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Towards the wastewater treatment plant of the future : integration of carbon redirection and nitrogen recovery technologies

Irene Sancho Lacalle

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Chemical Engineering Department
PhD Program: Chemical Processes Engineering

TOWARDS THE WASTEWATER TREATMENT PLANT OF THE FUTURE: INTEGRATION OF CARBON REDIRECTION AND NITROGEN RECOVERY TECHNOLOGIES

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Abstract

A change in the wastewater treatment paradigm is required for the sustainability of urban water cycle; where the actual loss of the value in wastewater should be recovered. The goal of a better capture of the full energy and nutrient resource potential present in the wastewater is an increased understanding of the importance of working toward greater sustainability in wastewater treatment systems. The research presented in this PhD thesis relies on evaluating an alternative wastewater treatment plant configuration (WWTP) presenting a sustainable solution for wastewater treatment.

Bio-sorption as a carbon redirection process (A-stage) and ion-exchange by using zeolites as nitrogen recovery system (B-stage) are experimentally validated in both laboratory and pilot scale. Furthermore, other alternatives to carbon redirection are evaluated; and also an experimental evaluation of the concentration of ammonium by means of natural inorganic ion-exchange and its purification by hollow fibre liquid-liquid membrane contactors is assessed. Finally, a technical and economic comparison of the innovative WWTP flowsheet with the reference scenario is conducted in order to define the potential of the proposed configuration in the sewage sector. The experimental work was conducted in Vilanova i la Geltrú WWTP (Barcelona, Spain), where a pilot plant was designed, constructed and operated over 18 months. Initial evaluation of the carbon redirection and nitrogen recovery processes were carried out at laboratory scale.

Keywords

Carbon redirection; High-rate activated sludge; bio-sorption; A-stage; self-sustainability; ion-exchange; zeolites; nitrogen recovery; Waste Water Treatment Plant.

Preface

Most of the urban wastewater treatment plants (WWTP), based on conventional activated sludge (CAS) systems, cannot be considered sustainable since the concept of resources (energy and nutrients) recovery is not taken into account. Notwithstanding, this paradigm can be changed by applying a new treatment concept. New technologies (or a combination of existing ones) are appearing on the scene in the recent years offering both a higher energy production (in terms of biogas generation from the anaerobic digestion of the sludge) and a recovery of essential nutrients present on water, such as nitrogen and phosphorus.

A CAS process uses large amounts of energy for aeration and loses the potential energy content of the organic load and the nutrients present in wastewater. Recently, it has been estimated that wastewaters contain more chemical energy (as organic pollution load) than it is needed for its treatment using CAS. However, in order to use this energy, the main barrier to overcome is the low organic content (1 to 2 g·L⁻¹). It is postulated that this situation can be solved by pre-concentrating sewage to redirect carbon through sludge to its valorisation as biogas and, thus, to achieve energy positive wastewater treatment plants.

The increasingly exigent discharge limits on nitrogen and phosphorous together with the concern for recovering nutrients to produce valuable fertilizers motivated the research of processes able to achieve this objective. One of the main used developed processes is the well-known Haber-Bosch, but nowadays, it is considered an expensive way to produce nitrogen for fertilizer. So, the challenge is finding not only an effective but also economical and sustainable technology comparable to the Haber-Bosch process.

This work is devoted to studying and validating of a new treatment concept of wastewater treatment plan configuration, based on the enhancement of resources recovery from wastewater at lower cost and in a sustainable way. The integration of a pre-concentration stage to redirect carbon (based on bio-sorption) and an ion-exchange unit with the purpose of recovering the inorganic nitrogen forms (e.g. ammonium) were studied in a pilot plant installed in a WWTP in Spain.

The technical and economic assessment of the proposed scheme and its comparison with conventional configuration has been also conducted, confirming the relevant role of new configurations to operate more sustainable and self-efficient plants.

Today, the final justification for this change of concept needs to be found in performance and environmental issues as some improvements in the costs are still required in some technologies.

Nonetheless, this thesis demonstrates that the economics for this new configuration is expected for the short-term.

