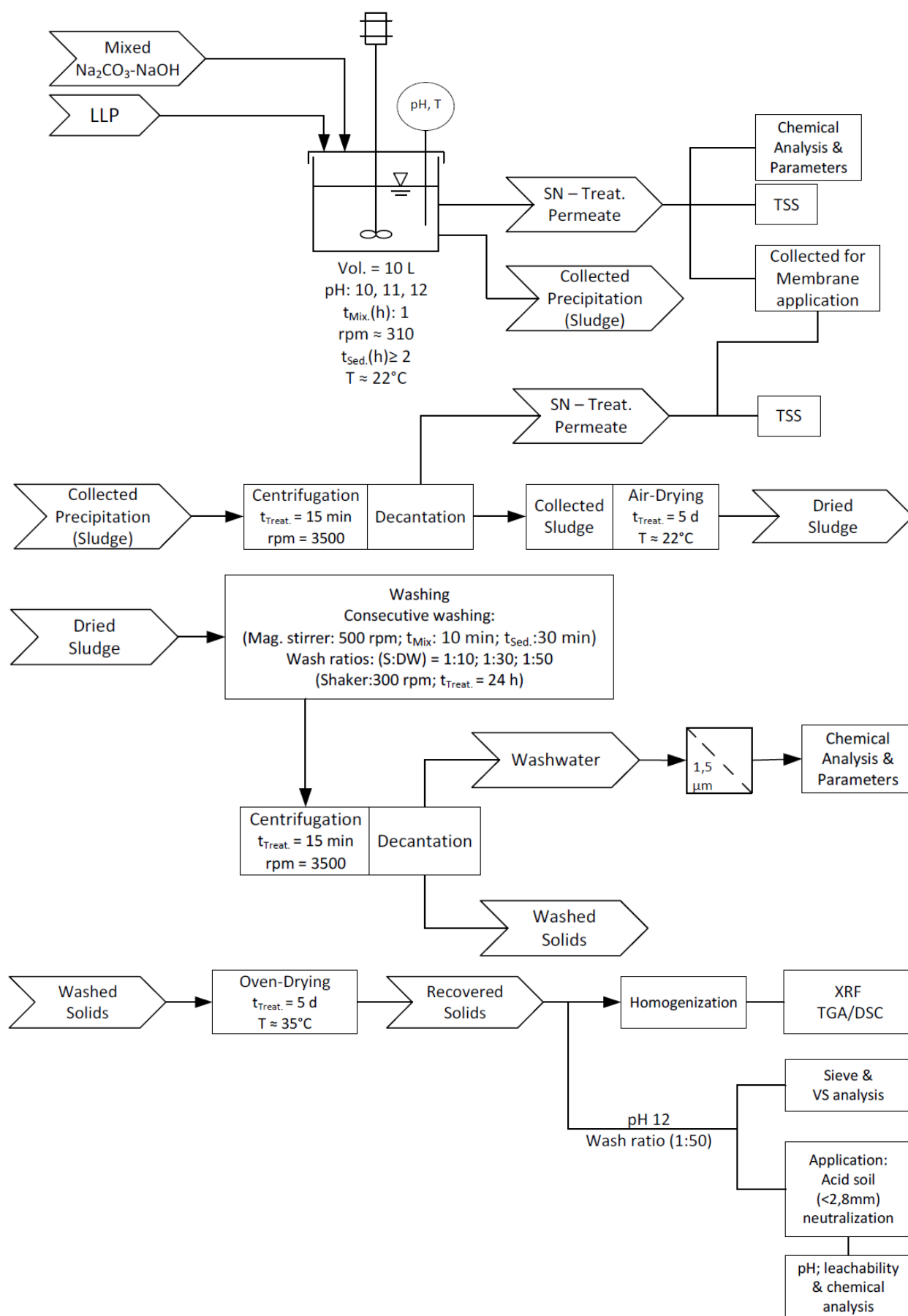


Figure 39. Overview of the procedures followed during the 10 L precipitation treatment of the LLP

3.3.2. Results and Discussion

3.3.2.1. Precipitating agent, pH, treatment time and organic content effect on precipitation

3.3.2.1.1. Analysis in Collected LLP and PAC treated LLP

The total average values and the sample standard deviations (SSD) calculated for each of the analyzed substances and/or parameters in the LLP collected during the spring and summer seasons and the PAC treated LLP are given in table 25. The raw data is given in appendix E.

Table 25. Average values LLP collected during spring & summer seasons and PAC treated LLP - Composition & measured parameters

Substance/Parameter	Average values	
	LLP	PAC-LLP
Ca ²⁺ (mg/L):	1205±77	1162±23
Mg ²⁺ (mg/L):	473±38	505±12
Hardness (°dH):	279±19	280±4
SO ₄ ²⁻ (mg/L):	9255±834	9680±85
COD (mg/L):	6370±280	4355±162
Ortho-PO ₄ ³⁻ -P (mg/L):	8,8±0,6	52,1±5,4
TOC (mg/L):	1342±89	575±54
TIC (mg/L):	235±20	159±4
TC (mg/L):	1577±95	734±50
TN (mg/L):	2029±155	2023±188
ANC (mmol H ⁺ /L) :	23,8±1,1	-
pH:	6,6±0,2	7,3±0,1
Conductivity (mS/cm):	87,6±1,7	89,3±0,2
T (°C):	23,1±2,0	24,0±1,9

As indicated in table 25 the lost in concentration of Ca and TN in the LLP after the adsorption treatment with respect to the average values were not considerable, with lost in concentration values less than 5% where the hardness in the LLP remained relatively constant after the PAC treatment. Also, for the case of SO₄²⁻ based on the average value and its SSD, it was seen that the concentration of this anion was not affected by the PAC treatment. On the other hand, after the PAC treatment the reduction of TOC concentration in the LLP was about 55%, which almost corresponded to the TOC removal discussed in section 3.2 for the same PAC dosage of 10 g/L at a treatment time of 2 h. However, after the PAC treatment the concentration of ortho-PO₄³⁻-P in the LLP was almost 6 times higher compared to the untreated LLP. The apparent increased in the concentration of orthophosphate after the PAC treatment was explained by the transferred of this substance from the used powdered activated carbon to the liquid phase since a pre-experiment with deionized water (DW) by using the same PAC material at the same dosage during 4 h revealed

the presence of the phosphate ion in the DW after the PAC treatment. Furthermore, after the adsorption treatment the pH and conductivity values increased slightly compared to the LLP average values.

Additionally, considering the permeate nature of the analyzed stream it was assumed that the analyzed TIC in the LLP corresponded to DIC. Therefore, based on the stoichiometric relation of 1 to 1 for Ca^{2+} and Mg^{2+} with CO_3^{2-} in the formation of CaCO_3 and MgCO_3 and by assuming that the average value of TIC in the LLP corresponded to the concentration of CO_3^{2-} , which as illustrated in figure 18 could be the case at high pH values, it was seen that the composition of CO_3^{2-} in the LLP is less than the stoichiometric value required for the ideal case of CaCO_3 precipitation and approximately equal to the stoichiometric value required for the ideal formation of MgCO_3 . The results are given in table 26.

Table 26. CO_3 excess in LLP with respect to Ca & Mg

Calculation based on Vol. _{LLP} = 0,5 L & Total average values LLP composition				
Reactants	v_i	Moles (mmol)	CO_3^{2-} Excess (%)	Product
Ca^{2+}	-1	15	-35	CaCO_3
Mg^{2+}	-1	9,7	0,6	MgCO_3
Ca^{2+} & Mg^{2+}	-	24,8	-60	Ca, MgCO_3
CO_3^{2-}	-1	9,8	-	-

v_i : Stoichiometric coefficient

The saturation index (SI) in the LLP was estimated in order to get a better understanding of the saturation degree of CaCO_3 with respect to pH. The results are illustrated in figure 40.

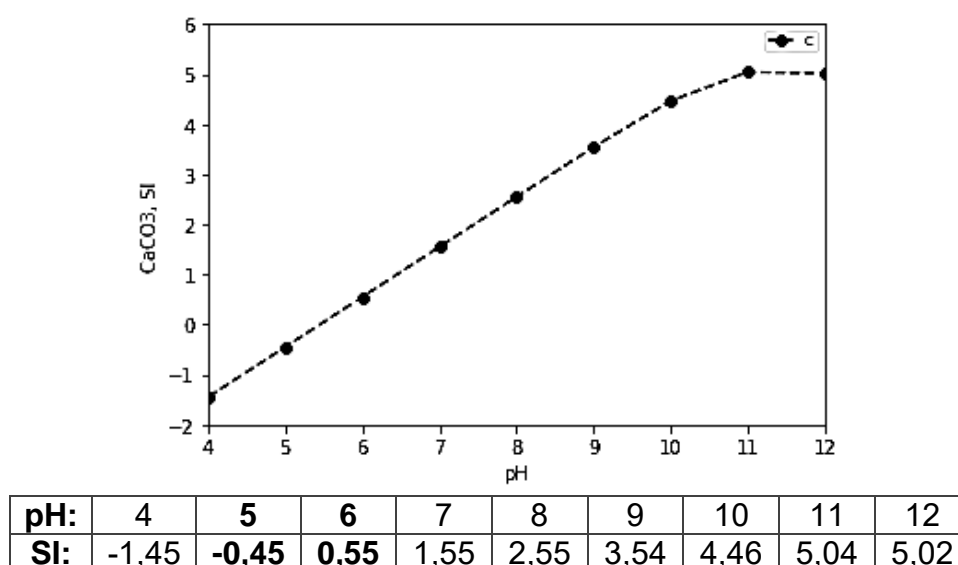


Figure 40. Saturation Index of CaCO_3 for LLP at different pH conditions

As illustrated in figure 40, the SI estimated for the LLP at the different pH conditions indicated that for pH values below 5 the LLP might be undersaturated with respect to CaCO_3 considering that the calculated SI yielded negative values. And, for pH values above 6 precipitation of CaCO_3 might be expected since the estimated SI yielded positive values, which meant oversaturation in the LLP with respect to CaCO_3 . Furthermore, the saturation point with respect to CaCO_3 , which corresponded to a SI value of zero could be located in between the pH values of 5 and 6.

3.3.2.1.2. NaOH as Precipitating Agent

The volume of caustic soda as 12M solution added to the 0,5 L permeate (LLP) and the average values of the parameters measured in the permeate during the precipitation treatment at the evaluated pH conditions are given in table 27.

Table 27. Reagent dosage, conductivity, pH and T in LLP during precipitation treatment with NaOH

LLP	Add. NaOH [12M] (mL)	Treatment conditions		
		pH	Cond. (mS/cm)	T (°C)
Initial:	-	6,6±0,2	86,6±2,7	22,6±0,2
pH 9:	2,6±0,2	9,10±0,02	83,7±0,2	22,2±0,8
pH 12:	10,0±0,5	12,02±0,01	92,0±0,2	23,5±0,9

As indicated in table 27, based on the calculated SSD it was observed that during the treatment times of 15, 60 and 120 min the conductivity in the LLP did not change considerably. However at pH 9 a slightly decreased in the conductivity value with respect to the initial condition was observed while at pH 12 the conductivity in the permeate increased to about 6% with respect to the initial value of 86,6 mS/cm.

The results obtained with NaOH as precipitating agent in the LLP at the pH values of 9 and 12 for the analysis of Ca and Mg at the treatment times of 15, 60 and 120 min are given in figure 41.

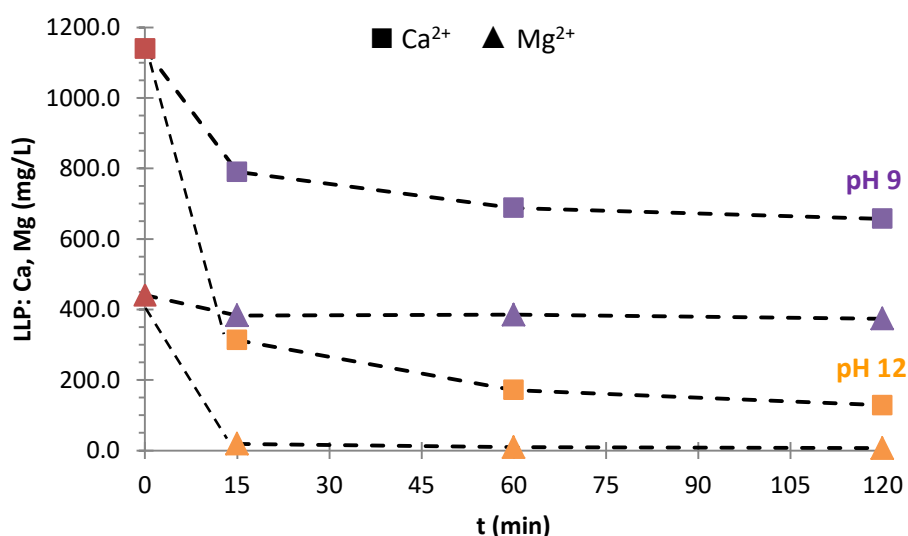


Figure 41. Ca & Mg Conc. vs. time at pH 9 and 12 with NaOH as precipitating agent; Red: Initial concentration; Purple: pH 9; Orange: pH 12

Figure 41, indicated that for both pH values only within the first hour of treatment the removal of Ca was more time dependent than Mg. For instance, for both pH values the concentration of Mg did not change considerably in between the treatment times of 15 and 60 min. However, for Ca a slightly decrease in concentration was observed in both pH values within the same treatment time. And, in between 60 to 120 min of treatment the concentration of Ca and Mg for both pH values did not change considerably. Furthermore, at the end of 2 h treatment for the pH 9 case, about 40% of Ca and 15% of Mg were removed and for pH 12 at the same treatment time 89% and 99% of Ca and Mg respectively were removed from the LLP. The reduction of hardness in the LLP at the evaluated pH and time conditions is illustrated in figure 42.

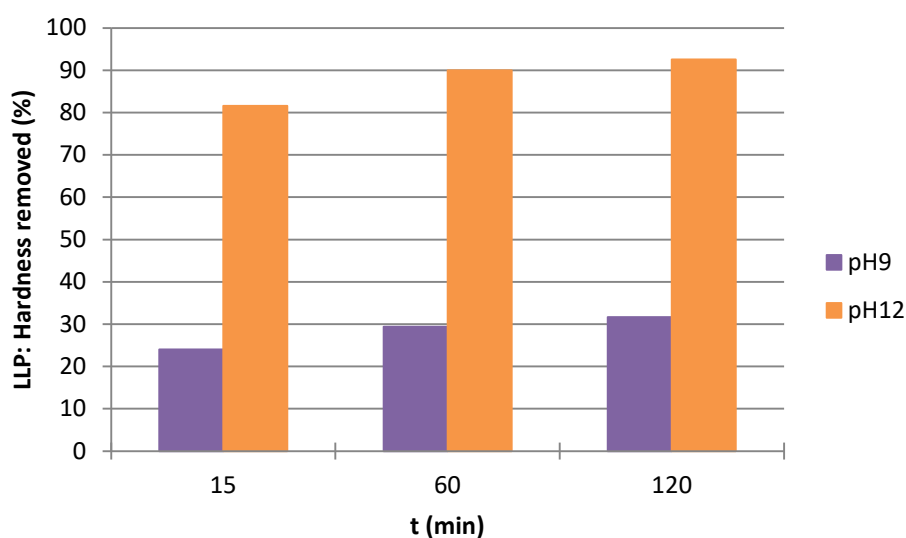


Figure 42. Hardness removed vs. time at pH 9 and 12 with NaOH as precipitating agent

As seen in figure 42, for the different treatment times at pH 9 the removal of hardness with caustic soda only reached a maximum value of about 30% removal at the treatment time of 120 min with a hardness value of 179 ± 9 °dH, which is approximately equal to a hardness of 3180 mg/L as CaCO_3 being approximately 18 times higher than the limit value of 180 mg/L as CaCO_3 characteristic of very hard water. However, for pH 12 at the same treatment time 93% of the hardness was removed from the LLP by the used of NaOH with a concentration value of $19,5 \pm 1,0$ °dH, which is equivalent to 347 mg/L as CaCO_3 and as indicated in table 8 this concentration is still consider to be characteristic of very hard water.

3.3.2.1.3. Mixed reagents (Na_2CO_3 & NaOH) as Precipitating Agent

The effect of the organic material for the precipitation treatment was analyzed by reducing the organic content in the LLP by about 50% with the used of PAC as indicated by the TOC concentration in table 25. The reagents dosage used for each of the evaluated pH and the average values of conductivity, pH and temperature measured during the precipitation treatment are given in tables 28 and 29 for the LLP and PAC-LLP respectively.

Table 28. Reagents dosage, conductivity, pH and T in LLP during precipitation treatment with Mixed Na_2CO_3 -NaOH

LLP	Add. Mixed Na_2CO_3 -NaOH			Treatment conditions		
	Mass fraction		Dosage (g/L)	pH	Cond. (mS/cm)	T (°C)
	Na_2CO_3	NaOH				
Initial:	-	-	-	6,6±0,2	88,3±0,3	23,4±2,7
pH 9:	0,80	0,20	8,06±0,01	9,05±0,02	90,3±0,4	21,4±0,4
pH 10:	0,52	0,48	12,32±0,01	10,07±0,01	88,9±0,6	26,2±0,1
pH 11:	0,44	0,56	14,78±0,03	11,29±0,12	89,8±0,8	24,7±0,8
pH 12:	0,39	0,61	16,36±0,03	12,13±0,03	91,2±0,7	23,4±0,6

Table 29. Reagents dosage, conductivity, pH and T in PAC-LLP during precipitation treatment with Mixed Na_2CO_3 -NaOH

PAC-LLP	Add. Mixed Na_2CO_3 -NaOH			Treatment conditions		
	Mass fraction		Dosage (g/L)	pH	Cond. (mS/cm)	T (°C)
	Na_2CO_3	NaOH				
Initial:	-	-	-	7,3±0,1	89,3±0,2	24,0±1,9
pH 9:	0,85	0,15	7,62±0,01	9,11±0,02	90,9±0,3	25,2±0,9
pH 10:	0,57	0,43	11,52±0,01	10,18±0,09	89,7±0,6	24,2±0,2
pH 11:	0,47	0,53	13,84±0,16	11,27±0,15	90,6±0,6	22,8±0,4
pH 12:	0,42	0,58	15,46±0,01	12,09±0,12	91,0±0,5	23,1±0,7

As see in tables 28 and 29, the amount of Na_2CO_3 added to the treated permeate with a value of $3,3\pm0,1$ g was kept constant at each evaluated pH and only the amount of NaOH was changed in order to reach the desire pH value. Based on the stoichiometric relation of CO_3 with Ca and Mg indicated in table 26, the fixed amount of Na_2CO_3 with the estimated initial mole composition of CO_3 in the permeates corresponded to about 50% excess of CO_3 with respect to the initial Ca and Mg composition. Furthermore, for a specific pH the calculated CV for the conductivity values were less than 1%; hence the conductivity remained almost unchanged during the treatment times of 1, 6 and 24 h for both permeates at the different pH conditions. However, as was the case with the NaOH treatment a slightly increase in conductivity was also observed in both permeates with the mixed Na_2CO_3 -NaOH reagents at the highest pH value of 12 with an increase in conductivity of about 2 to 3% with respect to their initial values, which was less than the increased in conductivity observed with the NaOH reagent.

The results obtained in the removal of Ca, Mg and hardness from the LLP and PAC-LLP at the treatment times of 1, 6 and 24 h are indicated in figures 43, 44 and 45 respectively.

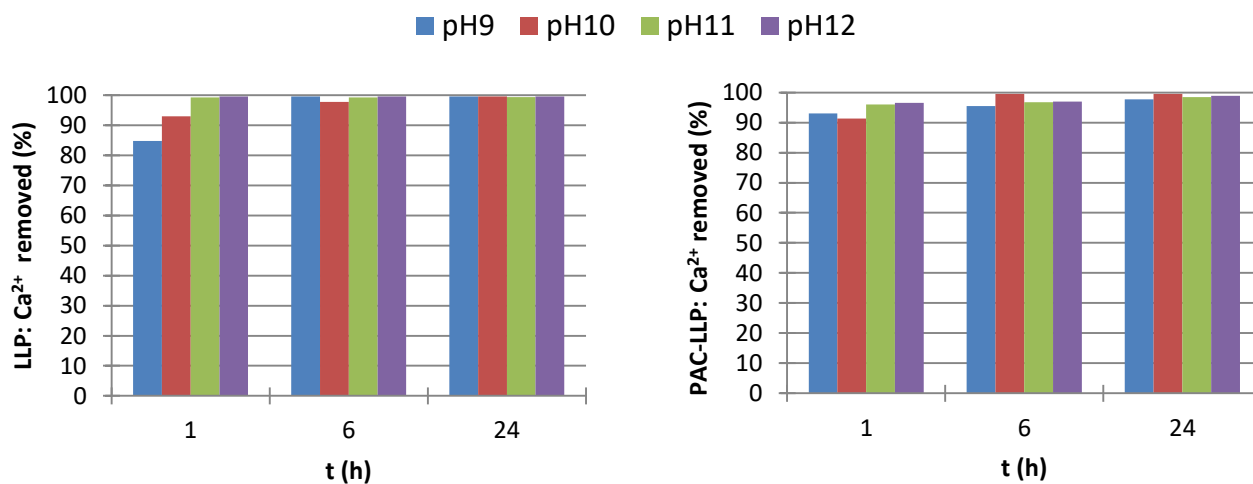


Figure 43. Ca removed in Left: LLP & Right: PAC treated LLP with Mixed Na_2CO_3 -NaOH reagents

As illustrated in figure 43, for the LLP at the higher pH values of 11 and 12 the removals of Ca were greater than 99% at all the evaluated treatment times while at the same pH conditions for the case of the PAC-LLP the removals of Ca were also steady at the treatment times of 1, 6 and 24 h ranging in between 96 and 99%. However, at the lower pH values of 9 and 10 the removals of Ca in both the LLP and PAC-LLP were more time dependent. For instance, in the LLP at pH 9 the removal of Ca for the 1 h treatment had a value of 85% and then at the treatment time of 6 and 24 h it reached a steady value of about 99%. The same was observed at pH 10 in the PAC-LLP whose removal was equal to 93% at the first hour of treatment and then it increased to a value of about 99% at the treatment time of 6 and 24 h.

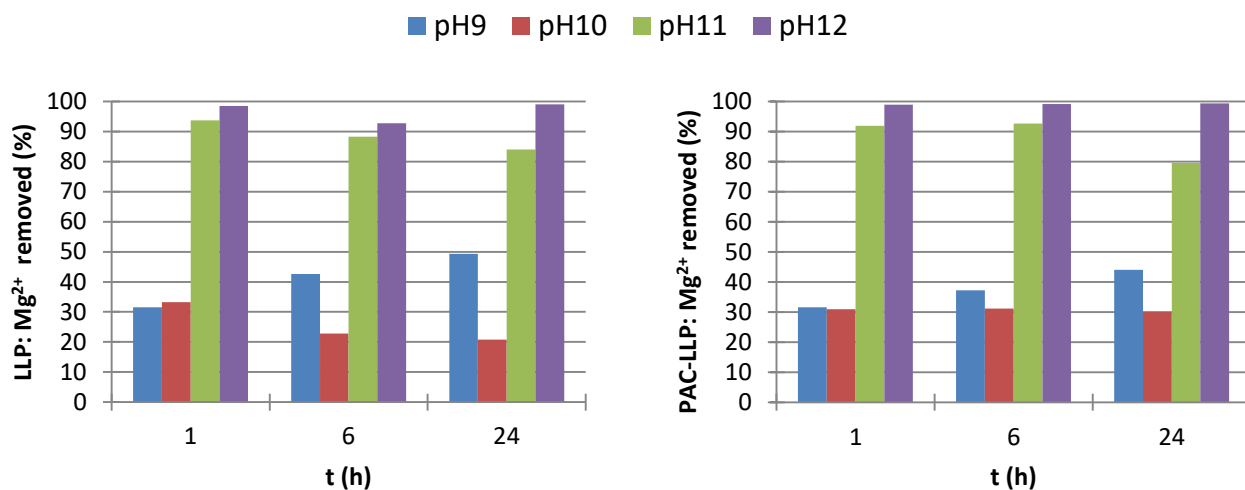


Figure 44. Mg removed in Left: LLP & Right: PAC treated LLP with Mixed Na_2CO_3 -NaOH reagents

As indicated in figure 44, during the treatment times of 1, 6 and 24 h in the LLP and PAC-LLP at the higher pH values of 11 and 12 the removal of Mg did not follow the same trend as did with Ca. For instance, only at pH 12 a relatively stable removal of about 99% was observed at the treatment times of 1 and 24 h. On the other hand, at pH 11 a decreased in the removal of Mg was observed in between the treatment of 1 and 24 h where for the case of the LLP it went from about 94 to 84% and in the PAC-LLP the removal decreased from about 92 to 80%. Furthermore, at pH 9 in the LLP

and PAC-LLP a stable percentage removal was not observed in neither permeate but rather it kept increasing with time reaching a maximum removal at 24 h with values of about 50 and 45% in the LLP and PAC-LLP respectively. Moreover, at pH 10 in the LLP as was the case with the pH 11 a decrease of about 10% in removal was observed in between the treatment time of 1 and 24 h reaching a value of about 21%. And, at the same pH condition in the PAC-LLP a stable removal percentage was observed at the different treatment times with values of about 30%.

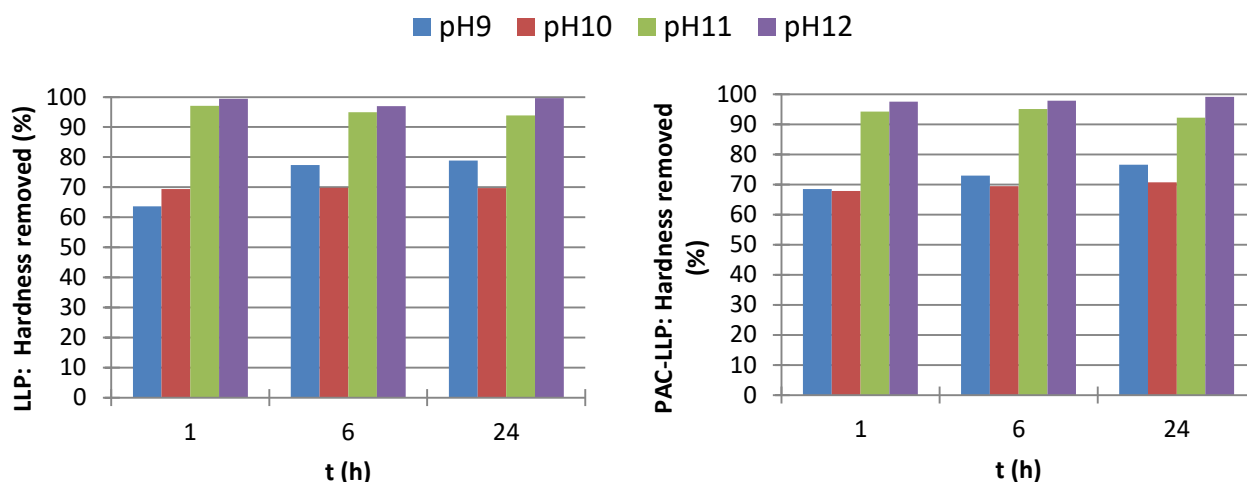


Figure 45. Hardness removed in Left: LLP & Right: PAC treated LLP with Mixed Na_2CO_3 -NaOH reagents

Figure 45 indicated that as expected the removal of hardness was higher in the LLP and PAC-LLP at the pH values of 11 and 12 being slightly higher at pH 12 for each of the treatment times where removals of about 99 and 98% were achieved in the LLP and PAC-LLP respectively at the treatment time of 1 h. The hardness value at pH 12 in the LLP and PAC-LLP at the treatment time of 1 h were equal to 1,7 and 6,7 °dH respectively, which corresponded to a hardness of about 40 and 120 mg/L as CaCO_3 . And, as indicated in table 8 these values corresponded to the range of soft and moderately hard water. Furthermore, at the lower pH values of 9 and 10 the removals ranged in between 60 and 80% in either permeate at the different treatment times.

Additionally, the removal of SO_4 , were also analyzed at the treatment time of 24 h for both permeates at the different pH conditions. The results are given in figure 46.

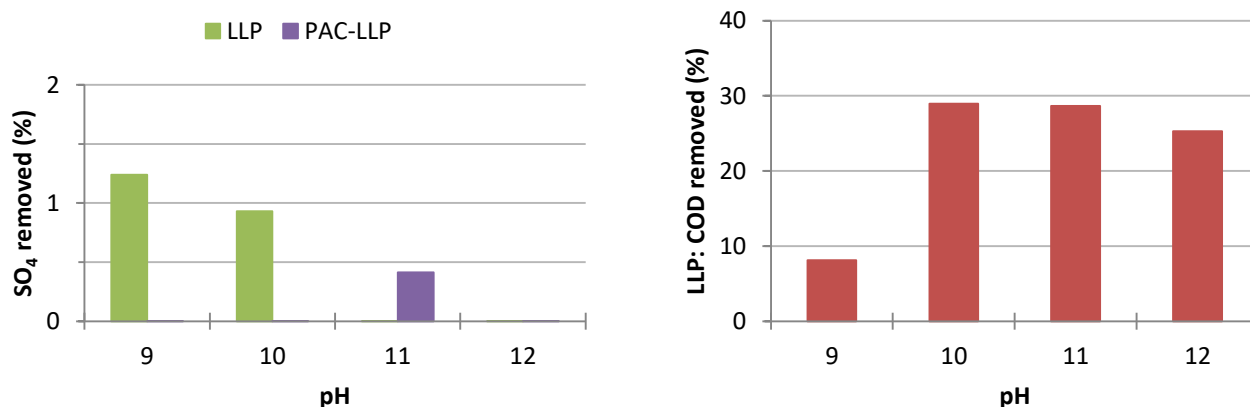


Figure 46. SO_4 and COD removed in LLP & PAC treated LLP with Mixed Na_2CO_3 -NaOH reagents at t=24 h

As shown in figure 46, less than 2 percent of the SO_4 concentration in the LLP and PAC treated LLP was removed during the precipitation treatment at the evaluated pH conditions. This might be an indication that the presence of SO_4 in the precipitation might not be substantial. Also, during the 24 h of precipitation treatment with the mixed Na_2CO_3 -NaOH less than 10% of the COD concentration was removed from the LLP at the pH of 9 and about 25 to 30% were removed at the pH conditions of 10, 11 and 12. These results provided an indication that some of organic matter might be found within the generated solids after the precipitation treatment at either pH condition.

3.3.2.1.4. NaOH vs. Mixed Na_2CO_3 -NaOH as Precipitating Agent

The results obtained at the different treatment times and pH conditions with NaOH and the mixed Na_2CO_3 -NaOH as precipitating agents indicated that the largest removal of hardness took place within the first hour of treatment. Thus, the removal of Ca, Mg and hardness were compared for both reagents at the treatment time of 1 h in the LLP and PAC treated LLP at the evaluated pH conditions of 9 and 12.

The reagents dosage used in the precipitation treatment are given in table 30.

Table 30. NaOH and Mixed Na_2CO_3 -NaOH dosages used at pH 9 and 12

pH:		pH 9			pH 12		
Reagent:		Mixed [‡] Na_2CO_3 (1) - NaOH (2)		NaOH ^{‡‡} (2)	Mixed [‡] Na_2CO_3 (1) - NaOH (2)		NaOH ^{‡‡} (2)
Permeate:		PAC-LLP	LLP	LLP	PAC-LLP	LLP	LLP
Dosage (g/L):		7,62	8,06	2,50	15,46	16,36	10,06
Mass ratio:	1	0,85	0,80	-	0,42	0,39	-
	2	0,15	0,20	1	0,58	0,61	1
Dosage ratio*:		3,1	3,2	1,0	1,5	1,6	1,0

‡ Added in solid form

‡‡ Calculated based on added NaOH (12M)

* Dosage ratio with respect to NaOH dosage in g/L-permeate

As indicated in table 30, at pH 9 the amount of mixed reagents used corresponded to about 3 times the amount of NaOH but at pH 12 the amount of mixed reagents added was only about 1,5 times higher than the amount of NaOH required to increase the pH to 12 in the permeate. Furthermore, as already mentioned the amount of Na_2CO_3 added was kept fixed at the evaluated pH conditions and with the estimated initial mole composition of CO_3 in the permeates it corresponded to about 50% excess with respect to the initial mole amounts of Ca and Mg. Thus, for the case of the mixed Na_2CO_3 -NaOH as precipitant, the CO_3 in the system at the evaluated pH conditions was about 4 times larger compared to the systems with NaOH as precipitant.

The pH, T and conductivity measured in the permeates during the treatment time of 1 h with their respective precipitating agents are given in table 31.

Table 31. Conductivity, pH and T in LLP & PAC-LLP during precipitation treatment at $t = 1$ h with NaOH & mixed Na_2CO_3 -NaOH reagents at pH 9 & 12

Precipitation Agent	Permeate	Treatment time	Parameters		
			pH	Cond. (mS/cm)	T (°C)
NaOH	LLP (Collected Spring)	Initial:	6,6±0,2	86,6±2,7	22,6±0,2
		1 h – pH9:	9,07±0,02	83,4±0,1	22,1±0,5
		1 h – pH12:	12,03±0,02	92,3±0,2	22,8±0,5
Mixed Na_2CO_3 -NaOH	LLP (Collected Summer)	Initial:	6,6±0,2	88,3±0,3	23,4±2,7
		1 h – pH9:	9,06±0,25	90,0±0,2	21,4±0,2
		1 h – pH12:	12,11±0,08	90,5±0,5	24,1±1,5
	PAC-LLP	Initial:	7,3±0,1	89,3±0,2	24,0±1,9
		1 h – pH9:	9,12±0,12	90,8±0,3	24,3±0,2
		1 h – pH12:	11,96±0,08	90,4±0,5	23,9±0,8

As seen in table 31, the parameters of the landfill leachate permeate (LLP) collected in the season of spring and summer were almost the same where the conductivity was slightly higher for the permeate collected on summer. Furthermore, for the treatment time of 1 h the only reagent that yielded a permeate with a conductivity value slightly lower than the initial value was NaOH at the pH of 9. At the same pH condition and treatment time the mixed Na_2CO_3 -NaOH reagent yielded permeates with slightly higher conductivities than their respective initial values with increases ranging in between 1,5 to 2%. Moreover, at the higher pH value of 12 the increase in conductivity was larger with respect to pH 9 for either precipitating agent reaching the maximum increase of about 6% for the case of NaOH in the LLP. The increase in conductivity in the permeates at pH 12 for the treatment time of 1 h with the different precipitating agents are illustrated in figure 47.

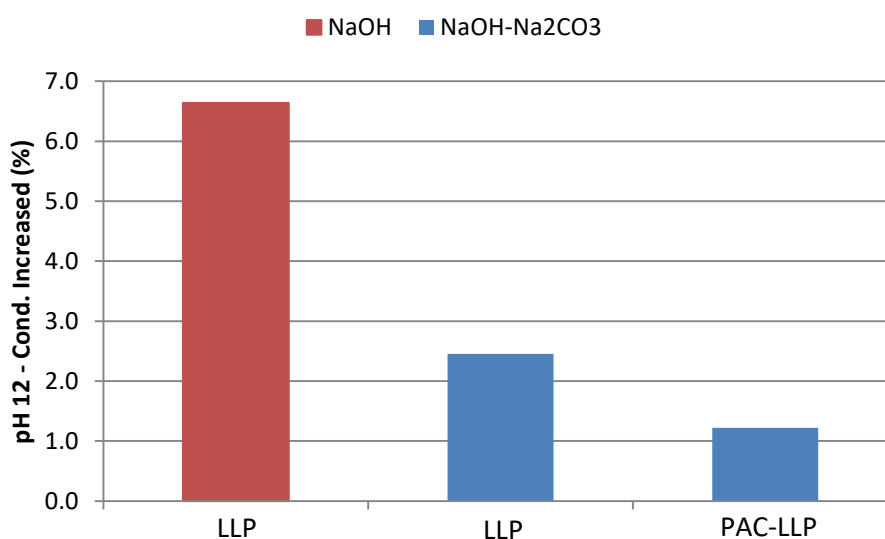


Figure 47. Conductivity increase at pH 12 in the permeates with NaOH and mixed Na_2CO_3 -NaOH for $t = 1$ h

The results obtained in the removal of Ca, Mg and hardness at the evaluated pH conditions are given in figure 48.

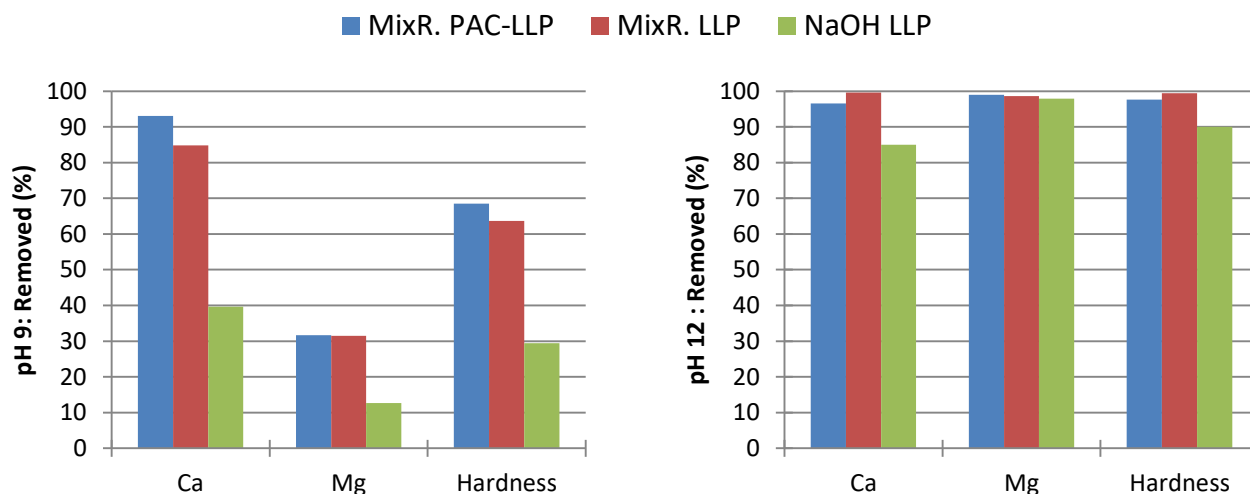


Figure 48. Ca, Mg and Hardness removed in LLP and PAC-LLP with NaOH and Mixed Na_2CO_3 -NaOH reagents (MixR.) at $t = 1$ h and pH conditions of 9 and 12

As seen in figure 48, at the lowest evaluated pH value of 9 the removal of Ca was greater than 90% in the PAC treated landfill leachate permeate (LLP) with the mixed Na_2CO_3 -NaOH reagent. Also, in the LLP at the same pH value about 85% of the Ca was removed with mixed reagents. On the other hand, in the LLP only about 40% of the Ca got removed with NaOH, which corresponds to less than half the removal obtained with the mixed Na_2CO_3 -NaOH reagent. At the same pH value of 9, the removal of Mg in the PAC treated LLP and LLP with the mixed reagents were almost the same with a value of about 30% and with NaOH only about 13% of the Mg was removed. Thus, the removal of hardness at pH pH 9 in the PAC-LLP and LLP were relatively close to each other with values of about 68 and 64% respectively and only about 30% of the hardness was removed with NaOH in the LLP. Furthermore, at pH 12 the mixed reagents removed more than 95% the Ca in the PAC-LLP and LLP and the removal with NaOH was also high but was 10% less compared to the mixed reagents. Moreover, the removal of Mg with either precipitant in the PAC-LLP and LLP was close to or greater than 98%. Thus, more than 98% of the hardness was removed from the PAC-LLP and LLP with the mixed Na_2CO_3 -NaOH reagents and about 90% of the hardness was removed from the LLP with NaOH.

Moreover, from the measured concentrations at the treatment time of 1 h the reacted moles of Ca, Mg and TIC were calculated. Then, based on the reacted moles, the ratios of reacted CO_3 to Ca-Mg were calculated at the evaluated pH conditions. For the calculations, it was assumed that the difference in TIC concentration with respect to the initial values corresponded to the reacted CO_3 . The assumption was made based on the carbonate equilibrium diagram illustrated in figure 18 where at pH 9 and 12 almost all of the inorganic carbon is in the form of either bicarbonate (HCO_3^-) or carbonate (CO_3^{2-}) and as indicated in figure 40 the SI at these pH conditions in the LLP showed oversaturated with respect to CaCO_3 . The results were compared to the hardness removed as indicated in figure 49.

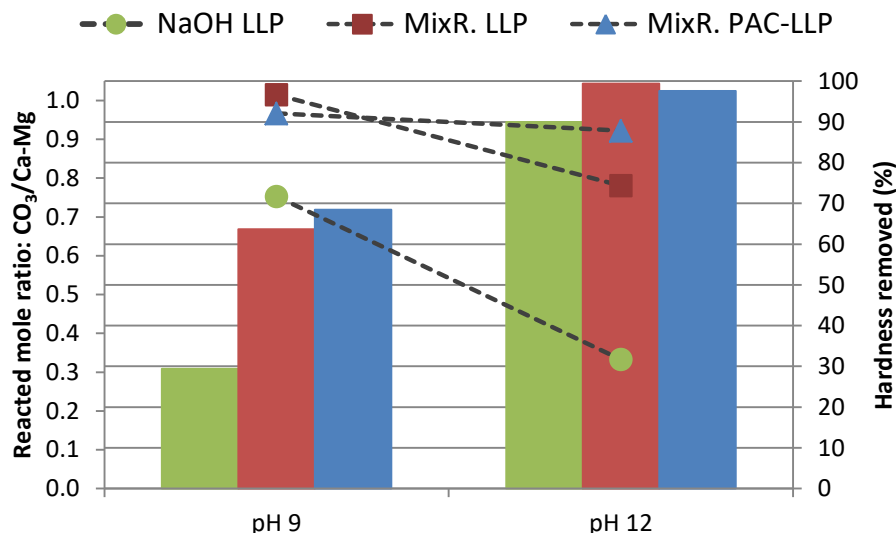


Figure 49. Points: Reacted CO_3 to Ca-Mg mole ratios; Bars: Hardness removed in LLP and PAC-LLP with NaOH and Mixed Na_2CO_3 -NaOH reagents (MixR.) at $t = 1$ h and pH conditions of 9 and 12

As indicated in figure 49 at pH 9 with NaOH as precipitant about 75% of the reacted Ca and Mg corresponded to the estimated CO_3 . However, only about 30% of the hardness was removed from the permeate and for the same reagent but at pH 12 the amount of CO_3 that reacted with respect to the reacted moles of Ca and Mg was even lower with a value of about 33% but the removal of hardness was about 90%. These ratios seemed relatively low considering the oversaturation in the LLP with respect to CaCO_3 and the stoichiometric relation discussed in table 26 where CO_3 was estimated as the limiting reagent. Thus, these results might provide an indication that at pH 12 with NaOH as precipitating agent the majority of the precipitated Ca and Mg were not in carbonate form but in different forms such as hydroxides and at pH 9 from the low amount of reacted Ca and Mg probably a considerable fraction was in carbonate form. Furthermore, in the LLP and PAC-LLP for the case of the mixed Na_2CO_3 -NaOH reagents at pH 9 the ratios between the reacted CO_3 and Ca-Mg were very close to their stoichiometric relation of 1 to 1 where about 65% of the hardness was removed in each permeate and at pH 12 the ratio decreased to values of about 0,8 and 0,9 for the LLP and PAC-LLP respectively with hardness removal greater than 98%. These decreased in the estimated ratio might be an indication of strong competition in the liquid system between the most abundant OH^- and CO_3^{2-} anions for the Ca^{2+} and Mg^{2+} cations. This observation might be explained by comparing the initial mole ratios of the added OH^- with respect to the estimated amount of CO_3 at the different pH conditions for each precipitating agent as indicated in table 32.

Table 32. Initial mole ratios in the LLP and PAC-LLP of PO_4^{3-} & added OH^- with respect to CO_3^{2-} at pH 9 and 12

INITIAL MOLE RATIO: $\text{OH}^-/\text{CO}_3^{2-}$				INITIAL MOLE RATIO: $\text{PO}_4^{3-}/\text{CO}_3^{2-}$			
Reagent:	NaOH [‡]	Na ₂ CO ₃ -NaOH*		Reagent:	NaOH	Na ₂ CO ₃ -NaOH	
Permeate:	LLP	LLP	PAC-LLP	Permeate:	LLP	LLP	PAC-LLP
pH 9	3,2	0,5	0,4	pH 9	0,014	0,004	0,023
pH 12	12,8	3,1	3,0	pH 12	0,014	0,004	0,023

‡ For NaOH reagent calculated based on initial CO_3 in LLP

* For Na₂CO₃-NaOH calculated based on total CO_3 (in LLP + Add.)

As described in table 32, due to its low concentration in the permeates the PO_4 anion played a small role in the competition of the anions for Ca and Mg considering that the PO_4 concentration only corresponded to 0,14 mmol as $\text{PO}_4\text{-P}$, which as compared to the mole amounts indicated in table 26 it was very small for the accounting of common forms of Ca^{2+} and PO_4 precipitation encounter in wastewater treatments such as hydroxyapatite with base formula of $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ (Ødegaard, 1979). On the other hand, for the case of the OH^- anion as the amount of OH^- increased to reach the pH of 12 also did the dominance of OH^- with respect to other anions including CO_3 in the competition for the cations Ca and Mg. This increased on dominance was stronger for the case of only NaOH as precipitating agent where at pH 12 the initial amount of OH^- was about 13 times higher compared to CO_3 . On the other hand, at the same pH condition with the mixed reagent the initial amount of OH^- was only about 3 times higher than CO_3 in either permeate, which might have made the conditions better for CO_3 dominance since stoichiometrically only one mole of CO_3 is required for the precipitation of Ca and/or Mg compare to the 2 moles require for OH^- . Thus, even at high pH conditions the use of only NaOH for the recovery of CaCO_3 -rich solids might not be ideal considering that a lot of the Ca present in the LLP might precipitate in OH^- forms and as indicated in table 7 of section 2.3, $\text{Ca}(\text{OH})_2$ is considered to be slightly soluble; hence having a less stable solid state compared to CaCO_3 , which is considered to be practically insoluble in aqueous medium.

The results obtained in the removal of TOC for each of the precipitating agents at the treatment time of 1 h and for the removal of ortho- $\text{PO}_4\text{-P}$ from the permeates with NaOH at the treatment time of 1 h and the mixed Na₂CO₃-NaOH at the treatment of 24 h at the pH conditions of 9 and 12 are given in figure 50.

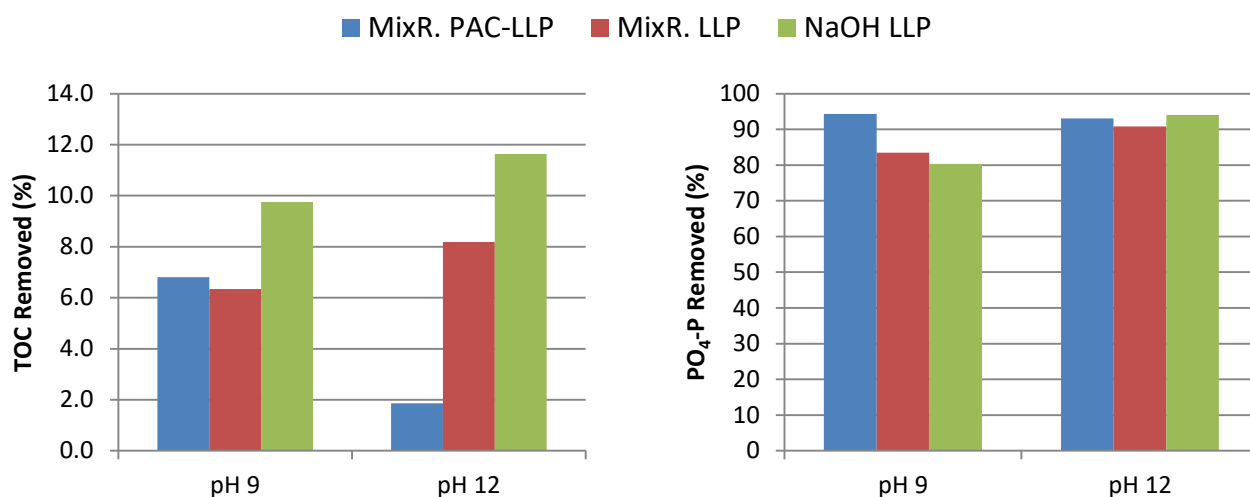


Figure 50. TOC and PO₄-P removed in LLP and PAC-LLP with NaOH and Mixed Na₂CO₃-NaOH reagents (MixR.)
 For TOC: All reagents at t = 1 h; For PO₄-P: NaOH: 1 h & Mixed reagents: 24 h at pH conditions of 9 and 12

As indicated in figure 50, the removal of TOC at the treatment time of 1 h was larger at both pH conditions in the LLP with NaOH compared to the permeates treated with the mixed Na₂CO₃-NaOH where at pH 12 almost 12% of the TOC got removed from the LLP with NaOH and for the same permeate and the PAC treated LLP about 8% and 2% respectively got removed with the used of the mixed Na₂CO₃-NaOH. Thus, as was already discussed for the case of COD in figure 46, besides the desire CaCO₃-rich solids also organic material might be found within the precipitation matrix from pH conditions greater or equal than 9. Furthermore, as indicated in table 25 even though the concentration of PO₄-P in the LLP is less than 10 mg/L, it was seen that more than 80% of this substances was precipitated at either pH condition by the used of the precipitating agents but it was slightly higher with NaOH in the LLP at pH 9 where unlike the others the removal was greater than 90%. And, at pH 12 the removals of PO₄-P at each of the evaluated conditions were very closed to each other with values of about 93%.

3.3.2.1.5. Collection of Generated Precipitation in LLP and PAC-LLP with Mixed Na₂CO₃-NaOH at Different pH Conditions

As indicated in figure 37 in order to separate the solids generated during the precipitation treatment, the generated precipitation went through a series of steps, which initially included centrifugation-decantation followed by its collection in the formed of sludge and left to air-dry at room temperature (T≈22°C) as illustrated in figure 51.



Figure 51. Collected precipitation in the form of sludge; Top: From LLP; Bottom: From PAC-LLP

In order to estimate the amount of dried sludge with respect to the treated permeate, the dried sludge collected from the precipitation treatment was weighted at the different pH conditions and divided by the volume of 0,5 L of treated permeate. Additionally, in order to verify the obtained results, a TSS analysis was performed. The results are given in table 33.

Table 33. TSS analysis and amount of dried sludge generated during the precipitation treatment in the LLP and PAC-LLP at the different pH conditions

pH	Mixed Na ₂ CO ₃ -NaOH						NaOH
	LLP			PAC-LLP			LLP
	Estimated (g/L _{Perm.})	TSS (g/L _{Perm.})	Error wrt TSS (%)	Estimated (g/L _{Perm.})	TSS (g/L _{Perm.})	Error wrt TSS (%)	TSS (g/L _{Perm.})
9	4,5±0,3	4,4	2	4,1±0,3	4,4	-8	2,2
10	5,0±0,5	4,8	3	4,8±0,5	4,6	4	3,1
11	7,0±0,7	7,4	-5	6,9±0,1	5,5	24	5,3
12	8,5±0,2	8,4	1	8,1±0,5	6,9	17	5,7

As seen in table 33, the TSS results served as indicators for the efficiency of the performed centrifugation-decantation in the dewatering of the generated precipitation. Thus, in general for most of the evaluated conditions the estimated values did not differ considerably from the TSS values but for the case of the PAC-LLP at the pH values of 11 and 12 the amount of dried sludge reached values close to or greater than 20% with respect to TSS, which indicated the presence of extra matter that might be of soluble nature and corresponded to the liquid fraction of the sludge. Additionally, the TSS analysis for the LLP treated with the mixed Na₂CO₃-NaOH yielded values that were in about 1,5 to 2,0 to times larger than the values obtained with NaOH as precipitating agent.

3.3.2.1.6. Washing of Collected Dried-Sludge and Recovery of Solids at Different pH Conditions

In order to obtain the stable solid fraction or insoluble part of the collected sludge, the dried sludge was washed with deionized water (DW) at a temperature of $22,1\pm0,3^{\circ}\text{C}$ in a ratio of 1 part of solids to 10 parts of water (100 g-dried sludge/L-DW) and allowed to air-dry at room temperature ($T\approx 22^{\circ}\text{C}$) for about 5 days. The dried solids were weighted before and after the washing steps and based on their weight difference the solids loss and also the amount of solids recovered per volume of permeate were estimated. The measured parameters in the filtered washwater and the results obtained in the calculations after the 24 h washing treatment are given in tables 34 and 35 respectively.

Table 34. pH and Conductivity in Washwater used on precipitation generated at different pH condition with the mixed $\text{Na}_2\text{CO}_3\text{-NaOH}$ reagents

Precipitation Generated at pH	Filtered Washwater Used on Precipitation from LLP ($T=22,0\pm0,3^{\circ}\text{C}$)			Filtered Washwater Used on Precipitation from PAC-LLP ($T=22,2\pm0,4^{\circ}\text{C}$)		
	pH	Cond. (mS/cm)	Inc. Cond Wrt pH 9	pH	Cond. (mS/cm)	Inc. Cond wrt pH 9
9	9,5	12,2	1,0	9,2	11,1	1,0
10	10,0	18,3	1,5	9,8	21,2	1,9
11	10,4	36,3	3,0	10,0	36,1	3,3
12	10,2	48,2	4,0	10,3	50,2	4,5

Table 35. Amount of recovered solids and washing losses from precipitation treatment in the LLP and PAC-LLP with mixed $\text{Na}_2\text{CO}_3\text{-NaOH}$ at different pH conditions

Precipitation Generated at pH	From LLP		From PAC-LLP	
	Recovered Solids (g-S/L _{Perm.})	Washing Loss (%)	Recovered Solids (g-S/L _{Perm.})	Washing Loss (%)
9	4,1	8	3,7	9
10	4,3	14	4,0	16
11	5,7	18	-	-
12	5,0	40	-	-

As indicated in tables 34 and 35, at the higher pH values of 11 and 12 the conductivity in both of the washwater used on the precipitation generated from both permeates were about 3 to 4 times larger than the conductivity values in the washwater from the generated precipitation at pH 9. This increase in conductivity was reflected in the higher increase of loss solids observed at the same pH conditions, which reached a loss of about 40% for the precipitation generated at the highest pH

value of 12. Furthermore, independently of the pH used during the precipitation and only with the exception of the pH 9 generated solids the pH in the analyzed washwater were all around 10. Moreover, the highest amount of recovered solid per volume of permeate were obtained for the pH 11 and 12 generated solids and in between the LLP and the PAC treated LLP the amount of generated solids were comparable to each other.

Furthermore, based on the fixed value used for the washing step of 100 g-dried sludge/L-DW and the estimated amount of dried-sludge per volume of permeate, a volume relation between washwater (DW) and permeate (Perm.) was estimated. Also, the ratios between the recovered solids (S) with respect to the reagents dosage (R) used during the precipitation treatment at the different pH conditions were estimated based on the amount of recovered solids per volume of permeate. The results are given in table 36.

Table 36. Precipitation Ratios: Amount of Recovered Solids per Total Mixed Na₂CO₃-NaOH Used & Volume of Washwater per Treated Permeate

Precipitation Generated at pH	Mass S/R		Vol. DW/Perm.	
	LLP	PAC-LLP	LLP	PAC-LLP
9	0,51	0,48	0,045	0,041
10	0,35	0,35	0,050	0,048
11	0,39	0,30	0,070	0,069
12	0,31	0,23	0,085	0,081

As seen in table 36, based on the amount of mixed reagents added the most optimal solid recovered to added reagents (S/R) ratio was obtained at the lowest pH value of 9 whose recovered value corresponded to about 50% of the added reagents and for the case of the LLP at higher pH values the ratio ranged in between 30 to 40%. Additionally, the values in between the untreated and PAC treated LLP did not differ from each other and were almost the same at the lower pH conditions of 9 and 10 but at the higher pH values the S/R ratio was lower for the PAC-LLP compared to the LLP. Furthermore, based on the performed steps for the separation of the precipitation for the treated permeate and on the solid to water ratio of 1 to 10, the amount of washwater required can range in between 4 to 8% of the permeate volume being lower for the lower pH values since the amount of solids generated was also less compare to the larger pH values of 11 and 12.

3.3.2.1.7. Chemical and XRD Analysis on Solids Generated with Mixed Na₂CO₃-NaOH at Different pH Conditions

The composition analysis was performed in order to determine the effect that the evaluated pH conditions and organic content of the LLP and PAC-LLP had on the recovered solids and their Ca concentration, precipitated by the addition of the mixed Na₂CO₃-NaOH reagent. Based on the results, the mass percentage concentrations of

Al, Ca, Fe, K, Mg, Mn, P and Si in their oxides forms were calculated. The results obtained for pH 9 and 10 and pH 11 and 12 are given in tables 37 and 38 respectively.

Table 37. Oxides in recovered solids with mixed Na_2CO_3 -NaOH reagent at pH 9 and 10

	pH 9			pH 10		
Substance	LLP	PAC-LLP	CV (%)	LLP	PAC-LLP	CV (%)
Al_2O_3 (%)	0,03	0,03	1	0,03	0,03	9
CaO (%)	30,4	32,9	6	30,8	31,8	2
Fe_2O_3 (%)	0,04	0,04	3	0,07	0,04	42
K_2O (%)	0,4	0,4	6	0,5	0,8	37
MgO (%)	2,6	2,8	3	2,3	2,6	9
MnO (%)	0,03	0,03	8	0,02	0,02	22
P_2O_5 (%)	0,9	3,2	79	0,9	6,0	104
SiO_2 (%)	<0,1	<0,1	0	1,2	1,4	8

Table 38. Oxides in recovered solids with mixed Na_2CO_3 -NaOH reagent at pH 11 and 12

	pH 11			pH 12		
Substance	LLP	PAC-LLP	CV (%)	LLP	PAC-LLP	CV (%)
Al_2O_3 (%)	0,02	0,02	2	0,04	0,05	18
CaO (%)	34,4	32,2	5	31,1	30,6	1
Fe_2O_3 (%)	0,05	0,03	41	0,05	0,02	49
K_2O (%)	0,8	1,1	22	1,3	1,3	4
MgO (%)	4,6	4,6	0	6,9	5,4	17
MnO (%)	0,03	0,03	5	0,03	0,03	1
P_2O_5 (%)	0,8	2,1	67	0,7	4,6	105
SiO_2 (%)	1,6	1,9	11	1,8	1,8	2

As indicated in tables 37 and 38, based on the coefficient of variation (CV) calculated for each of the oxides at the corresponding pH value and only with the exception of P_2O_5 it was seen that the concentration of the oxides in the solids recovered from the LLP and PAC-LLP did not differ considerably from each other. For instance, only with the exception of MgO at pH 12 the CV calculated for CaO and MgO at each of the pH conditions were less than 10% with CaO mass percentage ranging in between 30,4 to 34,4% and MgO concentration ranged in between 2,3 to 6,9% being higher at pH values of 11 and 12 in the solids recovered from both permeates. The concentration ranges of CaO and MgO at the different pH conditions generated from either permeates were very close to the values found during the production of cement in the feed of cement kiln, which can be around 44 and 5% for CaO and MgO respectively (Oates, 1998). Moreover, for the case of Fe_2O_3 the calculate CV were around 45% at

pH values of 10, 11 and 12 where the concentrations of Fe_2O_3 were higher for the solids recovered from the LLP. Furthermore, the higher concentration of P_2O_5 measured in the solids recovered from the PAC treated permeate corresponded to the higher concentration of PO_4 observed in the LLP after the adsorption treatment indicated in table 25. The sum of the oxides and the CaO mass percentage are illustrated in figure 52.

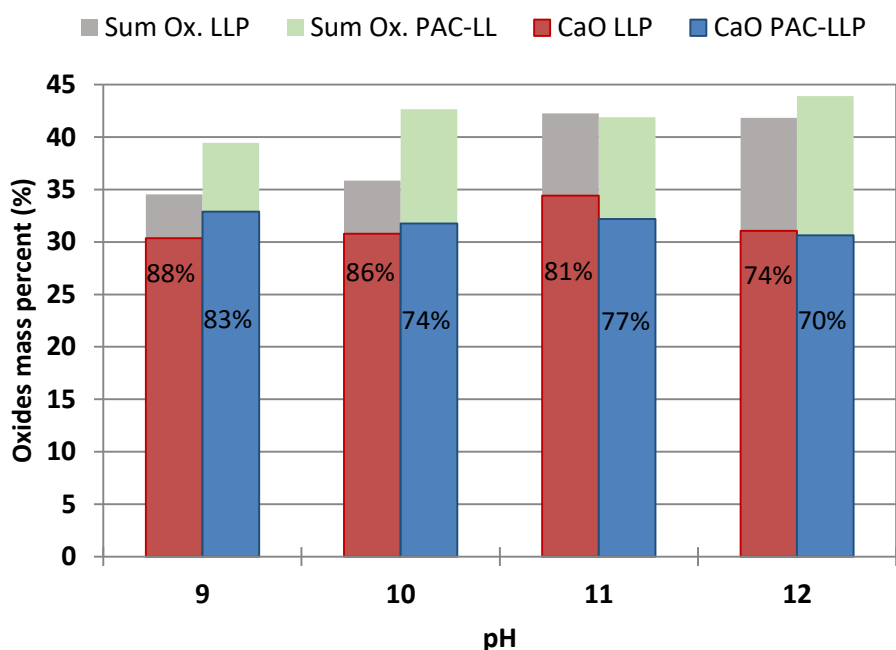


Figure 52. Mass percentage of CaO and Oxides in Recovered Solids at different pH conditions

As seen in figure 52, the sum of the analyzed oxides in the recovered solids generated from the LLP and PAC-LLP ranged in between 34 to 44% having the lowest value at pH 9 for the solids recovered from the LLP and the largest value at pH 12 for the solids recovered from the PAC-LLP. However, at pH 9 the percentage of CaO in the oxides were higher with values greater than 80% compared to pH 12 with values around 70%, which indicated larger concentration of oxides in the solids at higher pH values such as MgO. Additionally, the CV calculated for the sum of the oxides at the pH conditions of 11 and 12 were less than 3% and for the pH values of 9 and 10 were about 10%. These indicated that at the pH values of 9 and 10 the concentration of the oxides in the recovered solids from the PAC-LLP were higher compare to the solids generated from the LLP at lower pH values. However, as already stated with respect to CaO the composition did not change considerably at either pH condition and permeate used but the concentrations of CaO in the recovered solids was so much higher than any other of the analyzed oxides.

Moreover, as indicated in table 16, the Ca to Mg ratio in the LLP was about 3 and also as indicated in table 25, this ratio was about 2,5 in the LLP and 2,3 in the PAC-LLP. Thus, the concentration of Ca in the recovered solids was expected to be higher than the Mg concentration, the Ca to Mg ratios calculated in the recovered solids from both permeates at the different pH conditions are illustrated in figure 53.

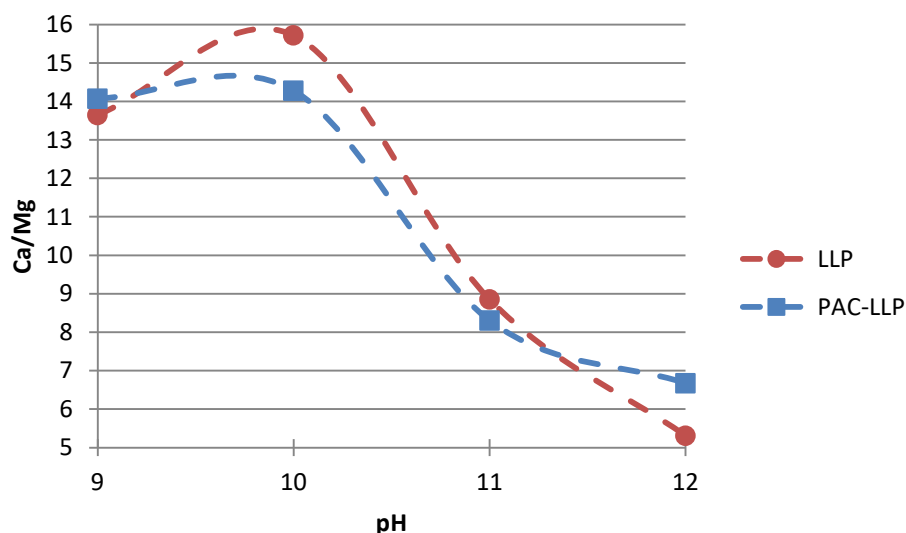


Figure 53. Ca to Mg ratio in recovered solids from LLP and PAC-LLP at different pH conditions

As seen in figure 53, at pH 9 the Ca to Mg ratios were almost the same for the solids recovered from both permeates but at pH 10 they deviated slightly reaching peak values of about 14 and 16 for the solids obtained from the PAC-LLP and LLP respectively. After reaching the maximum points the Ca to Mg ratios decreased until reaching a minimum value of about 5 and 7 in the solids recovered from the LLP and PAC-LLP respectively but still higher than the source Ca to Mg ratios found in the permeates, which ranged in between 2 to 3. Furthermore, based on the Ca to Mg ratio, pH 10 might be seen as an optimal point for the recovery of CaCO_3 -rich solids. However, as already indicated in figure 45, at this pH condition about 30% of the hardness still remained in the treated permeates; hence issues related to scaling might still be a problem in downstream membrane processes.

Additionally, besides the oxide substances, others including the heavy metals regulated by the EU Directive for Sewage sludge and Soil were analyzed at the different pH conditions. The results obtained for the regulated substances are given in tables 39 and 40 for the solids generated from the LLP and PAC-LLP respectively.

Table 39. Concentration of substances regulated by EU Directives in Solids Recovered from LLP

Solids recovered from LLP				
Substance	pH 9	pH 10	pH 11	pH 12
Hg (ppm)	<0,01	<0,01	<0,01	<0,01
Cd (ppm)	<10	<10	<1	<1
Pb (ppm)	<10	<10	<2	<2
Cr (ppm)	<10	<10	7,7	8,0
Cu (ppm)	<10	<10	2,1	<2
Ni (ppm)	<10	<10	<2	<2
Zn (ppm)	<50	<50	-	-

Table 40. Concentration of substances regulated by EU Directives in Solids Recovered from PAC-LLP

Solids recovered from PAC-LLP				
Substance	pH 9	pH 10	pH 11	pH 12
Hg (ppm)	<0,01	<0,01	<0,01	<0,01
Cd (ppm)	<10	<10	<1	<1
Pb (ppm)	<10	<10	2,2	2,8
Cr (ppm)	<10	<10	2,3	3,3
Cu (ppm)	<10	<10	<2	<2
Ni (ppm)	<10	<10	<2	2,2
Zn (ppm)	<50	<50	-	-

As indicated in tables 39 and 40 and based on the limit values indicated in the EU Directive of 1986 “on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture” described in table 3, the concentration of the analyzed heavy metal in the recovered solids were below the limit values indicated in the regulation. Moreover, the results obtained in the analysis of other substances, which are known to have some effect in the quality of soil, are given in tables 41 and 42 for the solids generated from the LLP and PAC-LLP respectively.

Table 41. Other analyzed substances in Recovered Solids generated from LLP with effects in soil quality

Solids recovered from LLP				
Substance	pH 9	pH 10	pH 11	pH 12
Na (ppm)	10400	7420	17400	24300
Cl ⁻ (ppm)	3100	4700	13000	25000
S (ppm)	1920	<800	1750	2780
N (ppm)	<1000	<1000	<1000	<1000
Mo (ppm)	<5	<5	<1	<1

Table 42. Other analyzed substances in Recovered Solids generated from PAC-LLP with effects in soil quality

Solids recovered from PAC-LLP				
Substance	pH 9	pH 10	pH 11	pH 12
Na (ppm)	8940	9350	19500	24400
Cl ⁻ (ppm)	3600	3400	17000	25000
S (ppm)	2180	<800	1970	2510
N (ppm)	<1000	<1000	<1000	<1000
Mo (ppm)	<5	<5	<1	<1

The results obtained in tables 41 and 42 were important specially for the potential application of the recovered solids in soil such as liming material for the correction of soil acidity (ISO, 2015) or as neutralizer of acid rain fall (Oates, 1998). For instance,

due to its large size the presence of Na^+ ions in soil has been known to affect soil structure since they induce dispersion within the soil matrix (MSU, 2003). Thus, in order to further decrease the amount of soluble substances such as Na^+ and Cl^- from the recovered solids a solid to washwater ratio larger than 1 to 10 might be required. Additionally, for the most part the concentration of S, N and Mo made up about 0,2 less than 0,1 and less than 0,0005% of the recovered solids respectively. As indicated in table 25 despite the high concentration of SO_4 in the permeates with values around 9500 mg/L, the low concentration of sulfur in the recovered solids correlated well with the low removal of SO_4 in the permeates illustrated in figure 46 during the precipitation treatment at the different pH conditions. Furthermore, for the case of the macronutrient N, low concentrations were also expected to be present in the precipitated solids since as indicated in table 16 about 90% of the N in the permeate is in the form of $\text{NH}_4\text{-N}$ whose salts are characterized by its high solubility.

The diffractograms obtained from the XRD analysis performed in the recovered solids obtained at the different pH conditions from the LLP and PAC-LLP are given in figures 54 through 61.

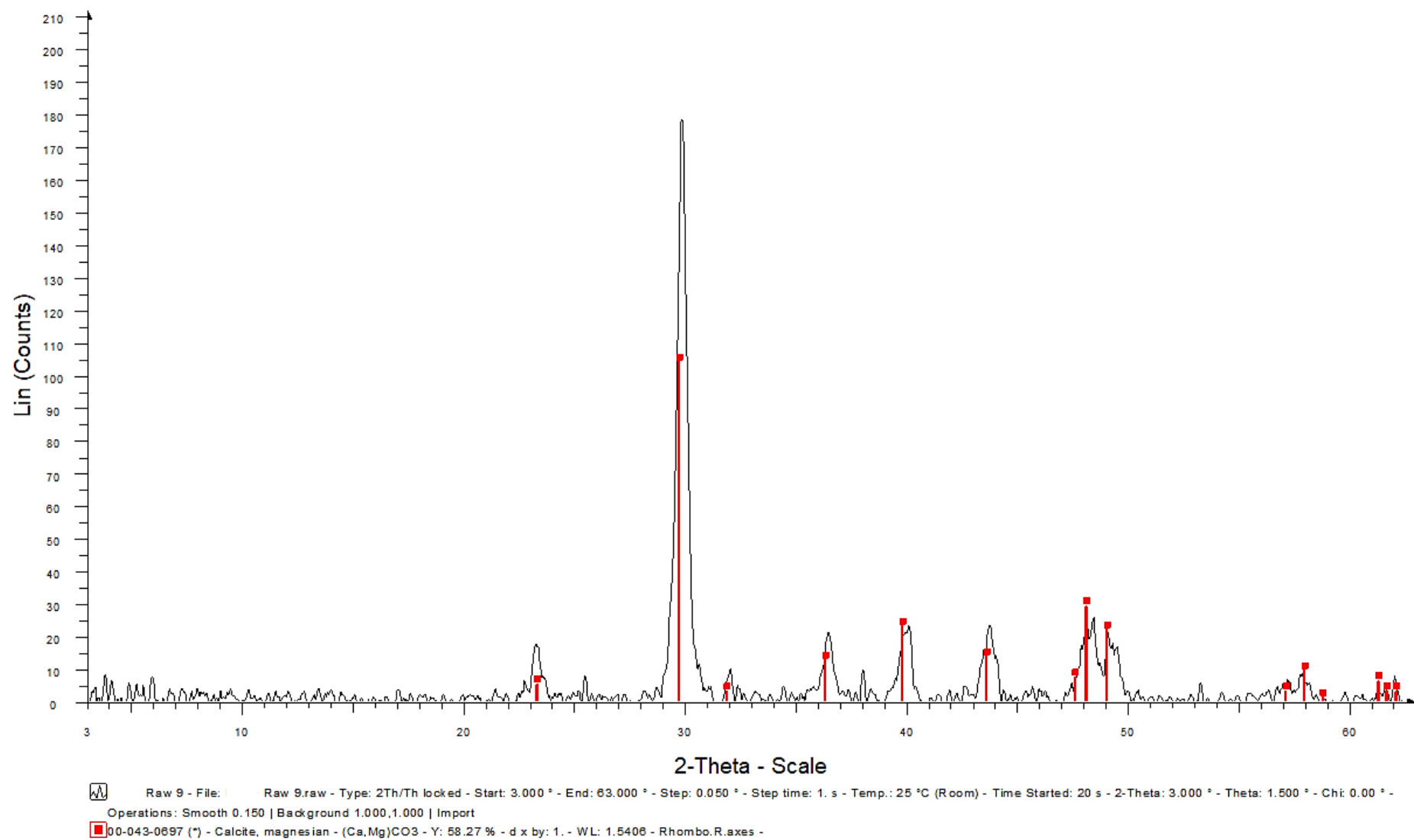


Figure 54. X-ray diffraction pattern for recovered solids at pH 9 from LLP

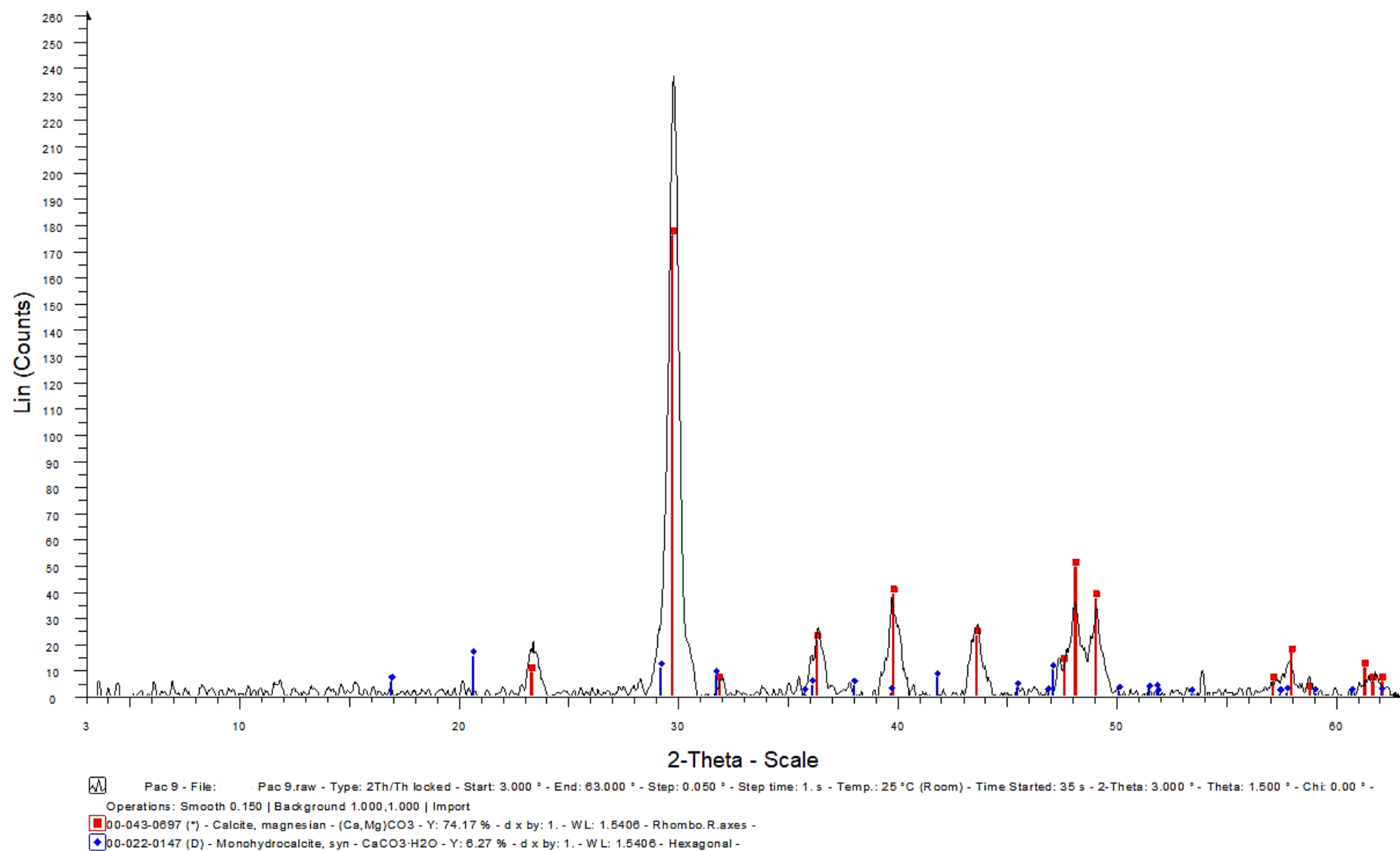


Figure 55. X-ray diffraction pattern for recovered solids at pH 9 from PAC-LLP

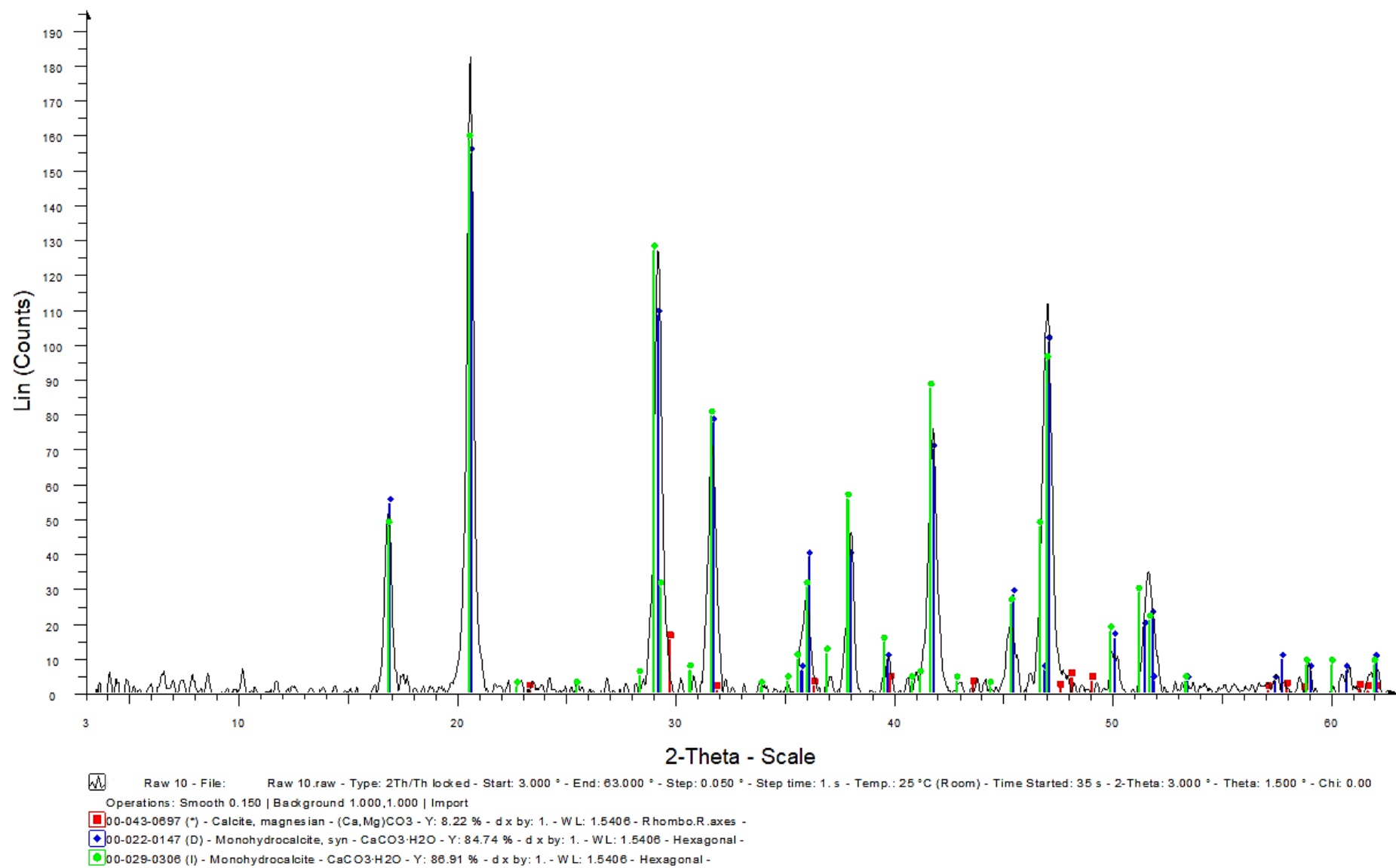


Figure 56. X-ray diffraction pattern for recovered solids at pH 10 from LLP

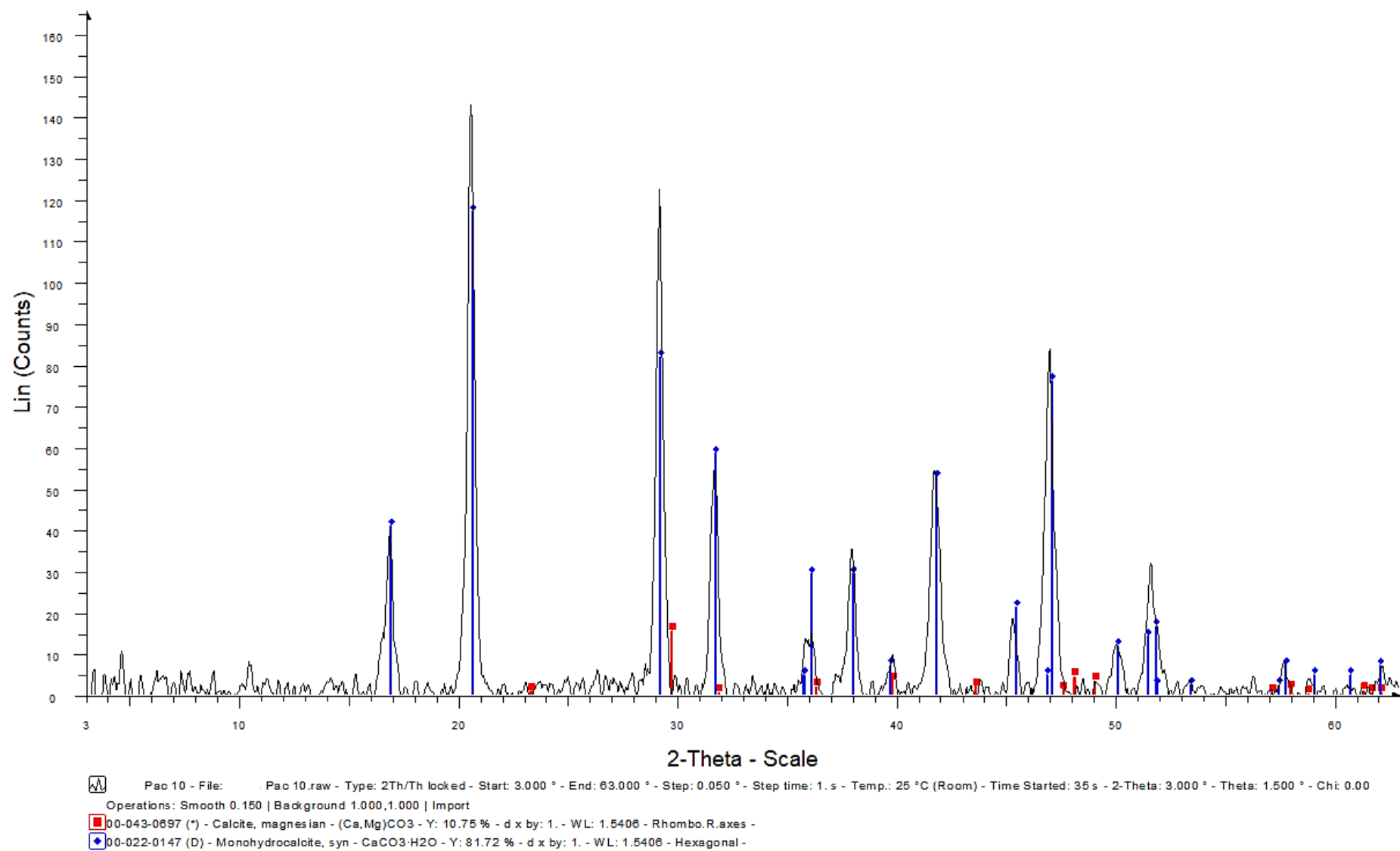


Figure 57. X-ray diffraction pattern for recovered solids at pH 10 from PAC-LLP

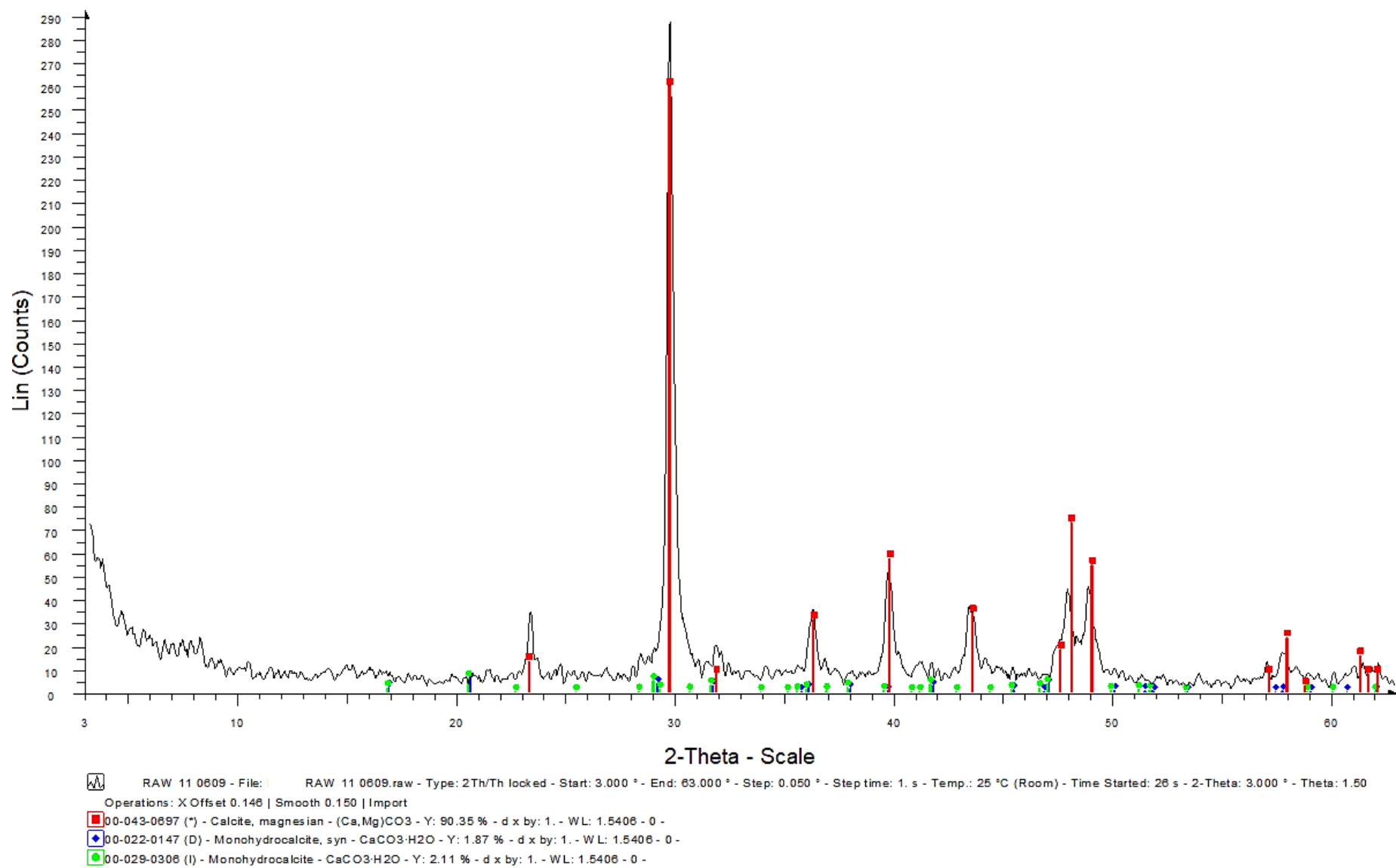


Figure 58. X-ray diffraction pattern for recovered solids at pH 11 from LLP

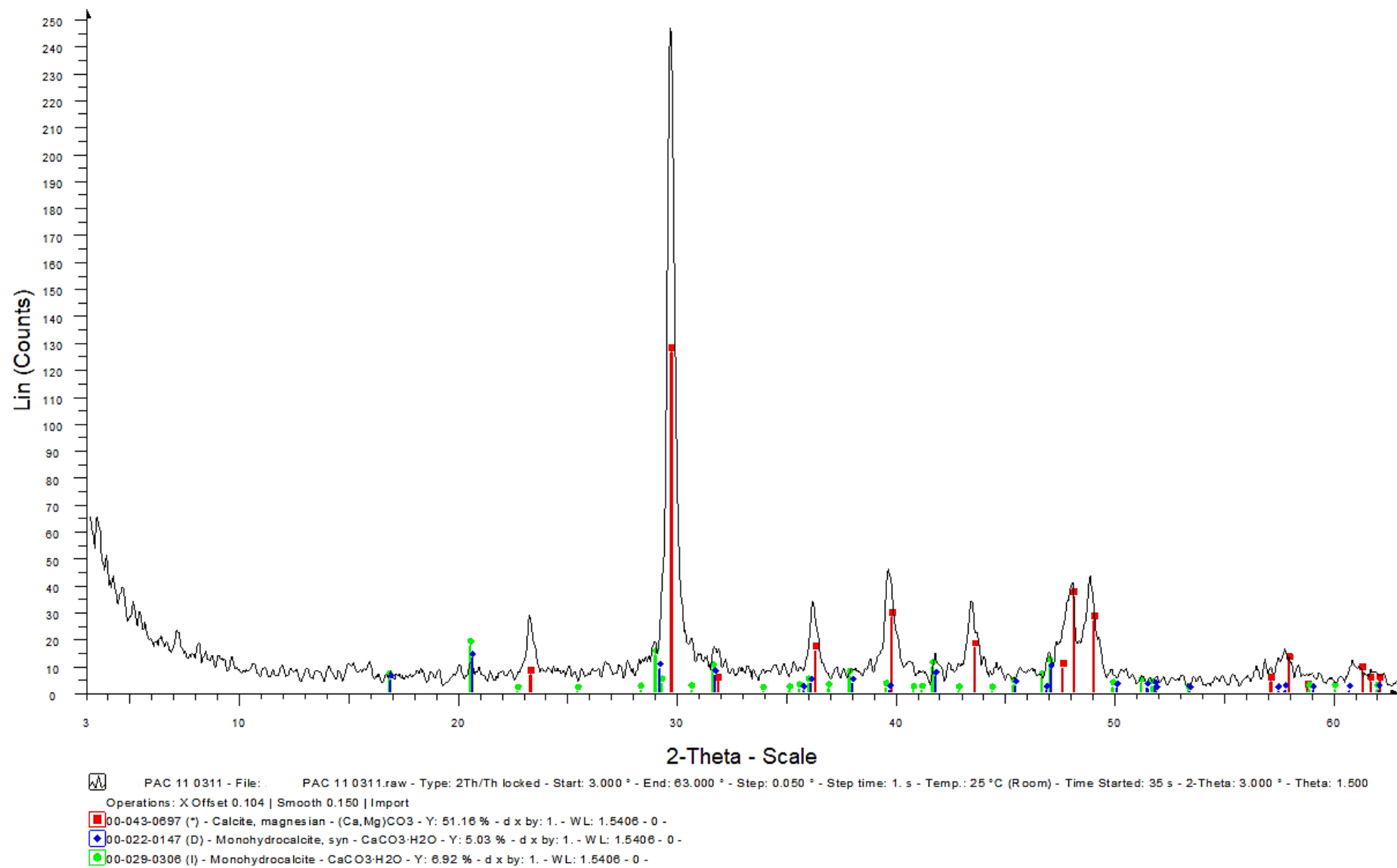


Figure 59. X-ray diffraction pattern for recovered solids at pH 11 from PAC-LLP

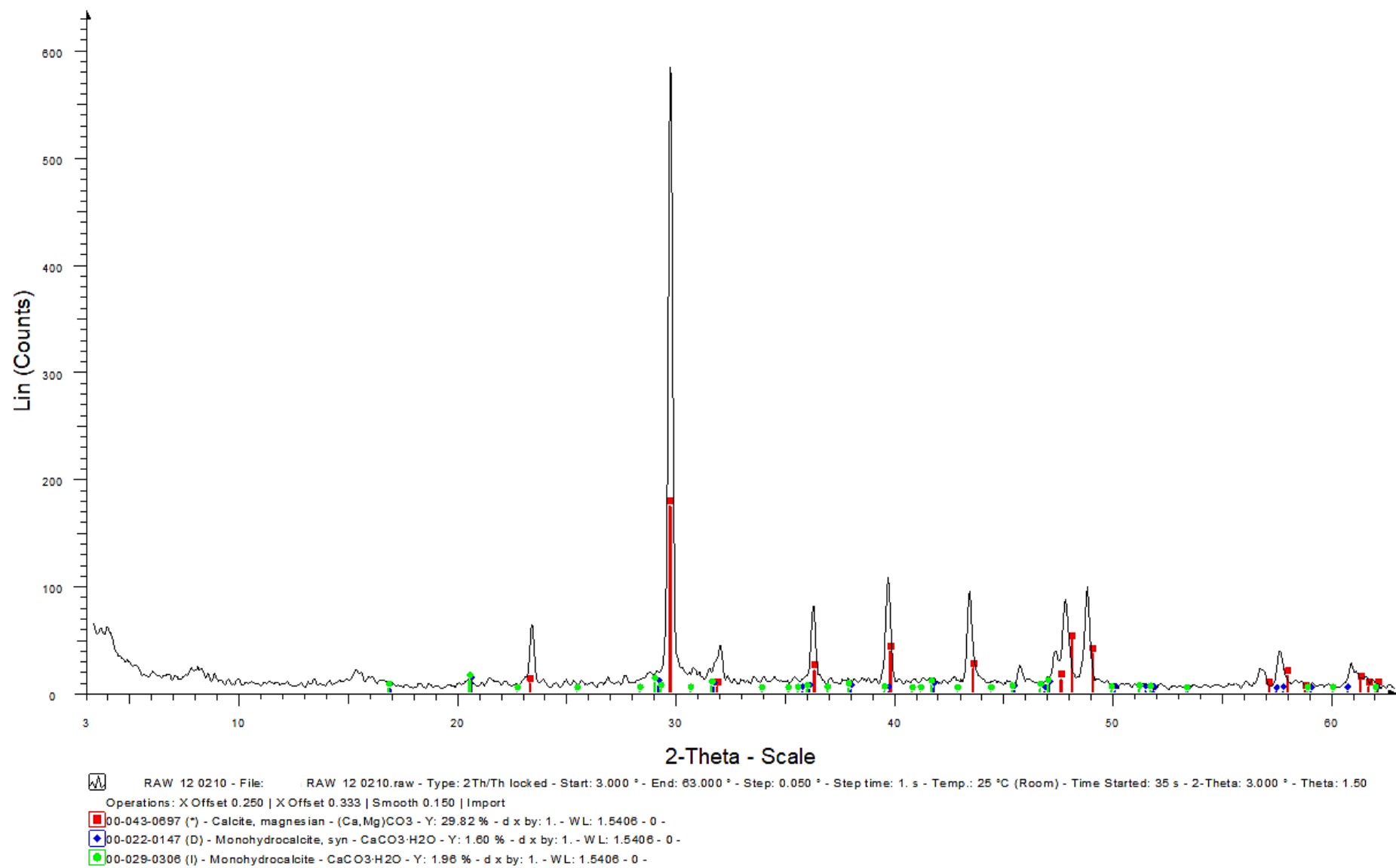


Figure 60. X-ray diffraction pattern for recovered solids at pH 12 from LLP

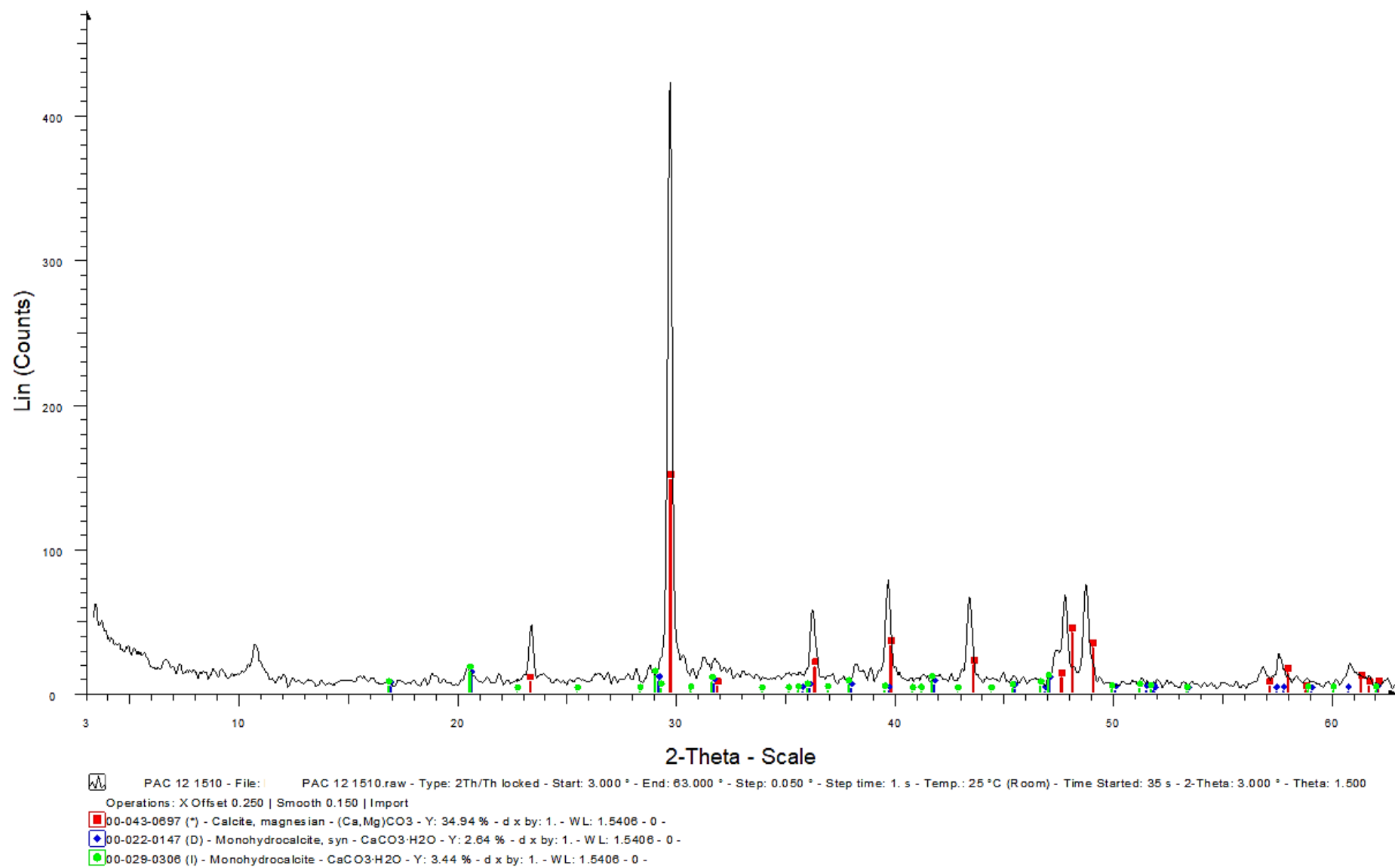


Figure 61. X-ray diffraction pattern for recovered solids at pH 12 from PAC-LLP

As observed in figures 54 through 61, at each pH condition the diffractograms obtained from the XRD analysis were almost identical for the solids recovered from the LLP and PAC-LLP and as expected from the CaCO_3 polymorphs calcite was the identified crystal structure in the analyzed solids. Other CaCO_3 polymorphs that can form in aqueous medium include aragonite and vaterite however calcite is the most stable CaCO_3 crystal form (Koutsoukos & Chen, 2010). The identified calcite in the recovered solids at the different pH conditions from the LLP and PAC-LLP are given in tables 43 and 44 respectively.

Table 43. Identified calcite in the recovered solids at different pH conditions from the LLP



pH:	pH 9	pH 10	pH 11	pH 12
Calcite, magnesian (Ca,Mg)CO₃	✓	✓	✓	✓
Monohydrocalcite CaCO₃·H₂O	-	✓	✓	✓

Table 44. Identified calcite in the recovered solids at different pH conditions from the PAC-LLP



pH:	pH 9	pH 10	pH 11	pH 12
Calcite, magnesian (Ca,Mg)CO₃	✓	✓	✓	✓
Monohydrocalcite CaCO₃·H₂O	✓	✓	✓	✓

3.3.2.2. Recovery of calcium carbonate-rich solids and explored application

3.3.2.2.1. Analysis in Collected LLP

The results obtained in the chemical analysis for the LLP collected in the fall season are given in table 45.

Table 45. LLP collected in fall season - composition & measured parameters

Substance/ Parameter	Concentration
Ca ²⁺ (mg/L):	1472±82
Mg ²⁺ (mg/L):	531±27
Hardness (°dH):	330±11
NH ₄ -N (mg/L)	2045±61
TN (mg/L):	2208±75
TOC (mg/L):	1229±246
TIC (mg/L):	323±58
TC (mg/L):	1552±287
SO ₄ (mg/L):	10620±531

As indicated in table 45, and as already discussed in table 16 and also showed in table 25 the Ca to Mg and NH₄-N to TN ratios in the LLP with values close to 3 and about 0,9 respectively were very consistent during the different collected seasons. Furthermore the concentrations of Ca, Mg, TOC and TN were also within a close range with values around 1300 mg/L for Ca and TOC, 500 mg/L for Mg and 2000 mg/L for TN.

3.3.2.2.2. 10 L Precipitation treatment

Based on the TIC concentration in the LLP collected in the fall season, the same 50% mole excess of CO₃ with respect to the initial moles of Ca and Mg was maintained in the precipitation treatment and adjusted by using a fix amount of Na₂CO₃. The precipitant dosage and the operating conditions measured during the treatment of the landfill leachate permeate at the different pH conditions are given in table 46.

Table 46. Reagents dosage, conductivity, pH and T in 10 L precipitator

LLP	Add. Mixed Na ₂ CO ₃ -NaOH			Operating conditions Mixing time = 1 h at 315 rpm		
	Mass fraction		Dosage (g/L)	pH	Cond. (mS/cm)	T (°C)
	Na ₂ CO ₃	NaOH				
Initial:	-	-	-	6,9±0,2	90,3±1,2	21,0±2,2
pH 10:	0,57	0,43	11,4±0,7	10,4±0,1	≈ 90	20,1±0,3
pH 11:	0,44	0,56	14,7±0,1	11,1±0,1	≈ 90	23,3±0,2
pH 12:	0,40	0,60	16,0±0,2	12,5±0,3	93,4±1,5	24,5±1,6

As seen in table 46, the average initial pH value in the LLP was 6,9, which was slightly higher than the average pH value of 6,6 in the LLP used in the 0,5 L precipitation treatment. Thus, the precipitant dosage used in the 10 L precipitator was slightly lower especially at pH 10 compared to the dosages used for the case of the smaller treated volume as indicated in table 28. Furthermore, as was the case in the 0,5 L treated permeate the conductivity with respect to the initial value at pH 10 and 11 did not change considerably but at pH 12 an increased in conductivity of about 3% with respect to the initial value was also observed in the 10 L treated permeate.

After the 1h mixing period the generated solids were allowed to sediment for at least 2h as illustrated in figure 62.



Figure 62. Generated solids in 10 L precipitator at pH 12 and 2 h sedimentation

As indicated in figure 62, for the case of pH 12 and sedimentation time of 2h it was possible to recover about 60% of the initial permeate volume as supernatant (LLP-SN) or treated permeate. Then, after decanting the LLP-SN the remained volume of sludge was unloaded from the precipitator and collected for further centrifugation and air-drying. The sludge collected from the 10 L precipitator after sedimentation and dewatering processes are illustrated in figure 63.



Figure 63. Left: Collected sludge after Sedimentation; Right: Collected sludge after Centrifugation

Moreover, at the pH 12 condition, in order to evaluate the separation efficiency of the 2h sedimentation and centrifugation steps the volumes of the recovered LLP-SN were measured and their percentage recovered were calculated based on the initial 10 L of permeate. The results are given in figure 64.

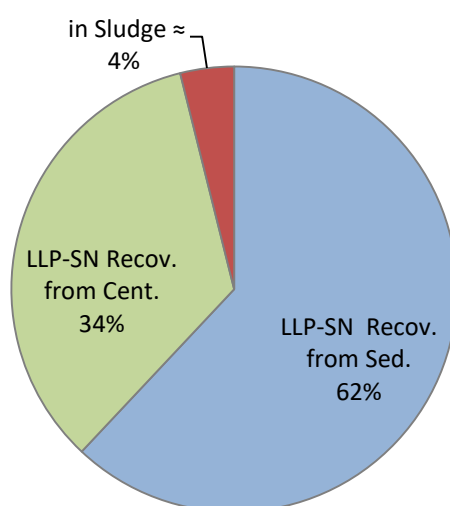


Figure 64. LLP-SN recovered from Sedimentation-Centrifugation separation steps

As illustrated in figure 64, the overall recovery of the precipitation treated permeate at pH 12 by decanting the supernatant after the 2h sedimentation and the 15 min centrifugation at 3500 rpm was about 96% and based on the percentage calculation the centrifuge recovered about 90% of the treated permeate from the sedimented sludge and a fraction of about 0,04 of the permeate might still remained within the sludge after the centrifugation step, which followed the air-drying.

Also, TSS analysis were performed in each of the supernatants obtained from the 2h sedimentation and centrifugations steps and the results were compared to the TSS values obtained for the landfill leachate and concentrates generated at the landfill leachate treatment facility given in table 12. The results are illustrated in figure 65.

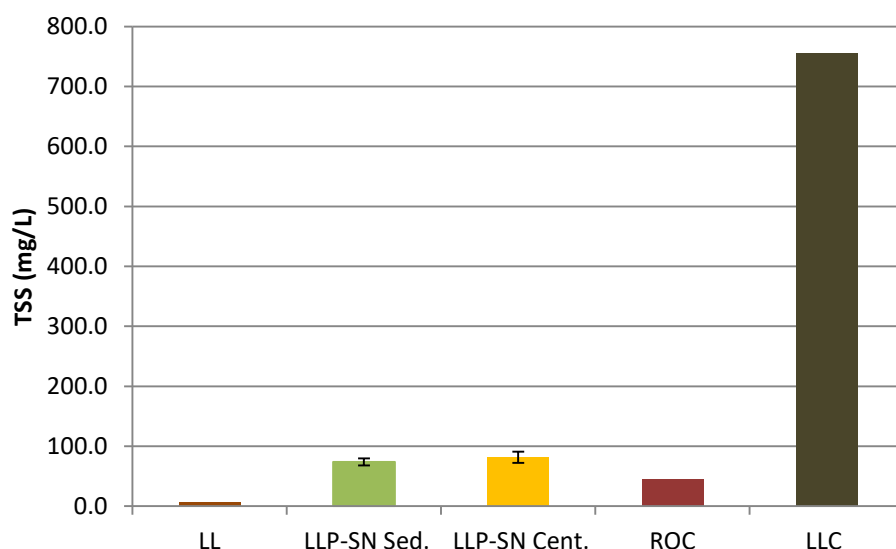


Figure 65. TSS in LLP-SN after sedimentation time of 1 and 24 h

As seen in figure 65, the TSS value of 81,4 mg/L corresponding to the supernatant collected after the centrifuge step was slightly higher than the one from the sedimentation step but both values were below 100 mg/L. Furthermore, in average the TSS values from the collected SN compared to the pre-filtered LL and ROC was about 10 and 2 times higher respectively but compared to the LLC its TSS was about 10 times lower. Moreover, after the 1h mixing period, the concentration of Ca, Mg and hardness were analyzed in the LLP-SN collected after sedimentation at the different pH conditions. The results obtained in the removal of Ca, Mg and hardness at the evaluated pH conditions are given in figure 66.