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List of Abbreviations and Acronyms

1,4-DB: 1,4 dichlorobenzene	FeCl ₃ : Iron chloride
A/B: Adsorption/Bio-oxidation	FeSO ₄ : Iron sulphate
AD: Anaerobic Digestion	FSEM: Field Scanning Electron Microscope
AEC: Annual Equivalent Cost	FTIR: Fourier Transform Infrared
Al: Aluminium	Microscopy
Anammox: Anaerobic Ammonium Oxidation	FU: Functional Unit
ASM: Activated Sludge Model	F/M: Food to Microorganisms ratio
AVG: Average	GHG: Greenhouse Gases
BOD: Biological Oxygen Demand	H ⁺ : Hydrogen ion or proton
BV: Bedvolume	H ₂ S: Hydrogen sulphide
Bv: Volumetric loading rate	H ₂ SO ₄ : Sulphuric acid
Bx: Sludge loading rate	HCl: Hydrochloric acid
C: Carbon	HFLLMC: Hollow Fibre Liquid-Liquid
Ca: Calcium	Membrane Contactor
CaCO: Calcite	HiCS: High-Rate Contact-Stabilisation
CaCO ₃ : Calcium carbonate	HNO ₃ : Nitric acid
CAPEX: Construction Cost Expenditure	H ₃ PO ₄ : Phosphoric acid
CAS: Conventional Activated Sludge	HRAS: High-Rate Activated Sludge
CEC: Cation Exchange Capacity	HRT: Hydraulic Retention Time
CEPT: Chemically Enhanced Primary	IC: Ionic Chromatograph
Treatment	ICP-MS: Inductively Coupled Plasma Mass
CF: Concentration Factor	Spectrometry
CH ₄ : Methane	IE: Inhabitant Equivalent
CHP: Combined Heat and Power unit	IE-CANON: Ion-Exchange assisted CANON
CO: Carbon monoxide	IWA: International Water Association
Cr: Chromium	K: Potassium
CO ₂ : Carbon dioxide	LCA: Life Cycle Assessment
COD: Chemical Oxygen Demand	LCC: Life Cycle Costing
CS: Contact-Stabilisation	LCCI: Life Cycle Costing Inventory
CSTR: Completely Stirred Tank Reactor	LCI: Life Cycle Inventory
DO: Dissolved Oxygen	LCIA: Life Cycle Impact Assessment
DAF: Dissolved Air Flotation	LOQ: Limit of Quantification
DSF: Dynamic Sand Filtration	LQC: Line Quality Control
EDX: Energy Dispersive X-ray Spectroscopy	O: Oxygen
EPS: Extracellular Polymeric Substances	PE: Population Equivalent
EU: European Union	PLC: Programmable Logic Controller
Fe: Iron	PP: Polypropylene

PVDF: Polyvinylidene fluoride	SPM: Shell Progressive Model
PZC: Point of Zero Charge	SRT: Sludge Retention Time
MBR: Membrane Bioreactor	SWOT: Strengths, Weaknesses, Opportunities, and Threats
Mg: Magnesium	T: Temperature
MgCO ₃ : Magnesium carbonate	TC: Total Carbon
MLSS: Mixed-Liquor Suspended Solids	TKN: Total Kjeldahl Nitrogen
MTZ: Mass Transfer Zone	TN: Total Nitrogen
N: Nitrogen	TOC: Total Organic Carbon
N ₂ : Dinitrogen gas	TP: Total Phosphorous
N ₂ O: Nitrous oxide	TPAD: Temperature-Phased Anaerobic Digestion
Na: Sodium	TSS: Total Suspended Solids
NaCl: Sodium chloride	UF: Ultrafiltration
NaOH: Sodium hydroxide	UPLC-MS/MS: Ultra Performance Liquid Chromatography Mass Spectrometer
NH ₃ : Ammonia	USA: United States of America
NH ₄ ⁺ -N: Ammonium nitrogen	VFA: Volatile Fatty Acids
NH ₄ Cl: Ammonium chloride	VSS: Volatile Suspended Solids
NH ₄ NO ₃ : Ammonium nitrate	WAC: Weak Acid Cation
(NH ₄) ₂ HPO ₄ : Ammonium phosphate	WAS: Waste Activated Sludge
Ni: Nickel	WRRFs: Water Resource Recovery Facilities
NO ₃ ⁻ -N: Nitrate nitrogen	WW: Wastewater
NPOC: Non-Purgeable Organic Carbon	WWTP: Wastewater Treatment Plant
OPEX: Operational Expenditure Costs	X _{HET} : Heterotrophic bacteria
OUR: Oxygen Uptake Rate	X _I : Particulate inert non-biodegradable organics
O&M: Operational and Maintenance	X _S : Slowly biodegradable organics
P: Phosphorus	XRD: X-Ray Diffraction
PO ₄ ³⁻ -P: Phosphate phosphorus	Z-N: Natural zeolite
RM: Rota Mining	Z-Na: Na-form zeolite
S _I : Soluble inert non-biodegradable organics	ZFA: Zeolite Fly Ash
S _X : Biodegradable organics	
SAC: Strong Acid Cation	
SGP: Specific Gas Production	
Si: Silicon	