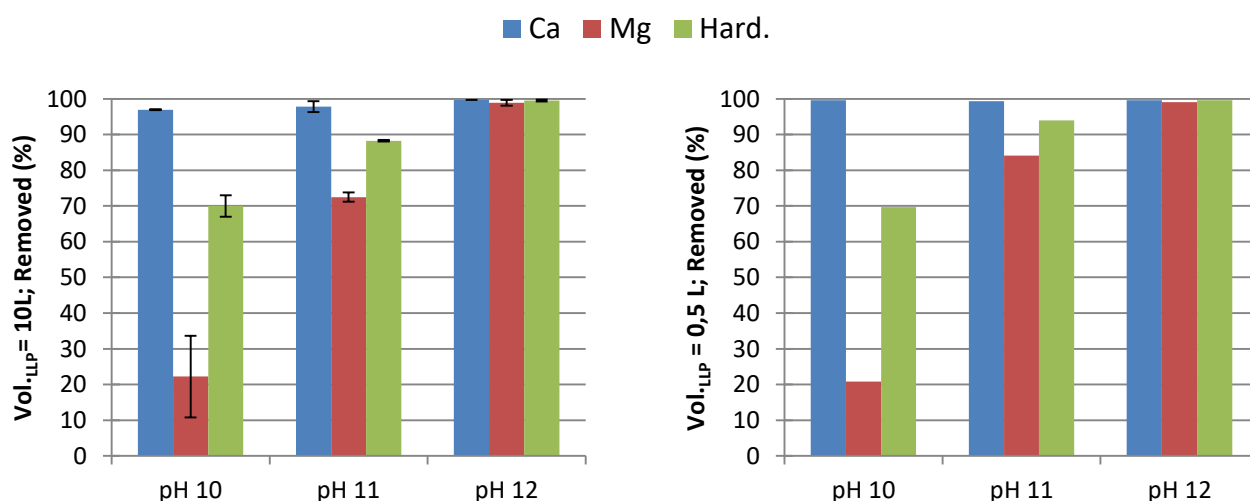


Figure 66. Ca, Mg and hardness removed in Left: LLP-SN from 10 L precipitator & Right: 0,5 L treated LLP at 24 h with mixed Na_2CO_3 -NaOH reagents

As illustrated in figure 66, the removal of hardness in the 10 L treated permeate was almost the same compared to the 24 h treated 0,5 L permeate specially at pH 12 where the removal of Ca, Mg and hardness were greater than 98% for both volumes and at pH 10 and 11 only a few differences were observed. For instance, at pH 10 and 11 almost complete removal of Ca was observed in the small volume of LLP. However, in the 10 L treated permeate about 5% of Ca still remained in the collected SN and at pH 11 there was about a 10% difference in the removal of Mg where almost 85% was removed from the 0,5 L permeate compared to about 70% removal in the larger volume. Thus, the removal of hardness at pH 10 and 12 with removals of 70 and 99% respectively were basically the same in both permeate volumes and at pH 11 they differed slightly with a value of 94% in the 0,5 L treated permeate and 88% in the 10 L treated permeate. The LLP-SN treated in the 10 L precipitator at the different pH conditions were collected and stored for further treatment in the membrane contactor for the recovery of NH_3 .

Moreover, the concentration of TOC and TN were analyzed in the collected LLP-SN at pH 12. The removals of TOC and TN by the precipitation treatment are illustrated in figure 67.

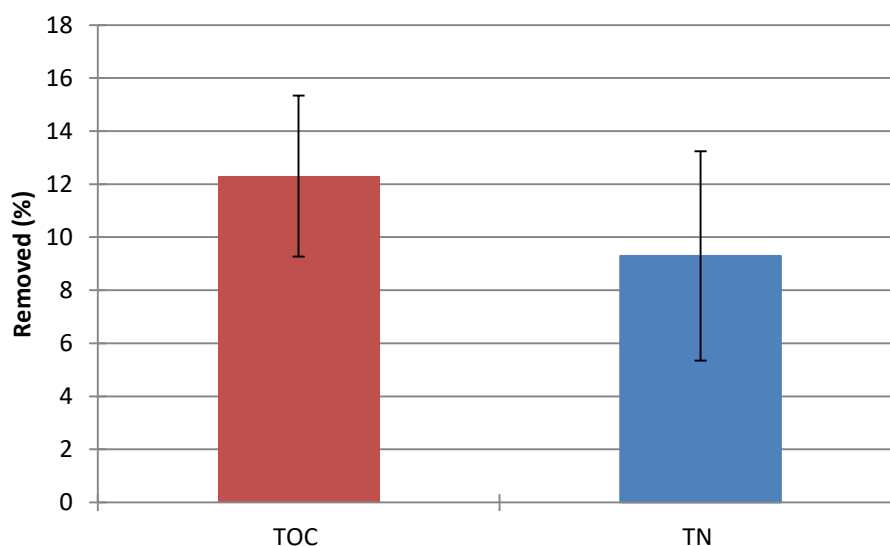


Figure 67. TOC and TN removed in 10 L precipitator from LLP at pH 12

As indicated in figure 67, about 12% of the TOC was removed from the LLP after the precipitation treatment and as illustrated in figure 50 this value was not that far from the one obtained for the 0,5 L treated permeate, which had a removal of about 8% for a treatment time of 1 h. Moreover, for the case of TN, in average only about 9% was lost during the treatment indicating that about 90% of the initial TN concentration still remained in the treated permeate at the pH condition of 12.

3.3.2.2.3. Washing of dried sludge

After the air-drying period the remaining dried sludge generated at pH 12 conditions were weighted in order to estimate the amount of solids per volume of permeate generated from the precipitation-sedimentation-centrifugation steps. The average

amount of dried sludge per volume of permeate was estimated as $5,4 \pm 0,7$ g/L and as indicated in table 33, this values was about 0,6 times lower than the value of 8,5 g/L obtained in the treated 0,5 L of LLP at the same pH condition. The collected dried sludge is illustrated in figure 68.



Figure 68. Collected dried sludge from 10L precipitator after 5 days Air-drying period

After the air-drying period, a sample of 150 g of the dried sludge generated at pH 12 from the LLP in the 10L precipitator went through a series of washes, which were performed in order to determine an acceptable washing condition for the recovered solids. The wash number 1, 4 and 7 are illustrated in figure 69.



Figure 69. Consecutive washes: Left: Wash No. 1 (Cond.= 46,9 mS/cm); Center: Wash No. 4 (Cond.= 3,3 mS/cm); Right: Wash No. 7 (Cond.= 0,65 mS/cm) performed on collected dried sludge from 10 L precipitator

Based on the conductivity measured in each washwater and the cumulative amounts of DW added during the washing procedure, a relation between conductivity and solids to DW mass ratios (S:DW) were estimated. The results are given in figure 70.

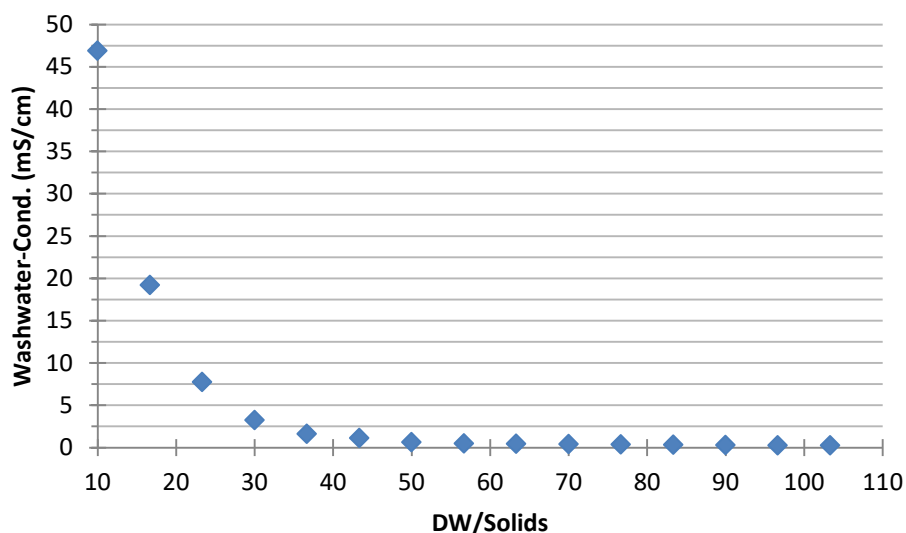


Figure 70. Relation of conductivity in washwater vs. Solids to DW ratio (S:DW)

As indicated in figure 70, in between the S:DW ratios of 1:30 to 1:40 the conductivity in the washwater was around 2,5 mS/cm and for the S:DW ratios of 1:50 or higher the conductivity in the washwater was close to or below 1,0 mS/cm. Furthermore, the pH value was almost the same in each of the analyzed washwater with an average value of $10,3 \pm 0,1$ at a temperature of $22,3 \pm 0,7^\circ\text{C}$.

3.3.2.2.4. Washing ratios of 1:10; 1:30 and 1:50

Based, on the results obtained in the washwater conductivity analysis the S:DW washing ratios of 1:10, 1:30 and 1:50 were separately analyzed with the collected dried sludge generated from the LLP at pH 12 with the mixed Na_2CO_3 -NaOH reagents as precipitant. The washes performed at the different washing ratios are illustrated in figure 71.



Figure 71. Washing of collected dried sludge for recovery of CaCO_3 -rich solids

After the 24 h shaking period at 300 rpm, the washwater was separated from the washed solids by centrifugation-decantation and about 200 mL of the washwater was filtrated for further analysis. The average pH, T and conductivity parameters

measured in the filtrated washwater were compared with the LLP as indicated in table 46. The results are given in table 47.

Table 47. pH, T & Cond. in washwater at different solids (S) to washwater (deionized water) ratios

Washing ratio (S:DW)	pH	Cond. (mS/cm)	T (°C)
LLP	6,9±0,2	90,3±1,2	21,0±2,2
1:10	10,2±0,4	47,3±0,5	21,8±1,0
1:30	10,1±0,1	19,4±1,9	21,4±0,2
1:50	10,2±0,1	12,3±1,1	21,4±0,5

As seen in table 47, the pH values in the washwater at the different washing ratios were almost the same with values around 10. However, the conductivity decreased with the increased in the amount of washwater, which might indicated only dilution of the soluble fraction present in the collected dried sludge as part of the permeate that remained in the sludge as indicated in figure 64.

Furthermore, in the filtrated washwater chemical analysis were performed at the different washing ratios and were compared to the LLP concentration indicated in table 45. The results for Ca, Mg and hardness are given in figure 72.

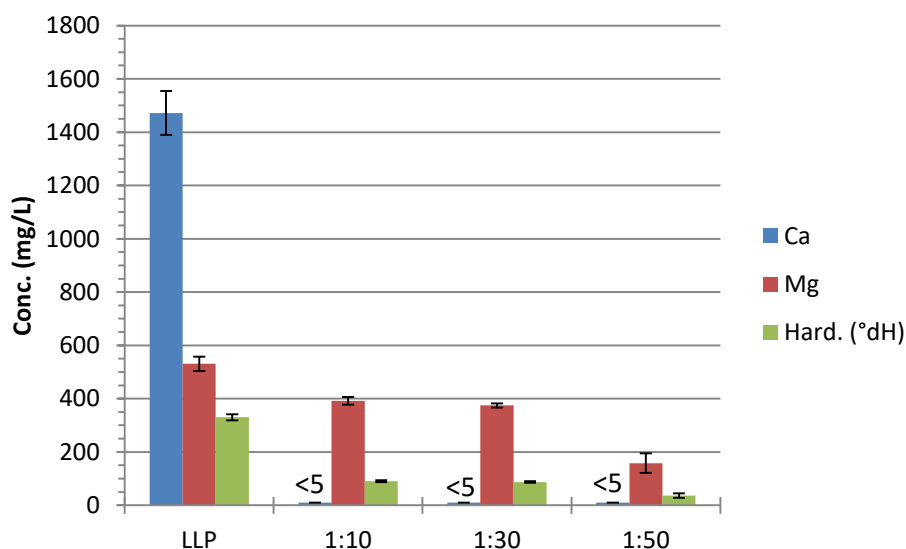


Figure 72. Ca, Mg and Hardness conc. in washwater at different solids to washwater ratios (S:DW)

As illustrated in figure 72, the concentration of Ca with values of less than 5 mg/L in each of the analyzed washwater at the different washing ratios was negligible compared to the LLP concentration, which indicated a stable Ca in the formed solid state. On the other hand, the precipitated form of Mg was less stable where significant amounts got dissolved by the washing treatment. However, based on the solids to washwater ratio of 1:50 it seemed that the dissolved amount reached a relatively finite value since its concentration decreased, which showed sign of dilution. And, the hardness in the LLP was about 4 and 9 times larger than the

washwater values in the 1:10, 1:30 and 1:50 washing ratios respectively. The results obtained in the chemical analysis performed in the different washwater ratios for TOC, TIC and TN are illustrated in figure 73.

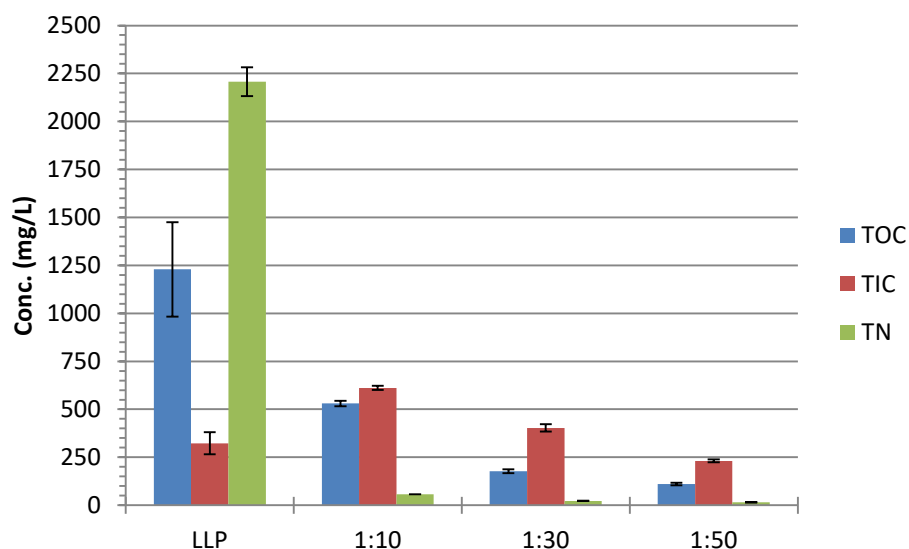


Figure 73. TOC, TIC & TN conc. in washwater at different solids to washwater ratios (S:DW)

Figure 73 indicated that the washing process removed organic content from the generated precipitation at the different washing ratios and the TIC concentration for the washing ratios of 1:30 and 1:50 were around the TIC value of 323 mg/L found in the LLP. Furthermore, the concentrations of TN in the washwater at each of the evaluated washing ratios were very low with values lower than 60 mg/L compared to the value of 2208 mg/L found in the LLP. Additionally, SO_4 was also measured in the washwater generated at the different solids to washwater ratios. The results given in figure 74 indicated that the washing process helped in removing the SO_4 salts formed after the drying of the collected sludge.

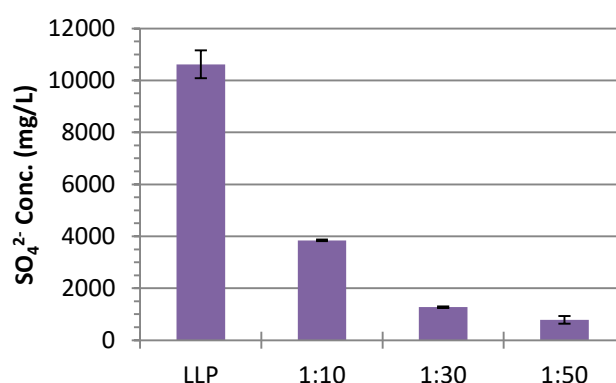


Figure 74. SO_4 conc. in washwater at different solids to washwater ratios (S:DW)

Furthermore, based on the average amounts of initial dried sludge and the recovered solids after the oven-drying step, the percentage losses of solids after the washing treatment were estimated, the results are given in figure 75.

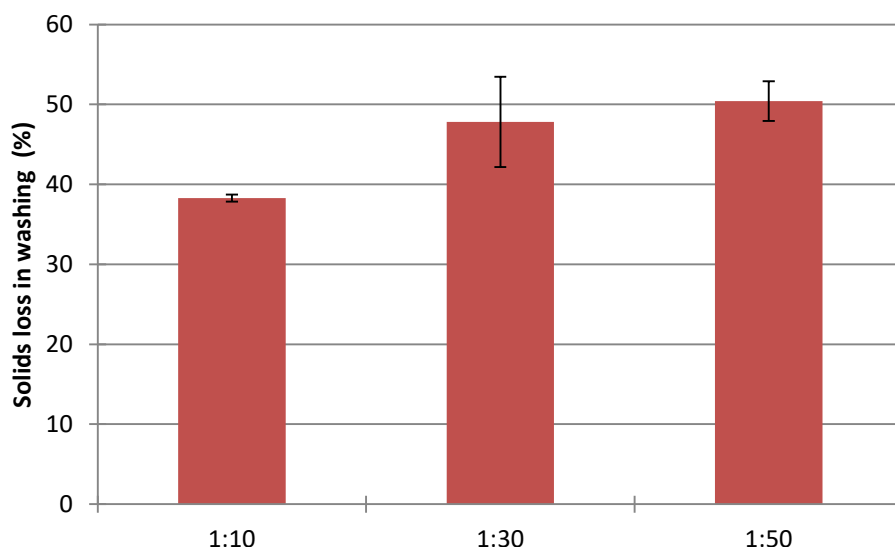


Figure 75. Percentage of solids loss after washing treatment at different wash ratios

As illustrated in figure 75, with the solids to washwater ratio of 1:10 the percentage of solids loss was about 40% and for the 1:30 and 1:50 washing ratios the loss percentage increased to about 50%, which might indicated further removal of soluble and/or undesired substance from the recovered solids. Furthermore, based on the amount of the dried solids recovered from the pH 12 precipitation treatment and washing ratio of 1:10; the amount of solids generated with respect to the permeate were estimated and the results were compared to the value obtained in the smaller LLP treated volume of 0,5 L. The results of the generated dried sludge and recovered solid obtained in both treated volumes of LLP are illustrated in figure 76.

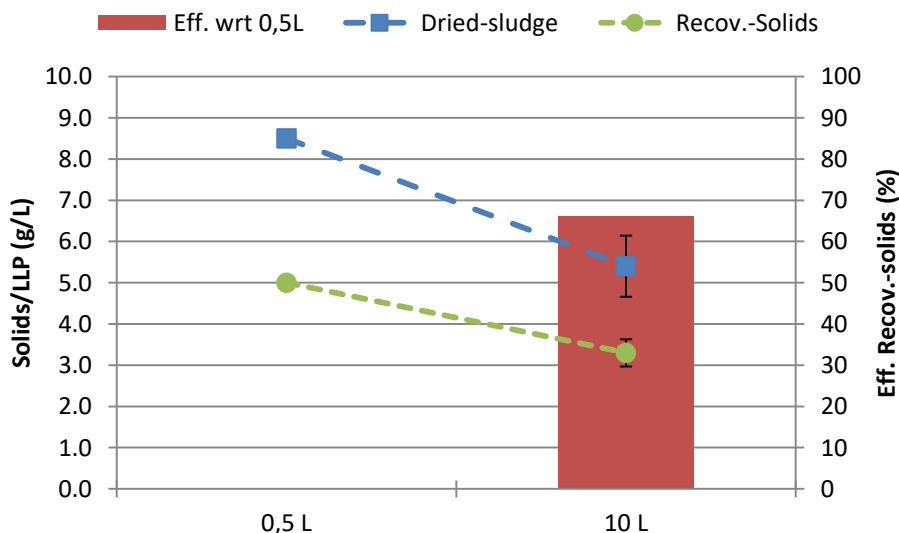


Figure 76. CaCO_3 -rich solids recovery efficiency in 10 L precipitation vs. 0,5 L precipitation

As seen in figure 76, compared to the 0,5 L treated permeate the overall efficiency of the recovery of solids in the larger treated volume of permeate was lower with a decreased of about 35% with respect to the values obtained in the smaller precipitation volume. This decreased in the efficiency could be linked directly to the

handling of larger amounts of permeate, generated precipitation and dried solids, which increased also the probability of losses.

As indicated in table 41, for the solids to washwater ratio of 1:10 generated from the LLP at pH 12, the concentration of substances known to form soluble salts such as Cl^- and S were found in the recovered solids with concentrations of 25000 and 2780 ppm respectively. Thus, in order to evaluate the removal of these substances by the evaluated washing ratios, the composition of the solids recovered after the washing ratios of 1:30 and 1:50 were analyzed through XRF. In the analysis, since the concentration of SO_4 in the LLP was relatively high it was assumed that the S found in the recovered solids was in the form of SO_4^{2-} salts and Cl^- was assumed to be as NaCl. The results obtained are given in figure 77.

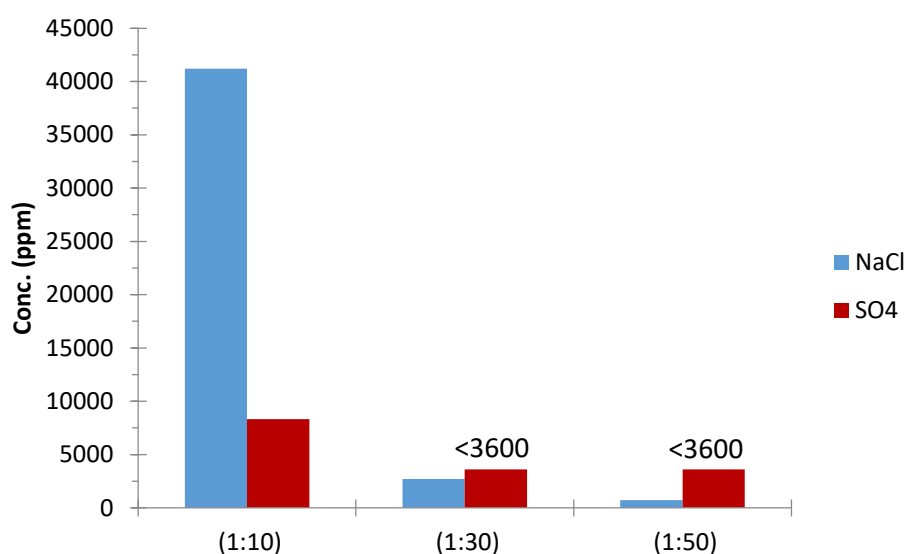


Figure 77. NaCl and SO_4 concentration in recovered solids after washing step at different solid to washwater (S:DW) ratios

Figure 77 indicated that the removal of soluble undesirable substance such as NaCl from the precipitation might be a function of the washing ratio. For instance, based on the solids to washwater ratio of 1:10 by increasing the washing ratio to 1:30 the estimated concentration of NaCl in the recovered solids decreased considerably from 41209 ppm to 2698 ppm. Moreover, the same was observed for the estimated SO_4 whose concentrations for the recovered solids after the washing ratios of 1:30 and 1:50 were lower than the LOD of 1208 ppm corresponding to sulfur.

Furthermore, the concentration of heavy metals in the recovered solids regulated by the EU Directive for Sewage sludge used in agriculture were below the limit ranges indicated in the regulation for each of the solids recovered after the evaluated washing ratios. The results are given in table 48.

Table 48. Heavy metals in recovered solids regulated by EU Directive for Sewage sludge used in agriculture

Substance	Sewage Sludge [‡]	Solids recovered with Washing ratio (S:DW)		
		1:10	1:30	1:50
Hg (ppm)	16 - 25	<0,01	-	-
Cd (ppm)	20 - 40	<1	<60	<60
Pb (ppm)	750 - 1200	<2	<25	<25
Cr (ppm)	1000 - 1750	8,0	<54	<54
Cu (ppm)	1000 - 1750	<2	<50	<50
Ni (ppm)	300 - 400	<2	<30	<30
Zn (ppm)	2500 - 4000	-	<30	<30

[‡] EU Directive of 1986 "on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture"

Additionally the oxides of Al, Ca, Fe, K, Mg, Mn, P and Si were estimated based on the XRF results for the solids recovered from the washing ratios of 1:30 and 1:50. The estimated oxides were compared with the oxides corresponding to the washing ratio of 1:10 already shown in table 38 and also with typical composition found in cement kiln fees. The results are given in table 49.

Table 49. Oxides composition in recovered solids after different wash ratios and found in cement kiln feed

Substance	1:10	1:30	1:50	Feed cement kiln [‡]
Al ₂ O ₃ (%)	0,04	-	-	3
CaO (%)	31	37	40	44
Fe ₂ O ₃ (%)	0,05	0,32	0,32	1
K ₂ O (%)	1,3	0,29	0,27	-
MgO (%)	6,9	2,8	<1,2	<3 - 5
MnO (%)	0,03	0,04	<0,01	-
P ₂ O ₅ (%)	0,70	0,53	0,50	-
SiO ₂ (%)	1,8	<1,6	<0,8	14
TiO ₂ (%)	-	0,06	0,07	-
Sum (%) =	42	42	42	-

[‡] (Oates, 1998)

Table 49 indicated that as the washing ratio increased from 1:10 to 1:30 to 1:50 a further decreased of K₂O and MgO was observed in the recovered solids and other substances such as Fe₂O₃ did not changed considerably with the increased of washing ratio from 1:30 to 1:50. However, for the case of CaO the mass percentage increased with increased of washing ratio approaching the common mass percentage value of 44% found in cement kiln feed and with respect to MgO the only recovered

solids whose concentration was above the limit of 5% found in cement kiln feed was the value from the washing ratio of 1:10. The CaO mass percentages with respect to the sum of the estimated oxides are represented in figure 78.

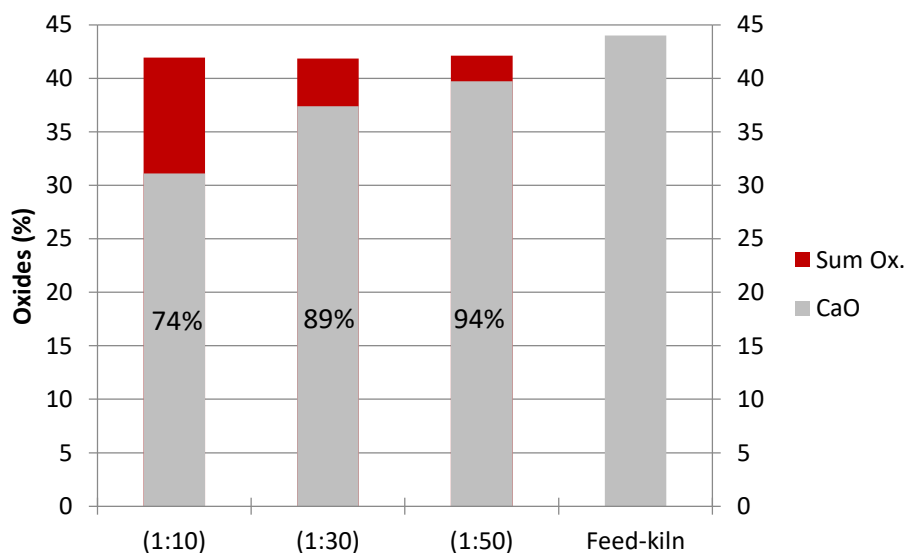


Figure 78. CaO mass percentage in recovered solids from different washing ratios & cement kiln feed (Oates, 1998)

Figure 78 showed that as some of the evaluated substances were washed out from the solids, the CaO mass percentage increased with increased in washing ratio approaching more to the mass percentage found in cement kiln feed and reaching a value of 94% with respect to the sum percentage of the estimated oxides for the washing ratio of 1:50. This indicated that the generated CaCO_3 -rich solids were very stable independently of the washing ratio conditions.

3.3.2.2.5. Further Characterization of Recovered Solids

The thermal decomposition of the most stable polymorph of CaCO_3 known as calcite has been widely analyzed where it has been proved that the thermal conversion of CaCO_3 to CaO initiates slowly and then decomposes rapidly at temperatures around or greater than 750°C (Karunadasa, et al., 2019). Thus, a TGA/DSC analysis was performed with the solids recovered from the 10 L precipitator at the pH conditions of 10, 11 and 12 and washing ratio of 1:30. The results are given in figure 80 and are compared with a TGA/DSC analysis found in the literature and performed with pure CaCO_3 (>99,9%) given in figure 79.

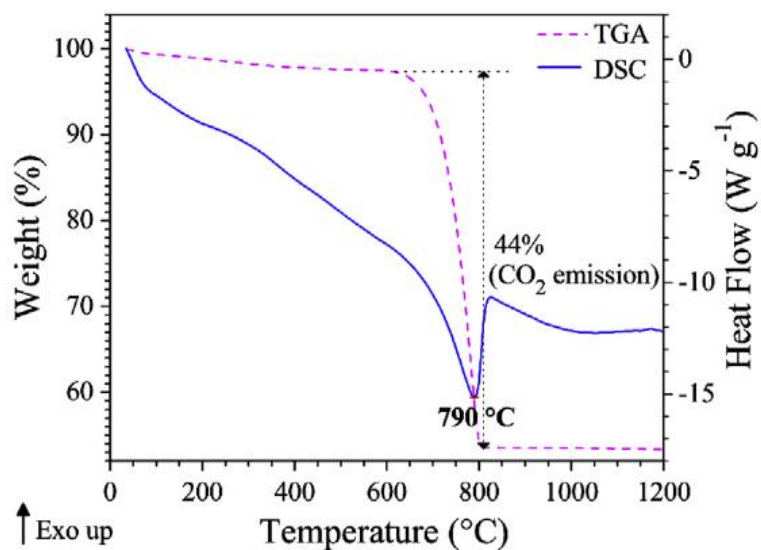


Figure 79. TGA/DSC analysis corresponding to pure calcite ($\text{CaCO}_3 >99.9\%$) (Karunadasa, et al., 2019)

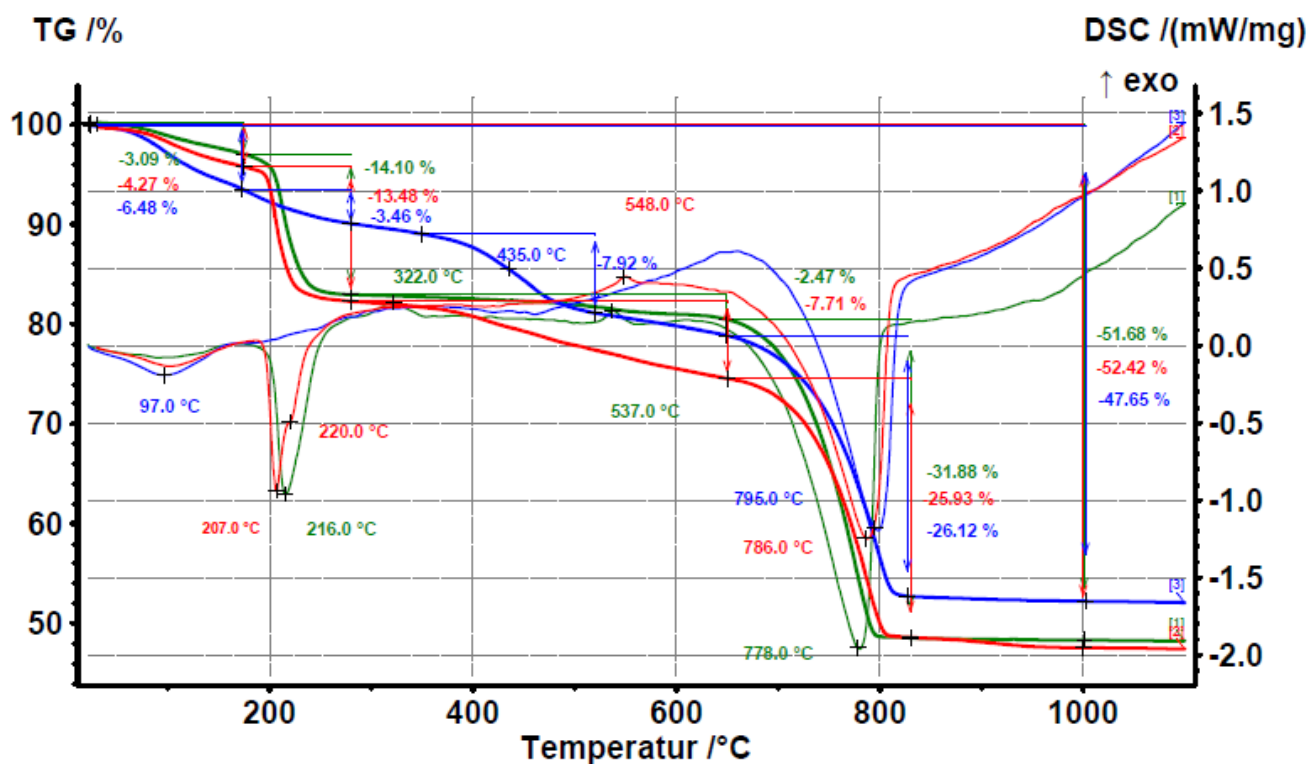


Figure 80. TGA/DSC analysis performed on recovered CaCO_3 -rich solids. Blue: pH 12; Red: pH 11; Green: pH 10

As indicated in figure 80, by comparing the DSC analysis of the pH 12 recovered solids with respect to the pure calcite it can be seen that its thermal conversion peak was very close to the one reported for pure calcite with a value of 795°C. Furthermore, for the pH 11 and 10 recovered solids the temperature peaks from the DSC analysis were also very close to 790°C with values of 786 and 778°C respectively. A summary of the main results obtained by the TGA/DSC analysis are given in table 50.

Table 50. Summary of TGA/DSC analysis performed in recovered solids

T-range (°C)	Solids recovered at Washing ratio (1:30)			Notes
	pH 10	pH 11	pH 12	
200 - 230	Loss of mass: -14,1% Exothermic reaction	Loss of mass: -13,5% Exothermic reaction	Loss of mass: -3,5% -	Possible contamination: Organic matter?
400 - 450	-	-	Loss of mass: -8% No DSC signal	Each change of mass is caused by a reaction, then a DSC signal was expected: * Unclear what it was
700 - 800	Loss of mass: -32% Exothermic reaction	Loss of mass: -26% Exothermic reaction	Loss of mass: -26% Exothermic reaction	Fits to CaCO ₃ signal: - pH 10 highest content

Furthermore, considering that the determination of volatile solids provides an estimate of the amount of organic material present in analyzed samples (APHA, 2005), the pH 12 recovered solids with washing ratio of 1:50 were analyzed as indicated in the Standard Method 2540G for the Determination of Volatile Solids in Solid Samples. The results indicated that $10,9 \pm 0,2\%$ corresponded to VS, which was very close to the loss of mass reported in the TGA analysis of 11,5% within the temperature range of 200 and 450°C for the pH 12 recovered solids.

Additionally, a sieve analysis was performed in order to determine the particle size distribution of the pH 12 recovered solids with the washing ratio of 1:50. The results from the sieving analysis are illustrated in figure 81.

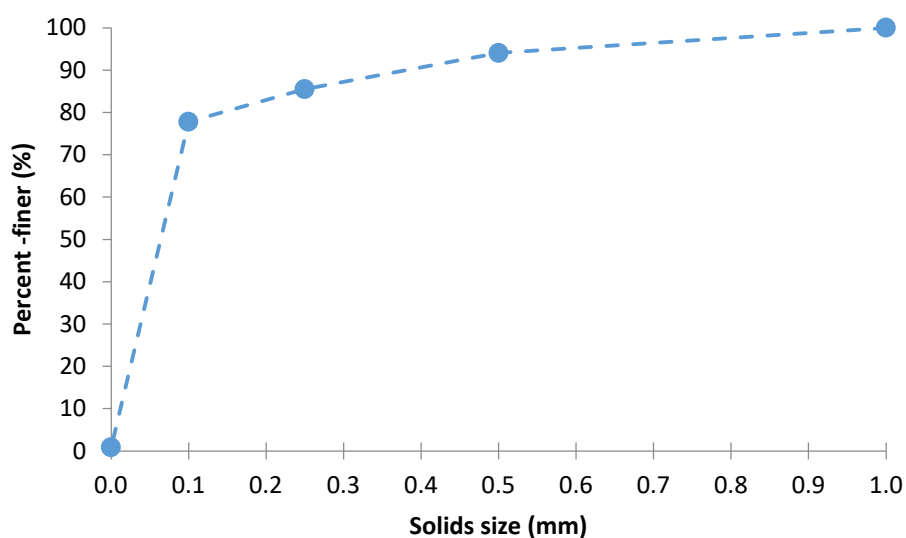


Figure 81. Sieve analysis of recovered CaCO₃-rich solids

Figure 81 indicated that about 94% of the recovered solids had a particle sizes less than 500 μm , only 6% in between 0,5 and 1 mm and most of the solid or about 80% of the recovered solids had a particle size less than 100 μm .

The solids recovered from the landfill leachate permeate at pH 12 conditions with the mixed Na_2CO_3 - NaOH reagents are illustrated in figure 82.



Figure 82. CaCO_3 -rich solids recovered from LLP with mixed reagents at pH 12. Left: CaCO_3 -rich solids; Middle: Recovered solids after heating 1000°C; Right: PAC-LLP CaCO_3 -rich solids

3.3.2.2.6. Application of CaCO_3 -Rich Solids

Limestone materials have been used in different sectors of the industry, which mainly includes construction, cement and agriculture. As already discussed throughout this section and based on the different analysis performed in the recovered solids, the results indicated that the composition of the solids recovered from the LLP at the evaluated pH conditions such as 12 were rich in CaCO_3 . Also, important features such as relatively low concentration of heavy metals and impurities such as organic matter and a large fraction of the solids with particle size less than 100 μm made the recovered solids a good material for potential applications, which might include those related to limestone material.

The explored application for the CaCO_3 -rich solids recovered from the landfill leachate permeate at pH condition of 12 with the mixed Na_2CO_3 - NaOH reagents as precipitant and washing ratio of 1:50 included the neutralization of acid soil from lignite mines as illustrated in figure 83.

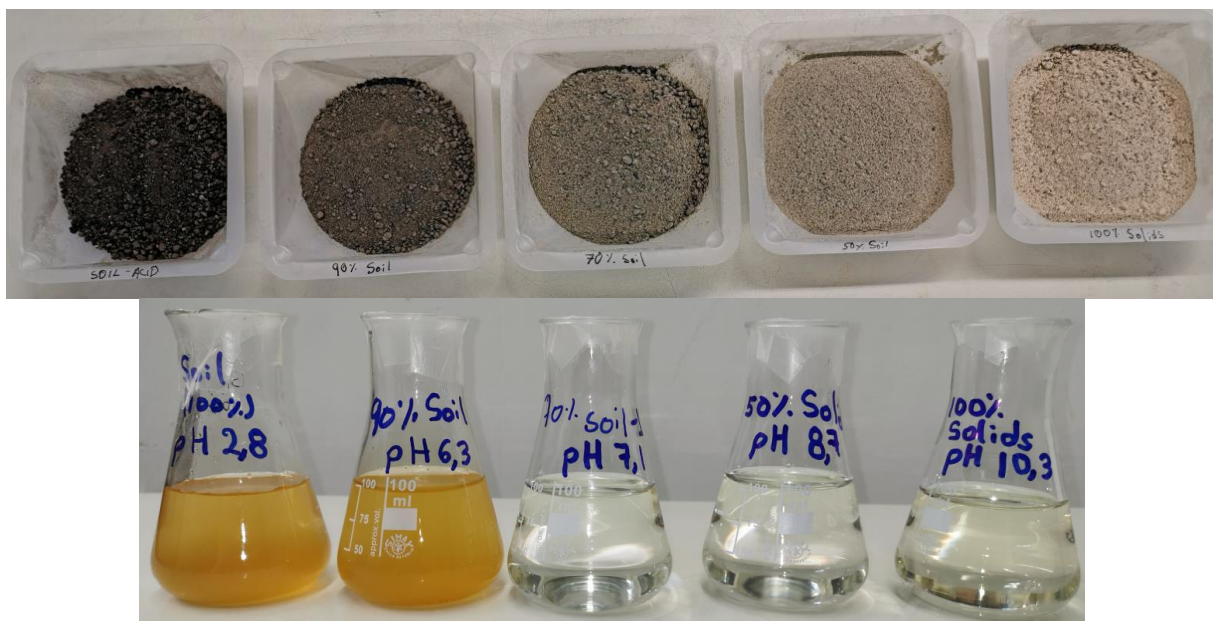


Figure 83. Acid soil neutralization with recovered CaCO_3 -rich solids from the LLP; Left: Acid soil from lignite mine; in Between: Acid soil to solids ratios; Right: CaCO_3 -rich solids

The results obtained in the pH analysis at the different acid soil to recovered solids mass fractions were compared with pure CaCO_3 at the same mass fraction conditions as illustrated in figures 84 and 85.

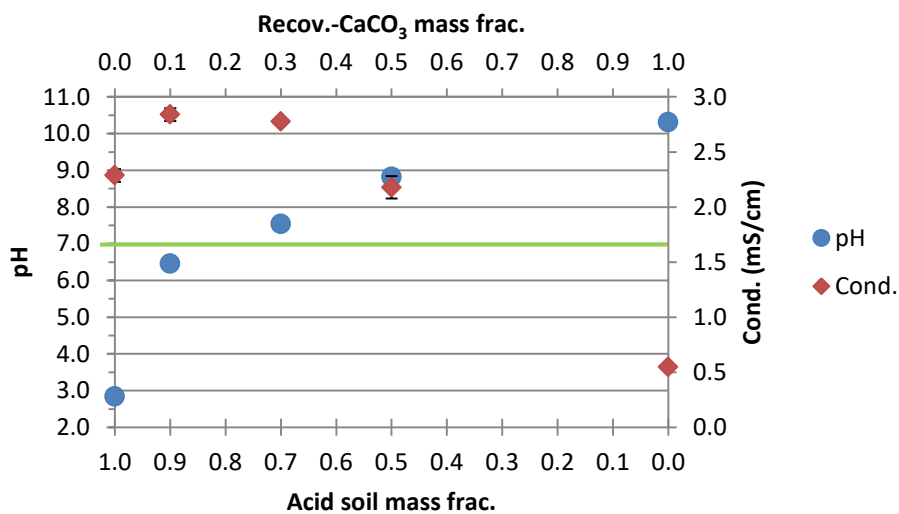


Figure 84. pH analysis: Neutralization of acid soil with recovered CaCO_3 -rich solids

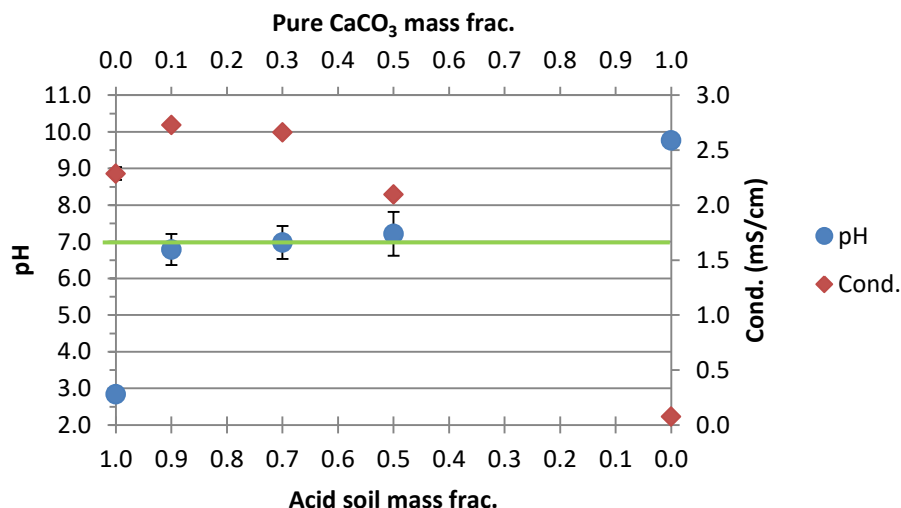


Figure 85. pH analysis: Neutralization of acid soil with pure CaCO₃

As illustrated in figures 84 and 85, for the mass fraction of 0,1 the neutralization effect of the recovered CaCO₃-rich solids with respect to the pure CaCO₃ was almost the same reaching pH values of 6.5 and 6.8 respectively. However, as the solids mass fraction increased a deviation with respect to the pH value was observed where for the solids mass fraction of 0,3 and 0,5 the recovered solids reached pH values of 7,5 and 8,8 respectively, which were larger than the pH values of 7,0 and 7,2 obtained with the pure precipitated CaCO₃ at the same mass fraction conditions respectively. Furthermore, the slightly increased in conductivity with respect to the acid soil value was observed with both neutralizers at mass fractions of 0,1 and 0,3 and then with solids mass fraction of 0,5 the conductivity values of the solids and acid soil mixture were below the value of $2,3 \pm 0,1$ mS/cm corresponding to the acid soil.

The optimum pH for a particular soil depends on the kind of plant that is planned to be grown. For example, conifers can tolerate acid soils with values around 4 but for grass the recommended pH value in soil is greater than 6 with optimum values found around the neutral pH value (Oates, 1998). Thus, based on the results, the mass fractions of CaCO₃-rich solids that seemed to be suitable for the increase of pH in the acid soil could range in between 0,1 to 0,3.

Additionally, leachability tests were performed in the acid soil, recovered CaCO₃ rich solids and the mixtures of 70% and 50% acid solid with the recovered solids. The results obtained for the pH and conductivity at a temperature of $23,0 \pm 0,2^\circ\text{C}$ are given in figure 86.

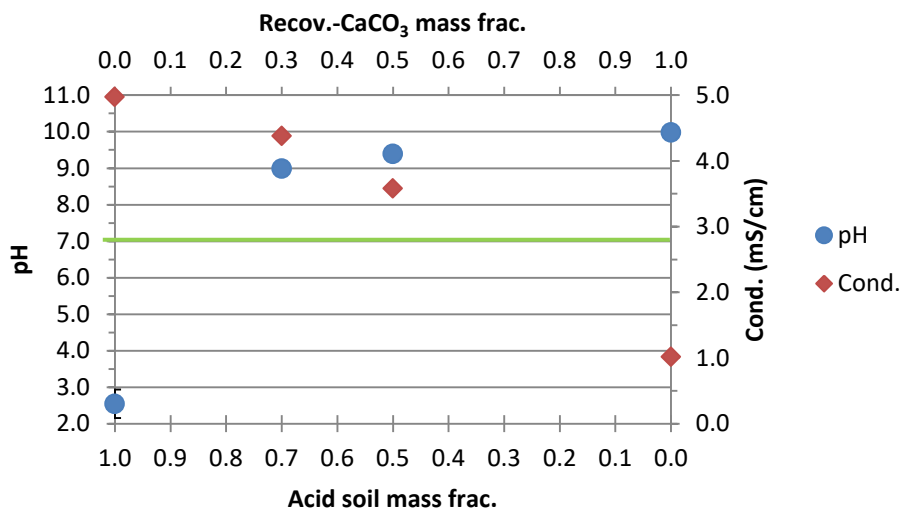


Figure 86. Leachability analysis: Neutralization of acid soil with recovered CaCO₃-rich solids

As seen in figure 86 and 84, the pH in the acid soil and recovered CaCO₃-rich solids were almost the same in both the pH and leachability analysis with pH values about 2,5 and 10 for the acid soil and recovered solids respectively. However, for the recovered solids mass fractions of 0,3 and 0,5 the pH were higher than the values obtained in the pH analysis and with respect to conductivity in average the values obtained in the leachability test were about twice the values obtained in the pH analysis for all of the solid conditions.

Furthermore, Ca, Mg, Fe, TOC and SO₄ were analyzed in the collected eluates collected from the leachability test. The results for Ca, Mg, TOC and Fe are given in figure 87 and for SO₄ in figure 88.

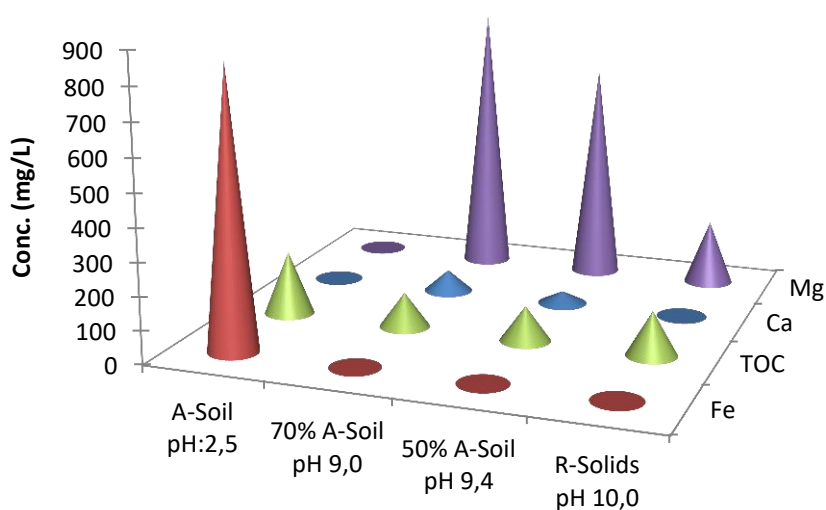


Figure 87. Leachability analysis: Ca, Mg, Fe and TOC conc. in Eluates generated from different mass percentages of acid soil and recovered CaCO₃-rich solids

As illustrated in figure 87, in the eluate from the acid soil the concentration of important nutrients in soil such as Ca and Mg were less than 5 and 3 mg/L respectively. However, with the addition of the recovered solids the concentration of Mg was considerable in the eluates corresponding to the acid soil mass percentage of 70 and 50% with value of about 800 and 650 mg/L respectively. The same was observed for Ca but at lower scale with a value of about 65 mg/L in the eluate from the acid soil mass percentage of 70%. Furthermore, the TOC leached from the acid soil was almost twice the TOC leached out by the solid mixtures and about 1,5 times higher than the TOC concentration in the eluate from the recovered solids. Furthermore, the concentration of Fe in the eluate generated by the acid soil was very high with a value of about 850 mg/L but this value decreased greatly compared to the eluate generated by the mixture with the recovered solids to values below 1 mg/L.

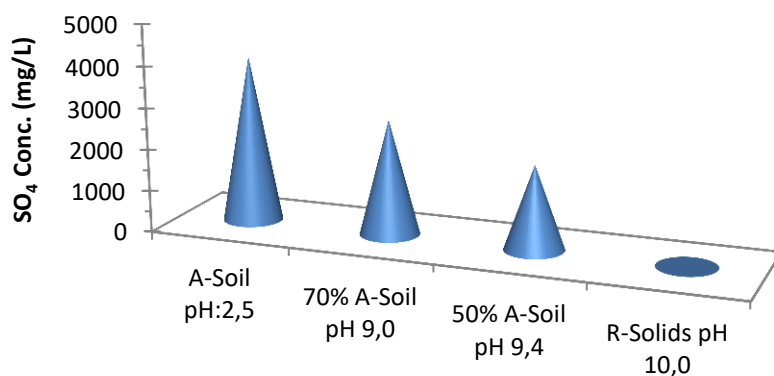


Figure 88. Leachability analysis: SO₄ conc. in Eluates generated from different mass percentages of acid soil and recovered CaCO₃-rich solids

Additionally, as seen in figure 88 for the case of SO₄ based on the high concentration of about 4000 mg/L measured in the eluate from the acid soil, the concentration of the eluates generated in the solids mixtures almost corresponded to the fraction of the acid soil in the mixture. Thus, SO₄ was not affected by the addition of the recovered CaO₃-rich solids. Other nutrients such as N and P were measured in the generated elutes but their concentrations were relatively low with values less than 10 mg/L as illustrate in figure 89.

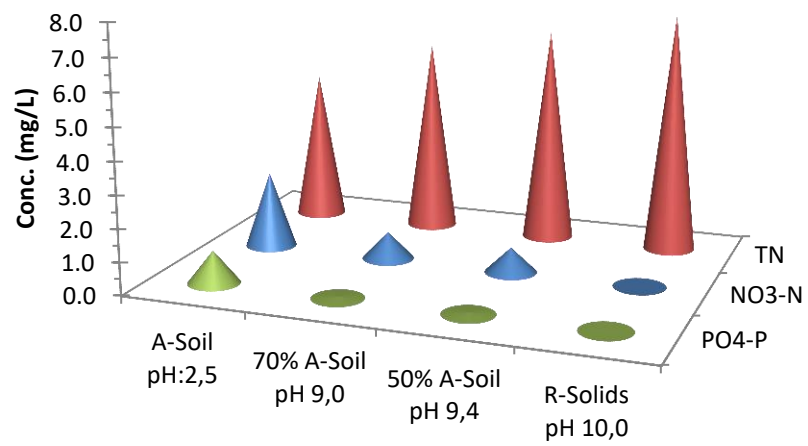


Figure 89. Leachability analysis: N and P conc. in Eluates generated from different mass percentages of acid soil and recovered CaCO_3 -rich solids

3.4. MEMBRANE CONTACTOR EVALUATION AND APPLICATION FOR THE RECOVERY OF AMMONIA AS AMMONIUM SULFATE SOLUTION

3.4.1. Materials and Methods

The landfill leachate permeates collected as supernatant from the precipitation treatment were used during this experimental work. Due to the corrosive nature of the process, the membrane contactor system was set up in a way that all the selected parts were resistant to corrosive environments; hence parts such as fittings, hoses, pumps and other used accessories were of PVC, PP or other material with good anticorrosive properties. The membrane contactor module used during this study and its main specifications are given in table 51. The raw data, and the analytical methods and equipment used are given in appendix F, A and B respectively.

Table 51. Specification of the membrane contactor module (3M, 2018)



Type:	Hollow fiber membrane, series 2,5x8x50
Material:	Polypropylene/Polyethylene
Membrane area:	1,4 m ²
Diameter:	67 – 77 mm
Length:	254 – 277 mm
Pore size (µm):	0,03

3.4.1.1. pH effect on membrane contactor treatment for the reduction and recovery of NH₃ from landfill leachate permeate

Before the start of each of the evaluated pH processes the membrane contactor was regenerated as suggested by the manufacturer cleaning guidelines, which can be summarized by washing and air drying steps and also the pre-filter was replaced.

First, the reduction of NH₃ from the LLP in the membrane contactor was evaluated at the pH conditions of 10, 11 and 12 where 8 L of the LLP and 7 L of a sulfuric acid solution (0,14M) were recirculated in countercurrent mode through the shell and the lumen side of the membrane module respectively. The sulfuric acid solution was prepared by mixing 7,5 mL of 95% H₂SO₄ per liter of deionized water. During the treatment, the pH was controlled by the use of NaOH (12M) and H₂SO₄ (65%) solutions and also NH₃-N was monitored with an ammonia ion selective electrode (ISE) probe. The membrane system was ran at each of the evaluated pH conditions until the removal of NH₄-N in the permeate was closed to 95%. The setup used during this experimental work is illustrated in figure 90.

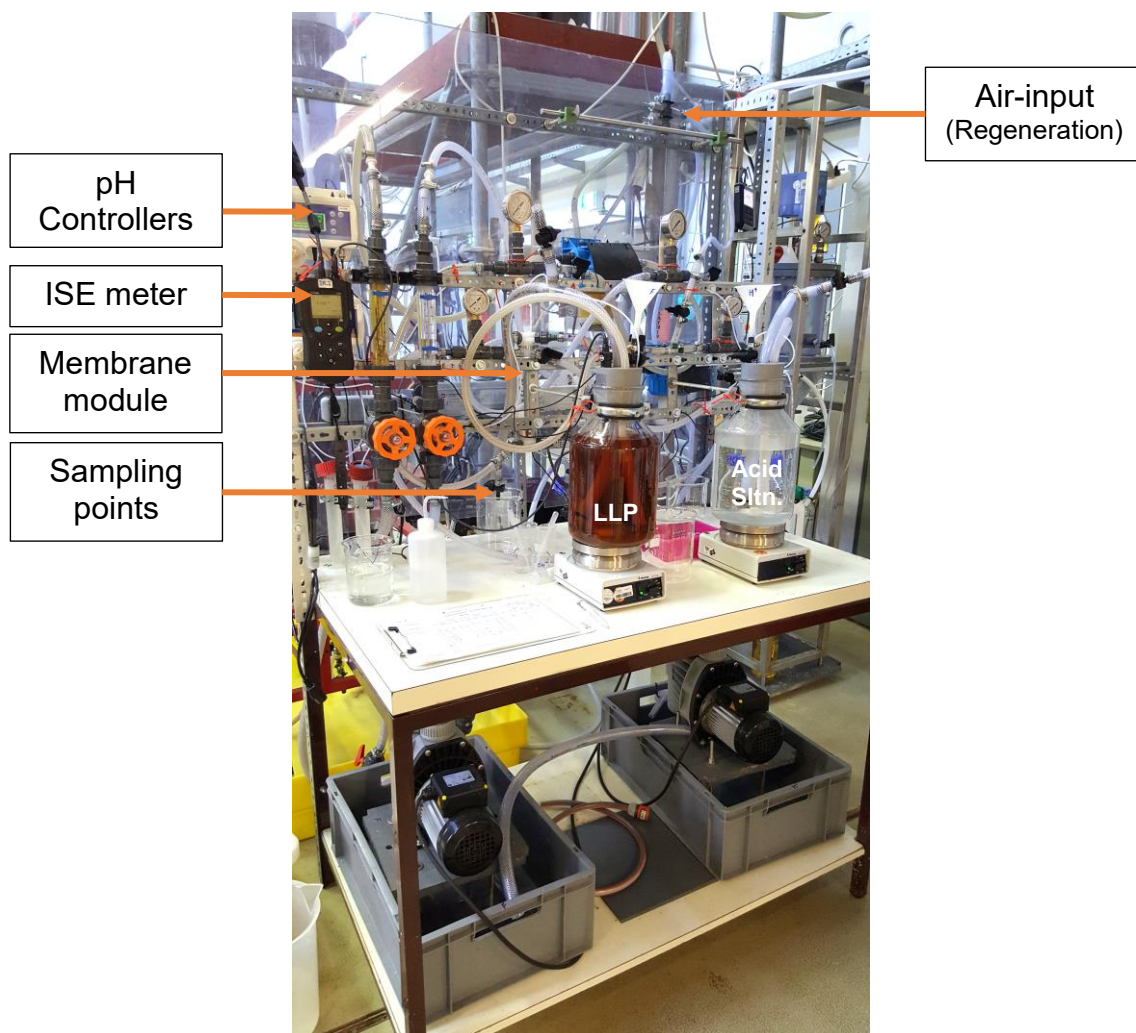


Figure 90. Setup used during the pH effect on membrane contactor treatment

3.4.1.2. Recovery of ammonia as concentrated ammonium sulfate solution ($\approx 20\%$) from landfill leachate permeate

Before the start of the recovery process the membrane contactor was regenerated by following the cleaning guide lines from the manufacturer. For the recovery of ammonia, about 380 L of the precipitation (pH12) pretreated landfill leachate permeate were treated in the membrane contactor module. First, 9 consecutive batches of 38 L each with treatment times of 5 h were performed with an initial 5 L acid solution (0,14M), which was recirculated through the lumen side of the membrane throughout all the consecutive batches until more than 90% of the N was reduced from the LLP and during the treatment the NH_3 -ISE was used as an indicator of N reduction. Then, in order to evaluate the regeneration step an extra 38 L batch was performed after the membrane cleaning where the volume of the acid solution was monitored throughout the 5h treatment time. For this last batch the glass bottle where the acid solution was previously collected was replaced by a 2 L PP volumetric cylinder. Moreover, during the membrane operation the pH values were fixed by setting the pH controllers to values of 12,0 and 1,1 where NaOH (12M) and H_2SO_4 (65 & 95%) solutions were used as pH control solutions respectively. The volumes of the pH control solution consumed during each batch were measured by using 100

mL and 250 mL PP volumetric cylinders. Furthermore, substances and/or parameters such as pH, T, $\text{NH}_4\text{-N}$, TN, TOC and SO_4 were measured during the ammonium sulfate enrichment process on both sides of the membrane. Furthermore, the liquids flow rate of the LLP and the acid solution were maintained during the treatment within the range of 240 to 260 and 220 to 240 L/h respectively. The setup used during the reduction and recovery of ammonia from the LLP is illustrated in figure 91.

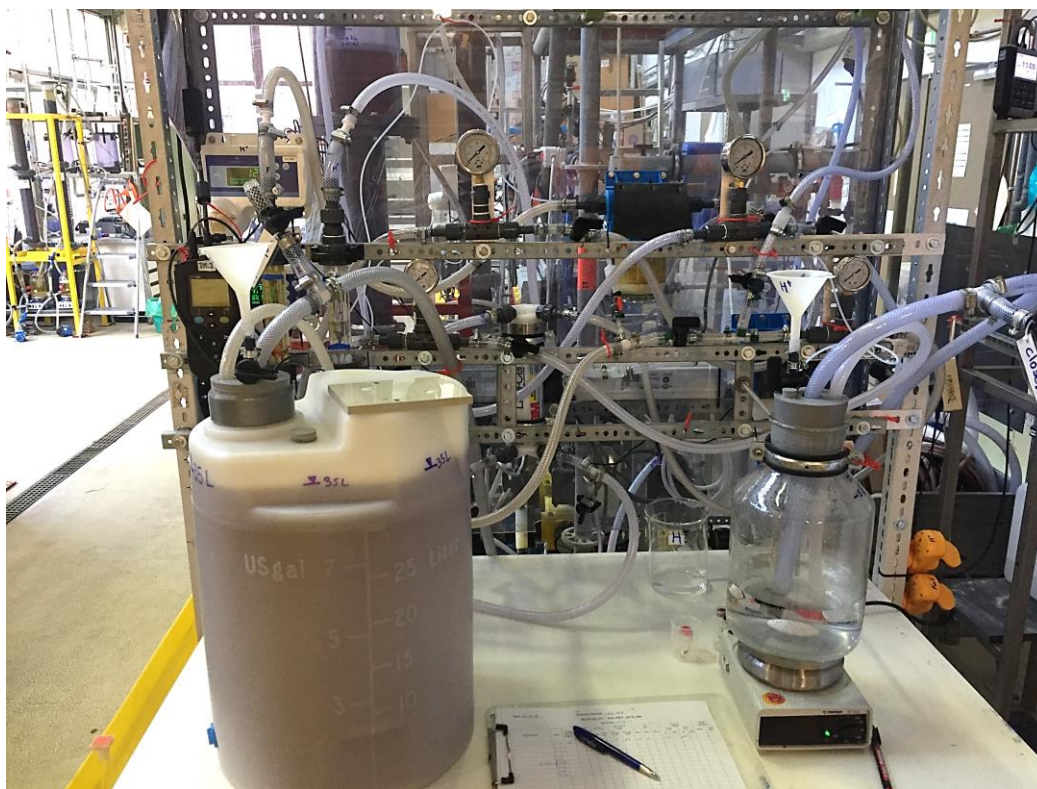


Figure 91. Setup used during the recovery of ammonia from LLP by the use of the membrane contactor module

3.4.1.3. Ammonium sulfate crystallization

A lab scale crystallization of $(\text{NH}_4)_2\text{SO}_4$ was performed as a potential application for the recovered ammonium sulfate solution ($\approx 20\%$) from the membrane contactor. Before cooling crystallization was performed the pH of the collected solution was adjusted to a pH value of about 5.5 ± 0.2 by using a NaOH (12M) solution. After the pH adjustment the ammonium sulfate solution was treated with PAC in order to remove impurities such as color. Then, 100 mL of the pretreated collected solution were concentrated by evaporation until reaching a close to ammonium sulfate saturated solution of 0,5 Kg/Kg-Sltn at a temperature range of 95 to 105°C. After, the concentration step, the solution was placed in an ice batch with temperature ranging in between 5 to 10°C. Then, during the cooling crystallization the concentrated solution was seeded with ammonium sulfate crystals in order to promote crystallization. After the crystallization process, the liquid was separated from the formed crystals by using vacuum filtration and then the collected crystals were let to air-dry, followed by homogenization and XRD analysis. The main steps followed during the ammonium sulfate crystallization from the recovered ammonium sulfate solution are illustrated in figure 92.

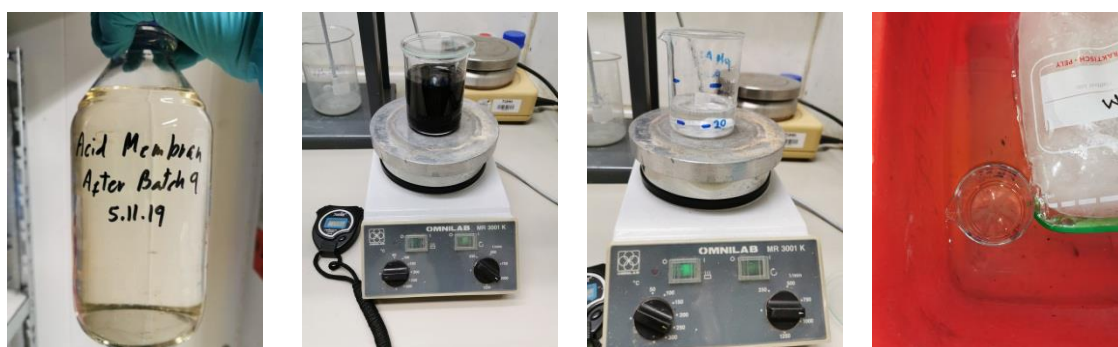


Figure 92. Procedures followed during ammonium sulfate crystallization; Left: Collected $(\text{NH}_4)_2\text{SO}_4$ solution ($\approx 20\%$); Middle: PAC and evaporation treatment; Right: Cooling crystallization

3.4.2. Results and Discussion

3.4.2.1. pH effect on membrane contactor treatment for the reduction and recovery of NH_3 from landfill leachate permeate

The operating conditions measured during the treatment of the landfill leachate permeate (LLP) at the different pH conditions in the membrane contactor and the acid solution are given in table 52.

Table 52. Operating conditions during membrane contactor treatment at pH 10, 11 & 12

LLP: Fed shellside; Acid Solution: Fed lumenside						
Parameter	pH 12 $t_{\text{Treat.}}: 90 \text{ min}$		pH 11 $t_{\text{Treat.}}: 120 \text{ min}$		pH 10 $t_{\text{Treat.}}: 150 \text{ min}$	
	LLP	Acid Sln.	LLP	Acid Sln.	LLP	Acid Sln.
Vol. Treat.: (L)	8,0 \pm 0,1	7,0 \pm 0,1	8,0 \pm 0,1	7,0 \pm 0,1	8,0 \pm 0,1	7,0 \pm 0,1
pH:	12,2 \pm 0,1	1,1 \pm 0,1	11,0 \pm 0,1	1,1 \pm 0,1	10,0 \pm 0,1	1,1 \pm 0,1
Vol. pH-cont.: (mL)	NaOH(12M): 0	H ₂ SO ₄ (65%): 10,5 \pm 12,0	NaOH(12M): 19,0 \pm 4,2	H ₂ SO ₄ (65%): 35,5 \pm 3,5	NaOH(12M): 43,5 \pm 3,5	H ₂ SO ₄ (65%): 62,0 \pm 17,0
Flow rate: (L/h)	240–260	200–220	220–260	200–220	140–260	200–220
P _{g in-mc} : (bar)	0,1	0,3	0,1	0,3	0 – 0,1	0,3
P _{g out-mc} : (bar)	0	0	0	0	0	0
T (°C):	30 \pm 5	30 \pm 5	30 \pm 6	30 \pm 5	29 \pm 6	30 \pm 5

As seen in table 52, the pH, P, T and flow rate conditions in the acid solutions side were almost the same during the permeate treatment for each of the evaluated pH conditions. However, with respect to the pH control acid solution the volumes consumed during the pH 11 and 10 treatment were about 3 and 6 times higher respectively compared to the average value of 10,5 \pm 12,0 mL of H₂SO₄ (65%) solution consumed during the pH 12 treatment. Also, in the permeate side during the

pH 10 treatment the consumed NaOH (12M) pH control solution was larger compared to the other pH values where it was about twice the volume consumed during the pH 11 treatment. Moreover, with respect to pressure, during the treatment the pressure at the membrane input of the acid solution side or lumenside was always slightly higher compared to the permeate side or shellside of the membrane and on average the temperatures were around 30°C on each side of the membrane. Furthermore, for the case of the LLP as indicated by the flow rate range, at pH 10 during the treatment the flow rate decreased and by the end of the treatment it reached a value of 140 L/h; a similar decrease in flow rate was observed at pH 11 but it was not as severe as for the case of pH 10. This decrease in flow rate was due to the accumulation of solid particles that formed during the membrane treatment and were retained by the installed pre-filter as illustrated in figure 93.



Figure 93. Pre-filter after LLP treatment in membrane contactor; Left: Pre-filter after pH 10 treatment; Right: Pre-filter after pH 11 treatment

The reason for the accumulation of the formed solids during the membrane treatment might be attributed to the relatively high hardness concentration that remained in the LLP at these pH conditions after the precipitation treatment as already indicated in figure 66. After the precipitation treatment the hardness in the LLP at pH 11 and 10 were equal to $38,8 \pm 0,8$ and $99,0 \pm 9,9$ °dH respectively, which corresponded to a hardness of about 681 and 1810 mg/L as CaCO_3 and as indicated in table 8 these values corresponded to very hard water. On the other hand the permeate obtained after the pH 12 precipitation treatment had a hardness of $1,6 \pm 0,8$, which corresponded to a hardness of about 37 mg/L as CaCO_3 being within the range of soft water. Thus, scaling problems might still be encountered downstream membrane processes after treating the landfill leachate permeate at precipitation pH conditions of 10 and 11 and might be more severe at pH 10.

Furthermore, the concentrations of TN were measured during the membrane treatment at the corresponding pH conditions. The results obtained in the reduction of N from the permeates are illustrated in figure 94.

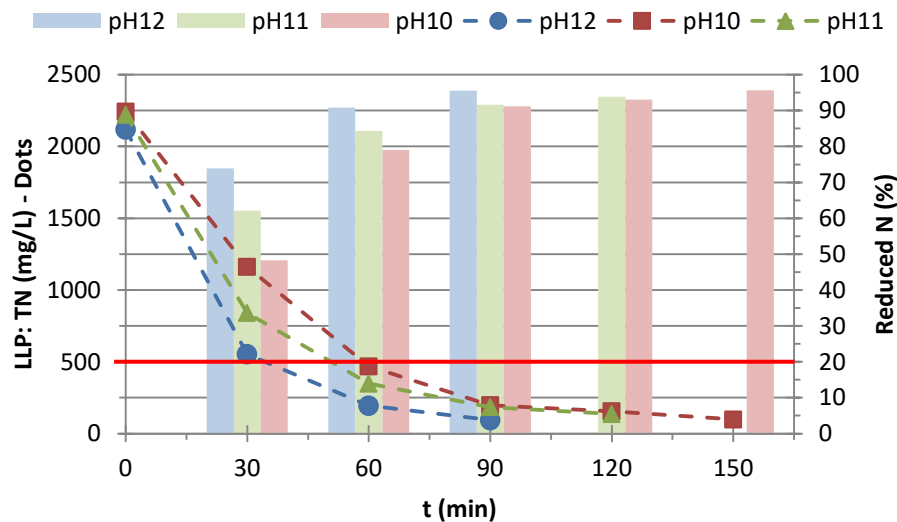
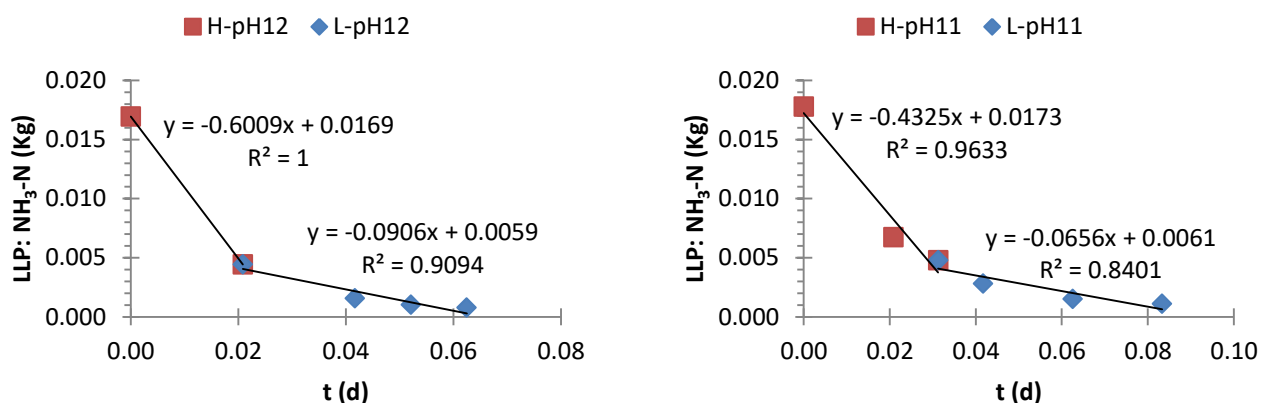


Figure 94. TN concentration in LLP during membrane treatment at pH 10, 11 & 12

As indicated in figure 94, based on the TN concentration in the LLP during the membrane treatment at the evaluated pH conditions when the TN concentrations reached values of around 500 mg/L the rates of N reduction were partitioned into two zones. The highest reduction of NH_3 took place in between the initial TN concentration with an average value of 2194 ± 68 mg/L down to the identified partition concentration of about 500 mg/L and with respect to time, the partition concentration corresponded to treatment times of 30, in between 30 to 60 (Approx. 45 min) and about 60 min with reduction values of about 74, 73 and 79% for pH 12, 11 and 10 respectively. Furthermore, below the TN concentration of about 500 mg/L the reduction of NH_3 in the membrane contactor was low where in general at all pH conditions with respect to time for a further reduction of about 20% it took about 1,5 to 2 times more the partition time to reached a final TN reduction of about 95%. The estimated reduction rates of $\text{NH}_3\text{-N}$ based on TN in the membrane contactor module at each of the pH conditions are illustrated in figure 95.



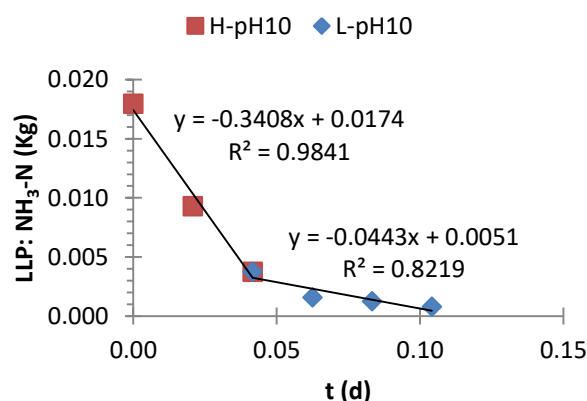


Figure 95. Estimated NH_3 reduction rate during treatment of LLP in membrane contactor at pH 10, 11 & 12; H: High reduction zone; L: Low reduction zone

As seen in figure 95, the estimated $\text{NH}_3\text{-N}$ reduction rate at pH 12 in the high reduction zone might be viewed as an ideal case since only two points were possible to consider in the linear model. However, it provided a numerical representation of the already observed higher TN reduction rate at pH 12 with respect to the other evaluated pH conditions. For instance, the N reduction rates at pH 11 and 10 were about 72 and 57% the value of 0,6 Kg-N/d obtained at pH 12 respectively. Furthermore, based on the R-squared values estimated for pH 10 and 11 it was seen that the high NH_3 reduction zone might followed linearity since the R^2 values were greater than 0,95. On the other hand, the R^2 values in the low $\text{NH}_3\text{-N}$ reduction zone were equal or less than 0,9; hence a linear model might not have represented the data accurately but it did provide an estimation in the degree of decrease in the N reduction rate, which in average was only about 15% the value obtained in the high N reduction zone at the corresponding pH condition.

Furthermore, in order to confirm the presence of $\text{NH}_4\text{-N}$ in the acid solution at the end of each pH treatment both TN and $\text{NH}_4\text{-N}$ were measured and it was seen that more than 98% of the N was in fact $\text{NH}_4\text{-N}$. The results are given in table 53.

Table 53. TN and $\text{NH}_4\text{-N}$ concentration in Acid solution after membrane treatment at pH 10, 11 & 12

pH	Time treatment (min)	TN (mg/L)	$\text{NH}_4\text{-N}$ (mg/L)
10	150	-	2370
11	120	2335	2300
12	90	2236	2200

Based, on the average N concentration measured in the acid solutions at the end of the membrane treatment and the initial TN concentration in the LLP, the recovery of N was estimated at each pH condition, the results are given in figure 96.

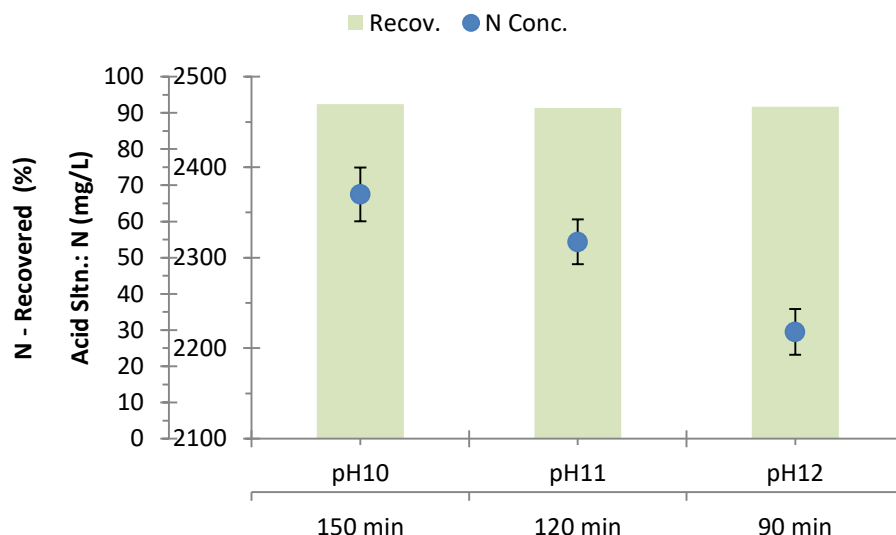


Figure 96. Nitrogen recovery & concentration in Acid solution after membrane treatment at pH 10, 11 & 12

Figure 96, illustrated that at the end of the treatment at each pH condition about 90% of the N was recovered in the acid solution reaching N concentrations in between 2200 to 2400 mg/L at the evaluated pH conditions. Furthermore, for pH 12 the recovery of nitrogen was estimated at each time interval as illustrated in figure 97.

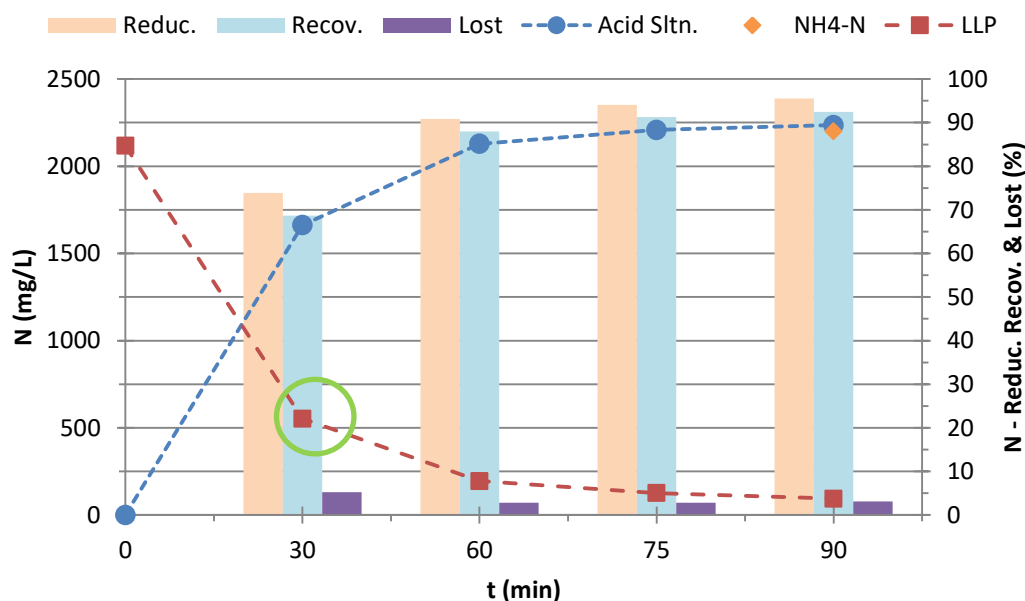


Figure 97. Nitrogen conc. during membrane treatment in LLP and Acid solution at pH 12

As seen in figure 97, for the treatment time of 30 min the N recovered in the acid solution was equal to 70%, which corresponded to the reduced N in the LLP of 74% and for the treatment time of 90 min the N recovered in the acid solution was equal to 92%, which corresponded to the reduced N in the LLP of 96%. These indicated that in average the N recovery efficiency in the membrane process at pH 12 was about 96% where only 4% of the TN was lost during the treatment.

Additionally, an NH_3 ion selective electrode (ISE) was evaluated during the process at the different pH conditions. The average $\text{NH}_3\text{-N}$ concentrations recorded by the instrument were compared to the TN values measure at the corresponding interval times; the results are given in figure 98.

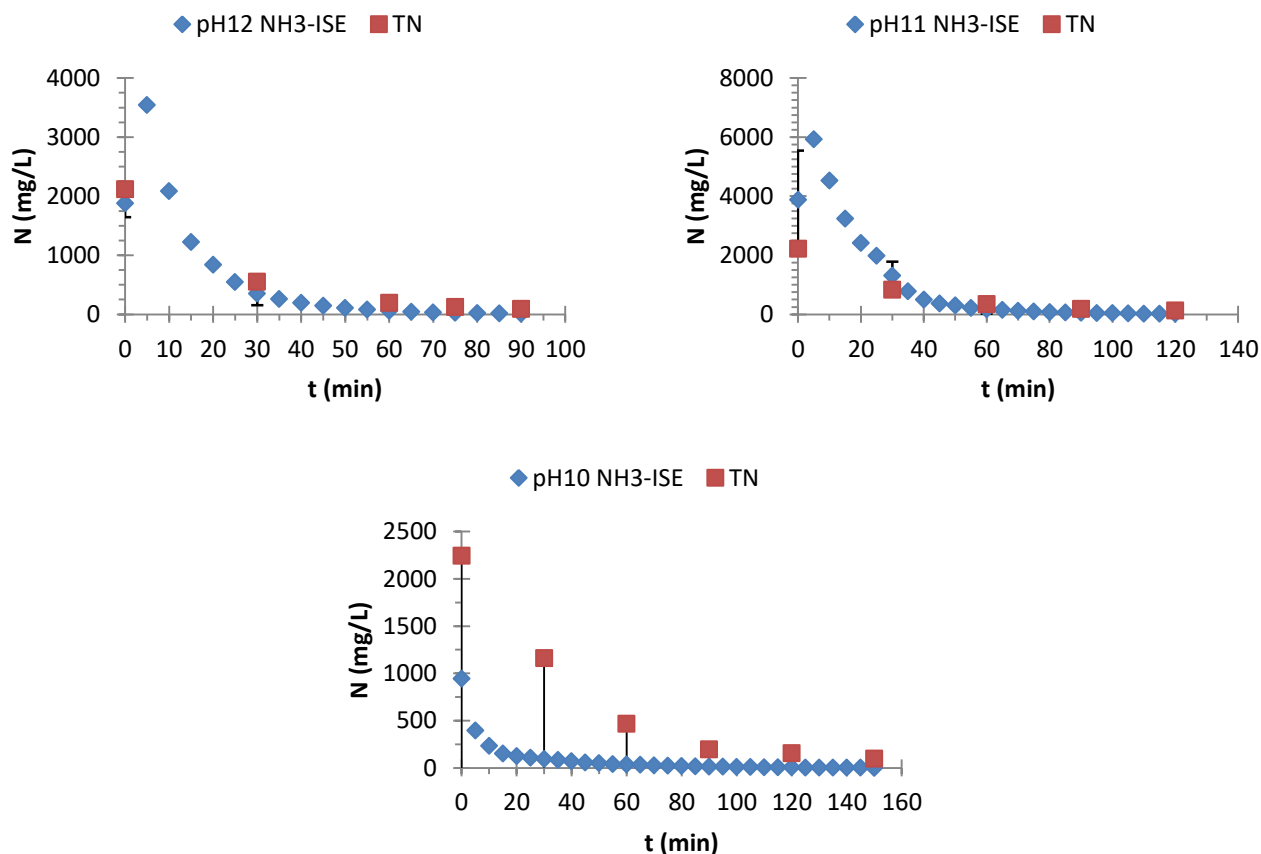


Figure 98. $\text{NH}_3\text{-N}$ conc. recorded by $\text{NH}_3\text{-ISE}$ and TN conc. during membrane treatment in LLP at pH 10, 11 & 12

As illustrated in figure 98, at pH 10 the $\text{NH}_3\text{-ISE}$ presented the largest error with respect to the measured TN with average errors of about 88%. For pH 11 and 12 the performance of the $\text{NH}_3\text{-ISE}$ seemed to be better where a sort of stabilization period was observed within the first 30 min of treatment, the average errors with respect to the measured TN were about 67 and 52% for pH 11 and 12 respectively. Even though, the $\text{NH}_3\text{-ISE}$ yielded large errors with respect to the relatively true N value, it did serve as an indicator since at pH 11 and 12 it was observed that in the system for a recorded $\text{NH}_3\text{-N}$ concentration of around 20 mg/L the TN concentration in the permeate was somewhere in between 150 to 100 mg/L, which indicated that already more than 90% of the N in the LLP was reduced.

Moreover, the conductivity in the LLP during the membrane treatment did not changed considerably with an average value of $93,4 \pm 0,9$ mS/cm but for the acid solution it did decrease from the initial average value of $59,5 \pm 0,6$ mS/cm to $45,7 \pm 3,3$ mS/cm.

3.4.2.2. Reduction and recovery of ammonia as concentrated ammonium sulfate solution ($\approx 20\%$) from landfill leachate permeate

The parameters measured during the consecutive batches for the recovery of ammonia from the landfill leachate permeate (LLP) and the after membrane regeneration batch are given in tables 54 and 55 respectively.

Table 54. Consecutive batches operating conditions during membrane contactor treatment

LLP: Fed shellside; Acid Solution: Fed lumenside $t_{\text{Treat.}}: 5 \text{ h per Batch}$				
Operating Mode:	Partially wet Batches: (1 – 6)		Wet out (Batches 7 – 9)	
Streams:	LLP	\ddagger Acid Sltn.	LLP	\ddagger Acid Sltn.
Vol. _{Treat.} (L):	Batch: 38,0 \pm 0,5	Initial: 5,0 \pm 0,1	Batch: 38,0 \pm 0,5	Initial: 7,3 \pm 0,1
	Total: 228 \pm 2	Final: 7,3 \pm 0,1	Total: 114 \pm 1	Final: 8,8 \pm 0,1
pH:	12,0 \pm 0,1	1,1 \pm 0,1	12,0 \pm 0,1	1,2 \pm 0,1
Aver. Vol. _{pH-cont.} : (mL/batch)	NaOH (12M): 303 \pm 108	H ₂ SO ₄ (65%): 386 \pm 19	NaOH (12M): 322 \pm 86	H ₂ SO ₄ (65%): 490 \pm 81
Flow rate (L/h):	240 – 260	200 – 220	240 – 260	200 – 220
P _{g in-mc} (bar):	0,1 – 0,2	0,3 – 0,4	0,1 – 0,3	0,4 – 0,5
P _{g out-mc} (bar):	0	0	0	0
T (°C):	28 \pm 7	28 \pm 6	27 \pm 8	27 \pm 7

\ddagger Acid Sltn. Final Vol.: Estimation based on volume of consumed pH control Sltn.

Table 55. After membrane regeneration batch operating conditions during membrane contactor treatment

LLP: Fed shellside; Acid Solution: Fed lumenside $t_{\text{Treat.}}: 5 \text{ h}$		
Operating Mode:	Batch: After regeneration	
Streams:	LLP	\ddagger Acid Sltn.
Vol. _{Treat.} (L):	38,0 \pm 0,5	Initial: 3,5 \pm 0,1
		Final: 4,0 \pm 0,1
pH:	12,0 \pm 0,1	1,1 \pm 0,1
Vol. _{pH-cont.} (mL):	NaOH (12M): 379 \pm 5	H ₂ SO ₄ (95%): 216 \pm 5
Flow rate (L/h):	240 – 260	200 – 220
P _{g in-mc} (bar):	0,1 – 0,3	0,3 – 0,4
P _{g out-mc} (bar):	0	0
T (°C):	29 \pm 9	30 \pm 8

\ddagger Acid Sltn. Final Vol.: Based on measured increase volume

As indicated in tables 54 and 55, the operating conditions during each of the performed consecutive and after membrane regeneration batches were relatively the same. For the case of the consecutive batches, only a slightly increase in the input pressure and a 6% increase in the average consumed volume of NaOH (12M) pH control solution were observed in the wet out batches compared to values obtained in the partially wet batches. However, in regards to the consumed volume of H₂SO₄ (65%) pH control solution a 27% increase was observed in the wet out batches compared to the average values obtained in the partially wet batches and a 44% volume reduction was observed by using the H₂SO₄ (95%) as pH control solution in the after membrane regeneration batch.

The average N concentration values obtained during the membrane treatment of the permeate corresponding to batches 1 through 6, batches 7 through 9 and the values obtained during the after membrane regeneration batch with their respective N reduction percentages are illustrated in figure 99.

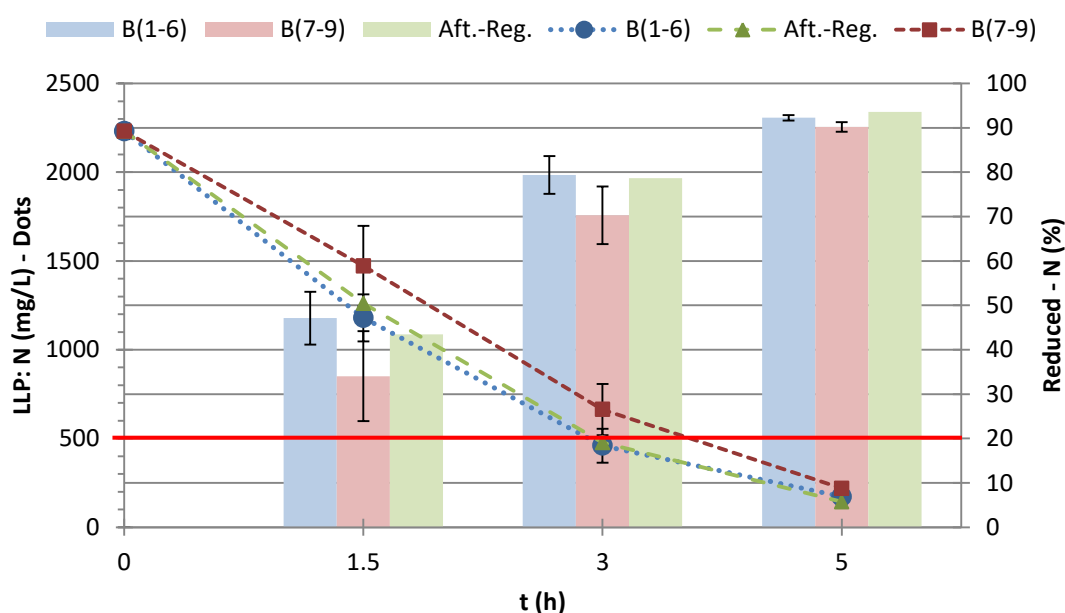


Figure 99. TN concentration and percentage reduction in LLP during membrane contactor treatment; B: Batch; Aft.-Reg.: After regeneration

Figure 99 indicated that in average for the consecutive batches 1 through 6 and the batch performed after membrane regeneration at the treatment time of 3 h about 80% of the N was reduced from the permeate. On the other hand for the wet out consecutive batches the reduction of N at the same treatment time only reached an average reduction value of about 70% and also with respect to the treatment time of 1,5 h the reduction of N was less with a value of about 34% compared to about 45% reduction obtained in the other batches. Moreover, the almost 80% N reduction time corresponded to the already identified permeate partition N concentration of around 500 mg/L, which separated the N reduction rate into high and low reduction zones also illustrated in figure 94 for the 8L batches where below this concentration the system took about 2h more, which corresponded to 40% of the total treatment time of

5h to reduce only an extra 10% of the N concentration and reaching a total N reduction in the LLP of about 90%.

In order to correlate the TN measured during the consecutive batches with the $\text{NH}_4\text{-N}$ concentration in the permeate, the concentrations of $\text{NH}_4\text{-N}$ during the first and after the membrane regeneration batches were measured during the 5 h treatment where the TN to $\text{NH}_4\text{-N}$ ratios were estimated based on the estimated average values as described in table 56.

Table 56. $\text{NH}_4\text{-N}$ & TN relation during membrane contactor treatment

Time _{Treat.} (h)	$\text{NH}_4\text{-N}$ (mg/L)	TN (mg/L)	$\text{NH}_4\text{-N}/\text{TN}$
0	2082±104	2231±112	0,9
1,5	930±47	1127±190	0,8
3	331±21	448±40	0,7
5	52±11	147±6	0,4

As indicated in table 56, with the membrane treatment time of 5h the $\text{NH}_4\text{-N}$ concentration in the permeate was below the N limit value indicated in the landfill German regulation of 70 mg/L also described in table 3. Furthermore, based on the estimated $\text{NH}_4\text{-N}$ to TN ratio of about 0,7 for the treatment time of 3h, the identified partition N concentration of about 500 mg/L corresponded to an $\text{NH}_4\text{-N}$ concentration of about 350 mg/L with an $\text{NH}_4\text{-N}$ reduction of about 85%. Furthermore, based on the measured N concentration the $\text{NH}_3\text{-N}$ reduction rates in the permeate were calculated for the different operating batches by using linear regression within the first 3h of treatment, which corresponded to about 80% reduction of N in the permeate. The calculated linear models are illustrated in figure 100.

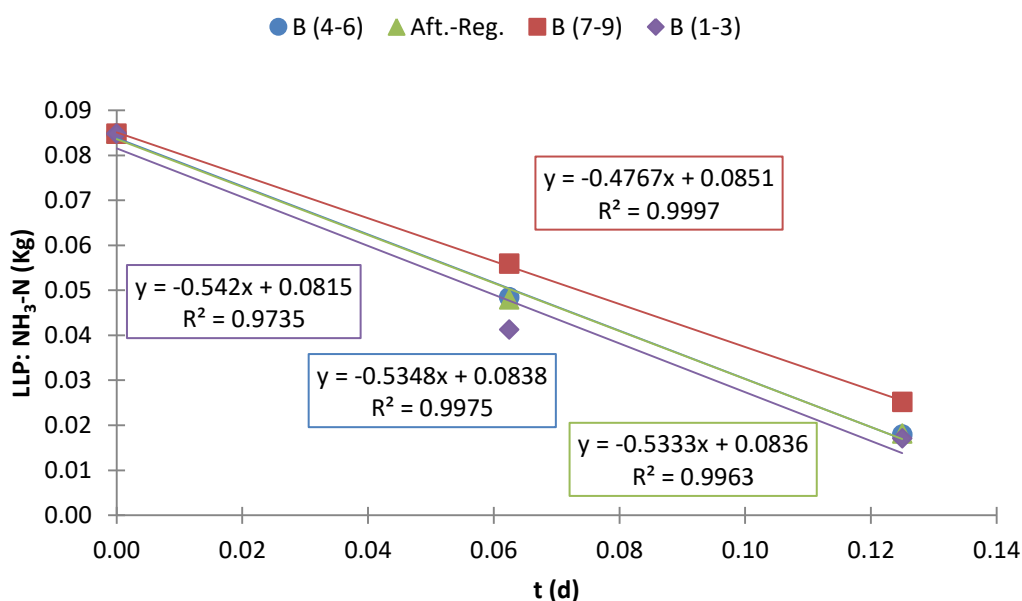


Figure 100. Estimated $\text{NH}_3\text{-N}$ reduction rate during the first 3h of membrane treatment for the reduction and recovery of NH_3 from LLP

As seen in figure 100, the results indicated that the N reduction rates obtained during the first 3h of membrane treatment for the partially wet and after regeneration batches were very close to each other with an average value of about 0,54 Kg/d, which was about 12% higher than the value of 0,48 Kg/d obtained in the wet out batches and about 11% lower than the value of 0,60 Kg/d illustrated in figure 95 for high reduction rate zone in the 8L batch at pH 12.

As already illustrated in figures 99 and 100, based on the results the N reduction efficiency from the permeate was regained in the membrane contactor module after performing the regeneration step. Furthermore, in order to evaluate the hydrophobicity of the membrane after regeneration, the volume of the acid solution was monitored during the 5h treatment in the after membrane regeneration batch. During the treatment, in order to better identify volume increases in the acid solution only due to crossing of the permeate from the shell- to the lumen- side of the membrane concentrated H_2SO_4 (95%) was used as pH control solution. The results obtained in the acid solution volume increase during the batch performed after the membrane regeneration step are illustrated in figure 101.

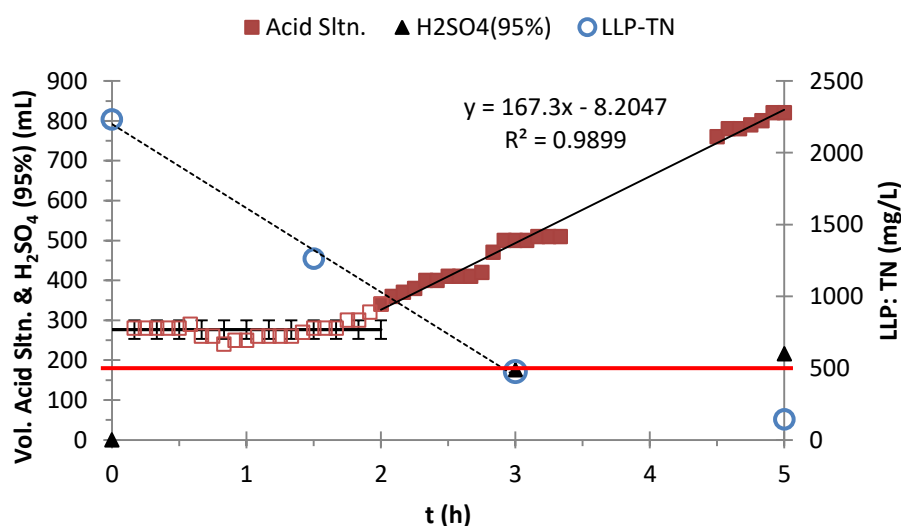


Figure 101. Monitored volume in acid solution during membrane contactor treatment

As indicated in figure 101, based on the average value of 277 ± 23 mL calculated from the recorded volumes, the acid solution volume remained relatively constant up to the treatment time of 2h, which based on the linear model it corresponded to a N concentration in the permeate side of about 1000 mg/L. Then, after the treatment time of 2h and based on the linear regression model the acid solution volume started to increase almost at a same rate until reaching a final volume of 820 ± 20 mL, which corresponded to a volume increase of 540 ± 20 mL with respect to the initial recorded volume of 280 ± 20 mL. Furthermore, at the treatment time of 3 and 5 h the consumed H_2SO_4 (95%) were measured as 176 ± 5 and 216 ± 5 mL respectively. Thus, even after the membrane regeneration the hydrophobicity of the membrane was partially lost during the batch where at the end of the treatment from the volume increase of 540 ± 20 mL and taking into account the consumed volume of the pH control solution

the fraction of LLP within the increase volume was about 0,6. Furthermore, based on the increase volume rate in the acid solution of 167,3 mL/h, for 1 h of treatment the increase in volume corresponded to almost the volume of pH control solution consumed up to the treatment time of 3 h, which also corresponded to the already discussed partition N concentration of 500 mg/L. This results indicated that the N concentration in the permeate of about 500 mg/L seemed to be a critical value during the membrane contactor treatment not only because it might divide the N reduction rates into high and low zones but also because it might have an effect on the hydrophobicity of the membrane.

As has been discussed throughout this section, the performed consecutive batches were classified as partially wet and wet out operating modes. The reason for this classification was obtained after analyzing the membrane treatment in the ideal case of completely hydrophobic membrane. For this ideal case, the volume in the acid solution would increase only due to the consumed volume of the pH control solution, which in this case was H₂SO₄ (65%). Thus, an indication of the membrane hydrophobicity during the process was obtained based on the initial NH₄-N concentration measured in the LLP, the cumulative TN concentration measured at the end of each batch in the acid solution and only taken into account that the increase in the acid solution volume was due only to the consumed pH control solution. The results are illustrated in figure 102.

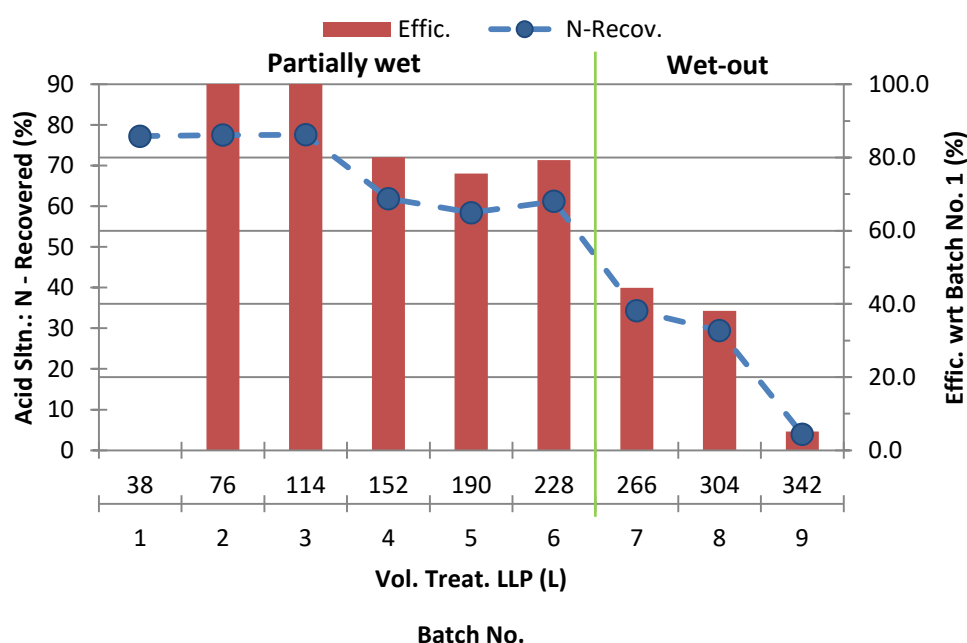


Figure 102. Estimated N recovery in acid solution during membrane contactor treatment

As illustrated in figure 102 and compared with figure 99 after the 5h membrane treatment about 90% of the N was reduced from the LLP. However, the estimated percent recovery of N in the first 3 batches of about 80% decreased to about 60% and 40% in batches 4 to 6 and batches 7 to 8 respectively and finally reaching a N recovery of about 4% in the last batch. These results indicated that the volumes in

the acid solution were larger than the estimated volumes, which suggested the crossing of permeate to the lumenside of the membrane. Also, they correlated well with what was observed during the experimental work, which was the unusual increase in the acid solution volume especially during the last consecutive batches. Thus, based on the percent recovery of N estimated for the first batch, efficiencies with respect to the first batch were calculated in each of the following batches, which yielded efficiencies of 100, about 80 and 40% or below for the consecutive batches in between 1 to 3, 4 to 6 and 7 to 9 respectively; hence the classification of partially wet and wet out membrane operating modes for batches 1 to 6 and 7 to 9 respectively.

Furthermore, based on the concentration of TN and $\text{NH}_4\text{-N}$ measured in the acid solution at the end of the evaluated consecutive batches, the mass percentages of ammonium sulfate solution recovered in the acid solutions and the percentage changes with respect to the increase in the ammonium sulfate concentration per batch were calculated. The results are illustrated in figure 103.

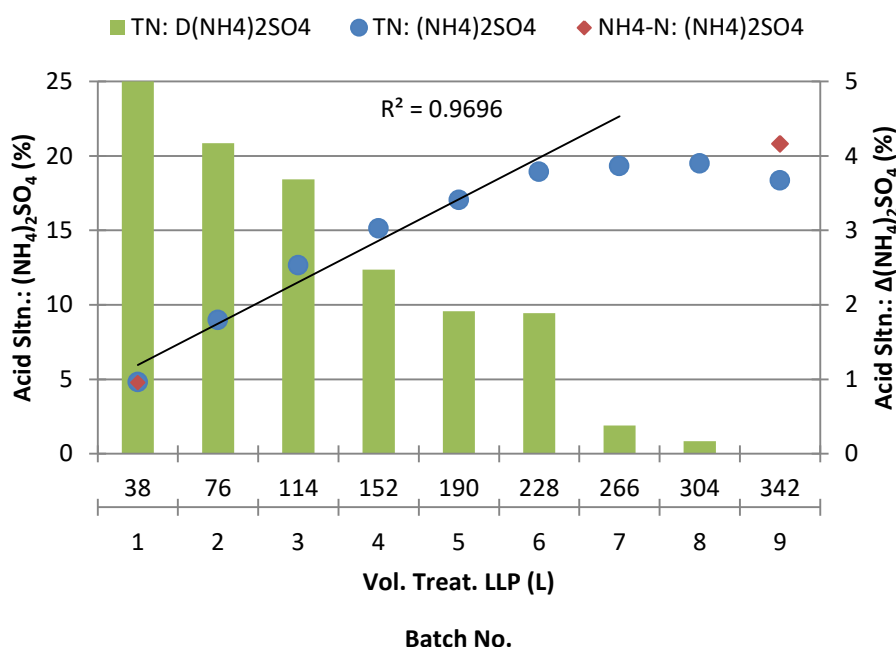


Figure 103. Concentration of Ammonium sulfate in acid solution during membrane contactor treatment

As indicated in figure 103, the increase in the concentration of ammonium sulfate in the acid solution seemed to followed linearity up to batch number 6 where about 228 L of the permeate were treated, which based on TN the acid solution reached an ammonium sulfate concentration of about 19%. Also, in between these batches the increased in ammonium sulfate percentage were above and close to a value of 2%. Furthermore, in between batches 7 to 9 the change in the percentage concentration decreased to values below 1%; hence the concentration of ammonium sulfate in the acid solution stayed relatively constant and started to decreased by batch 9 where the concentration of ammonium sulfate base on $\text{NH}_4\text{-N}$ was equal to about 21%. The results indicated that an acid solution with about 20% in weight of ammonium sulfate solution was achieved in between batches 1 to 6 without membrane regeneration.

However, as previously discussed during these batches the membrane was not completely hydrophobic but rather a partially wet operating mode was observed.

Additionally, the performance of the process in between the batches 1 to 3 was compared to the results obtained in the more control 8L membrane treatment at pH 12. For the larger scale treatment, the recovery on N in the acid solution was estimated based on the increase in volume rate of 167,3 mL/h per batch indicated in figure 101 where the volume increase was assumed to take place during the last 3 h of treatment. Also for each case the estimated reduction rates of NH₃-N obtained during the first 3h of membrane treatment were calculated with respect to the area of the membrane contactor module. The results are given in table 57.

Table 57. 8 L control batch vs. 38 L consecutive batches during membrane contactor treatment

LLP: Fed shellside; Acid Solution: Fed lumenside				
Parameter	8 L Batch pH 12 $t_{\text{Treat.}}: 1,5 \text{ h}$		Consecutive Batches (1 - 3) $t_{\text{Treat.}}: 15 \text{ h}$	
	LLP[‡]	Acid[‡] Sltn.	LLP[‡]	Acid[‡] Sltn.
Vol._{Treat.} (L):	8,0±0,1	7,0±0,1	114±1	6,0±0,5
pH:	12,2±0,1	1,1±0,1	12,0±0,1	1,2±0,1
Vol._{pH-cont.}: (mL/batch)	NaOH(12M): 0	H ₂ SO ₄ (65%): 10,5±12,0	NaOH (12M): 397±46	H ₂ SO ₄ (65%): 382±11
Flow rate (L/h):	240–260	200–220	240–260	200–220
P_{g in-mc} (bar):	0,1	0,3	0,1 – 0,2	0,3 – 0,4
P_{g out-mc} (bar):	0	0	0	0
T (°C):	30±5	30±5	30±6	30±6
N-reduced (%):	96		93	
N-recovered (%):	92		82±3	
N-loss (%):	4		10±4	
[‡]N-Reduction rate: (Kg-N/d·m²)	0,43		0,39	

[‡] Estimated for about 80% N-reduction in the LLP

As seen in table 57, based on the treatment time and operating conditions the controlled 8L batch seemed to approached an ideal case of membrane operation for the recovery of NH₃-N from the permeate. Thus, compared to the smaller scale treatment the average N reduction percentage obtained in the larger scale process with a value of 93% did not differ that much from the value of 96% obtained in the more control process. On the other hand, the estimated percent recovery of N in the acid solution and loss of N obtained in batches 1 through 3 with average values of 82±3 and 10±4% were about 11% less efficient and 2,5 times higher than the values of 92 and 4% respectively obtained in the more control 8L membrane treatment at pH 12.

Additionally, SO_4 and TOC were measured during the membrane treatment process. For the case of SO_4 , it was measured in the permeate side in order to identify abnormal increases in sulfate concentration due to possible crossing of the acid solution. The measured average concentration of SO_4 at the end of the membrane treatment in the LLP was equal to 9450 ± 240 mg/L, which compared to the initial value of 9660 ± 483 mg/L was within the concentration range. Furthermore, for the case of TOC in the LLP the average concentration at the end of each batch was 1172 ± 45 mg/L, which corresponded to about 5% removed from the initial TOC concentration with value of 1239 ± 23 mg/L. Moreover, as expected the TOC concentration in the acid solution was increasing as more permeate was treated. The results are illustrated in figure 104.