CHAPTER 1

Introduction

1. Introduction

1.1. Conventional urban wastewater treatment trains

Wastewater treatment plants (WWTPs) treat urban wastewaters before they can be discharged again for their domestic, industrial or any other uses without any risk to human or natural ecosystems. In this way, WWTPs are operating to accomplish the discharge standards established, in the case of European Union (EU), by the European Directive 91/271 [1] (*Table 1.1*) and the Water Framework Directive 2000/60/CE [2].

Table 1.1. Requirements for discharges from urban WWTPs subject to the Directive 91/271. The values for concentration or for the percentage of reduction shall apply.

Parameter	Limit concentration (mg·L⁻¹)	Minimum percentage reduction (%)
Biochemical oxygen demand (BOD ₅)	25	70–90
Chemical oxygen demand (COD)	125	75
Total suspended solids (TSS)	35	90
Total phosphorous (TP)	2	80
Total nitrogen (TN)	15	70–80

To achieve their main objective, technologies for wastewater treatment must be selected with a view to the purpose of the use of the treated water. Established in the early 20th century [3], a biological treatment via the conventional activated sludge (CAS) process followed by an anaerobic digestion (AD) is the configuration worldwide selected and most currently extended for the development of wastewater reuse for industrial and agronomical applications because of its robust and stable performance in providing the effluent quality requirements for the intended use [4]. Despite its consistency and strength in the expected result regarding discharge guidelines, WWTPs cannot be considered sustainable since the concept of resources recovery is not taken into account [5]. Nitrogen (N) is removed by biological nitrification-denitrification process and phosphorus (P) is removed by biological or chemical treatments. From the energy point of view, WWTPs are energy consuming (only part of the total energy produced in the AD stage is recovered in the form of biogas) and this leads to high operational expenditure costs (OPEX). Actually, in the vast majority of WWTPs, the equivalent to the 60–70% of the total energy consumption comes from the aeration of the biological CAS reactors [6].

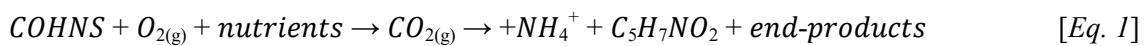
Moreover, due to the degradation of the organic matter via aerobic mineralization to carbon dioxide (CO₂) not only losses an important part of the potential energy present in wastewater [7] as organic matter, but also contributes to the climate change by the releasing of a greenhouse gas (GHG) [4].

Over the years, the CAS system has grown more complex, more restrictive with nutrient limits and also intrinsically more energy intensive. In addition, the recent developments towards nitrogen removal as well as the desire to minimize the excess sludge production (relatively high sludge ages and low sludge loading rates) have led to systems which employ more extended aeration. As a result, when traditional approaches are used, more energy is consumed in wastewater treatment that is gained through sludge digestion.

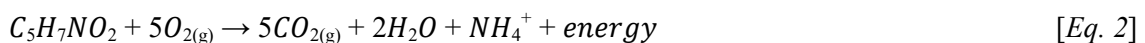
1.1.1. Conventional Activated System (CAS)

The most common treatment system for domestic wastewater depicted in *Figure 1.1*, currently in massive use, is a primary treatment followed by CAS system. It is based on aerobic systems where suspended bacterial biomass forming larger particles, called flocs, anabolises part of the organic compounds present in the wastewater and mineralizes another part of it into CO_{2(g)} through aerobic respiration according to *Equations 1–2* [8].

Oxidation and synthesis:



Endogenous respiration:



If appropriate conditions are given, the process is able to incorporate biological nitrogen removal through nitrification-denitrification, enhanced biological phosphorus removal and adsorb complex metals ions [9].