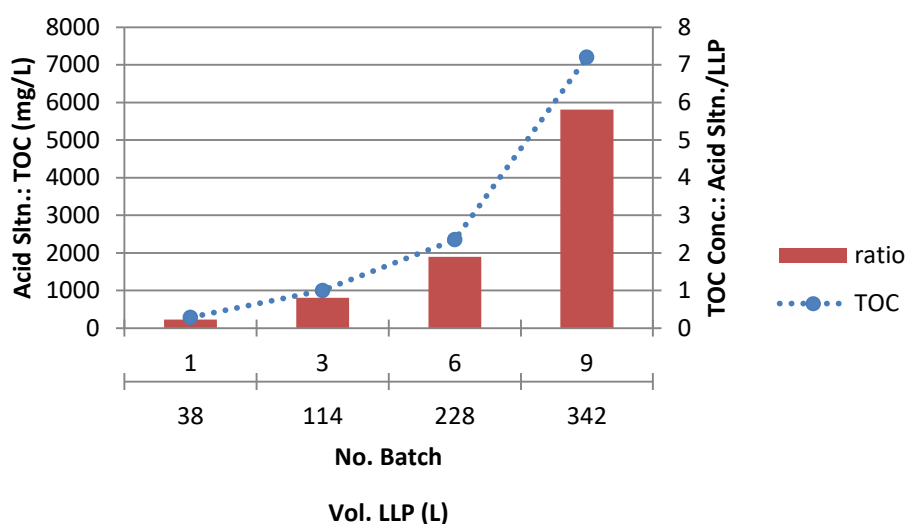


Figure 104. TOC concentration in acid solution during membrane contactor treatment

As indicated in figure 104, during the membrane treatment not only the acid solution was concentrated with ammonium sulfate but also with organic content. Based on the about 5% TOC loss in the LLP, the increased TOC in the acid solution might have been due to volatile organic matter and also as already discussed the crossing of the permeate into the acid solution side also increased the TOC content, which was more severe during the wet out batches corresponding to batches 7 through 9 and by the end of batch 9 the TOC concentration was almost 6 times higher than the TOC in the landfill leachate permeate.

3.4.2.3. Effect of pH control solution on ammonium sulfate enrichment

The evaluated process was not only limited by the identified critical N concentration of about 500 mg/L with respect to the reduction efficiency and possible effects on the membrane wet out during operation but also the pH control solution used in the acid solution side might have important effects during the enrichment of ammonium sulfate. As indicated in tables 54 and 55 the average volumes of the 65% and the 95% of pH control sulfuric acid solutions consumed during the 5 h treatment per batch were 386 ± 19 and 216 ± 5 mL respectively. Therefore by increasing the pH control solution concentration to about 1,5 times there was about 40% decreased in volume of required pH control solution per batch. Furthermore, by assuming the ideal case of hydrophobic membrane during operation and by considering a fixed amount of transfer N of about $61,28 \pm 0,14$ g per batch and the fixed consumed volumes of pH control H_2SO_4 (65 & 95%) solutions, it was calculated that as the process advances the percentage increase of ammonium sulfate concentration in between batches decreases with each batch reaching values below the 2% also obtained in the wet out batches. The results are given in figure 105.

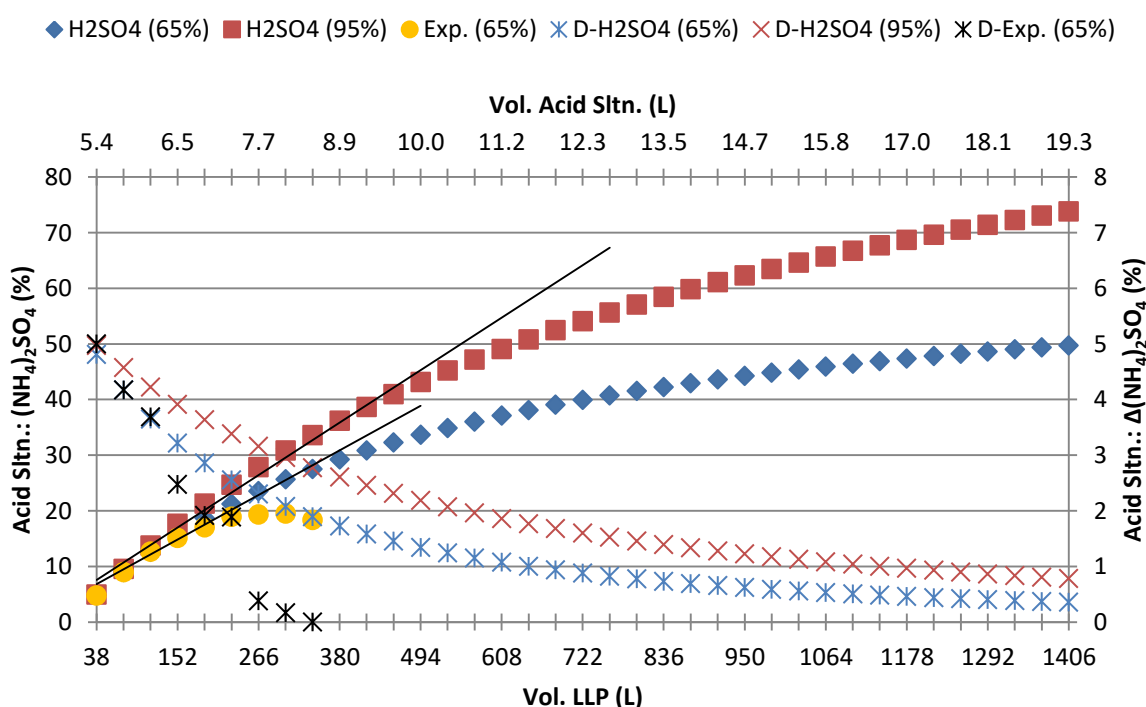


Figure 105. Calculated ammonium sulfate conc. in acid solution based on consumed H_2SO_4 (65 & 95%) as pH control solutions

As indicated in figure 105, based on the linear models, for the ideal case of completely hydrophobic membrane with H_2SO_4 (65%) as pH control solution from the initial acid solution [H_2SO_4 (0,14M)] with volume of 5 L an efficient ammonium sulfate concentration in the acid solution of about 25% could have been achieved with an increased in the ammonium sulfate concentration per batch larger than or about 2%, which corresponded to a permeate volume of about 304 L. Also, with the same pH

control solution an ammonium sulfate concentration of about 50% could have been reached in the acid solution but in order to double the concentration it would have required about 4 times more the volume of about 304 L of permeate. Furthermore, the efficiency in the acid solution might have been improved by the use of H_2SO_4 (95%) as pH control solution where the 2% change in concentration was shift to the right corresponding to an ammonium sulfate concentration in the acid solution of about 40% for about 456 L of treated LLP. Thus, for a volume of 304 L of treated permeate with H_2SO_4 (95%) as pH control solution the concentration of ammonium sulfate in the acid solution could have been about 30%, which corresponded to an increase of 20% with respect to the efficient concentration of 25% estimated for the H_2SO_4 (65%) as pH control solution. Despite the larger efficiency in the acid solution with the concentrated sulfuric acid (95%) as pH control solution operational and safety challenges can be faced during operation for example the need of equipment with very high anticorrosive properties and also the respective personal protective equipment would be require to handle this kind of extreme substance.

3.4.2.4. Ammonium sulfate crystallization

During the evaporation step it was expected that the desire ammonium sulfate saturated solution of about 0,5 Kg/Kg-Sltn at the temperature condition of 95 to 105°C would be reached when the volume in the solution decreased to around 50 mL from the initial volume of 100 mL. This was confirmed experimentally considering the formation of solids when the solution reached the estimated volume of about 50 mL, which were redissolved by the addition of a few milliliters of deionized water. This observation is illustrated in figure 106.



Figure 106. Evaporation step during ammonium sulfate crystallization from concentrated ammonium sulfate solution ($\approx 20\%$)

Then, the close to saturation ammonium sulfate solution at the temperature range of 95 to 105°C was transfer to the ice bath with temperature range in between 5 to 10°C for cooling crystallization. The crystals formed are illustrated in figure 107.

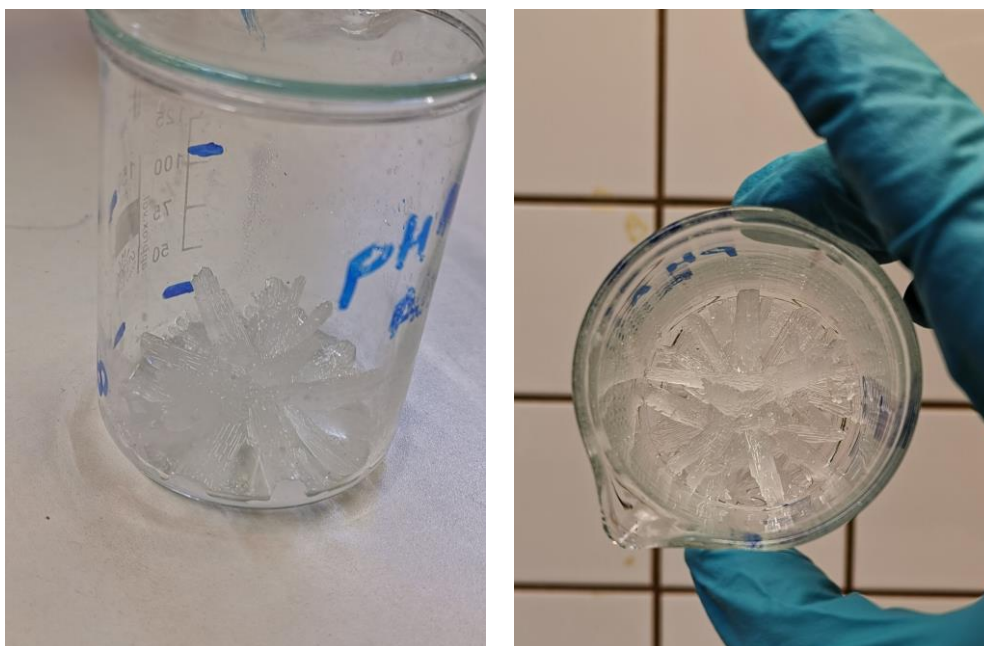


Figure 107. Crystals formed from concentrated ammonium sulfate solution ($\approx 20\%$)

After the air-drying step, the collected crystals were homogenized for XRD analysis. The obtained ammonium sulfate crystals and their X-ray diffraction pattern are given in figures 108 and 109 respectively.



Name:	Mascagnite	Lecontite
Formula:	$(\text{NH}_4)_2\text{SO}_4$	$(\text{K,Na})\text{NH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$

Figure 108. Ammonium sulfate crystals obtained from the concentrated ammonium sulfate solution ($\approx 20\%$) recovered from the LLP with the membrane contactor

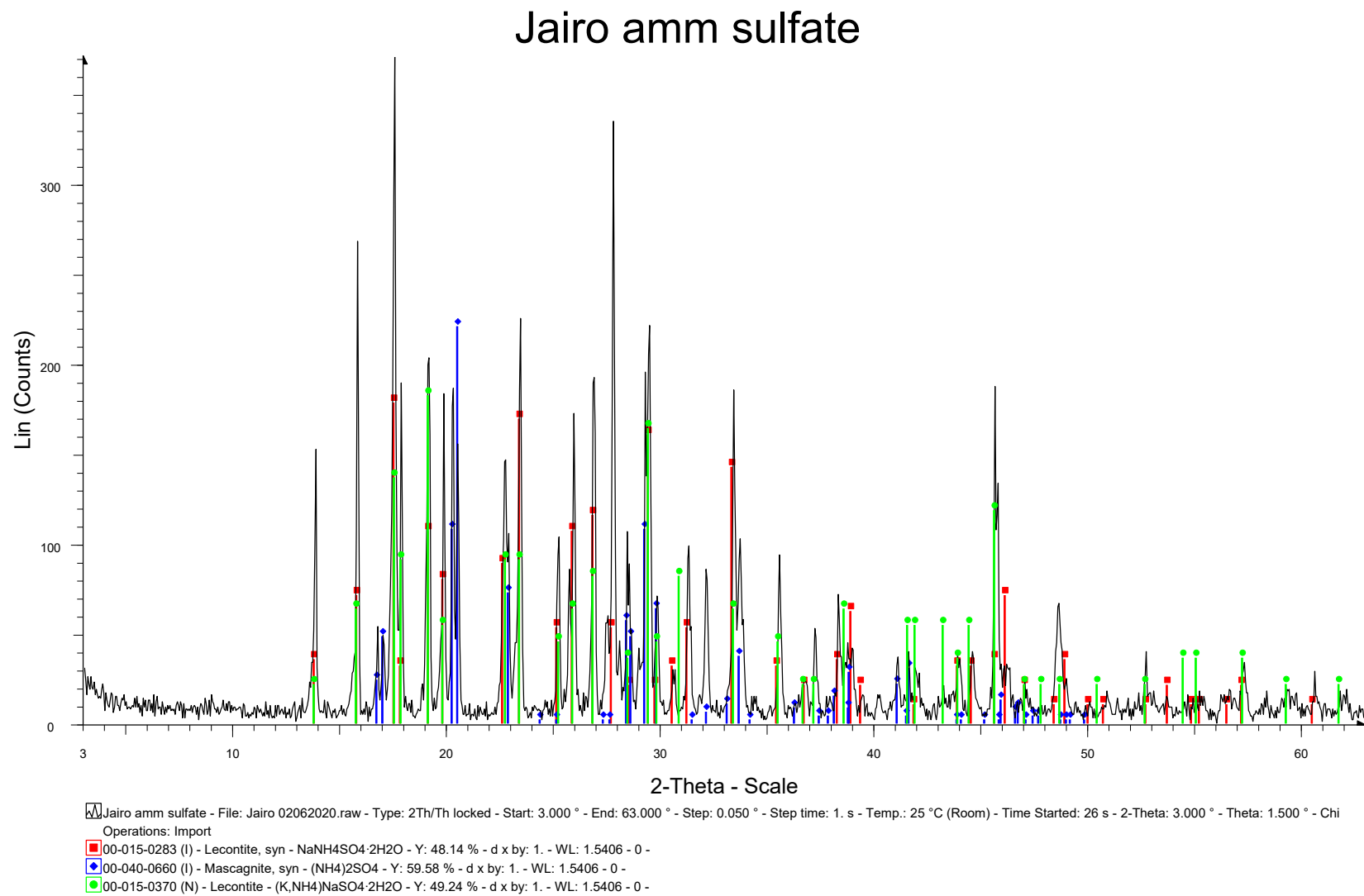


Figure 109. X-ray diffraction pattern for ammonium sulfate crystals obtained from the concentrated ammonium sulfate solution ($\approx 20\%$) recovered from the LLP with the membrane contactor

3.5. BIOLOGICAL REMOVAL OF NUTRIENTS IN FIXED-BED BIOREACTORS

3.5.1. Materials and Methods

The fixed-bed bioreactors (FBBs) used during the nitrification and denitrification treatment of the landfill leachate permeates were operated in batch mode for about 2 years and 6 months respectively. Initially, the development of biofilm on the packing material started by using the ROP and collected nitrification treated landfill leachate mixed-permeates in the nitrification and denitrification FBBs respectively. The nitrification bioreactor was inoculated with supernatant from activate sludge collected from a local wastewater treatment facility and the denitrification bioreactor was inoculated with landfill leachate collected from the landfill leachate treatment facility after a biological treatment stage.

The evaluated batches were analyzed after a stable biofilm and/or regular AOR and DNR were reached in both bioreactors at the corresponding operating conditions, which included biofilm maturation and also adaptation batches performed every time working conditions such as pH and salinity were changed during the study. Furthermore, the salinity in the treated permeates were adjusted by mixing the corresponding volume ratios of the LLP with the ROP where volumes of $12,0 \pm 1,0$ L and $13,0 \pm 1,0$ L of the permeates and/or mixed-permeates were treated in the nitrification and denitrification bioreactors respectively.

Moreover, during the biological treatment the pH controllers were set at the evaluated pH conditions of 6,5, 7,5 and 8,5 and the selected pH value was kept relatively constant during nitrification by the used of Na_2CO_3 (100g/L) and H_2SO_4 (1M) solutions and during denitrification by the used of HCl (1M) solution. Also, before the start of each batch the pH in the permeate was adjusted to the desire pH value by using either NaOH (2M) or HCl (1M) solutions.

Furthermore, for the denitrification batches methanol (Me-OH) and Na_3PO_4 were used as exogenous C- and P-sources where the added volume of methanol with value of 27 ± 1 mL was calculated based on a COD to $\text{NO}_3\text{-N}$ ratio of 4 and the Na_3PO_4 was added to keep a $\text{PO}_4\text{-P}$ concentration in the system of about 5 mg/L. Furthermore, for the batches evaluated during the effect of DO, salinity and $\text{NH}_4\text{-N}$ concentration on nitrification and the effect of pH on denitrification the liquid flow rate was maintained at 100 ± 10 L/h ($12,7 \pm 1,3$ m/h) and for the effect of pH on nitrification the liquid flow rate was kept at 170 ± 10 L/h ($21,6 \pm 1,3$ m/h). Moreover, during nitrification treatment based on the evaluated conditions the DO was maintained at concentration ranges of <1, 2 to 3 and >5 mg/L with the help of an air flow controller and its respective software and during denitrification the DO was kept below 0,5 mg/L.

The specifications of the packing material and the FBBs used during nitrification and denitrification are illustrated in tables 58 and 59 respectively.

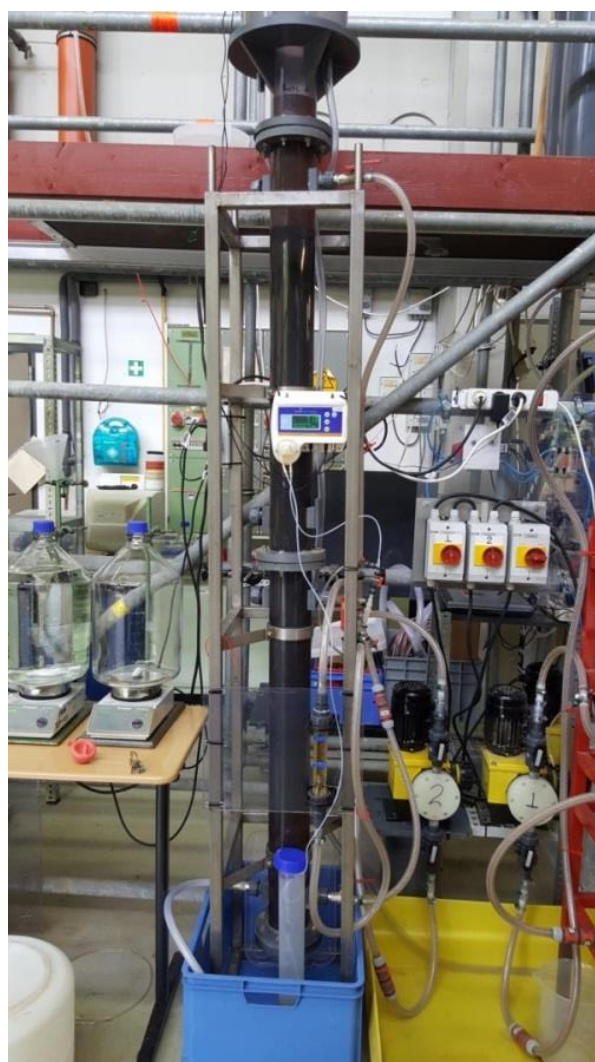
The raw data, and the analytical methods and equipment used during the biological treatment are given in appendices G, A and B respectively.

Table 58. Specifications of packing material used in bioreactors



Material:	Polyethylene
SSA \approx	$660 \text{ m}^2/\text{m}^3$
Diameter:	$12,3 \pm 0,5 \text{ mm}$
Height:	$12,1 \pm 0,5 \text{ mm}$

Table 59. Specifications of bioreactors and setups used during Nitrification and Denitrification for the treatment of landfill leachate permeates



Nitrification	Denitrification
Column ID: 100 mm	Column ID: 100 mm
Column material: PVC _{clear}	Column material: PVC _{clear}
Height _{Biofilter} $\approx 760 \pm 10 \text{ mm}$	Height _{Biofilter} $\approx 1440 \pm 10 \text{ mm}$
Vol. Biofilter $\approx 6 \text{ L}$	Vol. Biofilter $\approx 11 \text{ L}$

3.5.2. Results and Discussion

3.5.2.1. Effect of DO, salinity and $\text{NH}_4\text{-N}$ concentration on Nitrification with LLP and ROP

The composition of the feed permeates to the nitrification bioreactor were analyzed before each of the evaluated batches. The average pH and T of the feed permeates were equal to $6,5 \pm 0,3$ and 20 ± 1 °C respectively and during nitrification treatment the pH was adjusted and kept at an approximate value of 7,5 with the help of the pH controllers. The results obtained in the chemical analysis for the reverse osmosis (ROP), landfill leachate (LLP) and mixed-permeates are given in table 60.

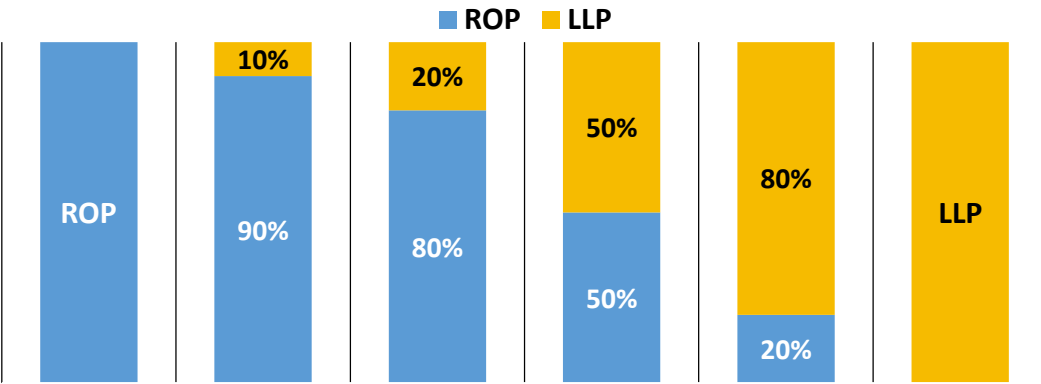
Table 60. Composition analysis in the feed permeates to the bioreactor during the effect of DO, salinity and $\text{NH}_4\text{-N}$ conc. on Nitrification with LLP and ROP

Substance/ Parameter	ROP	10% LLP	20% LLP	50% LLP	80% LLP	LLP
$\text{NH}_4\text{-N:}$ (mg/L)	$68,9 \pm 3,4$	244 ± 12	409 ± 20	1065 ± 53	1510 ± 76	2010 ± 101
$\text{NO}_2\text{-N:}$ (mg/L)	$<0,6$	$<0,6$	$<0,6$	$<0,6$	$<0,6$	$<0,6$
$\text{NO}_3\text{-N:}$ (mg/L)	$<0,23$	$<0,23$	$<0,23$	$<0,23$	$<0,23$	$<0,23$
$\text{PO}_4\text{-P:}$ (mg/L)	$<0,5$	$0,90 \pm 0,04$	$1,7 \pm 0,1$	$5,2 \pm 0,3$	$11,2 \pm 0,6$	$13,2 \pm 0,7$
COD: (mg/L)	131 ± 13	713 ± 71	1245 ± 125	2890 ± 289	5380 ± 538	6870 ± 687
TOC: (mg/L)	$25,0 \pm 2,5$	160 ± 16	298 ± 30	682 ± 68	1284 ± 128	1609 ± 161
TN: (mg/L)	$74,2 \pm 3,7$	273 ± 14	456 ± 23	1140 ± 57	1609 ± 80	2088 ± 104

As illustrated in table 60, the concentration of $\text{NH}_4\text{-N}$ in the different feed permeates ranged approximately in between 70 to 2000 mg/L where in average the $\text{NH}_4\text{-N}$ to TN ratio was approximately equal to $0,91 \pm 0,02$, which indicated that the organic-N content in the different permeates was about 9% considering that the concentration of the other inorganic N species including NO_2 and NO_3 were very low. Also the COD concentration range was very wide from about 130 to 6900 mg/L with an average TOC to COD ratio of $0,23 \pm 0,01$. Furthermore, the LLP and ROP used during the biological treatment were collected at different times of the year; hence some of the concentrations and/or parameters especially for the case of TOC and COD do not correlate exactly with the volumetric relations. However, most of the obtained values are within the estimated 10% errors.

Furthermore, the operating conditions measured during the nitrification treatment of the permeates and mixed-permeates at the different volumetric ratios are described in table 61.

Table 61. Operating conditions measured during effect of DO, salinity and $\text{NH}_4\text{-N}$ conc. on Nitrification with LLP and ROP



	ROP	10% LLP	20% LLP	50% LLP	80% LLP	LLP
$t_{\text{Treat.}} (d)$	3	13	5	11	30	90
$\text{Vol.}_{\text{Treat.}} (L)$	12 ± 1	12 ± 1	12 ± 1	12 ± 1	12 ± 1	12 ± 1
Salinity: (dS/m)	$2,8 \pm 0,3$	$13,1 \pm 0,3$	$22,5 \pm 0,3$	$49,0 \pm 0,3$	$78,1 \pm 0,4$	$90,5 \pm 0,4$
DO: (mg/L)	<1	<1	2 – 3	2 – 3	>5	>5
pH:	$7,5 \pm 0,3$	$7,5 \pm 0,3$	$7,5 \pm 0,3$	$7,5 \pm 0,3$	$7,5 \pm 0,3$	$7,5 \pm 0,3$
T: ($^{\circ}\text{C}$)	19 ± 1	20 ± 2	24 ± 1	22 ± 1	20 ± 1	22 ± 1
$V_{\text{Liq.}} (m/h)$	$12,7 \pm 1,3$	$12,7 \pm 1,3$	$12,7 \pm 1,3$	$12,7 \pm 1,3$	$12,7 \pm 1,3$	$12,7 \pm 1,3$

As indicated in table 61, in order to properly correlate the effect of DO in the treated permeate by substrate limitation, only the ROP and the 10% LLP mixed-permeates were analyzed at the low DO concentration range considering that the $\text{NH}_4\text{-N}$ concentration and salinity were relatively low ranging approximately in between 70 to 250 mg/L and 2,5 to 13,0 dS/m respectively. Thus, minimizing potential inhibitions during nitrification due to the presence of FA, FNA and organic and/or inorganic toxic substances. For instance, for FA based on the $\text{NH}_4\text{-N}$ concentration of 250 mg/L and figure 12 at pH and T values of 7,5 and 20°C the concentrations of FA during nitrification in the ROP and 10% LLP mixed-permeates were below 10 mg/L, which as indicated in section 2.5, around this value FA might have inhibition effects in AOB. Furthermore, as indicated in table 15 the concentration of Ni, Cr and Cu in the LLP were about 0,68 mg/L and smaller than 0,2 and 0,08 mg/L respectively, which also as discussed in section 2.5, these concentration values were higher or close to the reported concentration levels of 0,25, 0,25 and 0,1 mg/L for Ni, Cr and Cu respectively where inhibition of ammonia oxidation might take place. Moreover, the pH, T and liquid superficial velocity in the evaluated batches were relatively close to each other during the nitrification treatment.

The results obtained in nitrification during the treatment of the permeates for each of the evaluated conditions of DO and different $\text{NH}_4\text{-N}$ and salinity concentrations are given in figures 110 through 115.

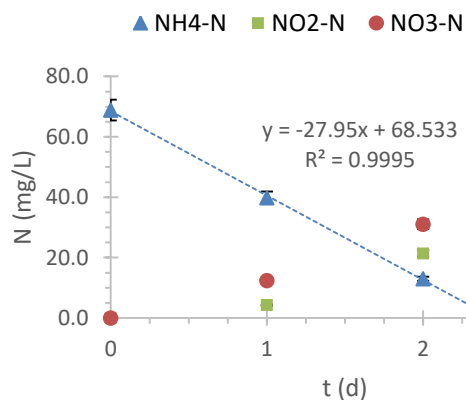


Figure 110. Nitrification in ROP; pH: $7,5 \pm 0,3$; Salinity: $2,8 \pm 0,3$ dS/m; DO: < 1 mg/L; v_{Liq} : $12,7 \pm 1,3$ m/h; T: $19 \pm 1^\circ\text{C}$

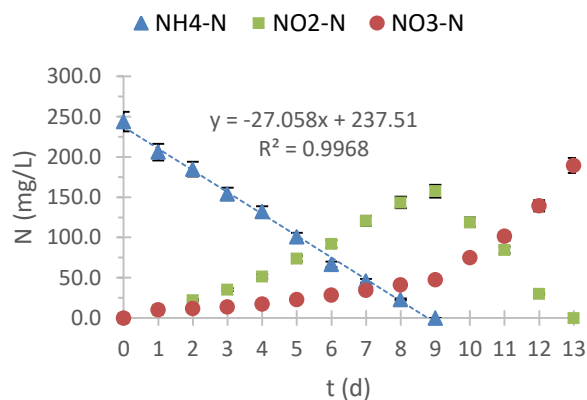


Figure 111. Nitrification in 10% LLP; pH: $7,5 \pm 0,3$; Salinity: $13,1 \pm 0,3$ dS/m; DO: < 1 mg/L; v_{Liq} : $12,7 \pm 1,3$ m/h; T: $20 \pm 2^\circ\text{C}$

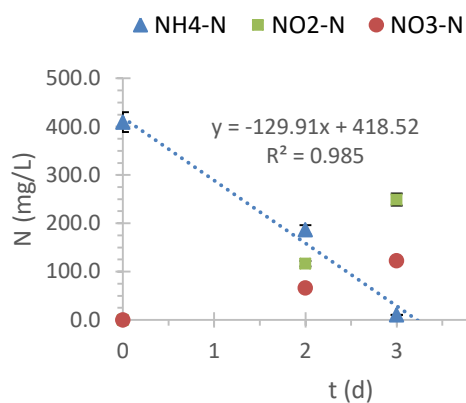


Figure 112. Nitrification in 20% LLP; pH: $7,5 \pm 0,3$; Salinity: $22,5 \pm 0,3$ dS/m; DO: $2 - 3$ mg/L; v_{Liq} : $12,7 \pm 1,3$ m/h; T: $24 \pm 1^\circ\text{C}$

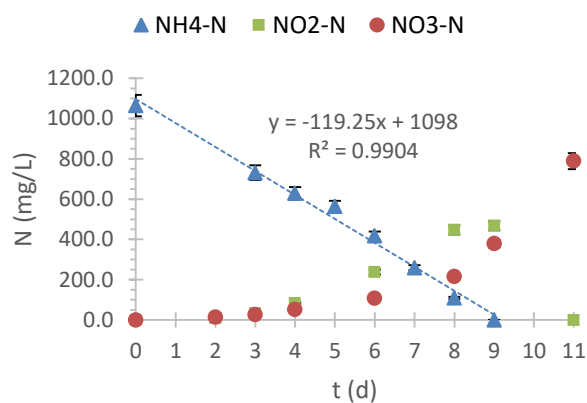


Figure 113. Nitrification in 50% LLP; pH: $7,5 \pm 0,3$; Salinity: $49,0 \pm 0,3$ dS/m; DO: $2 - 3$ mg/L; v_{Liq} : $12,7 \pm 1,3$ m/h; T: $22 \pm 1^\circ\text{C}$

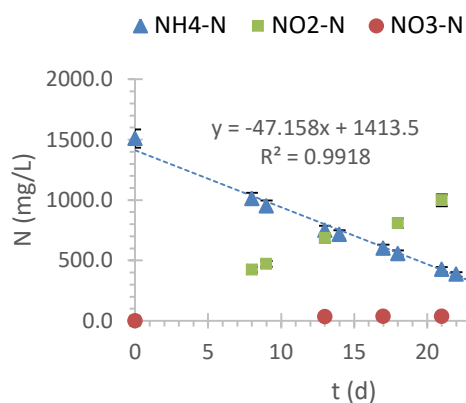


Figure 114. Nitrification in 80% LLP; pH: $7,5 \pm 0,3$; Salinity: $78,1 \pm 0,4$ dS/m; DO: > 5 mg/L; v_{Liq} : $12,7 \pm 1,3$ m/h; T: $20 \pm 1^\circ\text{C}$

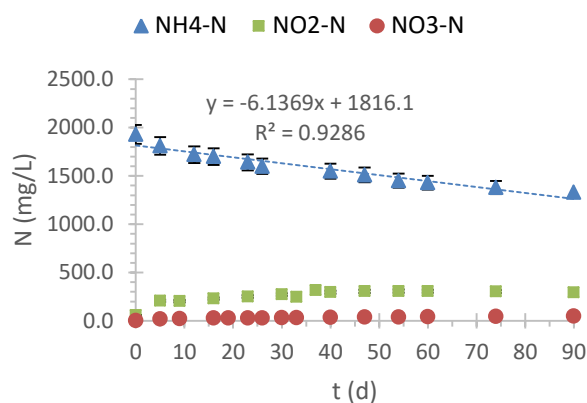


Figure 115. Nitrification in LLP; pH: $7,5 \pm 0,3$; Salinity: $90,5 \pm 0,4$ dS/m; DO: > 5 mg/L; v_{Liq} : $12,7 \pm 1,3$ m/h; T: $22 \pm 1^\circ\text{C}$

As illustrated in figures 110 through 113 at the relatively similar operating conditions the AORs were independent of the initial $\text{NH}_4\text{-N}$ concentrations in the permeates, which based on the linear regressions with R^2 values of about 0,99 obtained from the concentration data as a function of time indicated linearity, which is characteristic of a

zero-order reaction. Also, as discussed in section 2.5 the obtained results correlated with the Monod model, which indicates low specific grow rates of microorganisms at low substrate concentration; hence the AOR estimated for the low DO concentration batches corresponding to ROP and 10% LLP decreased in average 79% with respect to the AOR obtained in the 20% LLP mixed-permeates batch. Furthermore, the AOR in the 20% LLP was about 10% higher than the AOR in the 50% LLP, this increase in the AOR might be correlated not only with the lower salinity but also with the slightly higher temperature condition in the 20% LLP considering that as discussed in section 2.5 for the case of AOB about 10% increase in the specific grow rate could be expected for an increase in 1°C. Moreover, based on salinity, no considerable inhibition was observed for the AOB up to the value of about 50 dS/m. But, inhibition by toxicity was observed in the AOB with salinity values of about 78 and 90 dS/m where even with DO concentrations above 5 mg/L their estimated AOR with respect to the 20% LLP batch decreased to 64 and 95% respectively. Furthermore, during the treatment of the 80% LLP batch with salinity of 78 dS/m severe nitrite accumulation was observed, which indicated very low activity of NOB and during the treatment of the LLP with salinity of about 90 dS/m the activities of both AOB and NOB were severely affected. Hence, complete nitrification or conversion from $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ was only possible at the different salinity conditions up to the 50% LLP batch with salinity value of about 49 dS/m where in average about $76\pm 2\%$ of the initial $\text{NH}_4\text{-N}$ was converted to $\text{NO}_3\text{-N}$. Additionally, for the batches up to the 50% LLP the average TOC percentage removed during nitrification treatment was equal to $50\pm 4\%$. The effect of salinity, DO and initial $\text{NH}_4\text{-N}$ concentration on Nitrification are summarized in figure 116, the percentage decreased in the estimated AORs was calculated with respect to the AOR value of about 130 mg/L·d obtained in the mixed-permeate with salinity of $22,5\pm 0,3$ dS/m corresponding to the 20% in volume LLP.

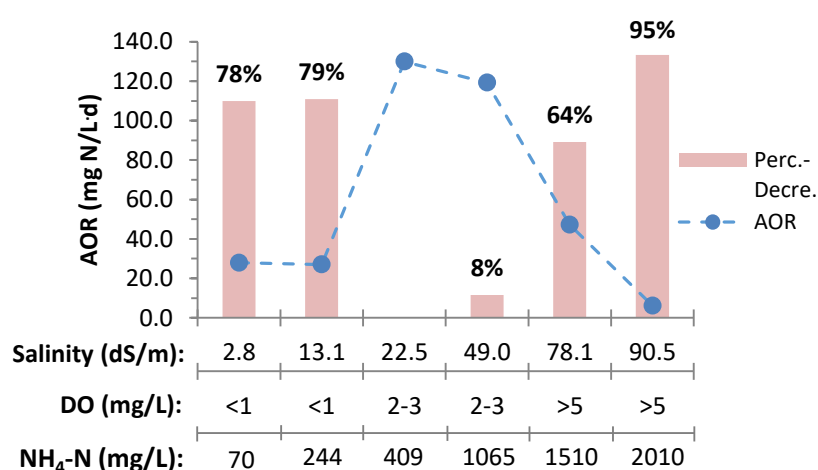


Figure 116. AOR in FBB with LL mixed-permeates during effect of DO, salinity and $\text{NH}_4\text{-N}$ conc. on Nitrification at pH: $7,5\pm 0,3$; $v_{\text{Liq.}}$: $12,7\pm 1,3$ m/h; T: $21\pm 2^\circ\text{C}$

Furthermore, based on salinity and considering the complex composition of the LLP and the potential inhibition effect of other substances, for the case of 80% LLP and LLP it was unclear to determine how large was the effect of salt toxicity in the nitrifying microorganisms but it did provide a reference point with respect to the AOB tolerance for the landfill leachate permeate. The AOR results obtained for the mixed-permeates and LLP with salinity values in between 20 to 90 dS/m are illustrated in figure 117.

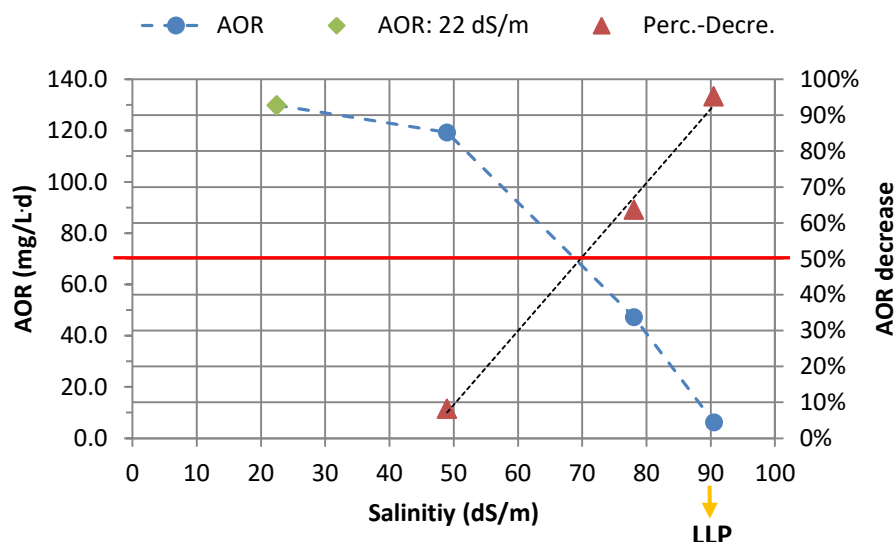


Figure 117. AOB tolerance with respect to salinity in LLP

As indicated in figure 117, based on the linear trend and with respect to the mixed-permeate with salinity of about 22 dS/m less than 10% of the AOB activity or AOR was affected up to salinity values of about 50 dS/m but more than 50% of their activity was lost at salinity conditions of 78 dS/m and reaching a 95% decrease in the AOR with the LLP. Hence, a decrease of less than 50% in AOB activity or AOR might be expected with landfill leachate permeates at salinity conditions ranging in between 50 to 70 dS/m.

3.5.2.2. Effect of pH on Nitrification and Denitrification

3.5.2.2.1. Effect of pH on Nitrification

In order to better evaluate potential inhibitions at the analyzed pH conditions of 6,5, 7,5 and 8,5 during nitrification, the transport of substrates to the biofilm was enhanced by operating at a liquid superficial velocity of about $21,6 \pm 1,4$ m/h and keeping the DO concentration at levels greater than 5 mg/L. The initial composition of the feed permeates are given in table 60 for the 50% LLP and the operating conditions measured during nitrification treatment are described in table 62.

Table 62. Operating conditions measured during effect of pH on Nitrification with 50% LLP mixed-permeates

pH:	6,5±0,1	7,5±0,1	8,5±0,1
t _{Treat.} (d):	15	5	6
Vol. _{Treat.} (L):	12±1	12±1	12±1
Salinity (dS/m):	49,4±1,3	49,3±1,2	49,6±1,1
DO (mg/L):	>5,0	>5,0	>5,0
T (°C):	23±1	21±1	21±1
v _{Liq.} (m/h):	21,6±1,4	21,6±1,4	21,6±1,4

Table 62, shows that except for the pH values all other working conditions were very similar during the nitrification treatment of the mixed-permeates with 50% LLP in volume and salinity of about 50 dS/m. The results obtained during the biological conversion of NH₄-N to NO₂-N and to NO₃-N are illustrated in figures 118, 119 and 120 for the pH conditions of 6,5, 7,5 and 8,5 respectively.

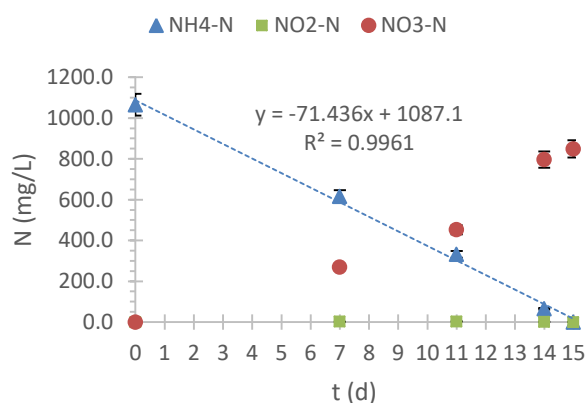


Figure 118. Nitrification at pH 6,5±0,1 with 50% LLP; Salinity: 49,4±1,3 dS/m; DO: > 5 mg/L; v_{Liq.}: 21,6±1,4 m/h; T: 23±1°C

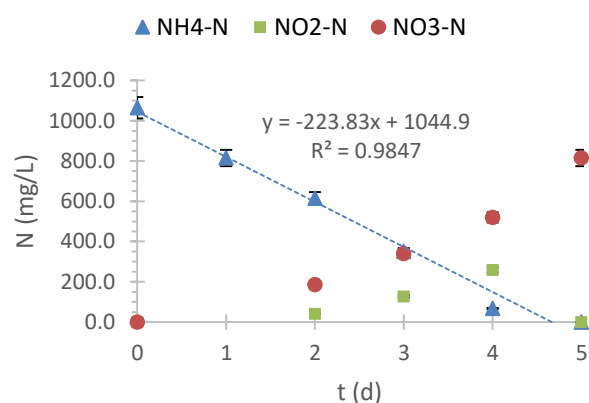


Figure 119. Nitrification at pH 7,5±0,1 with 50% LLP; Salinity: 49,3±1,2 dS/m; DO: > 5 mg/L; v_{Liq.}: 21,6±1,4 m/h; T: 21±1°C

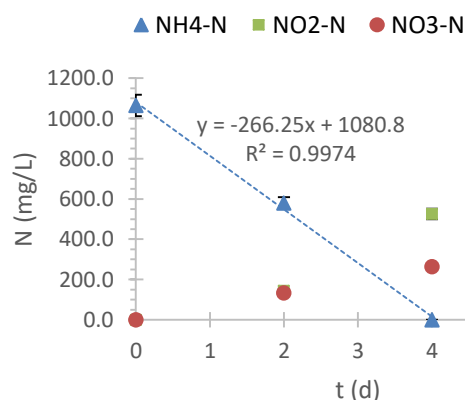


Figure 120. Nitrification at pH 8,5±0,1 with 50% LLP; Salinity: 49,6±1,1 dS/m; DO: > 5 mg/L; v_{Liq.}: 21,6±1,4 m/h; T: 21±1°C

As seen in figures 118 through 120, the nitrifying microorganisms had opposite responses with respect to the evaluated pH conditions in the mixed-permeates with salinity of about 50 dS/m. For instance, at pH 8,5 the activity of the AOB was the highest since for the same volume of permeate it oxidized the initial $\text{NH}_4\text{-N}$ concentration of about 1065 ± 53 mg/L within the 4 days of treatment being longer for the other pH conditions of 7,5 and 6,5, which took almost 5 and about 15 days of treatment respectively. On the other hand, for the case of the NOB accumulation of $\text{NO}_2\text{-N}$ was not observed at pH 6,5 but for the case of pH 7,5 and 8,5, the $\text{NO}_2\text{-N}$ concentration reached peak values of about 250 and 500 mg/L respectively. The results obtained in the estimated AORs at the different pH conditions are illustrated in figure 121.

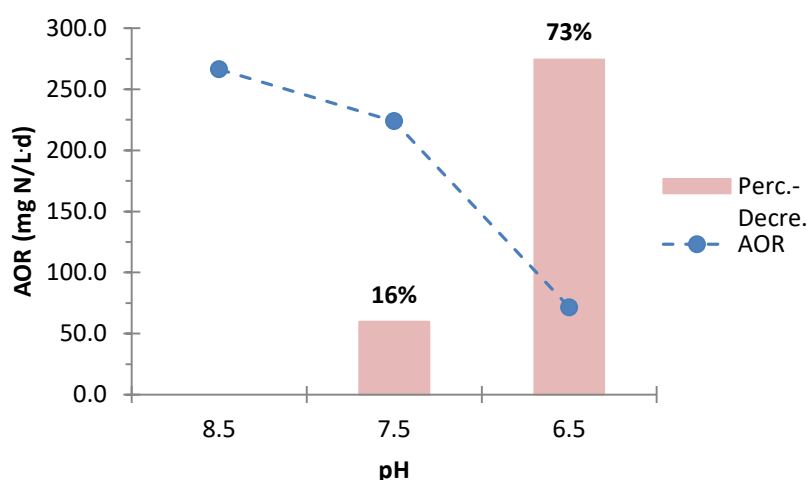


Figure 121. AOR in FBB with LL mixed-permeates 50% LLP in volume during effect of pH on Nitrification at Salinity: $49,4 \pm 1,2$ dS/m; $\text{DO} > 5,0$ mg/L; $v_{\text{Liq.}}$: $21,6 \pm 1,4$ m/h; T : $21 \pm 1^\circ\text{C}$

As indicated in figure 121, the highest AOR with value of 266 mg/L·d was obtained at the pH condition of 8,5 and started to decrease with the decrease of pH with estimated AOR values of 224 and 71 mg/L·d at pH 7,5 and 6,5, which corresponded to percentage decreases of about 16 and 73% respectively. The comparison, between the inhibitions cases with respect to the AORs percentage decrease are illustrated in figure 122.

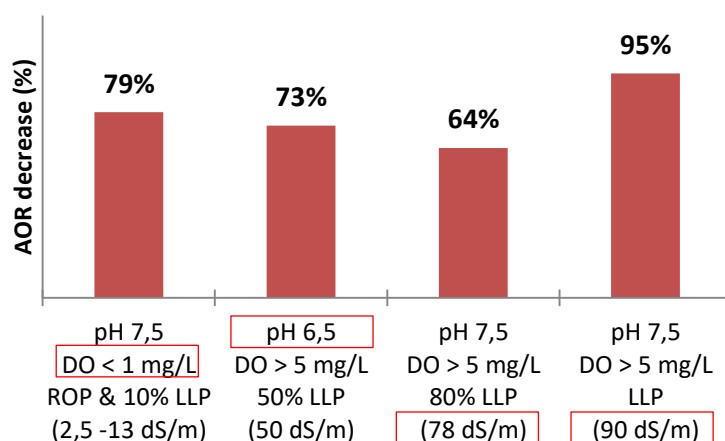


Figure 122. Inhibition cases during nitrification and their effect in AOR

As seen in figure 122, based on the percentage decreased in the AOR obtained at pH 6,5 it was seen that the inhibition at this pH condition was comparable to the inhibitions by DO limitation and mixed-permeate with salinity of 78 dS/m where the 73% decreased in AOR at pH 6,5 was almost in between the 79 and 64% in AOR decrease obtained in the cases of substrate limitation and toxicity inhibition respectively.

Furthermore, from the initial $\text{NH}_4\text{-N}$ concentration, an average of $77\pm 2\%$ was converted to $\text{NO}_3\text{-N}$ and from the initial TOC concentration of 682 ± 68 mg/L in average about $50\pm 2\%$ was removed during nitrification treatment at the evaluated pH conditions, which were very consistent with the results obtained in the previous analyzed batches. Additionally, as indicated in figures 113 and 119 for the 50% LLP at approximately the same pH, T and salinity conditions and assuming little influence by DO excess it was observed that in the FBB the increase of almost two times the liquid flow rate from about 13 to 22 m/h yielded almost the same increase in the AORs from about 119 to 224 mg/L·d.

3.5.2.2.2. Effect of pH on Denitrification

The nitrification treated landfill leachate mixed-permeates were collected and further treated in the denitrification FBB for the removal of N. The operating conditions with the exception of pH during the denitrification treatment were kept relatively constant. The parameters measured during denitrification at the evaluated pH conditions of 6,5, 7,5 and 8,5 are given in table 63.

Table 63. Operating conditions during effect of pH on Denitrification with mixed-permeates

pH:	6,5±0,2	7,5±0,2	8,5±0,2
t_{Treat.} (h):	25	32	56
Vol._{Treat.} (L):	13±1	13±1	13±1
Vol._{Me-OH} (mL):	27±1	27±1	27±1
Salinity (dS/m):	38,1±0,5	38,1±0,5	37,9±0,5
DO (mg/L):	<0,5	<0,5	<0,5
T (°C):	20±1	20±1	20±1
v_{Liq.} (m/h):	12,7±1,3	12,7±1,3	12,7±1,3

As indicated in table 63, the DO concentration was less than 0,5 mg/L; hence anoxic conditions were kept along the denitrification treatment and the biofilm was adapted to treat the collected mixed-permeates with salinity of about 38 dS/m at a liquid superficial velocity of about 13 m/h at each of the evaluated pH conditions.

The average composition of the collected mixed-permeates after nitrification treatment and before methanol (Me-OH) addition fed to the denitrifying FBB are given in table 64.

Table 64. Composition in mixed-permeates fed to denitrifying FBB before Me-OH addition

Substance/ Parameter	Mixed-permeates (LLP&ROP)
TN (mg/L):	668±33
NO ₂ -N (mg/L):	<0,6
NO ₃ -N (mg/L):	622±31
PO ₄ -P (mg/L):	0,51±0,06
COD (mg/L):	895±45
TOC (mg/L):	216±11

As seen in table 64, the average ratios of TOC to COD and NO₃-N to TN in the mixed-permeates were approximately equal to $0,23 \pm 0,01$ and $0,91 \pm 0,02$ respectively, which were similar to the ratios obtained in the permeates before nitrification treatment. Furthermore, due to the relatively low PO₄-P concentration in the mixed-permeates of 0,5 mg/L about 0,1 to 0,5 g of Na₃PO₄ were added to the feed permeates in order to keep a PO₄-P concentration during the treatment of about 5 mg/L, which as indicated in table 60 was approximately equal to the initial PO₄-P concentration corresponding to the 50% LLP before nitrification treatment.

The results obtained during the denitrification treatment are given in figures 123 through 125.

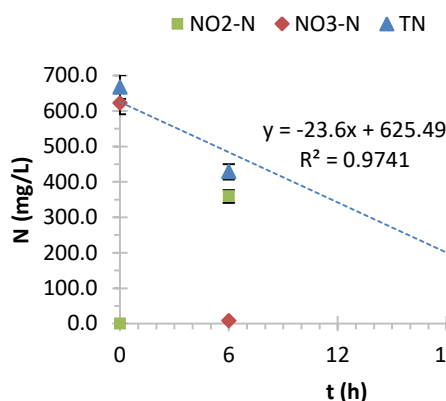


Figure 123. Denitrification at pH $6,5 \pm 0,1$ with mixed-P;
Salinity: $38,1 \pm 0,5$ dS/m; DO: $< 0,5$ mg/L; $v_{\text{Liq.}}$: $12,7 \pm 1,3$ m/h;
C-source: Me-OH; T: $20 \pm 1^\circ\text{C}$

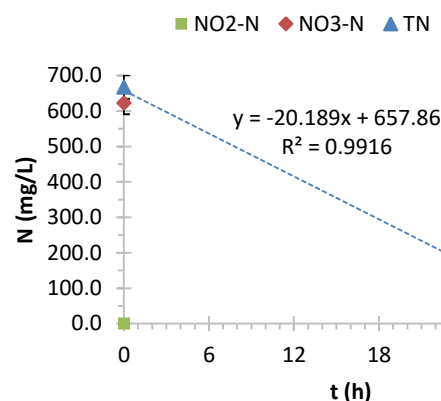


Figure 124. Denitrification at pH $7,5 \pm 0,1$ with mixed-P;
Salinity: $38,1 \pm 0,5$ dS/m; DO: $< 0,5$ mg/L; $v_{\text{Liq.}}$: $12,7 \pm 1,3$ m/h;
C-source: Me-OH; T: $20 \pm 1^\circ\text{C}$

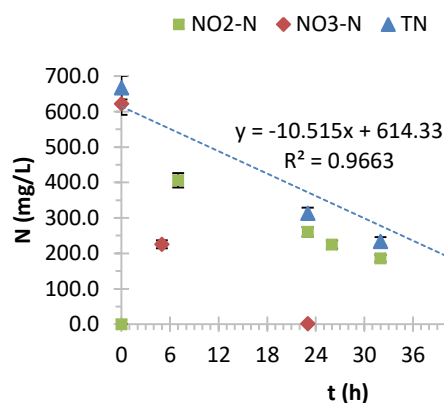


Figure 125. Denitrification at pH 8.5 ± 0.1 with mixed-P; Salinity: 37.9 ± 0.5 dS/m; DO: < 0.5 mg/L; $v_{\text{Liq.}}$: 12.7 ± 1.3 m/h; C-source: Me-OH; T: $20 \pm 1^\circ\text{C}$

As illustrated in figure 123 through 125, in the FBB at the end of denitrification treatment at the analyzed pH conditions more than 99% of the inorganic nitrogen including NO₃-N and NO₂-N was removed from the landfill leachate mixed-permeates. Furthermore, the TN concentration measured at the end of the denitrification treatment with average value of 52.2 ± 3.9 mg/L corresponded to an approximate 8% of the initial TN concentration with value of 668 ± 33 mg/L, which correlated well with the estimated organic-N concentration in the feed mixed-permeates of about 9% of the initial TN concentration. Moreover, with respect to the effect of pH on the rate of N consumed by the facultative heterotrophic microorganisms or denitrification rate (DNR) based on the TN concentration it was seen that the highest DNR was achieved at the pH condition of 6,5 followed by pH 7,5 and 8,5. The effect of pH in the DNR is illustrated in figure 126.

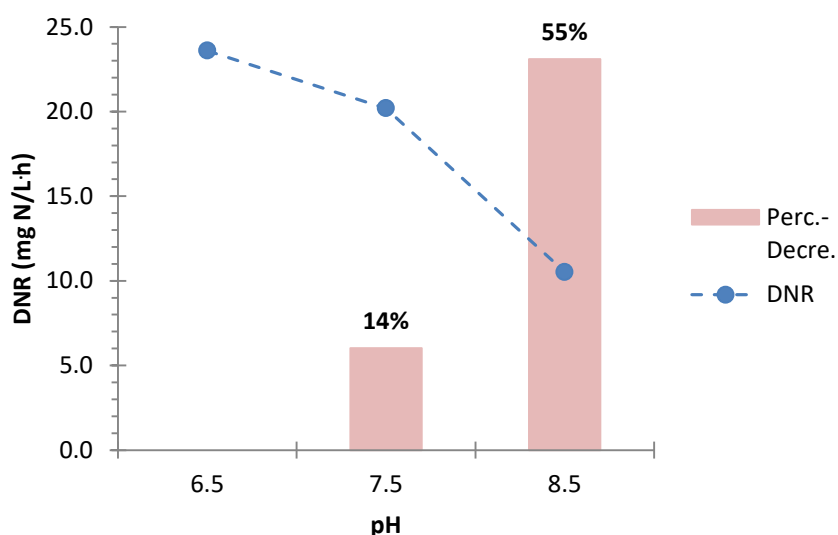


Figure 126. Effect of pH on denitrification rate (DNR) in FBB with LL mixed-permeates at Salinity: 38.0 ± 0.5 dS/m; DO: < 0.5 mg/L; $v_{\text{Liq.}}$: 12.7 ± 1.3 m/h; C-source: Me-OH; T: $20 \pm 1^\circ\text{C}$

Figure 126, indicated that based on the estimated DNR value of 23,6 mg-N/L·h obtained at the pH condition of 6,5, the DNR decreased about 14 and 55% with DNR values of about 20,2 and 10,5 mg-N/L·h at the pH conditions of 7,5 and 8,5 respectively. Thus, the denitrification system performed better at the pH condition of 6,5, which based on nitrification this pH value was more favorable for the NOB but considerably affected the activity of the AOB; hence decreasing the efficiency of the nitrification treatment or the AOR. Additionally, the TOC concentration measured at the end of the denitrification treatment with average value of 344 ± 17 mg/L was about 60% higher than the initial TOC concentration of 216 ± 11 mg/L indicated in table 64. But, based on the average 50% TOC removed during nitrification, even with the addition of organic-C in the form of Me-OH, at the end of the biological Nitrification/Denitrification treatment overall about 20% of the TOC load was still removed from the permeates.

CHAPTER 4: INTEGRATION OF EVALUATED PROCESSES WITH THE LANDFILL LEACHATE TREATMENT FACILITY

Based on the results obtained from the experimental work and data analysis the evaluated unit operations were integrated with the NF-stage from the landfill leachate treatment facility, which has the landfill leachate concentrate as the input stream in a process flow diagram (PFD) named in this Doctoral work as “Alternative Sustainable Approach”.

The proposed flow diagram for the recovery of Ca and NH_3 from the landfill leachate permeate as CaCO_3 -rich solids and concentrated $(\text{NH}_4)_2\text{SO}_4$ solutions ($\approx 20\text{-}40\%$) was divided into two sections. The first section included the unit operations where the recovery of substances takes place, which included the precipitation and membrane contactor units and in the second section a membrane bioreactor (MBR) was proposed where nitrification or nitrification/denitrification FBBs are integrated with a RO-stage ($P \approx 60$ bars) for the efficient removal of nutrients from the treated permeate. The main characteristic of the second section is that the proposed MBRs are given as an alternative to the high pressure RO systems (HPRO - $P \approx 120$ bars) require for the acceptable removal of TN as indicated in the German landfill regulation to values below 70 mg/L. For instance, for the configuration MBR case of Nitrification FBB/RO-Stage from the MW point of view better membrane selectivity might be expected for $\text{NO}_3\text{-N}$ compared to $\text{NH}_4\text{-N}$ and in the optional proposed MBR with Nitrification/Denitrification-FBBs/RO-stage more than 99% of the inorganic-N might be removed during the biological step before entering the membrane treatment.

Furthermore, in the developed flow diagram steady state conditions were assumed and the flow rates indicated in the PFD were based on the volumetric flow rates corresponding to the NF-stage at the landfill leachate treatment facility where about 50% of the permeate is recovered from the feed landfill leachate concentrate at a flow rate of about $1,3 \text{ m}^3/\text{h}$. Some general advantages and disadvantages of the evaluated processes are given in table 65 and the first and second sections of the integrated process are illustrated in figures 127 and 128 respectively. The assumptions made in each of the evaluated unit operations in the proposed PFD are given in appendix H.

Additionally, the explored application of the recovered CaCO_3 -rich solids included the neutralization or pH correction of acid soil. Thus, by assuming an acid soil bulk density of about $1,8 \text{ g/cm}^3$ (USDA, 2020), field depth of about 1 cm and recovered solids to acid soil mass ratios in between 0,07 and 0,1 the average neutralization dosage was estimated as 15 tonne per hectare, which was equal to the recommended dosage of 15 t/ha for the neutralization of acid rainfall with limestone (Oates, 1998). Furthermore, with the estimated neutralization dosage of 15 t/ha and at a CaCO_3 -rich solids production rate of 120 Kg/d indicated in figure 122 about 0,25 hectares of acid soil can be treated per month or about 1 hectare every four months.

Table 65. Evaluated processes: General advantages and disadvantages

Unit Operation	Advantages	Disadvantages
Adsorption	<ul style="list-style-type: none"> - Removal of pollutants including organic substances and heavy metals from the landfill leachate permeate 	<ul style="list-style-type: none"> - Relatively high PAC dosage for the 50% removal of TOC from the LLP - Management of spent PAC, e.g. Regeneration process
Precipitation	<ul style="list-style-type: none"> - Recovery of CaCO_3-rich solids with relatively low concentration of heavy metals and organic content - Simple and/or relatively economical unit operation - More than 99% of the hardness remove from the landfill leachate permeate - Considerable decrease of scaling might be expected downstream within the membrane systems and reflected on: <ul style="list-style-type: none"> • Less dosage of anti-scaling chemicals • Less frequent maintenance and/or manual cleaning • Less frequent replacement of pre-filters and membranes • Overall, a more efficient membrane process 	<ul style="list-style-type: none"> - Require high dosage of precipitating agents (Na_2CO_3-NaOH) with respect to recovered solids where at pH 12 the ratio of mixed-reagents to recovered solids was about 3 - Handling of recovered solids might be troublesome due to particle size, considering that about 80% of the recovered solids had particle size less than $100\text{ }\mu\text{m}$ - Unknown organic substances making up the organic fraction of the recovered solids - Might require the use of more complex unit operations such as dewatering systems
Membrane Contactor	<ul style="list-style-type: none"> - Recovery of NH_3 from landfill leachate permeate as Concentrated $(\text{NH}_4)_2\text{SO}_4$ Solution (20 – 40%) - More compact process compare to other conventional processes such as NH_3 stripping: <ul style="list-style-type: none"> • The estimated membrane area of 112 m^2 needed to treat approximately $1\text{ m}^3/\text{h}$ of LLP was equivalent to about 80 modules, which only require a space of about $0,1\text{ m}^3$ 	<ul style="list-style-type: none"> - Corrosive operating conditions, need of special equipment for safe operation, e.g. Dosage pumps for pH control solutions: <ul style="list-style-type: none"> • Concentrated H_2SO_4 ($\approx 95\text{-}98\%$) and NaOH ($\approx 50\%$)
Nitrifying and Denitrifying FBBs	<ul style="list-style-type: none"> - Lower footprint compared to other physical conventional processes for the removal of NH_3 and organic load such as stripping and adsorption respectively - Assimilation of pollutants including inorganic-N (NH_4, NO_2 & NO_3) and organic matter within biofilm formed on carrier material - For Nitrification/Denitrification more than 99% of inorganic-N and about 20% of the TOC load removed from the landfill leachate permeates - Less suspended biomass in treated permeate due to retention in biofilter and less require space compared to suspended biological treatment 	<ul style="list-style-type: none"> - Sensitive to changes in operating conditions such as DO, pH and temperature - Sensitive to landfill leachate permeate conditions, for example inhibitions might take place at salinity values greater than 50 dS/m - Removal of biomass from FBBs is required in order to avoid severe biofouling problems downstream within the membrane units, e.g. frequent backwash in bioreactors etc. - Management of generated biomass, for example anaerobically etc.

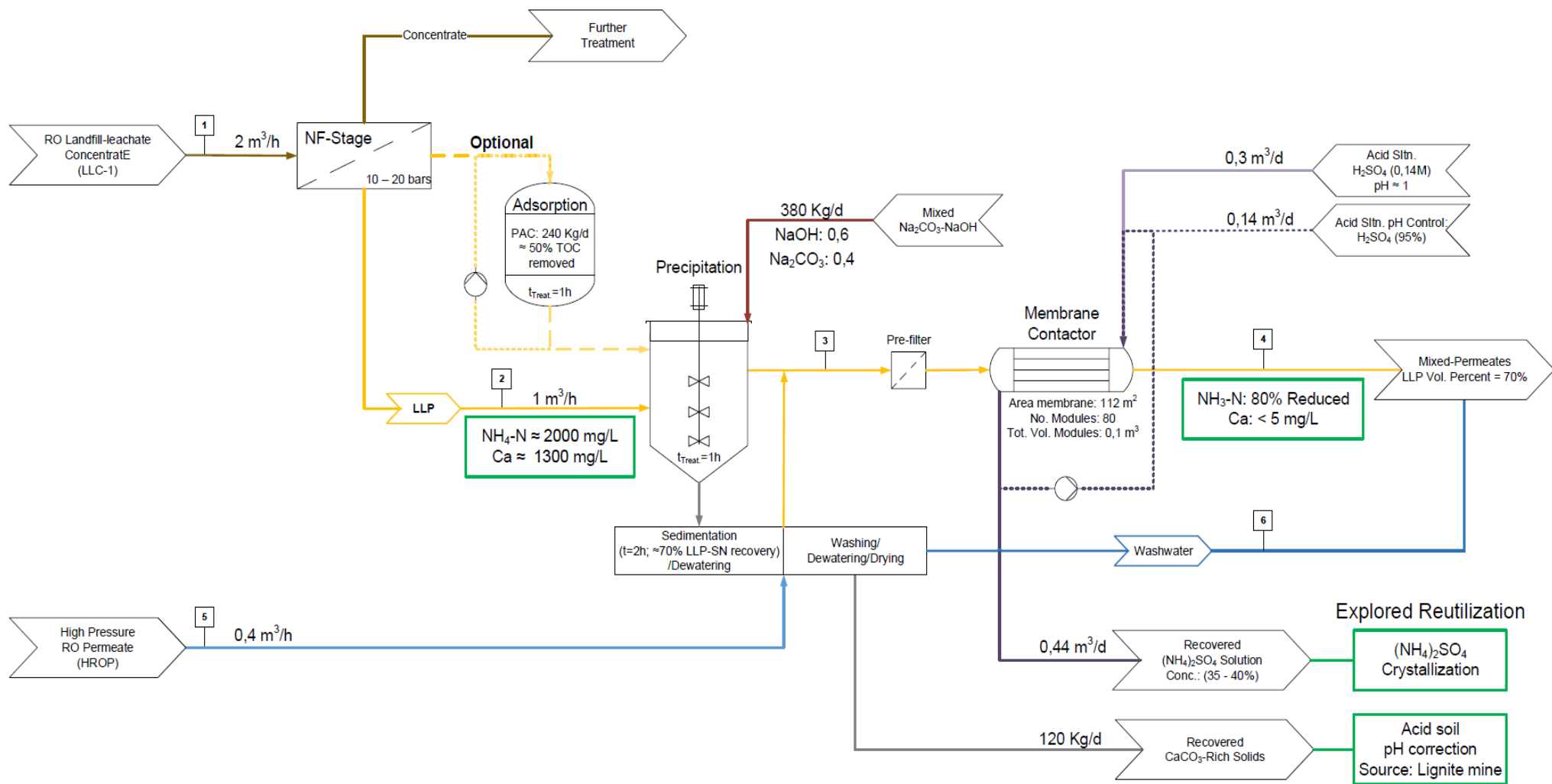


Figure 127. First Section: Recovery of Ca and NH_3 from LLP - Integrated Process “Alternative Sustainable Approach” (Stream conditions provided on next page)

Parameters	Unit	1	2	3	4	5	6
Salinity:	dS/m	96	92	92	92	0,0874	12
pH:	-	6,2	6,2	12	12	6,2	10
T:	°C	30 - 35	30 - 35	30 - 35	30 - 35	30 - 35	30 - 35
Ca:	mg/L	1470	1278	<5	<5	<5	<5
Mg:	mg/L	595	488	4,9	4,9	<3	158
Hardness:	°dH	344	292	1,5	1,5	<1	37
NH ₄ -N:	mg/L	1942	1920	1920	384	3,5	3,5
NO ₃ -N:	mg/L	19	<0,23	<0,23	<0,23	<0,23	<0,23
TN:	mg/L	2322	2088	2088	552	3,8	3,8
TOC:	mg/L	2106	1348	1240	1178	2,7	114
PO ₄ -P:	mg/L	-	13	1,2	1,2	<0,5	<0,5

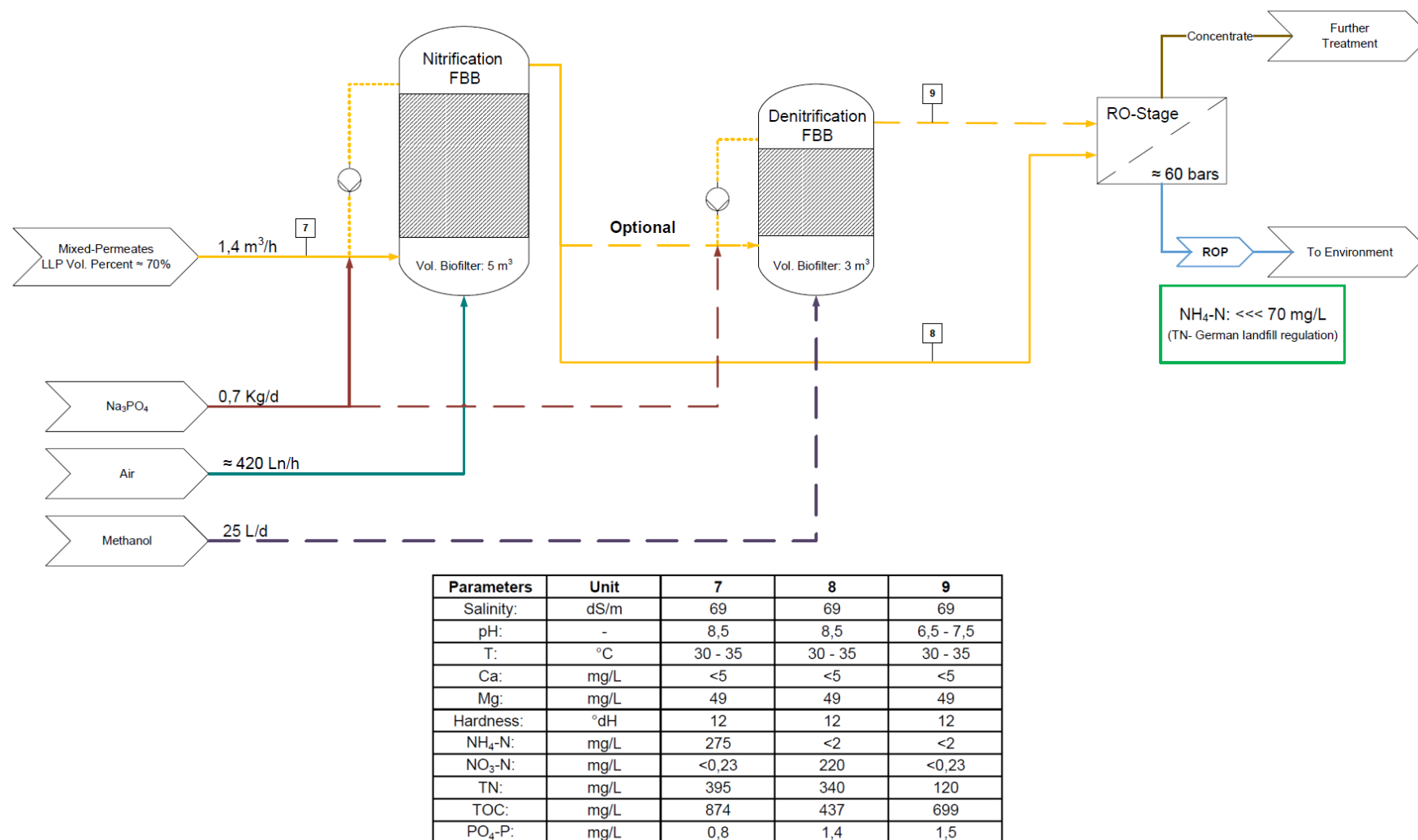


Figure 128. Second Section: MBRs Configurations for Removal of Nutrients from Permeates - Integrated Process "Alternative Sustainable Approach"

CHAPTER 5: CONCLUSIONS

5.1. Composition Analysis

The composition analysis performed with the different streams generated at the landfill leachate treatment facility was the started point of this Doctoral work since based on the results and the German landfill regulation it was possible to evaluate the degree of pollution of the analyzed streams and also they provided indicators for the potential recovery of substances including Ca and NH_3 from the landfill leachate streams.

From the analyzed macro-substances in the landfill leachate (LL) the ones with the highest concentration ranging in between 1 to 10 g/L were Cl^- , Na, COD and SO_4^{2-} with values of about 9,3, 4,5, 2,4 and 1,7 g/L respectively and with a conductivity of about 31 ± 1 mS/cm at $22 \pm 2^\circ\text{C}$. The landfill leachate differed from the landfill leachate permeate (LLP) and the landfill leachate concentrates (LLC-1 & LLC-2) where SO_4^{2-} was the third highest in concentration and their conductivities were about twice the value of 53 mS/cm commonly found in ocean waters. Also, based on their average pH value of $6,5 \pm 0,2$ at $22 \pm 2^\circ\text{C}$, it might indicated large additions of sulfuric acid for pH adjustment during their respective membrane treatment. For instance, in the LLP the concentrations of Cl^- , Na, SO_4^{2-} and COD were equal to 33,0, 15,6, 9,3 and 6,0 g/L respectively, which characterized this stream as a very salty permeate with a conductivity value of about 92 ± 2 mS/cm at $22 \pm 2^\circ\text{C}$. These indicated that the COD concentration in the LLP compared to the LL was about 2,5 times higher but compared to the concentrates it was about 30 and 50% less than the COD values of about 9,0 and 13,0 g/L corresponding to the LLC-1 and LLC-2 respectively. Moreover, based on the COD limit value (LV) of 0,2 g/L indicated in the German landfill regulation the COD concentration in the LLP was about 30 times higher than the LV, which was almost in between the LL and LLC-2, which were 12 and 65 times higher than the COD-LV respectively. Furthermore, for the case of the reverse osmosis permeates including the high pressure RO (HROP) and RO (ROP) their COD concentration with values of <0,10 and 0,11 g/L respectively were below the LV indicated in the regulation.

Moreover, the concentration of $\text{NH}_4\text{-N}$ and Ca in the LLP with values of about 1920 and 1280 mg/L respectively were about 3 times higher than the concentrations in the LL with values of 598 and 443 mg/L for $\text{NH}_4\text{-N}$ and Ca respectively. And, compared to the concentrates the $\text{NH}_4\text{-N}$ concentration in the LLP was almost equal to the concentration in the LLC-1 and only less than 9% of the LLC-2 with value of about 2120 mg/L. And, with respect to Ca, the concentration in the LLP was only about 13 and 30% less than the values of 1470 and 1875 mg/L corresponding to the LLC-1 and LLC-2 respectively. Furthermore, the concentration of Ca and $\text{NH}_4\text{-N}$ in the HROP were very low with values less than 5 mg/L and in the ROP the concentration of Ca and $\text{NH}_4\text{-N}$ were also low with values of about 9,4 and 80,5 mg/L respectively. Based, on the German landfill regulation the LV for TN is 70 mg/L, which indicated that the only stream that complied with the regulation was the HROP.

Furthermore, based on the LVs indicated in the German landfill regulation for the trace substances including $\text{NO}_2\text{-N}$, Ni, Cu, Zn, CN^- , Cr, As, Pb, Cd and Hg, only with the exception of CN^- and As the concentrations of the analyzed trace substances in the LLP and LL were below the limit values. For the case of CN^- , the concentration in the LLP was about 1,5 times higher than the LV of 200 $\mu\text{g/L}$ while the concentration of CN^- in the LL was approximately equal to the LV. and for the LLP and the LL their As concentrations were about 3 and 1,5 times higher than the LV of 100 $\mu\text{g/L}$ respectively. On the other hand, in the landfill leachate concentrates their concentrations of Ni, Cu, CN^- , Cr and As were higher than the limit values of 1000, 500, 200, 500 and 100 $\mu\text{g/L}$ respectively described in the regulation.

These results indicated that based on the LVs specify in the German landfill regulation for COD and trace substances, the landfill leachate permeate (LLP) might be categorized as more extreme than the landfill leachate but not as polluted as the landfill leachate concentrates. Thus, considering the larger concentration of Ca and $\text{NH}_4\text{-N}$ in the LLP with respect to the LL and the small differences with respect to the concentrates, the LLP might be an acceptable choice for the recovery of Ca and NH_3 from the landfill leachate streams.

Furthermore, the RO permeates including the HROP and ROP were categorized as soft water since their hardness values were below 60 mg/L and their conductivities were comparable to water intended for human consumption since their values were below the limit value of 2,5 mS/cm at 20°C indicated in EU Directive of 1998 “on the quality of water for human consumption”. The high quality of the HROP and ROP made them suitable for their reutilization as process water in applications such as water for pH control solutions, washwater, etc.

Additionally, the rejection curve estimated for the NF-stage indicated a trend in the increase of membrane selectivity with respect to MW. This increase in selectivity might be advantageous for the removal of inorganic-N species from the landfill leachate streams but in the form of NO_3 and/or NO_2 rather than the typical form of NH_4 commonly found in wastewater.

5.2. Adsorption

The PAC treatment showed that in general the adsorption of color, TOC and heavy metals onto PAC increased with the increased of PAC dosage. For the case of TOC and color the adsorption equilibrium was reached within the first hour of treatment after this time their concentrations in the treated permeate did not changed considerably. After the 2 h of treatment with PAC more than 50% of the TOC and 95% of the color got removed from the LLP at PAC dosages of 10, 15 and 20 g/L. For the same treatment time, the 5 g/L PAC dosage removed 34% of the TOC and 86% of the color. The maximum percentage removal of TOC and color was achieved with the 20 g/L PAC dosage with removals of 73 and 100% for TOC and color respectively. Furthermore, a relation between TOC and color was made by plotting the color and TOC percentage removals as a function of CU to TOC ratios where it was found that approximately 60% of the initial TOC concentration in the permeate with a value of $1490,2 \pm 103,8$ mg/L corresponded to the yellowish color characteristic of the LLP. Furthermore, for the case of the removal of heavy metals and halogens, despite the challenges that arose when targeting the analyzed substances, which were not only located in low concentration ranges such as pg/L– $\mu\text{g/L}$ –mg/L but also in a complex matrix such as the saline LLP; from the 20th analyzed substances including 17 heavy metals and 3 halogens, it was possible to determine the removal efficiency with PAC at different PAC dosages of 7 heavy metals and 3 halogens, which included Cr, Fe, Co, Ni, Cu, Mn, As, Cl^- , Br^- and F^- . The substances that did not showed any removal at any of the PAC dosages of 5, 10, 20 and 40 g/L were Mn, As, Cl^- , Br^- and F^- . On the other hand, for the 4 h treatment Cr, Fe, Co, Ni and Cu presented removals greater than 20% at all PAC dosages and maximum removals were achieved with the 40 g/L dosage with values of 81, >58, 90, >90 and >74% for Ni, Co, Fe, Cr and Cu respectively. Additionally, it was found that the adsorption equilibrium of Fe, Ni and TOC was well described by the Freundlich isotherm with R-squared values of 0,99, 0,92 and 0,99 respectively. Also, the Langmuir isotherm fitted well the data of Fe and TOC with R-squared values of 0,97 and 0,99 respectively. Finally, based on the Langmuir isotherm the maximum adsorption capacity for the analyzed adsorbates was 137 mg/g for TOC followed by 61 and 54 $\mu\text{g/g}$ for Iron and Nickel respectively.

5.3. Precipitation

The concentrations of calcium in the landfill leachate permeate (LLP) collected during the different seasons of the year including spring, summer and fall did not change considerably with an average value of 1294 ± 167 mg/L and the Ca to Mg concentration ratio also stayed relatively constant with a value of $2,6 \pm 0,1$.

For the 0,5 L precipitation treatment, for both LLP and PAC treated LLP (PAC-LLP) at the evaluated pH conditions of 9, 10, 11 and 12 with their respective precipitating agents NaOH and the mixed Na_2CO_3 -NaOH most of the Ca was removed from the permeate during the first hour of treatment and after 1h of treatment the removal of Ca was lower in which an equilibrium concentration was observed in the treated permeate. For instance, for the case of the mixed Na_2CO_3 -NaOH reagents at pH 12 the concentration of Ca was less than 5 mg/L at each of the evaluate treatment times of 1, 6 and 24 h with removals greater than 99% and for the case of NaOH at pH 9 in between the treatment time of 15 min and 1h the removal of Ca increased about 10% and for the treatment times of 1 and 2h the concentration of Ca stayed relatively the same in the permeate with removal values of about 40%. Moreover, it was found that in the LLP at pH 12 and treatment time of 1h the selection of the precipitating agent might have important effects in the recovery of CaCO_3 -rich solids. For instance, for the case of NaOH the estimated initial OH^- to CO_3^{2-} mole ratio was about 13, which yielded a hardness removal of 90% but the estimated reacted CO_3 to Ca-Mg mole ratio was about 0,3, which indicated that less than 50% of the reacted Ca and Mg was in carbonate form. However, for the case of the mixed Na_2CO_3 -NaOH reagents the initial OH^- to CO_3^{2-} mole ratio was only about 3, which yielded a hardness removal of about 99% and the estimated reacted CO_3 to Ca-Mg mole ratio was about 0,8, which indicated that more than 50% of the reacted Ca and Mg was in carbonate form. Thus, at the pH value of 12 the used of only NaOH as precipitating agent for the recovery of CaCO_3 -rich solids might not be the best option since most of the precipitated Ca might be in hydroxide forms and as it is known Ca-hydroxide forms are more soluble in water compared to Ca-carbonate forms; hence having a less stable solid state. Additionally, based on the Ca to Mg ratios estimated in the solids recovered from the LLP with the mixed Na_2CO_3 -NaOH reagents at the pH conditions of 9, 10, 11 and 12; it was possible to determine that the optimal pH value for precipitation was pH 10 reaching a maximum Ca/Mg ratio of about 16, but at this pH condition the hardness removed in the LLP was only about 70%, which might still be a factor in downstream membrane processes. Also, based on the chemical and XRD analysis performed in the solids recovered from the LLP and PAC-LLP it was observed that the organic content reduction of about 50% in the permeate did not have a major impact in the recovered solids, other than the physical appearance of the solids being whiter for the solids recovered from the PAC-LLP permeate compared to the solids from the LLP. For instance, in the solids recovered at pH 12 with the mixed reagents after the solids to washwater ratio of 1:10, the estimated CaO mass percentage in the solids generated from the LLP and PAC-LLP were equal to 31%. Moreover, the XRD patterns at each of the pH conditions were almost

identical for the solids recovered from the LLP and PAC-LLP where from the CaCO_3 polymorphs, Calcite was identified in the recovered solids in the form of Calcite, magnesian $(\text{Ca,Mg})\text{CO}_3$ and Monohydrocalcite $(\text{CaCO}_3 \cdot \text{H}_2\text{O})$. Additionally, the concentration of the heavy metals including Hg, Cd, Pb, Cr, Cu, Ni and Zn in the recovered solids at all pH conditions were considerably less than the limit values indicated in the EU Directive of 1986 concerning the protection of soil when sewage sludge is used in agriculture.

The precipitation generated in the 10L precipitator at pH 12 with the mixed Na_2CO_3 -NaOH reagents as precipitant presented good sedimentation properties since after the 1h of mixing at 310 ± 5 rpm and sedimentation time of 2h about 60% of the treated permeate was recovered as supernatant from the precipitator with a hardness removal and TSS values of greater than 99% and $73,6 \pm 4,5$ mg/L respectively. Furthermore, the efficiency of the 10 L precipitator compared to the more controlled 0,5 L precipitation treatment in the recovery of CaCO_3 -rich solids at pH 12 conditions, by the use of a series of separation steps, which included decantation of the SN from the sedimentation-centrifugation and the washing-drying of the collected solids; a recovered solids to treated permeate ratio of 3,3 g/L was obtained, which corresponded to about 65% the value obtained in the lower scale volume of 0,5 L. Moreover, the solids to washwater ratio became important since the excess amounts of soluble matter and/or impurities in the recovered solids might be a function of the washing ratio. For instance, with the solids to washwater ratio of 1:10 the concentration of the estimated NaCl and SO_4 in the recovered solids were equal to about 41000 and 8300 ppm respectively, but after using the washing ratios of 1:30 and 1:50 the concentration of these substances decreased to values of about 2600 and 700 ppm for NaCl with the washing ratios of 1:30 and 1:50 respectively and for SO_4 the concentrations decreased to values less than 3600 ppm in the solids recovered after both 1:30 and 1:50 washing ratios. Besides the washing of undesirable substances from the precipitation, the stability of the precipitated Ca was also evaluated and it showed to be very stable since the CaO mass percentage did not decrease but rather compared to the 1:10 washing ratio it increased with values of 37 and 40% of CaO for the washing ratios of 1:30 and 1:50 respectively, which were very close to the common value of 44% of CaO composition found in the feed of cement kiln. Additionally, the TGA/DSC analysis performed in the recovered solids confirmed that the solids recovered from the landfill leachate permeate were rich in CaCO_3 since the obtained signals from the analysis were characteristic of those found in pure CaCO_3 and also showed the presence of impurities, which were confirmed after performing a VS analysis where it was determined that the content of organic material present in the recovered solids was about 11%.

The characteristics of the recovered CaCO_3 -rich solid such as small particle size where about 80% of the solids were smaller than 100 μm , also relatively low concentration of heavy metals and organic content and about 40% of Ca as CaO made of the recovered solids a suitable material for applications related to limestone including the neutralization of acid soils. The application of the recovered CaCO_3 -rich

solids for the neutralization of acid soils indicated that its neutralization power was at the same level compared to pure precipitated CaCO_3 , where for the recovered solid mass fraction of 0,1 the pH in the acid soil increased from 2,8 to 6,5, which is known to be an acceptable pH value for plants such as grass. Additionally, the leachate analysis indicated that Fe and SO_4 leached from the acid soil in relatively high concentrations with values of about 850 and 4000 mg/L respectively. Thus, besides the neutralization effect, for the analyzed recovered solids mass fractions of 0,3 and 0,5 it was possible to determine the capture of Fe and reduced its concentration in the leachate by more than 99%. However, for SO_4 no reduction in the leachate concentration was observed at each of the evaluated solids and acid soil mass fractions.

5.4. Membrane Contactor

The temperature conditions in the evaluated streams during the pH effect on the membrane contactor treatment were about $30\pm 5^{\circ}\text{C}$. For the LLP side from the initial TN concentration with average value of 2194 ± 68 mg/L about 95% of the N was reduced from the permeate with treatment times of 150, 120 and 90 min at pH conditions of $10,0\pm 0,1$, $11,0\pm 0,1$ and $12,2\pm 0,1$ respectively. However, during the membrane treatment it was observed that when the TN concentration approached values around 500 mg/L the N reduction rates switched to a low reduction rate zone; hence a N reduction rate partition concentration of about 500 mg/L was identified during the membrane treatment at the working conditions. For instance, in between the initial TN concentration down to values around 500 mg/L about 70 to 80% of the N was reduced from the permeate with approximate treatment times of 60, 45 and 30 min but for the further 20% N reduction it took about 1,5 to 2 times more the respective partition times. Furthermore, based on the linear models, in between the initial TN concentration down to the values around the partition concentration the estimated $\text{NH}_3\text{-N}$ reduction rates were equal to 0,43, 0,31 and 0,24 $\text{Kg/d}\cdot\text{m}^2$ for pH 12, 11 and 10 respectively and for concentrations below 500 mg/L the N reduction rates decreased in average 86% with respect to the higher reduction rates. Additionally, based on both the estimated high and low N reduction rates with respect to pH 12 the reduction rates decreased about 28 and 47% for pH 11 and 10 respectively. Moreover, for all pH values on the acid solution side with respect to the initial N concentration in the permeate at the end of the respective treatment times, in average about 92% of the N was recovered and with respect to the reduced N it corresponded to a recovery efficiency of about 97% where only about 3% of the N was loss during the membrane treatment. Additionally, at pH 12 the hardness in the LLP was about 37 mg/L as CaCO_3 , which was characteristic of soft water but at pH 11 and 10 the hardness in the permeate was about 681 and 1810 mg/L as CaCO_3 respectively, which corresponded to hard water; hence from the hardness point of view the pH conditions of 10 and 11 in the permeate might not be suitable for the reduction and recovery of NH_3 from the LLP considering that scaling problems might still be encounter downstream in the membrane processes, which could be more severe at pH 10.

The temperature conditions for the case of the reduction and recovery of NH_3 as concentrated $(\text{NH}_4)_2\text{SO}_4$ solution ($\approx 20\%$) in the LLP and acid solution were approximately equal to $28\pm 7^{\circ}\text{C}$. The consecutive batches were run for 5 h until about 93% of the N was reduced from the initial TN concentration of 2231 ± 112 mg/L. Moreover, the process was very compact not only with respect to the module design but also to the amount of reagents used during the consecutive batches. For instance with respect to the treated 228 L of permeate only a volume percentage of about 0,8 and 3% of pH control NaOH (12M) solution and acid solution respectively were used during the ammonium sulfate enrichment process. Furthermore, as was the case in the more control 8 L membrane treatment, the switched in N reduction rate was also observed during each of the consecutive batches around the permeate N

concentration of 500 mg/L at the treatment time of 3 h where about 80% of the N was reduced from the permeate. Also, for the batch performed after membrane regeneration, it was observed that in between the treatment time of 3 to 5 h the volume in the acid solution experienced an abnormal increase at an estimated rate of about 167,3 mL/h. This volume increase was more than the total consumed volume of 216 ± 5 mL of the pH control H_2SO_4 (95%) solution where by the treatment time of 3 h about 80% of the pH control solution volume was already consumed. Thus, for the recovery of NH_3 from the permeate the TN concentration of about 500 mg/L was identified as a critical concentration since by further running of the membrane process below this concentration the efficiency in N reduction and potentially the hydrophobicity of the membrane might be affected. The TN critical concentration was correlated with the $\text{NH}_4\text{-N}$ concentration measured at the treatment time of 3 h in the treated permeate where the $\text{NH}_4\text{-N}$ to TN ratio was about 0,7 corresponding to a critical $\text{NH}_4\text{-N}$ concentration in the permeate of about 350 mg/L. Also, by the end of the 5 h treatment the $\text{NH}_4\text{-N}$ concentration in the permeate was equal to 52 ± 11 mg/L, which was below the limit value of 70 mg/L indicated in the German landfill regulation. Furthermore, the wet out membrane was observed after treating 228 L of the permeate but at this point the concentration of ammonium sulfate in the acid solution was already equal to about 20%; hence the target ammonium sulfate concentration in the acid solution was achieved without membrane regeneration but it was not operated as an ideal hydrophobic membrane but rather in a partially wet mode. Moreover, the performance of the ammonium sulfate enrichment process with percent recovery, percent loss and estimated reduction rate of N with values of 82%, 10% and $0,4 \text{ Kg-N/d}\cdot\text{m}^2$ respectively were 11% less, 2,5 times higher and approximately equal compare to the values obtained in the smaller and more control 8 L permeate treatment at pH 12 conditions.

Additionally, for the evaluated system from the initial 5 L acid solution (0,14M) by assuming the ideal case of completely hydrophobic membrane, also the same N recovery efficiency and based on the consumed volumes of pH control solution. During the 5 h membrane treatment the system could have reached efficiently an ammonium sulfate solution with concentrations of about 25 and 40% with treated LLP volumes of 304 and 456 L with concentrated 65 and 95% H_2SO_4 as pH control solutions respectively. Also, by using the H_2SO_4 (95%) as pH control solution and for a treated permeate volume of about 304 L the concentration in the acid solution could have been increase by 20% from the ammonium sulfate concentration value of 25% estimated with the consumed H_2SO_4 (65%) solution. Thus, the efficiency of the membrane treatment for the recovery of NH_3 might not only be affected by a critical concentration but also the pH control solution for the acid solution side might have considerable effects during the enrichment process. Finally, in the permeate during the membrane treatment about 5% of the TOC was removed from the initial concentration of 1239 ± 23 mg/L and by the end of the treatment the SO_4 concentration remained almost unchanged within the initial concentration of 9660 ± 483 mg/L, which indicated that there was no crossing from the acid solution side to the shell side of the membrane.

Furthermore, ammonium sulfate crystals in the form of Mascagnite $(\text{NH}_4)_2\text{SO}_4$ and Lecontite $(\text{K,Na})\text{NH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ were obtained from the recovered concentrated ammonium sulfate solution ($\approx 20\%$). Thus, in general the TMCS process by using the hollow fiber membrane contactor module proved to be an alternative for the reduction and recovery of NH_3 from the landfill leachate permeate.

5.5. Nitrification-Denitrification

In the FBB during nitrification, for the ROP and mixed-permeates up to the 50% LLP in volume with salinities in between 2,5 to 50 dS/m at the same pH, T and liquid flow rate conditions with values of $7,5 \pm 0,3$, $21 \pm 2^\circ\text{C}$ and $12,7 \pm 1,3$ m/h respectively and DO concentrations of less than 1 and in between 2 to 3 mg/L; complete nitrification was achieved where in average $77 \pm 2\%$ of the initial $\text{NH}_4\text{-N}$ concentration, which ranged approximately in between 70 to 1050 mg/L was converted to $\text{NO}_3\text{-N}$ and the initial average $\text{NH}_4\text{-N}$ to TN ratio was estimated as $0,91 \pm 0,02$, which indicated an organic-N content in the analyzed permeates of about 9%. Moreover, at the same operating conditions, based on the linear regressions performed in the $\text{NH}_4\text{-N}$ concentration data plotted as a function of time with R^2 values greater than 0,99 indicated that the AOR was independent of the initial $\text{NH}_4\text{-N}$ concentrations; thus, following a zero-order reaction. Furthermore, the effect of salinity in the nitrifying microorganisms were evaluated at the same operating conditions with the different ROP and LLP volume ratios where for the mixed-permeates with 20% LLP in volume and salinity of about 22 dS/m an AOR of about 130 mg/L·d was achieved but as the volume percentage of the LLP increased so did the salinity but with decrease in the AORs. For instance, for the mixed-permeate with 50% LLP in volume and salinity of about 50 dS/m there was only an 8% decrease in AOR with respect to the value of 130 mg/L·d but for the mixed-permeates with 80% LLP in volume and the LLP with salinities of about 78 and 90 dS/m the AOR decreased 64 and 95% respectively with respect to the 22 dS/m batch; hence the activity of the AOB was severely affected at these salinity conditions and being more extreme with the LLP. Furthermore, for the case of the NOB severe accumulation of $\text{NO}_2\text{-N}$ was observed with the 80% LLP where only about 3% of the initial $\text{NH}_4\text{-N}$ concentration with value of about 1500 mg/L was converted to $\text{NO}_3\text{-N}$ during the 30 days of treatment and with the LLP the activity of NOB was also extremely affected where only about 2% of the initial $\text{NH}_4\text{-N}$ concentration with value of about 2010 mg/L was converted to $\text{NO}_3\text{-N}$ during the 90 days of treatment. Thus, due to the complex composition of the landfill leachate permeate it was unclear to determine the degree of salt toxicity since other substances in the permeate might have influenced the inhibition effects in the microorganisms but the results did provide a reference with respect to the tolerance of the nitrifiers to the landfill leachate permeates. Therefore, based on the AOR obtained during the nitrification treatment at the more favorable salinity condition of about 22 dS/m corresponding to the mixed-permeates with 20% LLP in volume and a linear regression performed with AOR percentage decrease as a function of salinity indicated that a percentage decrease in the AOR of less than 50% might be expected in landfill leachate mixed-permeates with salinities in between 50 to 70 dS/m. Furthermore, the treatment of the mixed-permeates with salinities in between 2,5 and 13 dS/m but with DO concentrations of less than 1 mg/L showed in average a decreased in the AOR of 79% with respect to the value of 130 mg/L·d obtained during the treatment of the 20% LLP mixed-permeates.

Besides the inhibition effect in the nitrifiers at salinity values greater than 78 dS/m and DO less than 1 mg/L; the nitrification treatment of the mixed-permeates with 50% LLP in volume at pH conditions of 6,5 with DO, liquid flow rate and T equal to greater than 5 mg/L, $21,6 \pm 1,4$ m/h and $21 \pm 1^\circ\text{C}$ respectively also yielded a 73% decrease in the AOR with respect to the optimal pH value of 8,5 where the AOR was the highest with a value of about 266 mg/L·d. However, at the pH condition of 6,5, NOB activity was favorable considering that there was no accumulation of $\text{NO}_2\text{-N}$, which was not the case at pH 7,5 and 8,5 where $\text{NO}_2\text{-N}$ concentrations reached peak values of about 250 and 500 mg/L respectively. Furthermore, at pH 7,5 the AOR with value of 224 mg/L·d decreased about 16% with respect to the value obtained at pH 8,5 but it was almost twice the AOR value of 119 mg/L·d obtained at the same pH condition but with almost half the liquid flow rate with value of $12,7 \pm 1,3$ m/h, which indicated a direct correlation in between the liquid flow rate and the AOR in the FBB.

Additionally, in the analyzed permeates and mixed-permeates the average initial TOC to COD ratio was equal to $0,23 \pm 0,01$ and for the batches where complete nitrification was achieved from the initial TOC concentration ranging approximately in between 25 to 700 mg/L at the end of the nitrification treatment in average about $50 \pm 4\%$ of the initial TOC concentration was removed from the treated permeates.

Furthermore, during the denitrification treatment of the landfill leachate mixed-permeates with salinity of about 38 dS/m at $T = 20 \pm 1^\circ\text{C}$ and Me-OH as exogenous C-source, the highest DNR was achieved at the pH condition of 6,5 with value of 23,6 mg-N/L·h followed by pH 7,5 and 8,5 whose DNRs were 14 and 55% less compared to the value obtained at pH 6,5. Moreover, the average TN concentration measured at the end of the denitrification treatment with value of $52,2 \pm 3,9$ mg/L was about 8% of the initial TN concentration with value of 668 ± 33 mg/L, which correlated with the initial estimated $\text{NO}_3\text{-N}$ to TN ratio of $0,91 \pm 0,02$ where the organic-N was approximately equal to 9% of the TN concentration. Additionally, at the end of the denitrification treatment the TOC concentration in the mixed-permeate increase about 60% from the initial value of 216 ± 11 mg/L before Me-OH addition. Hence, despite the addition of Me-OH during denitrification and considering the TOC reduction during nitrification of about 50%, overall the biological Nitrification/Denitrification treatment in FBBs removed about 20% and more than 99% of the TOC and inorganic-N load from the fed landfill leachate mixed-permeates.

5.6. Integration of Evaluated Processes with the Landfill Leachate Treatment Facility

The proposed flow diagram for the landfill leachate treatment facility by integrating the evaluated processes with the NF-stage, which is the first step in the reduction treatment of landfill leachate concentrate; where from a generated landfill leachate permeate at a flow rate of 1 m³/h about 120 Kg/d of CaCO₃-rich solids might be recovered and more than 99% of the hardness removed from the permeate during the precipitation treatment. Moreover, with a PAC dosage of 10 g/L about 50% of the TOC might be removed from the landfill leachate permeate leading to the formation of CaCO₃-rich solids with lower organic and heavy metals content improving the quality and appearance of the recovered solids.

Based, on the production rate of the recovered CaCO₃-rich solids and considering its main characteristics, which included relatively low concentration of heavy metals and organic content and also small particle size where about 80% of the bulk material is less than 100 µm a potential reutilization of the recovered solids was as pH correction agent for acid soil such as the one found in lignite mines. It was estimated that a dosage of about 15 t/ha might be suitable for the pH correction of the acid soil, which corresponded to a recovered solids mass fraction of about 0,07 to 0,1 and with the production rate of 120 Kg/d about 0,25 ha of acid soil could be treated per month or 1 hectare every 4 months.

Furthermore, in the membrane contactor about 80% of the NH₃-N might be removed from the permeate and recovered as concentrated ammonium sulfate solution (35 - 40%) at a production rate of about 0,44 m³/d, which makes of this unit operation a compact process where compared to the treated permeate volume the produced acid solution represents only 2% and with respect to space requirement the estimated membrane area of about 112 m² is equivalent to about 80 modules, which require only a space volume of about 0,1 m³. Moreover, the recovered concentrated ammonium sulfate solution can be potentially reutilized as raw material for the crystallization of (NH₄)₂SO₄.

Additionally, based on the lower NH₄-N concentration in the permeates feed to the nitrifying FBB with values of about 280 mg/L and the estimated higher membrane selectivity for NO₃-N compared to NH₄-N with respect to their MWs, the proposed MBR configuration, which included Nitrification FBB/RO-stage (P≈60 bars) might be an alternative to the high pressure RO-stage (HPRO - P≈120 bars) currently used in the landfill leachate treatment facility for the reduction of NH₄-N to concentrations below the limit value of 70 mg/L for TN as indicated in the German landfill regulation. Also, the second proposed MBR configuration, which included Nitrification-/Denitrification-FBBs/RO-stage (P≈60 bars) might also be another alternative to the high pressure RO system where more than 99% of the inorganic-N could be removed from the permeate before entering the RO-stage (P≈60 bars).

Finally, some of the general disadvantages of the evaluated processes included for example, in the adsorption step the relatively high PAC dosage estimated as 240

kg/d require for approximately 50% reduction of TOC from the landfill leachate permeate at a flow rate of 1 m³/h and also the management of the spent PAC or the need for a regeneration process. Also, in the precipitation system the need for more complex unit operations such as dewatering systems, and the relatively high dosage of precipitant added with respect to the obtained recovered solids where about 1/3 of the mass added as precipitating agents corresponded to the recovered solids. Furthermore, in the membrane contactor system the need of special equipment due to corrosive operating conditions, which include the handling of concentrated pH control solutions such as H₂SO₄ (95%) and NaOH (50%). Finally, the sensitivity of the desire microorganisms including nitrifiers for changes in operating conditions such as pH, T, DO and salinity where optimal values must be kept during operation in order to avoid inhibitions during the biological treatment and if not manage properly the biomass generated in the FBBs might lead to severe biofouling problems downstream within the membrane systems.