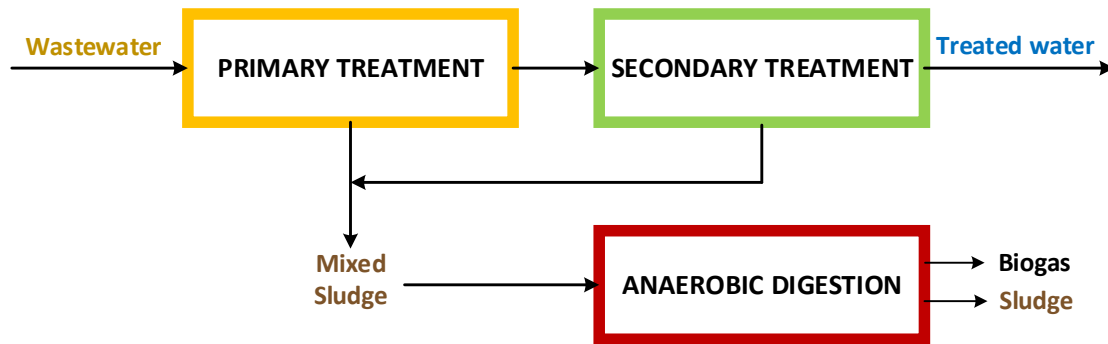


Figure 1.1. Conventional configuration of a wastewater treatment plant (WWTP) using activated sludge reactors (CAS).

The large population size and rapid growth of organotrophs in the aeration tank (90–97%) in comparison to the small population size (3–10%) and slow growth of nitrifying bacteria (*Nitrosomonas* and *Nitrobacters*), make it difficult to achieve and maintain desired nitrification. The competence for oxygen to stimulate both microorganism’s growth, full-scale WWTPs require a transfer of oxygen to water by compressors, leading to an enormous energy demand, representing $0.6 \text{ kWh} \cdot \text{m}^{-3}$ [4].

1.1.2. Anaerobic digestion (AD)

McCarty et al. (2011) [4] states that the production of methane by AD is regarded, among many choices, as the more mature technology for sewage energy recovery. Hence, as it is commonly extended in current WWTPs, the excess sludge from primary and secondary treatment is later treated by means of AD to recover some of the energy in the form of methane-rich biogas: a mixture mainly composed by methane (CH_4 ; 60–75%_{v/v}) and CO_2 (19–33%_{v/v}) as well as other gases in minor fractions, which can be burnt in order to obtain energy and thus reduces the energetic demand of the WWTP. This process, as shown in *Figure 1.2*, comprehends a set of sequential chemical reactions carried out by microorganisms and reaches sufficient low pollutant effluent levels, but has higher energy consumption.

However, through the conventional practice of aerobic wastewater treatment combined with anaerobic sludge digestion, only a portion of the energy potential of wastewater is recovered [11]. Depending on the AD process performance, conventional WWTPs with AD allow covering a minimum of 20% [12], around 33% [13] and up to 40% [14] of the electricity needs

of the plant. Taking into account that AD is carried out on thickened sludge, thus heating a matrix with 93–95% of water, it does not help to improve the WWTP energy balance [15].

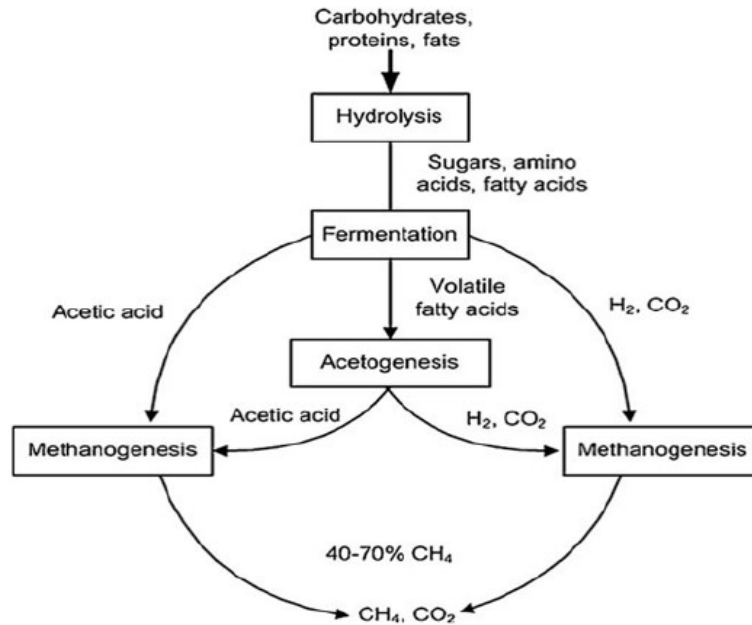


Figure 1.2. Schematic diagram of the anaerobic digestion (AD) process [10].

1.2. Change on energy paradigm in wastewater treatment plants (WWTPs): from consumption to recovery

Energy speaking, the conventional and current configuration of WWTPs, as presented above, has the following drawbacks: (i) it requires more aeration and thus more energy consumption and (ii) it leads to the creation of less and worse digestible sludge, which leads to an unfavourable energy recovery.