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APPENDICES

APPENDIX A: Analytical Methods and Standards

Substance/Parameter	Method	Operation range/Units
Ammonium	Hach Cuvette Test – LCK303 (HACH, 2020)	2,0 – 47 mg/L NH ₄ -N
ANC	DIN 38409-7:2005-12	mmol H ⁺ /L
COD	Hach Cuvette Test – LCK1014 (HACH, 2020)	100 – 2000 mg/L O ₂
Color	Standard Method: 2120C (APHA, 2005)	CU
Elemental: V, Cr, Mo, Mn, Co, Ni, Pb, Cu, Zn, Cd, Tl, As, Sb, Se, U, Th, Rb	ICP-MS (Cöllen & Frerichs, 2018)	pg/L – µg/L
Elemental: Na, K, Mg, Ca, Mn, Ba, Fe, Zn, Si, Sr, Li, Al, Sb, P, S	ICP-OES (Fütterer, 2018)	µg/L – mg/L
Elemental: N	NCHS Analyzer (Diedrich, 2019)	1 g/Kg
Halogens: F ⁻ , Cl ⁻ , Br ⁻	IC (Romann & Carstens, 2017)	mg/L – g/L
Hardness, Ca, Mg	Hach Cuvette Test – LCK327 (HACH, 2020)	1 – 20 °dH
Hg	AAS (Fütterer, 2017)	0,1 µg/L – 100 µg/L
Iron	Hach Cuvette Test – LCK321 (HACH, 2020)	0,2 – 6,0 mg/L Fe
Leachability of Water	DIN 38414 part 4 (S4)	-
Nitrate	Hach Cuvette Test – LCK339 (HACH, 2020)	0,23 – 13,5 mg/L NO ₃ -N
Nitrite	Hach Cuvette Test – LCK342 (HACH, 2020)	0,6 – 6,0 mg/L NO ₂ -N
Orthophosphate	Hach Cuvette Test – LCK348 (HACH, 2020)	0,5 – 5,0 mg/L PO ₄ -P
	Hach Cuvette Test – LCK349 (HACH, 2020)	0,05 – 1,5 mg/L PO ₄ -P
Saturation Index (SI)	Standard Method: 2330B (APHA, 2005)	-
pH Value – Sludge	DIN EN 12176:1998-06 (S5)	-
Cyanide (CN ⁻)	Spectrophotometric (Scholz, 2018)	mg/L
Sulfate	Hach Cuvette Test – LCK353 (HACH, 2020)	150 – 900 mg/L SO ₄
TIC	Multi N/C 3000	mg/L
TOC	Multi N/C 3000	mg/L
TN	Multi N/C 3000	mg/L
TSS	Standard Method: 2540D (APHA, 2005)	mg/L
VS	Standard Method: 2540G (APHA, 2005)	-

APPENDIX B: List of Equipment and Materials

Specification	Equipment/Instrument & Materials
AAS	Perkin Elmer FIAS 400 (Fütterer, 2017)
Air Flow Control	Vögtlin Instruments GSC-B9SA 250Ln/h
Ammonia	HACH Portable Multimeter HQ40D with Intellical™ ISENH3181 ammonia ion selective electrode probe
Centrifuge	ThermoFisher Scientific Heraeus Multifuge X3 Centrifuge
Conductivity	WTW Benchtop Multimeter 9620 IDS with IDS TetraCon® 925 conductivity probe
	Greisinger electronic Portable conductivity meter GLF100
DO	HACH Portable DO meter sensION™+ DO6 with sensION™+ 5130 polarographic DO probe
DSC	Netzsch STA 409 PC/PG
Filters & Filter housing	Merck nylon membrane filters, 0,45 µm HNWP type
	Whatman glass microfiber filters, 934-AH grade
	Whatman paper filters, 41 grade
	Hydro-s® 5" clear filter housing
IC	Thermo Fischer Scientific Dionex ICS1100 (Romann & Carstens, 2017)
ICP-MS	Perkin Elmer NexION 300 D (Cöllen & Frerichs, 2018)
ICP-OES	Perkin Elmer Optima 8300 DV (Fütterer, 2018)
Liquid Flow Meter	Cepex® 25-250 L/h & 60-630 L/h
Liquid Pump	Milton Roy Diaphragm pumps GA-170
	Speck Corrosive resistant M1 pumps
Magnetic Stirrer	Heidolph MR 3000 D
Membrane contactor	3M Liqui-Cel® 2,5x8 CN X50 PP
Micropipette	Eppendorf Research® plus G, variable single channel 100-1000 µL & 0,5-5 mL
Multi N/C 3000	Analytik Jena Multi N/C 3000 Analyzer
Overhead Stirrer	IKA® EUROSTAR digital (50-2000 rpm)
pH	HACH Portable Multimeter HQ40D with Intellical™ PHC101 pH electrode probe
	WTW Benchtop Multimeter 9620 IDS with IDS pH electrode probe
	Knick Portable Multimeter Portavo® 907 MULTI with SE 515/1 – MS pH sensor
	Bluelab® pH controllers
Photometer	HACH Spectrophotometer DR3900 (Hach cuvette test)
	JASCO Spectrophotometer V-550 (Color determination)
	Perkin Elmer Lambda 25 (Cyanide determination)
Shaker	Edmund Bühler Shaker KL 2
Vacuum Filtration	Leybold Vacuum pump DIVAC 2,2 L with Büchi Vacuum controller B-721
XRD	Siemens D500 with Cu-Ceramic tube Type K FL Cu 2K & Bruker DIFFRACplus Version 11
XRF	Thermo Fischer Scientific Niton™ XL3t XRF 980

Specification	Reagents*
Reagents Color Determination	Cobaltous chloride hexahydrate from ROTH
	Potassium chloroplatinate from Acros-Organics
Reagents for pH Adjustment	Hydrochloric acid 32% from VWR Chemicals
	Sodium carbonate water free (99,5%) from ORG Laborchemie
	Sodium hydroxide pellets (99%) from ORG Laborchemie
	Sulfuric acid 95% from VWR Chemicals
Other Reagents	Ammonium sulfate from ROTH
	Calcium carbonate precipitated pure from Merck
	Methanol from VWR Chemicals
	Sodium phosphate, tribasic, anhydrous from Alfa-Aesar
	Sulphamic acid from Merck

*All reagents were of Analytical Grade

APPENDIX C: Composition and Selectivity Analysis – Raw Data

C1. Composition Analysis:

Landfill leachate
(LL)

Substance	Unit	Df	Photometer
NH ₄ -N	mg/L	20	29,9
NO ₃ -N	mg/L	1	6,06; 5,11
NO ₂ -N	mg/L	1	<0,6
SO ₄	mg/L	10	169
COD	mg/L	20	119
Ca	mg/L	10	44,3
Mg	mg/L	10	16,9
Hardness	°dH	10	10,1

High Pressure - RO Permeate
(HROP)

Substance	Unit	Df	Photometer
NH ₄ -N	mg/L	2,5	1,38
NO ₃ -N	mg/L	1	<0,23
NO ₂ -N	mg/L	1	<0,6
SO ₄	mg/L	1	<150
COD	mg/L	1	<100
Ca	mg/L	1	<5
Mg	mg/L	1	0,93
Hardness	°dH	1	0,215

Landfill Leachate Concentrate-1
(LLC-1)

Substance	Unit	Df	Photometer
NH ₄ -N	mg/L	200	9,71
NO ₃ -N	mg/L	50	0,383
NO ₂ -N	mg/L	1	<0,6
SO ₄	mg/L	20	523
COD	mg/L	50	178
Ca	mg/L	50	29,4
Mg	mg/L	50	11,9
Hardness	°dH	50	6,88

Landfill Leachate Permeate
(LLP)

Substance	Unit	Df	Photometer
NH ₄ -N	mg/L	100	19,2
NO ₃ -N	mg/L	1	<0,23
NO ₂ -N	mg/L	1	<0,6
SO ₄	mg/L	20	463
COD	mg/L	20	303
Ca	mg/L	20	63,9
Mg	mg/L	20	24,4
Hardness	°dH	20	14,6

Landfill Leachate Concentrate-2
(LLC-2)

Substance	Unit	Df	Photometer
NH ₄ -N	mg/L	200	10,6
NO ₃ -N	mg/L	50	1,12
NO ₂ -N	mg/L	1	<0,6
SO ₄	mg/L	100	208
COD	mg/L	100	129
Ca	mg/L	50	37,5
Mg	mg/L	50	14,3
Hardness	°dH	50	8,55

RO Permeate
(ROP)

Substance	Unit	Df	Photometer
NH ₄ -N	mg/L	10	8,05
NO ₃ -N	mg/L	1	<0,23
NO ₂ -N	mg/L	1	<0,6
SO ₄	mg/L	1	<150
COD	mg/L	1	116; 105
Ca	mg/L	1	9,44
Mg	mg/L	1	3,24
Hardness	°dH	1	2,07

Stream	Df	TOC (mg/L)	TIC (mg/L)	TN (mg/L)
LL	10	66,2	56,07	65,73
HROP	1	2,67	18,05	3,82
LLC-1	50	42,11	12,29	46,44
LLP	20	67,41	14,21	101,6
LLC-2	50	78,74	6,71	50,93
ROP	1	18,67	48,72	89,91

C2. Comparative matrix with respect to limit values indicated in German landfill regulation:

>: Value greater than limit value (LV)

<: Value less than limit value

≈: Value Approx. equal to limit value

U: Uncertain

Substance	Units	DE-Regulation (LV)	LLC-2		LLC-1		LLP		LL		ROP		HROP	
			Mark	LLC-2/LV	Mark	LLC-1/LV	Mark	LLP/LV	Mark	LL/LV	Mark	ROP/LV	Mark	HROP/LV
COD	(g/L)	0,2	>	65	>	45	>	30	>	12	<	0,55	<	U
TN	(mg/L)	70	>	36	>	33	>	29	>	9,4	>	1,3	<	0,054
NO ₂ -N	(µg/L)	2000	<	U	<	U	<	U	<	U	<	U	<	U
Ni	(µg/L)	1000	>	2,8	>	1,5	<	0,68	<	0,40	<	U	<	U
Cu	(µg/L)	500	>	3,8	>	1,5	<	U	<	0,48	<	U	<	U
Zn	(µg/L)	2000	<	0,67	<	0,31	<	0,045	<	0,11	<	U	U	U
CN ⁻	(µg/L)	200	>	7,5	>	4,5	>	1,5	≈	1,1	<	0,050	<	U
Cr	(µg/L)	500	>	3,0	>	1,2	<	U	<	0,36	<	U	<	U
As	(µg/L)	100	>	5,7	>	3,2	>	2,9	>	1,5	<	U	<	U
Pb	(µg/L)	500	<	0,72	<	U	<	U	<	0,10	<	U	<	U
Cd	(µg/L)	100	U	U	U	U	U	U	<	U	<	U	<	U
Tl	(µg/L)	50	U	U	U	U	U	U	<	U	<	U	<	U
Hg	(µg/L)	50	<	U	<	U	<	U	<	U	<	U	<	U
Total No. :			13		13		13		13		13		13	
Total No. >:			7		7		4		3		1		0	
Total No. > (%):			54%		54%		31%		23%		8%		0%	

Orange: Macro-substances, based on landfill leachate composition

Black: Trace-substances, based on landfill leachate composition

C3. Rejection curve in NF stage:

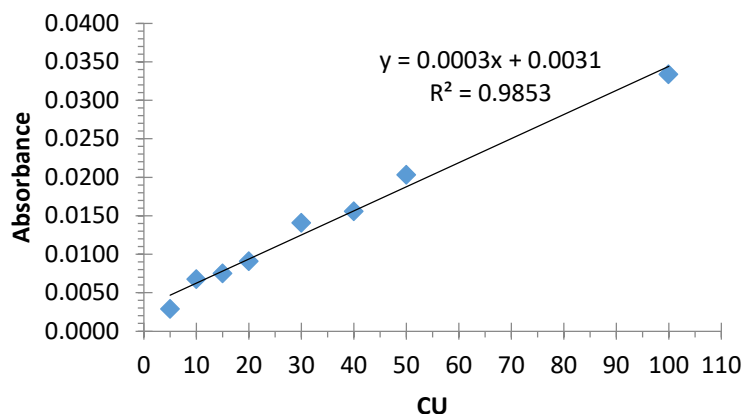
Substance	Units	LLC-1 _{In}	LLP	MW
Li	(mg/L)	15,7	14,9	6,9
Na	(g/L)	17,0	15,6	23,0
K	(g/L)	1,61	1,66	39,1
Rb	(mg/L)	3,9	4,0	85,5
Mg	(mg/L)	595	488	24,3
Ca	(mg/L)	1470	1278	40,1
Sr	(mg/L)	15,1	12,5	87,6
Mo	(µg/L)	750	150	95,9
Mn	(µg/L)	2600	1400	54,9
Ni	(µg/L)	1500	680	58,7
Zn	(µg/L)	610	90	65,4
Si	(mg/L)	45,7	45,9	28,1
As	(µg/L)	320	290	74,9
F ⁻	(mg/L)	16	14	19,0
Cl ⁻	(g/L)	33	33	35,5
Br ⁻	(mg/L)	430	420	79,9
CN ⁻	(µg/L)	890	290	26,0
SO ₄ ²⁻	(g/L)	10,46	9,26	96,1
NH ₄ -N	(mg/L)	1942	1920	18,0

C4. TSS – Standard Method 2540D:

Stream	Vol. filtrated (mL)	Filter setup	
		Initial weight (g)	Final weight (g)
LL	500	0,4818	0,4854
LLC-1	250	0,4754	0,4865
LLC-2	140	0,4718	0,5775

APPENDIX D: Adsorption – Raw Data

D1. Color Calibration Curve – Standard Method: 2120C:



$\lambda = 456 \text{ nm}$

Standards (CU)	Absorbance	
5	0,0031	0,0026
10	0,0065	0,0070
15	0,0081	0,0069
20	0,0094	0,0087
30	0,0141	0,0140
40	0,0159	0,0152
50	0,0200	0,0206
100	0,0332	0,0335

D2. Color Determination:

PAC dosage: 5 g/L

Time (min)	Df	Absorbance	
LLP	20	0,0180	0,0189
LLP	20	0,0204	0,0198
10	20	0,0086	0,0083
20	20	0,0068	0,0071
30	20	0,0053	0,0058
60	20	0,0058	0,0052
120	20	0,0058	0,0051

PAC dosage: 15 g/L

Time (min)	Df	Absorbance	
LLP	20	0,0241	0,0286
10	1	0,0186	0,0186
20	1	0,0154	0,0164
30	1	0,0097	0,0093
60	1	0,0074	0,0074
120	1	0,0059	0,0053

PAC dosage: 10 g/L

Time (min)	Df	Absorbance	
LLP	20	0,0205	0,0233
10	1	0,0262	0,0270
20	1	0,0247	0,0234
30	1	0,0238	0,0243
60	1	0,0208	0,0214
120	1	0,0186	0,0177

PAC dosage: 20 g/L

Time (min)	Df	Absorbance	
LLP	20	0,0230	0,0211
10	1	0,0053	0,0049
20	1	0,0042	0,0057
30	1	0,0033	0,0032
60	1	0,0035	0,0037
120	1	0,0022	0,0024

D3. Color Determination: Multi N/C 3000 Analyzer:

PAC dosage: 5 g/L

Time (min)	Df	TOC (mg/L)	TIC (mg/L)	TC (mg/L)	TN (mg/L)
LLP	20	76,16	13,26	89,43	95,4
LLP	20	78,67	11,44	90,11	105,9
10	20	56,03	10,95	66,98	97,2
20	20	54,79	11,04	65,86	101,9
30	20	54,29	9,24	63,53	95,8
60	20	52,52	8,77	61,29	95
120	20	51,88	8,52	60,4	95,6

PAC dosage: 10 g/L

Time (min)	Df	TOC (mg/L)	TIC (mg/L)	TC (mg/L)	TN (mg/L)
LLP	20	77,77	10,37	88,14	119
10	20	38,6	10,72	49,32	111,1
20	20	37,37	6,15	43,53	108,7
30	20	36,34	9,72	46,05	107,1
60	20	36,56	9,58	46,13	106,9
120	20	35,22	9,33	44,55	105,6

PAC dosage: 15 g/L

Time (min)	Df	TOC (mg/L)	TIC (mg/L)	TC (mg/L)	TN (mg/L)
LLP	20	74,22	10,24	84,46	106
10	20	27,07	10,19	37,27	95,21
20	20	26,48	9,96	36,44	96,5
30	20	26,65	9,99	36,64	96,96
60	20	25,87	9,54	35,41	95,33
120	20	25,85	8,98	34,83	93,75

PAC dosage: 20 g/L

Time (min)	Df	TOC (mg/L)	TIC (mg/L)	TC (mg/L)	TN (mg/L)
LLP	20	65,74	11,26	77	97,66
10	20	17,67	11,81	29,48	88,9
20	20	17,73	11,57	29,3	86,99
30	20	17,48	10,76	28,24	85,22
60	20	18,17	10,31	28,47	84,9
120	20	17,92	9,9	27,81	84,71

D4. Color & TOC Correlation – Treated Data:

LLP

No.	Color (CU)	TOC (mg/L)	CU/TOC ratio
1	1023,3	1523,2	0,67
2	1133,3	1573,4	0,72
3	1253,3	1555,4	0,81
4	1550,0	1484,4	1,04
5	1263,3	1314,8	0,96
Average =	1244,7	1490,2	0,84
SDS =	196,9	103,8	0,16

PAC dosage: 5 g/L

time (min)	Color (CU)	TOC (mg/L)	CU/TOC ratio	Removed Color (%)	Removed TOC (%)
0	1133,3	1573,4	0,72	-	-
10	356,7	1120,5	0,32	68,5	28,8
20	256,7	1095,8	0,23	77,4	30,4
30	163,3	1085,8	0,15	85,6	31,0
60	160,0	1050,4	0,15	85,9	33,2
120	156,7	1037,6	0,15	86,2	34,1

PAC dosage: 10 g/L

time (min)	Color (CU)	TOC (mg/L)	CU/TOC ratio	Removed Color (%)	Removed TOC (%)
0	1253,3	1555,4	0,81	-	-
10	78,3	772,0	0,10	93,8	50,4
20	69,8	747,4	0,09	94,4	51,9
30	69,8	726,8	0,10	94,4	53,3
60	60,0	731,2	0,08	95,2	53,0
120	50,2	704,4	0,07	96,0	54,7

PAC dosage: 15 g/L

time (min)	Color (CU)	TOC (mg/L)	CU/TOC ratio	Removed Color (%)	Removed TOC (%)
0	1550,0	1484,4	1,04	-	-
10	51,7	541,4	0,10	96,7	63,5
20	42,7	529,6	0,08	97,2	64,3
30	21,3	533,0	0,04	98,6	64,1
60	14,3	517,4	0,03	99,1	65,1
120	8,3	517,0	0,02	99,5	65,2

PAC dosage: 20 g/L

time (min)	Color (CU)	TOC (mg/L)	CU/TOC ratio	Removed Color (%)	Removed TOC (%)
0	1263,3	1314,8	0,96	-	-
10	6,7	353,4	0,02	99,5	73,1
20	6,2	354,6	0,02	99,5	73,0
30	0,5	349,6	0,00	100,0	73,4
60	1,7	363,4	0,00	99,9	72,4
120	0,0	358,4	0,00	100,0	72,7

D5. Heavy Metal & Halogen Analysis:

- LLP-PAC5: Treated Permeated with PAC dosage of 5 g/L
- LLP-PAC10: Treated Permeated with PAC dosage of 10 g/L
- LLP-PAC20: Treated Permeated with PAC dosage of 20 g/L
- LLP-PAC40: Treated Permeated with PAC dosage of 40 g/L

	V		Cr		Mo	Mn	
	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
Sample	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
LLP	39	< 200	97	<200	150	820	1400
LLP-PAC5	42	< 100	35	<10	< 100	1100	490
LLP-PAC10	34	< 100	30	<10	< 100	1100	420
LLP-PAC20	32	< 10	16	<10	< 100	1000	310
LLP-PAC40	-	< 10	-	<10	< 100	-	520

	Fe		Co		Ni		Pb
	ICP-OES	ICP-OES	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
Sample	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L
LLP	0,81	<4	24	<200	460	680	< 200
LLP-PAC5	0,58	0,176	19	<10	510	230	< 10
LLP-PAC10	0,43	0,172	16	<10	440	220	< 10
LLP-PAC20	0,34	0,120	< 10	<10	370	170	< 10
LLP-PAC40	-	0,081	-	<10	-	130	< 10

	Cu		Zn		Cd		Hg	
	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	AAS	AAS
Sample	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
LLP	38	<80	<10	90	< 10	<200	< 0,2	<0,25
LLP-PAC5	14	<10	280	n.r.	< 10	-	< 0,2	-
LLP-PAC10	8,8	<10	250	n.r.	< 10	-	< 0,2	-
LLP-PAC20	16	<10	480	n.r.	< 10	-	< 0,2	-
LLP-PAC40	-	<10	-	n.r.	-	-	-	-

	Al		Ti	As		Sb		Se
	ICP-OES	ICP-OES	ICP-MS	ICP-MS	ICP-MS	ICP-OES	ICP-MS	ICP-MS
Sample	mg/L	mg/L	µg/L	µg/L	µg/L	mg/L	mg/L	µg/L
LLP	0,67	<4	< 200	220	290	-	< 0,08	n.r.
LLP-PAC5	0,60	0,208	< 10	230	200	< 0,1	-	n.r.
LLP-PAC10	0,54	0,206	< 10	230	230	< 0,1	-	n.r.
LLP-PAC20	0,58	0,202	< 10	230	220	< 0,1	-	n.r.
LLP-PAC40	-	0,203	< 10	-	260	< 0,1	-	n.r.

	F ⁻		Cl ⁻		Br ⁻	
	IC	IC	IC	IC	IC	IC
Sample	mg/L	mg/L	g/L	g/L	mg/L	mg/L
LLP	19	14	29	33	430	420
LLP-PAC5	19	21	29	33	430	480
LLP-PAC10	17	18	29	32	430	470
LLP-PAC20	14	15	29	33	430	480
LLP-PAC40	-	15	-	34	-	490

D6. Adsorption Isotherms:

Chromium						
PAC dosage (g PAC/L)	C _e (µg/L)	ΔC _e (µg/L)	q _e (µg/g)	LN C _e (µg/L)	LN q _e (µg/g)	C _e /q _e (g/L)
0	97					
5,0	35	62	12,4	3,6	2,5	2,8
10,0	30	67	6,7	3,4	1,9	4,5
20,0	16	81	4,1	2,8	1,4	4,0
40,0	< 10	-	-	-	-	-

Iron						
PAC dosage (g PAC/L)	C _e (µg/L)	ΔC _e (µg/L)	q _e (µg/g)	LN C _e (µg/L)	LN q _e (µg/g)	C _e /q _e (g/L)
0	810					
5,0	580	230	46,0	6,4	3,8	12,6
10,0	430	380	38,0	6,1	3,6	11,3
20,0	230	580	29,0	5,4	3,4	7,9
40,0	81	729	18,2	4,4	2,9	4,4

Nickel						
PAC dosage (g PAC/L)	C _e (µg/L)	ΔC _e (µg/L)	q _e (µg/g)	LN C _e (µg/L)	LN q _e (µg/g)	C _e /q _e (g/L)
0	680					
5,0	510	170	34,0	6,2	3,5	15,0
10,0	440	240	24,0	6,1	3,2	18,3
20,0	270	410	20,5	5,6	3,0	13,2
40,0	130	550	13,8	4,9	2,6	9,5

TOC						
PAC dosage (g PAC/L)	C _e (mg/L)	ΔC _e (mg/L)	q _e (mg/g)	LN C _e (mg/L)	LN q _e (mg/g)	C _e /q _e (g/L)
0	1490,2					
5,0	1037,6	452,6	90,5	6,9	4,5	11,5
10,0	704,4	785,8	78,6	6,6	4,4	9,0
15,0	517,0	973,2	64,9	6,2	4,2	8,0
20,0	358,4	1131,8	56,6	5,9	4,0	6,3

D7. Validation of Freundlich & Langmuir Isotherm Models:

Validation for Chromium				
		Experimental	Freundlich Model	
PAC dosage (g PAC/L)	C _e (µg/L)	q _e (µg/g)	q _e (µg/g)	Error (%)
5,0	35	12,4	10,2	18
10,0	30	6,7	8,4	26
20,0	16	4,1	3,8	5
			Average =	16

Validation for Iron						
		Experimental	Freundlich Model		Langmuir Model	
PAC dosage (g PAC/L)	C _e (µg/L)	q _e (µg/g)	q _e (µg/g)	Error (%)	q _e (µg/g)	Error (%)
5,0	580,0	46,0	43,3	6	43,4	6
10,0	430,0	38,0	37,8	1	39,6	4
20,0	230,0	29,0	28,4	2	30,5	5
40,0	81,0	18,2	17,7	3	16,0	12
			Average =	3	Average =	7

Validation for Nickel						
		Experimental	Freundlich Model		Langmuir Model	
PAC dosage (g PAC/L)	C _e (µg/L)	q _e (µg/g)	q _e (µg/g)	Error (%)	q _e (µg/g)	Error (%)
5,0	510	34,0	30,9	9	29,8	12
10,0	440	24,0	28,4	18	27,8	16
20,0	270	20,5	21,3	4	21,3	4
40,0	130	13,8	13,8	1	12,9	6
			Average =	8	Average =	10

Validation for TOC						
		Experimental	Freundlich Model		Langmuir Model	
PAC dosage (g PAC/L)	C _e (mg/L)	q _e (mg/g)	q _e (mg/g)	Error (%)	q _e (mg/g)	Error (%)
5,0	1037,6	90,5	91,6	1	90,8	0
10,0	704,4	78,6	76,8	2	78,3	0
15,0	517,0	64,9	66,8	3	67,8	5
20,0	358,4	56,6	56,5	0	55,4	2
			Average =	2	Average =	2

APPENDIX E: Precipitation – Raw Data

E1. Collected landfill leachate permeate (LLP):

Chemical Analysis and Measured Parameters

Substance/ Parameter	Season – Value		DF
	Spring	Summer	
Ca ²⁺ (mg/L):	56,6; 57,4	64,4; 62,6	20
Mg ²⁺ (mg/L):	21,5; 22,6	24,9; 25,6	
Hardness (°dH):	12,9; 13,3	14,8; 14,7	
SO ₄ ²⁻ (mg/L):	480; 403	469; 499	
COD (mg/L):	318; 303	316; 337	
TOC (mg/L):	61,39; 64,14	72,87; 67,85; 69,25	
TIC (mg/L):	10,38; 13,15	11,71; 12,08; 11,45	
TC (mg/L):	71,77; 77,29	84,58; 79,93; 80,7	
TN (mg/L):	91,25; 98,8	106,8; 99,18; 111,2	
Ortho-PO ₄ ³⁻ P (mg/L):	1,62; 1,74	1,92; 1,88// 1,76; 1,79	5

Spring collected permeate	
Parameter	Measured values
pH:	6,38;6,47;6,43;6,45;6,42;6,6//6,72;6,73;6,71;6,83
Conductivity (mS/cm):	85,2;84,5;84,4;84,5;84,7;84,5//88,5;88,5;88,2;88,7
T (°C):	23,1;22,9;22,2//21,6;22,7;23,1;22,5

Summer collected permeate	
Parameter	Measured values
pH:	6,52;6,5;6,5//7,6;85;6,95;6,86;6,87//6,48;6,47;6,52
Conductivity (mS/cm):	88,4;88,5;88,6;88,3//88,7;87,7;87,6;88;87,7//88,5;88,7;88,4
T (°C):	21;21;20,8//23,8;28;27//23;23,2;22,7

ANC (Alkalinity) – DIN 38409-7:2005-12

HCl (0,1N); Vol. Sample: 100 mL; Magnetic stirrer								
No.	Acid Add. (mL)	pH	T (°C)		No.	Acid Add. (mL)	pH	T (°C)
1	0,0	6,68	22,3		1	0,0	6,67	26,5
2	0,5	6,63	22,3		2	0,5	6,61	26,4
3	1,0	6,60	22,4		3	1,0	6,57	26,4
4	1,5	6,55	22,4		4	1,5	6,52	26,4
5	2,0	6,51	22,4		5	2,0	6,47	26,4
6	2,5	6,47	22,5		6	2,5	6,41	26,3
7	3,0	6,43	22,6		7	3,0	6,38	26,3
8	3,5	6,39	22,6		8	3,5	6,32	26,3
9	4,0	6,35	22,6		9	4,0	6,30	26,1
10	4,5	6,32	22,6		10	4,5	6,25	26,1
11	5,0	6,28	22,6		11	5,0	6,22	26,1
12	5,5	6,24	22,6		12	5,5	6,18	26,1
13	6,0	6,21	22,7		13	6,0	6,14	26,0
14	6,5	6,17	22,7		14	6,5	6,10	26,0
15	7,0	6,14	22,7		15	7,0	6,06	26,0
16	7,5	6,10	22,7		16	7,5	6,03	26,0
17	8,5	6,06	22,7		17	8,0	5,98	26,0
18	9,0	6,03	22,7		18	8,5	5,95	25,9
19	9,5	5,99	22,7		19	9,2	5,90	25,9
20	10,0	5,96	22,9		20	9,5	5,88	25,9
21	10,5	5,93	22,9		21	10,0	5,85	25,9

22	11,0	5,89	22,9	22	10,5	5,81	25,8
23	11,5	5,86	22,9	23	11,0	5,78	25,8
24	12,0	5,82	22,9	24	11,5	5,74	25,8
25	12,5	5,79	23,0	25	12,0	5,71	25,8
26	13,0	5,76	23,0	26	12,5	5,68	25,8
27	13,5	5,72	23,0	27	13,0	5,63	25,8
28	14,0	5,68	23,0	28	13,5	5,59	25,7
29	14,5	5,65	23,0	29	14,0	5,55	25,7
30	15,0	5,60	23,0	30	14,5	5,51	25,7
31	15,5	5,56	23,0	31	15,0	5,48	25,7
32	16,0	5,52	23,0	32	16,0	5,37	25,7
33	16,5	5,47	23,0	33	17,0	5,27	25,7
34	17,0	5,42	23,0	34	18,0	5,15	25,6
35	17,5	5,38	23,0	35	19,0	5,02	25,6
36	18,5	5,28	23,1	36	20,0	4,87	25,6
37	19,0	5,23	23,1	37	21,0	4,70	25,6
38	19,5	5,17	23,1	38	22,1	4,48	25,6
39	20,0	5,10	23,1	39	22,8	4,36	25,5
40	20,5	5,05	23,1	40	23,2	4,24	25,5
41	21,5	4,88	23,1				
42	22,0	4,80	23,1				
43	22,5	4,70	23,1				
44	23,0	4,60	23,2				
45	23,5	4,50	23,2				
46	24,0	4,41	23,2				
47	24,5	4,32	23,2				

SI Determination: Standard Method 2330B – Section 2. Saturation Index by Calculation

Assumed: CaCO ₃ in Calcite form; T = 20°C; pKs = 8,45; All alkalinity due to bicarbonate ion (HCO ₃ ⁻)				
Substance	Charge	MW (g/mol)	Conc. (mg/L)	Conc. (mol/L)
Ca:	+2	40,078	1278	0,03189
Mg :	+2	24,305	488	0,02008
Na:	+1	22,989	15600	0,6786
K:	+1	39,09	1660	0,04247
Cl:	-1	35,45	33000	0,9309
Br:	-1	79,90	420	0,005257
SO ₄ :	-2	96,06	9260	0,09640
NH ₄ :	+1	18,04	2474,2	0,1372
Alkalinity*:	-1	-	-	0,024

* Units: mol H⁺/L

E2. PAC treated landfill leachate permeate:

Chemical Analysis and Measured Parameters

Substance/ Parameter	Value	DF
Ca ²⁺ (mg/L):	58,8; 56,8; 58,7	20
Mg ²⁺ (mg/L):	24,7; 25,2; 25,9	
Hardness (°dH):	14; 13,8; 14,2	
SO ₄ ²⁻ (mg/L):	481//486; 488	
COD (mg/L):	432;433// 453;421	10
TOC (mg/L):	27,66; 26,74; 31,85	20
TIC (mg/L):	8,01; 8,16; 7,73	
TC (mg/L):	35,67; 34,9; 39,58	
TN (mg/L):	91; 102,8; 109,6	
Ortho-PO ₄ ³⁻ P (mg/L):	2,42;2,41// 2,8;2,79	

Parameter	Measured values
pH:	7,32;7,39;7,29//7,22;7,16;7,16//7,36;7,31;7,37
Conductivity (mS/cm):	89,6;89,6;88,3//89,7;89,3;89,6//88,9;89,4;89,4
T (°C):	30,2;24,24,3//22,2;23,4;22,6//22,7;23,6;22,7

E3. NaOH as precipitation agent (Used permeate collected on spring season):

Landfill leachate permeate (LLP)

pH 9 – LLP; NaOH

Parameter	Measured values
Add. NaOH [12M] (mL):	2,6
pH:	9,12;9,12//9,1;9,06;9,07;9,05//9,16;9,12;9,1;9,05;9,02
Conductivity (mS/cm):	83,7//83,5;83,3;83,6;83,3//83,6;84;84,1;84,1;83,7
T (°C):	21,7//22,1//22,2;20,3;20,5

	t = 15 min		t = 60 min		t = 120 min	
Substance/ Parameter	Value	DF	Value	DF	Value	DF
Ca ²⁺ (mg/L):	79	10	68,8	10	65,7	10
Mg ²⁺ (mg/L):	38,3	10	38,5	10	37,4	10
Hardness (°dH):	19,9	10	18,5	10	17,9	10
TOC (mg/L):	-	-	57,59; 55,69	20	-	-
TIC (mg/L):	-	-	6,18; 5,07	20	-	-
TC (mg/L):	-	-	63,76; 60,76	20	-	-
Ortho-PO ₄ ³⁻ P (mg/L):	-	-	1,65	1	-	-

pH 12 – LLP; NaOH

Parameter	Measured values
Add. NaOH [12M] (mL):	10,0
pH:	12,02;12,03//12,02;12,03;12,05;12//12;12,01;12,04;12,02;12,01;12
Conductivity (mS/cm):	91,8;91,9;91,9//92,1;92,2;92,5;92,4//91,8;91,9;91,9;91,9;91,9;91,8
T (°C):	23,7;23,4//23,5;22,8;22,4;22,4//24,5;24,1;22,8;22,21,6

	t = 15 min		t = 60 min		t = 120 min	
Substance/ Parameter	Value	DF	Value	DF	Value	DF
Ca ²⁺ (mg/L):	62,6	5	85,6	2	64,1	2
Mg ²⁺ (mg/L):	3,76	5	4,59	2	3,23	2
Hardness (°dH):	9,65	5	13,1	2	9,73	2
TOC (mg/L):	-	-	58,08; 52,85	20	-	-
TIC (mg/L):	-	-	3,85; 2,92	20	-	-
TC (mg/L):	-	-	61,93; 55,78	20	-	-
Ortho-PO ₄ ³⁻ P (mg/L):	-	-	<0,5	1	-	-

E4. Mixed reagents (NaOH & Na₂CO₃) as precipitation agent (Used permeate collected on summer season):

Landfill leachate permeate (LLP)

pH 9 – LLP; Mixed reagents

Parameter	Measured values
Add. NaOH (g):	0,8058; 0,8058; 0,8088
Add. Na ₂ CO ₃ (g):	3,2273; 3,2229; 3,2265
pH:	8,69;9,18;9,19;9,19//8,69;9,16;9,19;9,11;9,08;9,06;8,99;9,08;9,06// 8,69;9,17;9,11;9,05;9,04;9,08;9,06;8,96;9,1;9,05;9,2;8,71;9,12;9,08;9,05
Conductivity (mS/cm):	90,3;89,9;89,8;89,8//90,2;90,89,9;90,90,1;90,2;90,5;90,3// 90,89,9;89,8;89,8;89,8;90,90,2;90,2;89,8;92,4;92,1;92,5;92,4
T (°C):	21,2;21,7;21,3;21,2//21,1;21,4;21,3;21,2;21,20,8;20,4;20,4// 21,21,4;21,6;21,8;22,22;22,2;22,2;22,2;22,3;21,7;21,8;21,6;21,7

	t = 1 h		t = 6 h		t = 24 h	
Substance/ Parameter	Value	DF	Value	DF	Value	DF
Ca ²⁺ (mg/L):	9,67	20	<5	1	<5	1
Mg ²⁺ (mg/L):	17,3	20	14,5	20	25,6	10
Hardness (°dH):	5,36	20	3,34	20	6,24	10
SO ₄ ²⁻ (mg/L):	-	-	-	-	478	20
COD (mg/L):	-	-	-	-	304;296	20
TOC (mg/L):	68,43; 62,67	20	-	-	-	-
TIC (mg/L):	30,71; 25,17	20	-	-	-	-
TC (mg/L):	99,15; 87,84	20	-	-	-	-
Ortho-PO ₄ ³⁻ P (mg/L):	-	-	-	-	1,51;1,52	1

pH 10 – LLP; Mixed reagents

Parameter	Measured values
Add. NaOH (g):	2,9345; 2,9335; 2,9328
Add. Na ₂ CO ₃ (g):	3,2226; 3,2289; 3,2280
pH:	10,08;10,07;10,07;10,06//9,95;10,11;10,12;10,15;10,1;10,07;10,06;10,09;10,03; 10//9,98;10,13;10,13;10,05;10,03;10,1;10,05;10,26;9,8;10,1;10,05;10,04
Conductivity (mS/cm):	89,8;88,4;88,9;88,4;88,5//89,5;88,1;87,1;87,7;88,2;88,2;88,3;88,4;88,4;88,4; 88,8//89,5;88,1;87,4;88,3;88,6;88,6;88,5;88,9;88,8;91,8;91,8;91,9;91,9
T (°C):	25,9;27,2;26,5;26,5;25,9//28,6;29,6;29,6;25,8;25,2;24,8;24,7;24,7;24,8;24,7// 27,8;28,8;28,9;26,5;25,8;25,9;25,9;26,2;26,3;23,8;23,9;24,5;24,7

	t = 1 h		t = 6 h		t = 24 h	
Substance/ Parameter	Value	DF	Value	DF	Value	DF
Ca ²⁺ (mg/L):	8,9	10	5,7	5	<5	1
Mg ²⁺ (mg/L):	33,7	10	39	10	40	10
Hardness (°dH):	9,04	10	17,4	5	17,3	5
	-	-	9,09	10	9,24	10
SO ₄ ²⁻ (mg/L):	-	-	-	-	479;480	20
COD (mg/L):	-	-	-	-	232	20
Ortho-PO ₄ ³⁻ P (mg/L):	-	-	-	-	1,74;1,89;1,93	1

pH 11 – LLP; Mixed reagents

Parameter	Measured values
Add. NaOH (g):	4,1656; 4,1534; 4,1869
Add. Na ₂ CO ₃ (g):	3,2219; 3,2225; 3,2233
pH:	11,45;11,39;11,4//11,15;11,15;11,22;11,21;11,19// 11,4;11,37;11,34;11,31;11,18;11,36;11,16;11,13
Conductivity (mS/cm):	90,1;88,6;89,5;90//89,3;87,6;87,8;89,3;89,5;90,2;90,2// 88,2;89,7;88,5;89,2;90,1;90,4;90,5;90,5;95,95,1
T (°C):	24,26,3;25,23,8//27,8;29,3;29,2;25,23,5;22,1;21,9// 24,8;25,27,2;24,8;23,8;23,8;23,9;23,9;20,9;21,2

	t = 1 h		t = 6 h		t = 24 h	
Substance/ Parameter	Value	DF	Value	DF	Value	DF
Ca ²⁺ (mg/L):	8,27;7,82	1,25	7,16	1,25	7,01	1,25
Mg ²⁺ (mg/L):	25,2;25,4	1,25	47,2	1,25	16,1	5
Hardness (°dH):	6,97	1,25	11,9	1,25	13,8	1,25
	-	-	-	-	3,71	5
SO ₄ ²⁻ (mg/L):	-	-	-	-	518;520	20
COD (mg/L):	-	-	-	-	233	20
Ortho-PO ₄ ³⁻ P (mg/L):	-	-	-	-	<0,5	1

pH 12 – LLP; Mixed reagents

Parameter	Measured values
Add. NaOH (g):	4,9573; 4,9349; 4,9583
Add. Na ₂ CO ₃ (g):	3,2292; 3,2262; 3,2287
pH:	12,07;12,2;12,05//12,02;12,21;11,98;12,21;12,16// 12,17;11,95;12,21;12,2;12,16;12,32;12,12
Conductivity (mS/cm):	90,4;90,4;91,1//90,6;89,8;90,4;91,5;92,3;92,3// 90,3;90,6;90,2;91,3;92,92,1;92,2;93,95,2
T (°C):	23,1;25,4;25,3;22,5//23,2;25,7;25,5;21,2;21,2;21,2// 22,8;24,3;24,2;22,6;22,7;23,1;23,1;23,2;21,6

	t = 1 h		t = 6 h		t = 24 h	
Substance/ Parameter	Value	DF	Value	DF	Value	DF
Ca ²⁺ (mg/L):	<5	1,25	<5	1,25	<5	1,25
Mg ²⁺ (mg/L):	5,77	1,25	29,2	1,25	3,66	1,25
Hardness (°dH):	1,33	1,25	7,2	1,25	0,846	1,25
SO ₄ ²⁻ (mg/L):	-	-	-	-	528	20
COD (mg/L):	-	-	-	-	245;243	20
TOC (mg/L):	63,82; 64,7	20	-	-	-	-
TIC (mg/L):	22,8; 24,99	20	-	-	-	-
TC (mg/L):	86,62; 89,68	20	-	-	-	-
Ortho-PO ₄ ³⁻ P (mg/L):	-	-	-	-	0,678	1,25

PAC treated Landfill leachate permeate (PAC-LLP)

pH 9 – PAC-LLP; Mixed reagents

Parameter	Measured values
Add. NaOH (g):	0,5514; 0,5545; 0,5518
Add. Na ₂ CO ₃ (g):	3,2573; 3,2541; 3,2559
pH:	8,98;9,22;9,15//8,87;9,14;9,13;9,09;9,06;9,03;9,19;9,17;9,12// 8,95;9,26;9,2;9,1;9,01;9,2;9,18;9,12;9,3;8,75;9,23;9,11
Conductivity (mS/cm):	91,1;90,6;90,6//90,6;90,6;90,6;90,7;90,8;90,8;90,7// 91,1;90,6;90,3;90,4;90,6;90,4;90,5;90,5;90,5;93,6;93,3;93,5
T (°C):	24,1;24,3;24,4//29,7;29,6;25,2;24,9;24,7;24,7;24,7;24,8// 24,4;24,7;25,6;25,9;26,1;26,26,6;26,5;24,2;24,4;24,7

	t = 1 h		t = 6 h		t = 24 h	
Substance/ Parameter	Value	DF	Value	DF	Value	DF
Ca ²⁺ (mg/L):	8,07	10	10,4	5	5,28	5
Mg ²⁺ (mg/L):	32,9	10	31,7	10	28,3	10
	18,1	20	-	-	-	-
Hardness (°dH):	8,73	10	14,6	5	13	5
	4,46	20	7,82	10	6,58	10
SO ₄ ²⁻ (mg/L):	-	-	-	-	491;492	20
TOC (mg/L):	26,67; 26,92	20	-	-	-	-
TIC (mg/L):	24,13; 26,63	20	-	-	-	-
TC (mg/L):	50,8; 53,55	20	-	-	-	-
Ortho-PO ₄ ³⁻ P (mg/L):	-	-	-	-	2,96;2,97	1

pH 10 – PAC-LLP; Mixed reagents

Parameter	Measured values
Add. NaOH (g):	2,5098; 2,5037; 2,5046
Add. Na ₂ CO ₃ (g):	3,2560; 3,2576; 3,2548
pH:	10,28;10,3;10,26//10,24;10,25;10,21;10,17;10,11;10,04// 10,23;10,23;10,15;10,09;10,04;10,10,01;10,31;9,72;10,15;10,18;10,1
Conductivity (mS/cm):	90,4;88,6;88,9;88,5//90,4;88,8;89,1;89,3;89,4;89,4;90,1// 89,7;88,1;89,1;89,2;89,2;89,6;89,5;89,6;89,2;92,7;92,7;92,7;93,4
T (°C):	25,1;26,5;24,22//26,5;28,23,4;22,9;22,9;20,7// 25,5;26,8;23,9;24,3;24,7;24,8;24,7;24,7;24,8;22,6;22,8;22,9;23

	t = 1 h		t = 6 h		t = 24 h	
Substance/ Parameter	Value	DF	Value	DF	Value	DF
Ca ²⁺ (mg/L):	10,1	10	<5	1	<5	1
Mg ²⁺ (mg/L):	33	10	34,8	10	35,4	10
	18,4	20	-	-	-	-
Hardness (°dH):	9,04	10	8,55	10	8,18	10
	4,48	20	-	-	-	-
SO ₄ ²⁻ (mg/L):	-	-	-	-	488	20
Ortho-PO ₄ ³⁻ P (mg/L):	-	-	-	-	2,44;2,43	1

pH 11 – PAC-LLP; Mixed reagents

Parameter	Measured values
Add. NaOH (g):	3,6228; 3,7640; 3,6133
Add. Na ₂ CO ₃ (g):	3,2560; 3,2514; 3,2550
pH:	11,31;11,21//11,53;11,38;11,37// 11,22;11,19;11,11;11,08;11,27;10,96;11,11
Conductivity (mS/cm):	91,2;89,1;90,2//90,9;89,2;90,6;90,9// 91,2;89,1;90,4;90,7;90,7;90,8;93,5;93,6
T (°C):	22,5;24,5;22,1//23,6;25,6;21,7;21,2// 22,7;24,6;22,4;22,3;22,4;22,6;21,1;21,2

Substance/ Parameter	t = 1 h		t = 6 h		t = 24 h	
	Value	DF	Value	DF	Value	DF
Ca ²⁺ (mg/L):	37,4;37	1,25	29,7	1,25	14,3	1,25
Mg ²⁺ (mg/L):	33;32,3	1,25	29,4	1,25	10,3	10
Hardness (°dH):	12,9;12,6	1,25	11	1,25	15,8	1,25
	-	-	-	-	2,38	10
SO ₄ ²⁻ (mg/L):	-	-	-	-	482	20
Ortho-PO ₄ ³⁻ P (mg/L):	-	-	-	-	1,01	1,25

pH 12 – PAC-LLP; Mixed reagents

Parameter	Measured values
Add. NaOH (g):	4,4770; 4,4760; 4,4753
Add. Na ₂ CO ₃ (g):	3,2535; 3,2586; 3,2516
pH:	11,88;12,02;11,9;12,05//12,2;12,24;12,21;12,15// 12,18;12,21;12,13;12,09;11,51;12,29;12,21;12,21
Conductivity (mS/cm):	90,4//90,7;90,9;91,3;92,2//90,8;90,6;90,9;91,7;92;92,1
T (°C):	22,7;24,8;24,6;23,7;23,7//23,6;25,8;22,9;20,9;20,9// 22,7;25;23,2;22,2;21,9;22,6;22,9;21,7;21,7

Substance/ Parameter	t = 1 h		t = 6 h		t = 24 h	
	Value	DF	Value	DF	Value	DF
Ca ²⁺ (mg/L):	31,7	1,25	28,4	1,25	10,2	1,25
Mg ²⁺ (mg/L):	4,01	1,25	3,33	1,25	<3	1,25
Hardness (°dH):	5,37	1,25	4,75	1,25	1,86	1,25
SO ₄ ²⁻ (mg/L):	-	-	-	-	515;522	20
TOC (mg/L):	27,77; 28,66	20	-	-	-	-
TIC (mg/L):	17,1; 18,8	20	-	-	-	-
TC (mg/L):	44,87; 47,47	20	-	-	-	-
Ortho-PO ₄ ³⁻ P (mg/L):	-	-	-	-	2,9;2,88	1,25

E5. Collected Air-drying Sludge and TSS:

Dried sludge from LLP with mixed reagents (Na ₂ CO ₃ -NaOH)			Dried sludge from PAC-LLP with mixed reagents (Na ₂ CO ₃ -NaOH)		
pH	Plastic dish (g)	Plastic dish+Dried sludge (g)	pH	Plastic dish (g)	Plastic dish+Dried sludge (g)
9	2,2324	4,3141	9	2,2133	4,1991
	2,2373	4,5545		2,2221	4,1340
	2,1940	4,5694		2,1806	4,3630
10	2,1963	4,9822	10	2,1744	4,8496
	2,2290	4,5046		2,2981	4,4585
	2,2284	4,5985		2,2451	4,5736
11	2,2272	5,4889	11	2,4866	5,9820
	2,2116	5,5352		2,2358	5,6327
	2,2889	6,1812		2,2575	5,6504
12	2,4785	6,7475	12	2,4501	6,5031
	2,5058	6,6298			
	2,4787	6,7848			

TSS from LLP with mixed reagents (Na ₂ CO ₃ -NaOH) Vol. sample = 0,1 L		
pH	Filter setup (g)	Filter setup+Dried solids (g)
9	2,6766	3,1215; 3,1213
10	2,6580	3,1382; 3,1385
11	2,6856	3,4233; 3,4236
12	2,7025	3,5418; 3,5422
TSS from LLP with NaOH Vol. sample = 0,1 L		
pH	Filter setup (g)	Filter setup+Dried solids (g)
9	2,6842	2,9084
10	2,6650	2,9709
11	2,6844	3,2163
12	2,6671	3,2388

TSS from PAC-LLP with mixed reagents (Na ₂ CO ₃ -NaOH) Vol. sample = 0,1 L		
pH	Filter setup (g)	Filter setup+Dried solids (g)
9	2,6854	3,1241
10	2,6816	3,1398
11	2,6810	3,2357
12	2,6725	3,3633

E6. Washing Step:

Washed solids from LLP with mixed reagents (Na ₂ CO ₃ -NaOH)				
Before washing			After washing	
pH	Dried sludge (g)	Dried sludge + DW (g)	Filter setup (g)	Filter setup+ Dried washed solids (g)
9	6,5105	71,6386	2,1822	8,1524
10	7,1770	78,9698	2,2001	8,3685
11	9,5477	105,2343	2,4644	10,3238
12	11,5846	127,5831	2,2511	9,1448

Washed solids from PAC-LLP with mixed reagents (Na ₂ CO ₃ -NaOH)				
Before washing			After washing	
pH	Dried sludge (g)	Dried sludge + DW (g)	Filter setup (g)	Filter setup+ Dried washed solids (g)
9	6,0012	66,0217	2,2669	7,7212
10	7,0241	77,2743	2,2322	8,1492

E7. Chemical Analysis:

Solids recovered from LLP with mixed reagents (Na ₂ CO ₃ -NaOH)				
Substance	pH 9	pH 10	pH 11	pH 12
Al (ppm)	70	79,8	57,6	96,6
Ca (ppm)	217000	220000	246000	222000
Fe (ppm)	139	239	165	176
K (ppm)	1710	1970	3210	5240
Mg (ppm)	15900	14000	27800	41800
Mn (ppm)	235	139	200	211
P (ppm)	2000	2000	1650	1490
Si (ppm)	<500	5820	7590	8350

Solids recovered from PAC-LLP with mixed reagents (Na ₂ CO ₃ -NaOH)				
Substance	pH 9	pH 10	pH 11	pH 12
Al (ppm)	69	70,7	56,1	125
Ca (ppm)	235000	227000	230000	219000
Fe (ppm)	145	129	91,1	86
K (ppm)	1570	3380	4380	5580
Mg (ppm)	16700	15900	27700	32800
Mn (ppm)	264	189	214	213
P (ppm)	7000	13000	4600	9930
Si (ppm)	<500	6520	8860	8590

E8: 10 L Precipitation:

Chemical Analysis and Measured Parameters in LLP

Substance/ Parameter	Season – Value	DF
	Beginning Fall	
Ca ²⁺ (mg/L):	76,5; 70,7	20
Mg ²⁺ (mg/L):	26,5; 26,6	
Hardness (°dH):	16,9; 16,1	
NH ₄ ⁺ -N (mg/L):	20,5; 20,4	100
TN (mg/L):	42,78; 42,98	50
	112,5; 114,6	20
TOC (mg/L):	20,85; 21,89; 21,57	50
	81,57; 64,96	20
TIC (mg/L):	7,06; 5,06; 5,34	50
	18,73; 18,40	20
TC (mg/L):	27,92; 26,95; 26,90	50
	100,3; 83,35	20
SO ₄ ²⁻ (mg/L):	531	20
pH	6,89; 6,95; 6,82; 6,69; 7,04; 7,28	-
Conductivity (mS/cm):	89,7; 89,6; 90,4; 90,0; 88,9; 92,0; 91,8	-
T (°C):	21,9; 22,8; 22,8; 22,1; 18,6; 17,9	-

pH 10 – LLP; Mixed reagents

Parameter	Measured values
Add. NaOH (g):	42,73; 42,72; 42,78; 55,93; 55,96; 55,87
Add. Na ₂ CO ₃ (g):	64,30; 64,36; 64,28; 64,29; 64,31; 64,29
pH:	10,53;10,58;10,58;10,31;10,31;10,31;10,31
Conductivity (mS/cm):	-
T (°C):	20,5;20,5;20,4;19,8;19,8;19,9;19,9

Substance/ Parameter	LLP-SN	
	Value	DF
Ca ²⁺ (mg/L):	9,34; 8,7	5
Mg ²⁺ (mg/L):	74	5
	22,8	20
Hardness (°dH):	18,4	5
	5,3	20

pH 11 – LLP; Mixed reagents

Parameter	Measured values
Add. NaOH (g):	83,02; 82,97; 83,00; 83,04; 82,99; 83,07
Add. Na ₂ CO ₃ (g):	64,30; 64,32; 64,30; 64,30; 64,30; 64,30
pH:	11,05; 11,16; 11,17; 11,16; 11,17
Conductivity (mS/cm):	-
T (°C):	23,2;23,4;23,5;23,1;23,5

Substance/ Parameter	LLP-SN	
	Value	DF
Ca ²⁺ (mg/L):	39; 13,5	1,25
Mg ²⁺ (mg/L):	113	1,25
	15,1	10
Hardness (°dH):	31,5	1,25
	3,82	10

pH 12 – LLP; Mixed reagents

Parameter	Measured values
Add. NaOH (g):	95,06; 94,96; 94,98; 94,93; 94,93; 99,06
Add. Na ₂ CO ₃ (g):	64,30; 64,30; 64,30; 64,30; 64,30; 64,30
pH:	11,55;12,62;12,72;12,70;12,69;12,44;12,68;12,68;12,65;12,60;12,57; 12,18;12,49;12,48;12,49;12,47;12,23;12,19
Conductivity (mS/cm):	96,2;95,9;94,1;93,8;91,1;92,9;92,0;93,2;93,4;93,4;93,0;92,0
T (°C):	23,9;23,9;23,9;23,9;26,1;26,9;26,9;26,6;23,4;23,4;23,4;26,2; 26,4;26,4;25,9;25,4;25,2;25,1;21,4;21,4;21,4; 21,4;24,3;24,5;24,5;24,6;24,7;22,5;25,0;25,4;25,4;25,3

	LLP-SN	
Substance/ Parameter	Value	DF
Ca ²⁺ (mg/L):	<5; <5; <5; <5	1,25
Mg ²⁺ (mg/L):	2,37	5
	4,78; <3; <3	1,25
Hardness (°dH):	0,546	5
	1,26; <1; <1	1,25
TN (mg/L):	20,01;19,16;20,9	100
TOC (mg/L):	11,01;10,27;11,1;10,74	100
TIC (mg/L):	6,93;6,55;6,83;6,58	100
TC (mg/L):	17,94;16,82;17,93;17,32	100

TSS for LLP-SN decanted from Separation Units (Precipitation with mixed Na ₂ CO ₃ -NaOH at pH 12) Vol. sample = 0,5 L			
Permeate	Separation Units	Filter setup (g)	Filter setup+Dried solids (g)
LLP-SN	Sedimentation	0,9106	0,9458
		1,0601	1,0985
	Centrifugation	0,7949	0,8389
		0,6273	0,6647

Volumes of LLP-SN decanted from Separation Units (Precipitation with mixed Na ₂ CO ₃ -NaOH at pH 12)		
Permeate	Separation Units	Volume (mL)
LLP-SN	Sedimentation	6000
		6400
	Centrifugation	3600
		3220

Dried collected sludge	
No.	Weight (g)
1	57,25
2	51,85
3	44,10
4	61,17

Consecutive washes

Initial amount dried sludge = 150 g				
Wash No.	Add. DW (mL)	Conductivity (mS/cm)	pH	T (°C)
1	1500	46,90	10,2	22,6
2	1000	19,21	10,2	22,2
3	1000	7,74	10,1	20,3
4	1000	3,27	10,3	22,0
5	1000	1,62	10,3	22,8
6	1000	1,12	10,3	22,5
7	1000	0,65	10,1	22,3
8	1000	0,509	10,2	23,0
9	1000	0,464	10,3	22,4
10	1000	0,427	10,5	23,0
11	1000	0,397	10,3	22,8
12	1000	0,341	10,4	21,7
13	1000	0,308	10,2	22,2
14	1000	0,281	10,5	22,5
15	1000	0,268	10,4	21,9

S:DW washing ratio= 1:10

Solids generated at pH 12 in 10L precipitator with mixed Na ₂ CO ₃ -NaOH reagents (After washing: Washwater vacuum filtrated through 1,5µm glass fiber filter)	
Parameter	Measured values
pH	9,82; 9,89; 9,85; 9,93// 10,47; 10,16; 10,52; 10,49; 10,50
Conductivity (mS/cm):	46,3; 43,0; 49,8; 48,6// 41,0; 45,4; 50,5; 53,5
T (°C):	20,2; 21,1; 21,4; 21,6// 24,0; 23,6; 21,3; 21,4; 23,2

S:DW washing ratio= 1:30

Solids generated at pH 12 in 10L precipitator with mixed Na ₂ CO ₃ -NaOH reagents (After washing: Washwater vacuum filtrated through 1,5µm glass fiber filter)	
Parameter	Measured values
pH	10,18; 10,2; 10,18; 10,15; 10,19// 10,1; 10,12; 10,15; 10,18; 10,18// 10,06; 10,19; 10,22; 10,23; 10,18// 10,11; 10,04; 10,09; 10,1; 10,04
Conductivity (mS/cm):	16,89; 16,52; 18,75; 17,51; 15,59// 19,8; 18,86; 17,9; 21,6; 18,88// 18,68; 18,52; 17,56; 19,77; 23,4// 21,3; 22,7; 21,8; 21,2; 21,2
T (°C):	22,4; 21,7; 21,3; 20,4; 21,4//21,8; 22; 21,5; 21,1; 21,5// 21,7; 21,5; 21,1; 20,5; 21,3; 21,1; 22; 21,6; 21,2; 20,6

S:DW washing ratio= 1:50

Solids generated at pH 12 in 10L precipitator with mixed Na ₂ CO ₃ -NaOH reagents (After washing: Washwater vacuum filtrated through 1,5µm glass fiber filter)	
Parameter	Measured values
pH	10,2; 10,24; 10,23; 10,24; 10,22// 10,14; 10,23; 10,27; 10,17; 10,3// 10,2; 10,43; 10,2; 10,26; 10,27// 10,26; 10,21; 10,23; 10,17; 10,24// 10,18; 10,25; 10,18; 10,25; 10,25
Conductivity (mS/cm):	9,72; 10,52; 14,15; 13,11; 17,4//16,31; 14; 12,12; 14,64; 11,62// 10,26; 12,87; 11,06; 9,3; 10,4// 12,07; 11,38; 12,56; 11,98; 11,92// 12,82; 12,43; 11,4; 11,51; 13,02
T (°C):	22,9; 22,4; 21,7; 21,4; 22,5// 22,3; 21,2; 21,4; 21,4; 20,6// 22,1; 21,2; 20,5; 21; 21,1// 22,1; 21,2; 21; 20,7; 20,6// 22,3; 21,1; 21; 20,6; 20,6

Solids generated at pH 12 in 10L precipitator with mixed Na ₂ CO ₃ -NaOH reagents (After washing: Washwater vacuum filtrated through 1,5µm glass fiber filter)						
Substance/Parameter	Washwater (1:10)		Washwater (1:30)		Washwater (1:50)	
	Value	DF	Value	DF	Value	DF
Ca ²⁺ (mg/L):	<5	1	<5	1	<5	1
	<5	1	<5	1	<5	1
Mg ²⁺ (mg/L):	19,1	20	36,9	10	26,4	5
	20,1	20	38,0	10	36,8	5
Hardness (°dH):	4,4	20	8,52	10	6,1	5
	4,64	20	8,9	10	8,51	5
SO ₄ (mg/L):	382	10	250;251	5	677;674	1
	387	10	257;259	5	885;882	1
TOC (mg/L)	27,04	20	15,98;17,99	10	10,88;10,26	10
	26,03	20	18,71;18,13	10	13,46;9,63	10
TIC (mg/L)	30,19	20	39,12;38,71	10	23,28;23,98	10
	30,97	20	41,26;42,12	10	22,77;22,47	10
TC (mg/L)	57,22	20	55,1;56,7	10	34,16;34,25	10
	57,00	20	59,97;60,25	10	36,23;32,1	10
TN (mg/L)	2,84	20	2,37;2,12	10	1,18;1,52	10
	2,82	20	2,44;2,18	10	1,71;1,45	10

Washed solids from LLP in 10 L precipitator with mixed reagents (Na ₂ CO ₃ -NaOH) At different Solids to washwater (S:DW) ratio conditions				
Before washing			After washing	
Washing ratio	Dried sludge (g)	Dried sludge + DW (g)	Plastic tray (g)	Plastic tray + Dried washed solids (g)
1:10	200,0	2200	13,2	136,0
	214,4	2358	13,3	146,3
1:30	83,3	2582,3	13,2	61,8
	83,3	2582,3	13,2	57,1
	83,3	2582,3	13,2	57,4
	83,3	2582,3	13,2	50,4
1:50	50	2550	13,2	37,7
	50	2550	13,2	37,2
	50	2550	13,2	36,2
	50	2550	13,2	39,6
	50	2550	13,2	38

XRF analysis in recovered solids from different solids to washwater ratios (S:DW)		
Substance	S:DW (1:30)	S:DW (1:50)
Cl (ppm)	1637	440
S (ppm)	<1208	<1208
Ca (ppm)	267193	283799
Fe (ppm)	2249	2215
K (ppm)	2415	2203
Mg (ppm)	16989	<15000
Mn (ppm)	324	<215
P (ppm)	2335	2182
Si (ppm)	<7470	<7470
Ti (ppm)	344	445

APPENDIX F: Membrane Contactor – Raw Data

F1. pH effect on membrane contactor treatment:

Parameters measured during membrane treatment at pH 12		
Parameter		Measured values
pH	Permeate	12,4; 12,4; 12,3; 12,3; 12,3; 12,2; 12,2; 12,2; 12,2// 12,3; 12,2; 12,2; 12,2; 12,2; 12,1; 12,1; 12,1; 12,1
	Acid Sltn.	1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,2; 1,1// 1,2; 1,1; 1,1; 1,1; 1,1; 1,2; 1,1; 1,1; 1,1
T (°C):	Permeate	14; 20; 22; 23; 24; 26; 27; 28; 29; 30; 31; 31; 32; 33; 33; 34; 34; 35; 35// 20; 23; 24; 26; 27; 28; 29; 30; 31; 32; 32; 33; 34; 35; 35; 36; 36; 37; 37
	Acid Sltn.	23; 21; 22; 23; 25; 26; 27; 28; 29; 30; 31; 31; 32; 33; 33; 34; 34; 35; 35// 23; 23; 24; 26; 27; 28; 29; 30; 31; 32; 32; 33; 34; 35; 35; 36; 36; 37; 37
Cond. (mS/cm)	Permeate	Initial: 93,2; 94,3 // Final: 94,4
	Acid Sltn.	Initial: 61,8; 58,1 // Final: 43,3
Vol. pH control Sltn. (mL)	Permeate	NaOH (12M): 0; 0
	Acid Sltn.	H ₂ SO ₄ (65%): 2; 19

Parameters measured during membrane treatment at pH 11		
Parameter		Measured values
pH	Permeate	11,1; 11,0; 11,0; 11,0; 11,0; 11,0; 11,0; 11,0; 11,0; 11,0; 11,0; 11,0// 11,0; 11,1; 11,0; 11,0; 11,1; 11,0; 11,0; 11,0; 11,0; 11,0; 11,0; 11,0
	Acid Sltn.	1,2; 1,2; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1// 1,1; 1,2; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1; 1,1
T (°C):	Permeate	12; 19; 21; 22; 24; 25; 26; 27; 28; 29; 30; 30; 31; 32; 32; 33; 33; 34; 34; 35; 35; 35; 36; 36; 36//16; 20; 22; 23; 25; 26; 27; 28; 29; 30; 31; 31; 32; 33; 33; 34; 34; 35; 35; 36; 36; 36; 37; 37; 37
	Acid Sltn.	23; 20; 21; 22; 24; 25; 26; 27; 28; 29; 30; 30; 31; 32; 32; 33; 33; 34; 34; 35; 35; 35; 36; 36; 36//21; 21; 22; 24; 25; 26; 27; 28; 29; 30; 31; 31; 32; 33; 33; 34; 34; 35; 35; 36; 36; 36; 37; 37; 37
Cond. (mS/cm)	Permeate	Initial: 93; 92 // Final: 92,6; 93
	Acid Sltn.	Initial: 59,3; 58,8 // Final: 48,5; 47,5
Vol. pH control Sltn. (mL)	Permeate	NaOH (12M): 16; 22
	Acid Sltn.	H ₂ SO ₄ (65%): 38; 33

Parameters measured during membrane treatment at pH 10		
Parameter		Measured values
pH	Permeate	10,2; 10; 10; 9,9; 9,9; 9,9; 9,9; 9,9; 10; 10,1; 10; 10,1; 10; 10; 10; 10,1; 10; 10; 10; 10,2; 10,1; 10,1; 10; 10; 10; 10; 10; 10; 10,2; 10,1; 10,1
	Acid Sltn.	1,1; 1,1; 1,1; 1,1; 1,2; 1,2; 1,1; 1,2; 1,2; 1,2; 1,1; 1,2; 1,2; 1,1; 1,2; 1,3; 1,3; 1,1; 1,1; 1,2; 1,1; 1,1; 1,2; 1,3; 1,3; 0,9; 0,9; 0,9; 0,9; 0,9; 0,9
T (°C):	Permeate	10; 18; 19; 21; 22; 23; 25; 26; 27; 28; 28; 29; 30; 30; 31; 32; 32; 32; 33; 33; 34; 34; 34; 35; 35; 35; 36; 36; 36; 36; 36//10; 20; 22; 22; 24; 25; 26; 27; 28; 29; 29; 30; 31; 31; 32; 32; 33; 33; 33; 34; 34; 34; 35; 35; 35
	Acid Sltn.	22; 19; 20; 21; 22; 24; 25; 26; 27; 28; 28; 29; 30; 30; 31; 32; 32; 32; 33; 33; 34; 34; 34; 35; 35; 35; 36; 36; 36; 36; 36; 23; 20; 22; 22; 24; 25; 26; 27; 28; 29; 29; 30; 31; 31; 32; 32; 33; 33; 33; 34; 34; 34; 35; 35; 35
Vol. pH control Sltn. (mL)	Permeate	NaOH (12M): 46; 41
	Acid Sltn.	H ₂ SO ₄ (65%): 74; 50

TN concentration in Acid Solution – pH 12		
Time (min)	TN (mg/L)	DF
0	0,087; 0,259	1
30	36,63; 29,86	50
60	46,08; 39,06	50
75	47,55; 40,78	50
90	47,91; 41,53	50

TN concentration in Permeate (LLP)						
Time (min)	pH 12		pH 11		pH 10	
	TN (mg/L)	DF	TN (mg/L)	DF	TN (mg/L)	DF
0	107,7; 106,1// 100,3; 109,3	20	112,3; 109,3// 110,1; 112,4	20	114,9; 107// 116,3; 110,6	20
30	12,07; 10,02	50	43,98; 40,06	20	58,05	20
60	10,48; 8,99	20	17,93; 16,96	20	21,76; 25,16	20
75	6,45; 6,1	20	-	-	-	-
90	4,83; 4,59	20	9,29; 9,21	20	9,9	20
120	-	-	6,28; 7,37	20	7,79	20
150	-	-	-	-	4,93	20

TN and NH ₄ -N in Acid Solution – End treatment					
pH	Treat. time (min)	TN (mg/L)	DF	NH ₄ -N (mg/L)	DF
10	150	-	-	23,7	100
11	120	48,06; 45,34	50	23,0	100
12	90	47,91; 41,53	50	22,0	100

NH ₃ -ISE Recorded values						
Time (min)	NH ₃ -N (mg/L)					
	pH10		pH11		pH 12	
0	941	948		3883		1882
5	404	388	9885	1979	5749	1337
10	216	255	7402	1657	3164	1011
15	152	155	5074	1401	1664	781
20	125	123	3803	1029	1069	615
25	111	105	3155	815	629	464
30	99,9	89,9	1945	682	361	345
35	88,3	79	1003	569	251	269
40	74,1	68,2	517	480	184	209
45	60,1	58,1	349	394	139	156
50	52,2	48,2	269	334	106	112
55	43,5	41	217	222	79,4	83,7
60	39,1	35,5	183	173	58,8	62,1
65	35,6	30,3	155	143	46	46,8
70	30,8	26,8	134	115	34,3	34,7
75	26,2	22,8	110	91,9	25,4	26,6
80	21,9	19,8	90,2	74,3	19,6	19,9
85	18,5	16,9	76,5	62,3	14,4	15,1
90	15,1	14,4	62,7	50,2	10,5	11,5
95	11,8	12,9	51,9	42,3		
100	10,4	11,1	43,8	35,2		
105	8,54	9,54	36	29,6		

110	6,92	8,26	29	24,3		
115	5,95	7,15	23,3	20,7		
120	4,97	6,19	18,8	18		
125	4					
130	3,25					
135	2,72					
140	3,31					
145	2,42					
150	2,01					

F2. Reduction and recovery of NH₃ from LLP:

Time (min)	pH									
	Batch No. 1		Batch No. 2		Batch No. 3		Batch No. 4		Batch No. 5	
	LLP	Acid Sltn.	LLP	Acid Sltn.	LLP	Acid Sltn.	LLP	Acid Sltn.	LLP	Acid Sltn.
0	11,8	1,2	12,0	1,1	12,0	1,1	12,2	1,0	12,2	1,1
5	11,7	1,3	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
10	11,7	1,3	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
15	11,8	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
20	11,8	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
25	11,9	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
30	12,0	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
35	12,0	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
40	12,0	1,1	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
45	12,0	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
50	12,0	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
55	12,0	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
60	12,0	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
65	12,0	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
70	11,9	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
75	12,0	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
80	11,9	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
85	12,0	1,2	12,0	1,1	12,0	1,1	12,2	1,1	12,2	1,1
90	11,9	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
95	11,9	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
100	11,9	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
105	11,9	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
110	11,9	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
115	11,9	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
120	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
125	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
130	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
135	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
140	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
145	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
150	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
155	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
160	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
165	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
170	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
175	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,2
180	12,0	1,1	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
185	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
190	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
195	11,9	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
200	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
205	11,9	1,1	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1

210	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
215	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
220	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
225	12,0	1,1	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
230	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
235	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
240	12,0	1,1	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
245	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
250	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
255	11,9	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
260	11,9	1,1	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
265	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
270	11,9	1,2	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
275	11,9	1,1	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
280	11,9	1,1	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
285	11,9	1,1	12,0	1,1	12,0	1,2	12,0	1,2	12,0	1,1
290	11,9	1,1	11,9	1,1	12,0	1,2	12,0	1,2	12,0	1,1
295	11,9	1,2	11,9	1,1	12,0	1,2	12,0	1,2	12,0	1,1
300	11,9	1,1	11,9	1,1	11,9	1,1	11,9	1,1	11,9	1,1

Time (min)	pH									
	Batch No. 6		Batch No. 7		Batch No. 8		Batch No. 9		After Regen.	
	LLP	Acid Sltn.	LLP	Acid Sltn.	LLP	Acid Sltn.	LLP	Acid Sltn.	LLP	Acid Sltn.
0	12,3	1,0	12,3	1,1	12,4	1,1	12,4	1,1	12,2	1,1
5	12,3	1,0	12,3	1,1	12,4	1,1	12,4	1,1	12,2	1,1
10	12,3	1,0	12,3	1,1	12,4	1,1	12,4	1,1	12,1	1,1
15	12,3	1,0	12,3	1,1	12,4	1,1	12,4	1,1	12,1	1,1
20	12,3	1,0	12,3	1,1	12,4	1,1	12,4	1,1	12,1	1,2
25	12,3	1,0	12,3	1,1	12,4	1,1	12,4	1,1	12,0	1,1
30	12,3	1,0	12,3	1,1	12,1	1,1	12,4	1,1	12,0	1,1
35	12,3	1,0	12,3	1,1	12,0	1,1	12,4	1,1	12,0	1,2
40	12,3	1,0	12,3	1,1	12,0	1,1	12,4	1,1	12,0	1,1
45	12,3	1,0	12,3	1,1	12,0	1,1	12,4	1,1	12,0	1,1
50	12,3	1,0	12,3	1,1	12,0	1,1	12,4	1,1	12,0	1,1
55	12,3	1,0	12,3	1,1	12,0	1,1	12,4	1,1	12,0	1,1
60	12,3	1,0	12,3	1,1	12,0	1,2	12,4	1,1	12,0	1,1
65	12,3	1,0	12,3	1,1	12,0	1,2	12,0	1,2	12,0	1,1
70	12,3	1,0	12,3	1,1	12,0	1,2	12,0	1,2	12,0	1,1
75	12,3	1,0	12,3	1,1	12,0	1,2	12,0	1,2	12,0	1,1
80	12,3	1,0	12,3	1,1	12,0	1,2	12,0	1,2	12,0	1,1
85	12,3	1,0	12,3	1,1	12,0	1,2	12,0	1,2	12,0	1,1
90	12,0	1,2	12,0	1,2	12,0	1,2	12,0	1,2	12,0	1,1
95	12,0	1,2	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2
100	12,0	1,2	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,1
105	12,0	1,2	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,1
110	12,0	1,2	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,1
115	12,0	1,2	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,1
120	12,0	1,2	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,1
125	12,0	1,2	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2
130	12,0	1,2	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,1
135	12,0	1,2	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,1
140	12,0	1,2	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,2
145	12,0	1,2	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,1
150	12,0	1,2	12,0	1,2	12,0	1,1	12,0	1,2	12,0	1,1
155	12,0	1,2	12,0	1,2	12,0	1,1	11,9	1,2	12,0	1,1
160	12,0	1,2	12,0	1,2	12,0	1,1	11,9	1,2	11,9	1,1
165	12,0	1,2	12,0	1,2	12,0	1,1	11,9	1,2	12,0	1,2

170	12,0	1,2	12,0	1,2	12,0	1,1	11,9	1,2	12,0	1,2
175	12,0	1,2	12,0	1,2	12,0	1,1	11,9	1,2	11,9	1,1
180	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
185	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
190	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,2
195	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,2
200	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
205	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
210	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
215	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
220	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
225	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
230	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
235	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
240	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
245	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
250	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
255	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
260	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
265	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
270	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	11,9	1,1
275	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	11,9	1,1
280	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	11,9	1,1
285	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	11,9	1,1
290	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,1
295	12,0	1,2	11,9	1,2	12,0	1,1	11,9	1,2	12,0	1,2
300	12,0	1,2	12,0	1,1	11,9	1,2	11,9	1,2	11,9	1,1

Time (min)	T (°C)									
	Batch No. 1		Batch No. 2		Batch No. 3		Batch No. 4		Batch No. 5	
	LLP	Acid Sltn.	LLP	Acid Sltn.	LLP	Acid Sltn.	LLP	Acid Sltn.	LLP	Acid Sltn.
0	16	22	15	20	14	20	9	20	9	19
5	18	19	17	18	15	15	13	14	10	10
10	18	20	17	17	16	16	13	13	11	11
15	19	20	17	17	16	16	13	13	12	12
20	20	21	18	18	17	17	14	14	13	13
25	20	22	19	19	18	18	15	15	14	14
30	21	22	19	19	19	19	16	16	15	15
35	22	23	20	20	19	19	16	16	16	16
40	22	23	21	21	20	20	17	17	16	16
45	23	24	22	22	21	21	18	18	17	17
50	24	24	22	22	22	22	19	19	18	18
55	24	25	23	23	22	22	20	20	19	19
60	25	26	23	23	23	23	20	20	19	19
65	25	26	24	24	23	23	21	21	20	20
70	26	26	25	25	24	24	22	22	21	21
75	26	27	25	25	25	25	22	22	21	21
80	27	27	26	26	25	25	23	23	22	22
85	27	28	26	26	26	26	24	24	23	23
90	28	28	27	27	27	27	25	26	24	25
95	28	28	27	27	27	27	25	25	24	24
100	28	28	28	28	27	27	25	25	24	24
105	29	29	28	28	28	28	26	26	25	25
110	29	29	29	29	28	28	26	26	25	25
115	30	30	29	29	29	29	27	27	26	26
120	31	31	29	29	29	29	27	27	26	26
125	31	31	30	30	29	29	28	28	27	27

130	31	31	30	30	30	30	28	28	27	27
135	32	32	31	31	30	30	29	29	28	28
140	32	32	31	31	31	31	29	29	28	28
145	33	33	31	31	31	31	29	29	28	28
150	33	33	31	31	31	31	30	30	29	29
155	33	33	32	32	32	32	30	30	29	29
160	33	33	32	32	32	32	30	30	29	29
165	33	33	32	32	32	32	31	31	30	30
170	33	33	33	33	32	32	31	31	30	30
175	33	33	33	33	33	33	31	31	30	30
180	33	33	33	33	33	33	32	32	30	31
185	33	34	33	33	33	33	32	32	31	31
190	34	34	34	34	34	34	32	32	31	31
195	34	34	34	34	34	34	32	32	32	32
200	34	34	34	34	34	34	32	32	32	32
205	34	34	34	34	34	34	33	33	32	32
210	34	35	34	34	34	34	33	33	32	32
215	34	35	35	35	35	35	33	33	32	32
220	35	35	35	35	35	35	34	34	33	33
225	35	35	35	35	35	35	34	34	33	33
230	35	35	35	35	35	35	34	34	34	34
235	35	35	35	35	35	35	34	34	34	34
240	35	35	35	35	36	36	34	34	34	34
245	35	36	35	35	36	36	34	34	34	34
250	36	36	36	36	36	36	34	34	34	34
255	36	36	36	36	36	36	34	34	34	34
260	36	36	36	36	36	36	34	34	34	34
265	36	36	36	36	36	36	34	34	34	34
270	36	36	36	36	36	36	34	34	34	34
275	36	36	36	36	36	36	35	35	34	34
280	36	36	36	36	36	36	35	35	34	34
285	36	36	36	36	36	36	35	35	34	34
290	36	36	36	36	36	36	35	35	34	34
295	37	36	36	36	36	36	35	35	34	34
300	37	36	36	36	36	36	35	35	35	35

T (°C)										
Time (min)	Batch No. 6		Batch No. 7		Batch No. 8		Batch No. 9		After Regen.	
	LLP	Acid Sltn.	LLP	Acid Sltn.	LLP	Acid Sltn.	LLP	Acid Sltn.	LLP	Acid Sltn.
0	9	18	9	19	9	19	9	19	10	20
5	10	10	10	10	10	10	10	10	13	14
10	11	11	11	11	11	11	11	11	13	15
15	12	12	12	12	12	12	12	12	14	16
20	13	13	13	13	13	13	13	13	15	17
25	13	13	14	14	14	14	14	14	16	17
30	14	14	15	15	15	17	15	15	17	18
35	15	15	16	16	16	18	16	16	18	20
40	16	16	16	16	17	18	17	17	18	19
45	17	17	17	17	18	19	18	18	19	20
50	17	17	18	18	19	20	18	18	20	21
55	18	18	18	18	19	20	19	19	20	21
60	19	19	19	19	20	21	20	20	21	22
65	19	19	20	20	21	22	22	22	22	23
70	20	20	20	20	21	22	22	22	22	23
75	21	21	21	21	22	23	23	23	23	24
80	21	21	22	22	22	23	23	23	24	24
85	22	22	22	22	23	24	24	24	24	25

90	23	24	23	23	23	24	24	24	25	26
95	23	23	24	25	24	25	25	25	25	27
100	24	24	24	24	25	25	25	25	26	26
105	24	24	24	24	26	26	25	25	26	27
110	25	25	25	25	26	26	26	26	27	27
115	25	25	25	25	27	27	26	26	27	28
120	25	25	26	26	27	27	27	27	28	28
125	26	26	26	26	28	28	27	27	28	29
130	26	26	27	27	28	28	28	28	28	29
135	27	27	27	27	28	28	28	28	29	29
140	27	27	28	28	29	29	29	29	29	30
145	28	28	28	28	29	29	29	29	30	30
150	28	28	28	28	30	30	29	29	30	30
155	28	28	29	29	30	30	30	30	30	31
160	29	29	29	29	30	30	30	30	31	31
165	29	29	29	29	31	31	30	30	31	31
170	29	29	30	30	31	31	31	31	31	32
175	29	29	30	30	31	31	31	31	32	32
180	30	30	30	30	31	31	31	31	32	32
185	30	30	31	31	32	32	32	32	32	32
190	30	30	31	31	32	32	32	32	32	33
195	31	31	31	31	32	32	32	32	32	33
200	31	31	31	31	32	32	32	32	33	33
205	31	31	32	32	33	33	33	33	34	34
210	31	31	32	32	33	33	33	33	35	35
215	31	31	32	32	33	33	33	33	36	36
220	32	32	32	32	33	33	33	33	37	37
225	32	32	33	33	33	33	33	33	38	38
230	32	32	33	33	34	34	34	34	39	39
235	32	32	33	33	34	34	34	34	40	40
240	32	32	33	33	34	34	34	34	41	41
245	33	33	33	33	34	34	34	34	42	42
250	33	33	34	34	34	34	34	34	43	43
255	33	33	34	34	34	34	34	34	44	44
260	33	33	34	34	35	35	35	35	45	45
265	33	33	34	34	35	35	35	35	46	46
270	33	33	34	34	35	35	35	35	35	35
275	33	33	34	34	35	35	35	35	35	35
280	34	34	34	34	35	35	35	35	35	35
285	34	34	34	34	35	35	35	35	35	35
290	34	34	34	34	35	35	35	35	35	35
295	34	34	34	34	35	35	35	35	35	35
300	34	34	34	34	35	35	35	35	35	35

Volume pH control solution (mL)		
Batch No.	NaOH (12M)	H ₂ SO ₄ (65%)
1	344	387
2	417	389
3	430	369
4	212	364
5	189	416
6	227	392
7	223	450
8	383	438
9	359	583
‡After Regen.	379	216

‡Used H₂SO₄ (95%)

Composition in Permeate (LLP)		
Substance	value	DF
TN (mg/L):	112,9; 111,1; 108,2; 114,1; 111,4	20
NH ₄ -N (mg/L):	21,2; 20,7; 20,8// 20,7; 20,8// 20,8	100
TOC (mg/L):	62,98; 60,64; 61,11; 63,27; 61,71	20
SO ₄ (mg/L):	482; 484	20

NH ₄ -N Conc. in (LLP) – During membrane treatment				
Time (h)	Batch No. 1		Batch After regeneration	
	NH ₄ -N (mg/L)	DF	NH ₄ -N (mg/L)	DF
1,5	18,6	50	-	-
3	15,8	20	17,3	20
5	5,96; 5,97	10	4,36	10

TN concentration in Permeate (LLP) – During membrane treatment										
Time (h)	Batch 1		Batch 2		Batch 3		Batch 4		Batch 5	
	TN (mg/L)	DF	TN (mg/L)	DF	TN (mg/L)	DF	TN (mg/L)	DF	TN (mg/L)	DF
1,5	49,62	20	54,55	20	58,49	20	59,98	20	62,08	20
3	21,01	20	22,88	20	23,3	20	15,06	20	27,46	20
5	7,57	20	8,44	20	8,37	20	8,58	20	9,35	20

TN concentration in Permeate (LLP) – During membrane treatment										
Time (h)	Batch 6		Batch 7		Batch 8		Batch 9		After Regen.	
	TN (mg/L)	DF	TN (mg/L)	DF	TN (mg/L)	DF	TN (mg/L)	DF	TN (mg/L)	DF
1,5	69,15	20	64,87	20	69,53	20	86,36	20	63,07	20
3	28,22	20	27,6	20	30,48	20	41,34	20	23,82	20
5	9,36	20	9,7	20	11,02	20	12,06	20	7,15	20

After regeneration Batch			
Time (min)	Vol. Acid solution (mL)	Time (min)	Vol. Acid solution (mL)
10	280	120	340
15	280	125	360
20	280	130	370
25	280	135	380
30	280	140	400
35	290	145	400
40	260	150	410
45	260	155	410
50	240	160	410
55	250	165	420
60	250	170	470
65	260	175	500
70	260	180	500
75	260	185	500
80	260	190	510
85	270	195	510
90	280	200	510
95	280	270	760
100	280	275	780
105	300	280	780
110	300	285	790
115	320	290	800
		295	820
		300	820

Acid Sltn. End Batch - TN		
Batch No.	TN (mg/L)	DF
1	115,6	100
	11,13	1000
2	21,2	1000
3	30,14	1000
	29,69	1000
4	14,67	2500
	13,94	2500
5	15,76	2500
	16,47	2500
6	17,44	2500
	18,36	2500
7	18,26	2500
8	9,21	5000
9	8,67	5000

Acid Sltn. End Batch - TOC		
Batch No.	TOC (mg/L)	DF
1	2,86	100
3	1,0	1000
6	0,939	2500
9	1,44	5000

Acid Sltn. End Batch – SO ₄		
No.	SO ₄ (mg/L)	DF
1	463;465	20
2	481	20

APPENDIX G: Nitrification - Denitrification – Raw Data

G1. Nitrification:

Parameters measured during nitrification with ROP	
Parameter	Measured values
Cond. (mS/cm)	2,5; 2,7; 2,8; 3,0; 3,2
T (°C):	19; 18; 20; 19

Parameters measured during nitrification with 10% LLP mixed-permeates	
Parameter	Measured values
Cond. (mS/cm)	13,1; 13,3; 12,6; 13,4
T (°C):	20; 21; 22; 22; 22; 18; 16; 19; 21; 20; 20; 20; 19; 18

Parameters measured during nitrification with 20% LLP mixed-permeates	
Parameter	Measured values
Cond. (mS/cm)	22,7; 22,5; 22,1; 22,6
T (°C):	24; 23; 25; 24; 23

Parameters measured during nitrification with 50% LLP mixed-permeates	
Parameter	Measured values
Cond. (mS/cm)	49,3; 48,8; 48,9; 48,5; 49,0; 49,2; 48,9; 49,1
T (°C):	21; 22; 22; 22; 22; 22; 22; 22; 22; 22; 23; 22

Parameters measured during nitrification with 80% LLP mixed-permeates	
Parameter	Measured values
Cond. (mS/cm)	77,9; 77,8; 77,9; 77,9; 77,8; 77,9; 77,8; 78,0; 77,9; 78,0; 78,2; 78,1; 78,3; 78,2; 78,1; 78,2; 78,3; 78,4; 78,2; 78,4; 78,5
T (°C):	20; 19; 19; 19; 19; 21; 20; 20; 21; 21; 21; 20; 20; 21; 21; 21; 21; 21; 20; 20; 20; 20; 19; 19; 20; 20; 21; 20; 20

Parameters measured during nitrification with LLP	
Parameter	Measured values
Cond. (mS/cm)	91,4; 91,9; 91,2; 90,7; 90,8; 90,8; 90,9; 90,5; 90,5; 90,5; 90,6; 90,7; 90,7; 90,4; 90,6; 90,1; 90,1; 90,3; 90,3; 90,8; 90,9; 90,6; 90,7; 90,7; 90,4; 90,5; 90,3; 90,4; 90,5; 90,0; 90,8; 90,2; 90,3; 90,0; 90,5; 90,1; 90,5; 90,0; 90,4; 90,5; 90,3; 90,2; 90,2; 90,3; 90,1; 90,4; 90,1; 90,1; 90,4; 90,2; 90,6; 90,6; 90,3
T (°C):	23; 18; 20; 20; 20; 21; 21; 21; 21; 21; 21; 21; 21; 21; 21; 21; 21; 21; 22; 21; 22; 23; 22; 22; 19; 20; 20; 20; 21; 21; 21; 21; 21; 21; 22; 23; 24; 23; 22; 23; 22; 23; 24; 25; 25; 21; 23; 23; 23; 22; 22; 22; 22; 22; 22; 22; 22; 21; 21; 22; 22; 23; 23; 23; 23; 23; 23; 22; 23; 25

Batch with ROP

Day 0

Substance	Df	Value	Unit
NH ₄ ⁺ -N	10	6,89	mg/L
NO ₂ ⁻ N	1	<0,6	mg/L
NO ₃ ⁻ N	1	<0,23	mg/L
o-PO ₄ ³⁻ P	1	<0,5	mg/L
COD	1	131	mg/L
TOC	1	25,02	mg/L
TN	1	74,19	mg/L

Day 1

Substance	Df	Value	Unit
NH ₄ ⁺ -N	10	3,98; 3,99	mg/L
NO ₂ ⁻ N	1	4,29	mg/L
NO ₃ ⁻ N	1	12,4	mg/L

Day 2

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	15,9; 10,1	mg/L
NO ₂ ⁻ N	10	1,93; 2,35	mg/L
NO ₃ ⁻ N	10	2,98; 3,23	mg/L

Day 3

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	1	<0,6	mg/L
NO ₃ ⁻ N	10	5,3	mg/L
TOC	1	13,68	mg/L

Batch with 10% LLP mixed-permeates

Day 0

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	12,1; 12,3	mg/L
NO ₂ ⁻ N	1	<0,6	mg/L
NO ₃ ⁻ N	1	<0,23	mg/L
o-PO ₄ ³⁻ P	1	0,866; 0,928	mg/L
COD	2,5	285	mg/L
TOC	2,5	64,01	mg/L
TN	2,5	109,2	mg/L

Day 1

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	10,3	mg/L
NO ₂ ⁻ N	10	1,02	mg/L
NO ₃ ⁻ N	10	0,999	mg/L

Day 2

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	9,24	mg/L
NO ₂ ⁻ N	10	2,22	mg/L
NO ₃ ⁻ N	10	1,16	mg/L

Day 3

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	7,71	mg/L
NO ₂ ⁻ N	10	3,52	mg/L
NO ₃ ⁻ N	10	1,36	mg/L

Day 4

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	6,6	mg/L
NO ₂ ⁻ N	10	5,16	mg/L
NO ₃ ⁻ N	10	1,72	mg/L

Day 5

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	5,04	mg/L
NO ₂ ⁻ N	20	3,68	mg/L
NO ₃ ⁻ N	10	2,28	mg/L

Day 6

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	3,33	mg/L
NO ₂ ⁻ N	20	4,6	mg/L
NO ₃ ⁻ N	10	2,83	mg/L

Day 7

Substance	Df	Value	Unit
NH ₄ ⁺ -N	10	4,61	mg/L
NO ₂ ⁻ N	30	4,02	mg/L
NO ₃ ⁻ N	10	3,45	mg/L

Day 8

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	23	mg/L
NO ₂ ⁻ N	50	2,87	mg/L
NO ₃ ⁻ N	10	4,1	mg/L

Day 9

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	50	3,18; 3,12	mg/L
NO ₃ ⁻ N	10	4,46; 5,04	mg/L

Day 10

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	20	6,16	mg/L
	50	2,29	
NO ₃ ⁻ N	20	3,54; 3,96	mg/L

Day 11

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	20	4,2; 4,24	mg/L
NO ₃ ⁻ N	20	5,13; 5,01	mg/L

Day 12

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	20	1,49; 1,52	mg/L
NO ₃ ⁻ N	20	7,01; 6,93	mg/L

Day 13

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	1	<0,6	mg/L
NO ₃ ⁻ N	20	9,47	mg/L
TOC	2,5	32,22	mg/L

Batch with 20% LLP mixed-permeates

Day 0

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	8,13; 8,24	mg/L
NO ₂ ⁻ N	1	<0,6	mg/L
NO ₃ ⁻ N	1	<0,23	mg/L
o-PO ₄ ³⁻ P	1	1,63; 1,68	mg/L
COD	5	245; 253	mg/L
TOC	5	59,51	mg/L
TN	5	91,22	mg/L

Day 2

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	3,68; 3,78	mg/L
NO ₂ ⁻ N	50	2,31; 2,34	mg/L
NO ₃ ⁻ N	50	1,37; 1,28	mg/L

Day 3

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	10,3; 10,2	mg/L
NO ₂ ⁻ N	50	4,96; 5,0	mg/L
NO ₃ ⁻ N	50	2,5; 2,38	mg/L

Day 4

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	50	2,09; 2,13	mg/L
NO ₃ ⁻ N	50	5,23; 5,14	mg/L

Day 5

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	1	<0,6	mg/L
NO ₃ ⁻ N	50	6,23	mg/L
TOC	5	29,53	mg/L

Batch with 50% LLP mixed-permeates

Day 0

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	21,8; 20,8	mg/L
NO ₂ ⁻ N	1	<0,6	mg/L
NO ₃ ⁻ N	1	<0,23	mg/L
o-PO ₄ ³⁻ P	2	2,46; 2,78	mg/L
COD	10	288; 290	mg/L
TOC	10	71,04	mg/L
	20	32,66	
TN	10	112,9	mg/L
	20	57,53	

Day 2

Substance	Df	Value	Unit
NH ₄ ⁺ -N	-	-	mg/L
NO ₂ ⁻ N	2	4,24	mg/L
NO ₃ ⁻ N	20	0,667	mg/L

Day 3

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	36,5; 36,6	mg/L
NO ₂ ⁻ N	10	3,22; 3,2	mg/L
NO ₃ ⁻ N	20	1,6; 1,06	mg/L

Day 4

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	31,4; 31,5	mg/L
NO ₂ ⁻ N	50	1,67; 1,69	mg/L
NO ₃ ⁻ N	20	2,88; 2,29	mg/L

Day 5

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	28,2	mg/L
NO ₂ ⁻ N	-	-	mg/L
NO ₃ ⁻ N	-	-	mg/L

Day 6

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	20,9	mg/L
NO ₂ ⁻ N	50	4,74; 4,76	mg/L
NO ₃ ⁻ N	20	5,76; 5,04	mg/L

Day 7

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	12,9; 13	mg/L
NO ₂ ⁻ N	-	-	mg/L
NO ₃ ⁻ N	-	-	mg/L

Day 8

Substance	Df	Value	Unit
NH ₄ ⁺ -N	10	11; 10,9	mg/L
NO ₂ ⁻ N	100	4,46; 4,48	mg/L
NO ₃ ⁻ N	50	4,47; 4,14	mg/L

Day 9

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	100	4,67; 4,69	mg/L
NO ₃ ⁻ N	100	3,88; 3,7	mg/L

Day 11

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	1	<0,6	mg/L
NO ₃ ⁻ N	100	7,89	mg/L
TOC	10	30,95	mg/L

Batch with 80% LLP mixed-permeates

Day 0

Substance	Df	Value	Unit
NH ₄ ⁺ -N	100	15,1	mg/L
NO ₂ ⁻ N	1	<0,6	mg/L
NO ₃ ⁻ N	1	<0,23	mg/L
o-PO ₄ ³⁻ P	20	0,561	mg/L
COD	20	269	mg/L
TOC	20	64,20	mg/L
TN	20	80,44	mg/L

Day 8

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	20,2	mg/L
NO ₂ ⁻ N	100	4,23	mg/L
NO ₃ ⁻ N	-	-	mg/L

Day 9

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	19	mg/L
NO ₂ ⁻ N	100	4,71	mg/L
NO ₃ ⁻ N	-	-	mg/L

Day 13

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	15	mg/L
NO ₂ ⁻ N	200	3,42	mg/L
NO ₃ ⁻ N	50	0,67	mg/L

Day 14

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	14,3	mg/L
NO ₂ ⁻ N	-	-	mg/L
NO ₃ ⁻ N	-	-	mg/L

Day 17

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	12	mg/L
NO ₂ ⁻ N	-	-	mg/L
NO ₃ ⁻ N	50	0,712	mg/L

Day 18

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	11,1	mg/L
NO ₂ ⁻ N	200	4,04	mg/L
NO ₃ ⁻ N	-	-	mg/L

Day 21

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	8,49	mg/L
NO ₂ ⁻ N	200	4,99	mg/L
NO ₃ ⁻ N	50	0,734	mg/L

Day 22

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	7,7	mg/L
NO ₂ ⁻ N	-	-	mg/L
NO ₃ ⁻ N	-	-	mg/L

Day 25

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	4,86	mg/L
NO ₂ ⁻ N	200	5,65	mg/L
NO ₃ ⁻ N	50	0,776	mg/L

Day 26

Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	4,16	mg/L
NO ₂ ⁻ N	-	-	mg/L
NO ₃ ⁻ N	-	-	mg/L

Day 28

Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	5,51	mg/L
NO ₂ ⁻ N	500	2,58	mg/L
NO ₃ ⁻ N	50	0,781	mg/L

Day 30

Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	20,5; 22,1	mg/L
NO ₂ ⁻ N	500	2,79	mg/L
NO ₃ ⁻ N	50	0,804; 0,808	mg/L

Batch with LLP

Day 0

Substance	Df	Value	Unit
NH ₄ ⁺ -N	100	20,0; 20,2	mg/L
NO ₂ ⁻ N	1	<0,6	mg/L
NO ₃ ⁻ N	1	<0,23	mg/L
o-PO ₄ ³⁻ P	20	0,659; 0,662	mg/L
COD	20	344; 343	mg/L
TOC	50	31,47; 31,81	mg/L
	20	82,41; 81,18	mg/L
TN	50	41,58; 42,37	mg/L
	20	104,6; 103,1	mg/L

Day 5

Substance	Df	Value	Unit
NH ₄ ⁺ -N	100	18,1	mg/L
NO ₂ ⁻ N	100	2,07	mg/L
NO ₃ ⁻ N	50	0,359	mg/L

Day 30

Substance	Df	Value	Unit
NH ₄ ⁺ -N	-	-	mg/L
NO ₂ ⁻ N	100	2,72	mg/L
NO ₃ ⁻ N	50	0,623	mg/L

Day 33

Substance	Df	Value	Unit
NH ₄ ⁺ -N	-	-	mg/L
NO ₂ ⁻ N	100	2,46	mg/L
NO ₃ ⁻ N	50	0,641	mg/L

Day 37

Substance	Df	Value	Unit
NH ₄ ⁺ -N	-	-	mg/L
NO ₂ ⁻ N	100	3,16	mg/L
NO ₃ ⁻ N	-	-	mg/L

Day 9				Day 40			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	-	-	mg/L	NH ₄ ⁺ -N	100	15,5	mg/L
NO ₂ ⁻ -N	100	2,04	mg/L	NO ₂ ⁻ -N	100	2,96	mg/L
NO ₃ ⁻ -N	50	0,459	mg/L	NO ₃ ⁻ -N	50	0,725	mg/L
Day 12				Day 47			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	100	17,2	mg/L	NH ₄ ⁺ -N	100	15,1	mg/L
NO ₂ ⁻ -N	-	-	mg/L	NO ₂ ⁻ -N	100	3,05	mg/L
NO ₃ ⁻ -N	-	-	mg/L	NO ₃ ⁻ -N	50	0,786	mg/L
Day 16				Day 54			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	100	17,0	mg/L	NH ₄ ⁺ -N	100	14,5	mg/L
NO ₂ ⁻ -N	100	2,29	mg/L	NO ₂ ⁻ -N	100	3,08	mg/L
NO ₃ ⁻ -N	50	0,542	mg/L	NO ₃ ⁻ -N	50	0,771	mg/L
Day 23				Day 60			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	100	16,4	mg/L	NH ₄ ⁺ -N	100	14,3	mg/L
NO ₂ ⁻ -N	100	2,51	mg/L	NO ₂ ⁻ -N	100	3,06	mg/L
NO ₃ ⁻ -N	50	0,579	mg/L	NO ₃ ⁻ -N	50	0,823	mg/L
Day 26				Day 74			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	100	16,0	mg/L	NH ₄ ⁺ -N	100	13,8	mg/L
NO ₂ ⁻ -N	-	-	mg/L	NO ₂ ⁻ -N	100	3,06;3,03	mg/L
NO ₃ ⁻ -N	50	0,587	mg/L	NO ₃ ⁻ -N	50	0,884;0,89	mg/L
				Day 90			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	100	13,3	mg/L	NH ₄ ⁺ -N	100	13,3	mg/L
NO ₂ ⁻ -N	100	2,94	mg/L	NO ₂ ⁻ -N	100	2,94	mg/L
NO ₃ ⁻ -N	50	0,985	mg/L	NO ₃ ⁻ -N	50	0,985	mg/L

Parameters measured during nitrification with 50% LLP – pH effect at pH 7,5	
Parameter	Measured values
Cond. (mS/cm)	52;52;48,6;48,4;48,4;48,1;48,2;48,5;48,2//48,2;48,3;48,3;48,4;48,3;48,3;48,4;48,3; 48,3;48,3//48,5;48,5;48,6;48,6;48,5;48,5;48,5;48,6;48,5//48,9;49;48,9; 48,9;48,9;48,9;48,9;49;49//49,1;49,2;49;49;49,1;49;49;49,2//49,6;49,5
T (°C):	18;19,1;20,6;21,6;21,7;21,3;21,7//21,2;21,3;21,4;21,7;22;22;21,5;21,9;22;21,9// 20,9;21,3;21,5;21,6;21,1;21,4;21,6;21,6;21,5;21,4//19,5;19,8;19,6;19,9; 20,1;20,2;20,1;20,3//20,2;20,4;20,5;20,1;20,2;20,5;20,4;20,8;20,9//19,3;19,5

Parameters measured during nitrification with 50% LLP – pH effect at pH 6,5	
Parameter	Measured values
Cond. (mS/cm)	52;51,8;47,8;47,9;47,9;47,9//48,1;48,1;48,2//48,2;48,2;48,1;48,3//48,3;48,3;48,3// 49;49;48,9;49//49;49;49,2;49//49;49,2;49;49,2//49,4;49,4;49,6// 49,6;49,6;49,6;49,6//50,1;50,2;50,2;50,2
T (°C):	20,1;23,4;23,3;23,5;23,2//23,2;23,2;23,1;23,2//22,9;22,7;23,2;23,3//23,1;23,4;23,3// 23;23;23,2;23,3//23,4;22,6;22,7;22,7//22,4;23,5;23;23,6//23,6;24;24,1;24// 23,6;23,7;23,6;23,4//22,5;22,7;22,9;23;23,1

Parameters measured during nitrification with 50% LLP – pH effect at pH 8,5	
Parameter	Measured values
Cond. (mS/cm)	52,1;51,8;48,3;48,4;48,4//48,5;48,6;48,5;48,6;48,5;48,6;48,5;48,6// 48,8;48,8;48,8;48,8;48,8;48,8;48,8;48,9//49,1;49,1;49,1;49,2;49,3;49,2;49,1;49,3;49,1// 49,6;49,7;49,6;49,6;49,6;49,7;49,4//49,9;49,9;49,7;49,6;49,7//49,7;49,6;49,8
T (°C):	20,1;20,8;21,3;21,1;21//20,2;20,3;21,3;22,1;22;20,8;21,3;22,4// 20,6;20,7;20,9;21;21,1;21,3;21,3;21,4//20,6;20,8;20,9;21,4;21,7;21,8;21,2;21,6;21,8// 20,6;20,8;21,2;21,9;21,8;21,4;22,1//18,7;18,9;19,2;19,3;19,5//18,8;19;18,9

Batch with 50% LLP – pH effect at pH 7,5

Day 1				Day 3			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	16,3	mg/L	NH ₄ ⁺ -N	50	7; 7,01	mg/L
NO ₂ ⁻ N	-	-	mg/L	NO ₂ ⁻ N	100	1,27	mg/L
NO ₃ ⁻ N	-	-	mg/L	NO ₃ ⁻ N	50	6,78	mg/L
Day 2				Day 4			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	12,3	mg/L	NH ₄ ⁺ -N	20	3,35; 3,34	mg/L
NO ₂ ⁻ N	50	0,824	mg/L	NO ₂ ⁻ N	100	2,59	mg/L
NO ₃ ⁻ N	50	3,69; 3,7	mg/L	NO ₃ ⁻ N	100	5,2	mg/L
Day 5				Day 5			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	<2	mg/L	NH ₄ ⁺ -N	1	<0,6	mg/L
NO ₂ ⁻ N	1	<0,6	mg/L	NO ₂ ⁻ N	100	8,15; 8,14	mg/L
NO ₃ ⁻ N	100	8,15; 8,14	mg/L	TOC	10	33,78	mg/L

Batch with 50% LLP – pH effect at pH 6,5

Day 7				Day 11			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	20	30,8	mg/L	NH ₄ ⁺ -N	20	16,6	mg/L
NO ₂ ⁻ N	2	1,04; 0,664	mg/L	NO ₂ ⁻ N	1	3,45; 2,67	mg/L
NO ₃ ⁻ N	50	5,38	mg/L	NO ₃ ⁻ N	50	9,03; 9,05	mg/L
Day 14				Day 15			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	2	32,7; 32,5	mg/L	NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	1	0,894; 0,895	mg/L	NO ₂ ⁻ N	1	<0,6	mg/L
NO ₃ ⁻ N	100	7,95; 7,97	mg/L	NO ₃ ⁻ N	100	8,49; 8,48	mg/L
				TOC	20	17,71	mg/L

Batch with 50% LLP – pH effect at pH 8,5

Day 2				Day 5			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	50	11,6	mg/L	NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	50	2,89	mg/L	NO ₂ ⁻ N	100	2,98	mg/L
NO ₃ ⁻ N	50	2,65; 2,64	mg/L	NO ₃ ⁻ N	50	9,97	mg/L
Day 4				Day 6			
Substance	Df	Value	Unit	Substance	Df	Value	Unit
NH ₄ ⁺ -N	1	<2	mg/L	NH ₄ ⁺ -N	1	<2	mg/L
NO ₂ ⁻ N	100	5,25	mg/L	NO ₂ ⁻ N	1	<0,6	mg/L
NO ₃ ⁻ N	50	5,26	mg/L	NO ₃ ⁻ N	100	8,07	mg/L
				TOC	20	16,72	mg/L

G2. Denitrification:

Parameters measured during denitrification at		
Parameter	pH 6,5	pH 7,5
	Measured values	Measured values
Cond. (mS/cm)	38,5;38,0;38,3;37,4	38,5;38,2;38,1;37,4
T (°C):	18,9; 20,7;21,0;20,0;21,0	19,1;20;20;21;21;21;20;20;21

Parameters measured during denitrification at pH 8,5	
Parameter	Measured values
Cond. (mS/cm)	38,5;38,3;38,3;38,4;37,8;37,7;37,4; 37,4
T (°C):	18,4;18,4;20;20;20;20;21;20;20;20;19;19;20;19

Denitrification – pH effect at pH 6,5

Feed (pH 6,5, 7,5 & 8,5)			
Substance	Df	Value	Unit
NO ₃ ⁻ -N	100	6,39; 6,15; 6,33; 6,15; 6,10	mg/L
NO ₂ ⁻ -N	1	<0,6	mg/L
o-PO ₄ ³⁻ -P	1	0,456;0,468// 0,551	mg/L
COD	5	183;175	mg/L
TOC*	20	11,11; 11,3; 10,13; 10,66	mg/L
TN	20	32,88; 33,84; 33,69; 32,94; 32,99; 33,96	mg/L

* Before Methanol Addition

t = 6h			
Substance	Df	Value	Unit
NO ₃ ⁻ -N	1	7,58;8,07	mg/L
NO ₂ ⁻ -N	100	3,59	mg/L
TN	20	21,42	mg/L

t = 23h			
Substance	Df	Value	Unit
NO ₃ ⁻ -N	-	-	mg/L
NO ₂ ⁻ -N	20	1,46	mg/L
TN	-	-	mg/L

t = 25h			
Substance	Df	Value	Unit
NO ₃ ⁻ -N	1	<0,23	mg/L
NO ₂ ⁻ -N	1	<0,6	mg/L
TN	20	2,44	mg/L
TOC	20	17,32	mg/L

Denitrification – pH effect at pH 7,5

t = 23h			
Substance	Df	Value	Unit
NO ₃ ⁻ -N	1	0,90	mg/L
NO ₂ ⁻ -N	100	1,47	mg/L
TN	20	8,13	mg/L

t = 26h			
Substance	Df	Value	Unit
NO ₃ ⁻ -N	-	-	mg/L
NO ₂ ⁻ -N	100	0,958	mg/L
TN	20	6,23	mg/L

t = 32h			
Substance	Df	Value	Unit
NO ₃ ⁻ -N	1	<0,23	mg/L
NO ₂ ⁻ -N	1	<0,6	mg/L
TN	20	2,57	mg/L
TOC	20	17,15	mg/L

Denitrification – pH effect at pH 8,5

t = 5h			
Substance	Df	Value	Unit
NO ₃ ⁻ -N	100	2,26	mg/L
NO ₂ ⁻ -N	-	-	mg/L
TN	-	-	mg/L

t = 7h			
Substance	Df	Value	Unit
NO ₃ ⁻ -N	-	-	mg/L
NO ₂ ⁻ -N	100	4,06	mg/L
TN	-	-	mg/L

t = 47h			
Substance	Df	Value	Unit
NO ₃ ⁻ -N	-	-	mg/L
NO ₂ ⁻ -N	50	1,24	mg/L
TN	20	5,8	mg/L

t = 50h			
Substance	Df	Value	Unit
NO ₃ ⁻ -N	-	-	mg/L
NO ₂ ⁻ -N	50	0,851	mg/L
TN	20	4,58	mg/L

t = 23h			
Substance	Df	Value	Unit
NO ₃ ⁻ N	1	1,36	mg/L
NO ₂ ⁻ N	100	2,61	mg/L
TN	20	15,66	mg/L

t = 26h			
Substance	Df	Value	Unit
NO ₃ ⁻ N	-	-	mg/L
NO ₂ ⁻ N	100	2,25	mg/L
TN	-	-	mg/L

t = 32h			
Substance	Df	Value	Unit
NO ₃ ⁻ N	-	-	mg/L
NO ₂ ⁻ N	100	1,86	mg/L
TN	20	11,7	mg/L

t = 54h			
Substance	Df	Value	Unit
NO ₃ ⁻ N	-	-	mg/L
NO ₂ ⁻ N	10	1,2	mg/L
TN	20	3,32	mg/L

t = 56h			
Substance	Df	Value	Unit
NO ₃ ⁻ N	1	<0,23	mg/L
NO ₂ ⁻ N	1	<0,6	mg/L
TN	20	2,82	mg/L
TOC	20	17,07	mg/L

APPENDIX H: Proposed PFD: “Alternative Sustainable Approach”

Assumptions in NF-Stage and Adsorption with PAC
<p>NF-Stage:</p> <ul style="list-style-type: none"> - Percent Permeate Recovered: 50% <p>Adsorption with PAC (Optional):</p> <ul style="list-style-type: none"> - PAC Dosage (g-PAC/L-LLP): 10 - TOC Removed: $\approx 50\%$ - $t_{\text{Treat.}}$: 1 h

Assumptions in Precipitation, Sedimentation, Washing & Recovered CaCO_3 -Rich Solids
<ul style="list-style-type: none"> - Negligible loss of permeate volumes and changes in TN and conductivity (Dewatering efficiency $\approx 100\%$) <p>Precipitation:</p> <ul style="list-style-type: none"> - Precipitating agent: <ul style="list-style-type: none"> • Mixed Na_2CO_3-NaOH reagents: <ul style="list-style-type: none"> ❖ Dosage (g-Reagents/L-LLP): 16 (Mass fractions: 0,6 NaOH & 0,4 Na_2CO_3) - $t_{\text{Treat.}}$: 1 h - Substances percent removed in LLP: <ul style="list-style-type: none"> • Ca Removed: $>99\%$ • Mg Removed: 99% • Hardness Removed: $>99,5\%$ • TOC Removed: 8% • $\text{PO}_4\text{-P}$ Removed: 91% <p>Sedimentation:</p> <ul style="list-style-type: none"> - Sedimentation time ≈ 2 h; LLP-SN Volume Recovery $\approx 70\%$ <p>Washing:</p> <ul style="list-style-type: none"> - Washwater: High pressure RO permeate (HROP) - Volume ratio Washwater to LLP (L-Washwater/L-LLP): 0,4 - Concentration in washwater after washing step without HROP composition: <ul style="list-style-type: none"> • Ca (mg/L): <5 • Mg (mg/L): 158 • Hardness ($^\circ\text{dH}$): 37 • $\text{NH}_4\text{-N}$ (mg/L): <2 • $\text{NO}_3\text{-N}$ (mg/L): $<0,23$ • TOC (mg/L): 111 • $\text{PO}_4\text{-P}$ (mg/L): $<0,05$ <p>Recovered CaCO_3-Rich Solids:</p> <ul style="list-style-type: none"> - Ratio Recovered solids to LLP (g-Solids/L-LLP): 5,0

Assumptions in Membrane Contactor
<ul style="list-style-type: none"> - Negligible changes in conductivity - Area per Module: 1,4 m² - Module Volume: 0,0013 m³ - Completely hydrophobic membrane: <ul style="list-style-type: none"> • Volume increase in Acid Solution only due to consume H₂SO₄ (95%) pH control solution - NH₃-N reduction rate in LLP (Kg-N/d·m²): 0,43 - Initial NH₄-N concentration in LLP: 2000 mg/L - NH₃-N Reduced in LLP: 80% - Recovery Efficiency: 100% - Initial volume ratio Acid Solution to LLP (L-Acid Sltn./L-LLP): 0,1 - Volume ratio H₂SO₄ (95%) pH control Sltn to LLP (L-Sltn/L-LLP): 0,0057 - TOC Removed: 5%

Assumptions in Nitrification and Denitrification FBBs
<ul style="list-style-type: none"> - Negligible loss of mixed-permeate volumes and changes in hardness and conductivity <p>Nitrification FBB:</p> <ul style="list-style-type: none"> - DO > 2 mg/L - Packing material SSA: 900 – 1000 m²/m³ (Larger SSA more available surface for biofilm development) - v_{Liq.} (m/h): ≈ 22 - Volumetric flow rate ratio Air to Liquid (Ln/h-q_{Air})/(L/h-q_{Liq}): ≈ 0,3 - Estimated AOR at pH 8,5 & adjusted at 33°C for AOB: 1,8 Kg/m³·d - NH₄-N to NO₃-N Conversion: ≈ 80% - Potential inhibition effect due to salinity value of about 70 dS/m balances with greater SSA - Ratio Na₃PO₄ to LLP (mg-Na₃PO₄/L-LLP): 20 - TOC Removed: 50% - PO₄-P Removed: 70% <p>Denitrification FBB (Optional):</p> <ul style="list-style-type: none"> - DO < 0,5 mg/L - Packing material SSA: 900 – 1000 m²/m³ - v_{Liq.} (m/h): ≈ 13 - Same effect of temperature on Denitrifying microorganisms at 33°C as with AOB: <ul style="list-style-type: none"> • Estimated DNR at pH 6,5 & adjusted at 33°C: 2,2 Kg-N/m³·d - Ratio Na₃PO₄ to LLP (mg-Na₃PO₄/L-LLP): 20 - Methanol dosage based on COD to NO₃-N ratio concentration of 4 <ul style="list-style-type: none"> • Ratio Methanol to LLP (mL-MeOH/L-LLP): 0,74 - TOC Increased: 60% - PO₄-P Removed: 70%