The electricity consumption of a WWTP with a design flow of around $20,000 \text{ m}^3 \cdot \text{d}^{-1}$ (or 100,000 population equivalent; PE) is around $0.35 \text{ kWh}_e \cdot \text{m}^{-3}$ treated [16]. Therefore, the annual electricity consumption for a WWTP of this type would be of around 2,500 MWh. It has been reported that sewage exceeds the electrical energy requirement of the treatment process by a factor of 1.2–6.0 [17] containing up to 10 times more chemical energy (as organic pollution or COD) than is needed for its treatment using CAS [4,14,18,19]. The organic carbon in municipal wastewater ($400\text{--}500 \text{ mgCOD} \cdot \text{L}^{-1}$ average value) represents a potential chemical energy content of $1.5\text{--}1.9 \text{ kWh}_{th} \cdot \text{m}^{-3}$ [20] that easily overcomes the energy requirements of the CAS system [3].

In the current economic and environmental context, the increase of energy prices and consumption lead to looking for newer alternatives to reduce the operational costs of WWTPs and to avoid the emissions of GHG. These alternatives must be able to increase the energy self-sufficiency of any WWTP up to, at least, 60% and they would reduce the CO₂ emissions around 1,250 tons CO₂·y⁻¹ (considering the Spanish electricity mix system). In order to increase this ratio, several options are possible: co-digestion of other organic substrates with WWTP sludge [13] and energy conversion equipment with high electrical energy efficiencies such, as fuel cells [21]. Moreover, pre-treatment of sludge prior AD (thermal hydrolysis or sonication) can contribute to increasing biogas production. However, other changes in the sludge line can also improve the biogas production, such as higher primary sludge recovery. This will reduce the energy requirements for the waterline residual pollution and will obtain more energy-rich sludge to be digested without the use of hydrolysis technologies which are mainly useful for secondary sludge [22]. Moreover, if this sludge is recovered at a higher concentration (pre-concentrated sewage), the necessary heat for the operation of the digester will also be optimised [4,14,18,19]. Higher biogas production efficiency will be obtained with the AD of the pre-concentrated sludge than conventionally due to more concentrated operating conditions: it is expected to reach 50–65% organic matter removal, instead of 40–50% for conventional anaerobic digesters of mixed sludge. The better energy efficiency allows producing heat and electricity to be used on-site, thus avoiding much of the energy requirements from fossil fuels of conventional WWTPs and emissions due to their production and use. If the electricity consumption of the overall WWTP was reduced (e.g. reduction of the electricity consumption for aeration), the associated emissions will also be reduced.

1.3. Change on nutrients (nitrogen and phosphorus) paradigm in wastewater treatment plants (WWTPs): from removal to recovery

Nutrients (N and P) are removed in WWTPs instead of being recovered despite it is highly known that those nutrients are important added value products in the farming and chemical industry. About 60–65% of the nitrogen present on wastewater influent is returned to the atmosphere, mainly as dinitrogen gas (N_{2(g)}), and 15–20% ends up as organic nitrogen in the sludge [23]. Although about 90% of the phosphorus is retained in CAS sludge [24], and 38% of this sludge is disposed of through land spreading in the EU27 [25], this phosphorus is not readily bio-available. Moreover, the COD/N/P ratio is often not high enough to bring about biological nutrient removal, requiring the addition of external COD, as exemplified in Dailey et al.(2007) [27], Fongsatitkul et al. (2008) [28] and Isaacs and Henze (1995) [26]. Normally, they are produced by applying chemical processes that are expensive and that normally fix nitrogen

and phosphorus present in the atmosphere and on the soil. According to U.S. Geological Survey, the reserves of phosphorus will last 300 years at most at the actual rate of mine production [29]. Because phosphorus is mined as a mineral, and thus it is a limited resource; its commercial value will inevitably increase as it is depleted [3]. The increasing market value of these wastewater components is acting as key drivers for resource recovery from wastewater. Therefore, considering that wastewater is an important source of concentrated nutrients and taking into account that fertilizer prices are also increasing, any alternative that considers their recovery at an acceptable cost must be considered to save money and resources, obtain added value products and increase the final effluent water quality.

The nutrients recovery potential on a WWTP with a treatment capacity of $20,000 \text{ m}^3 \cdot \text{d}^{-1}$, considering $50 \text{ mgTN} \cdot \text{L}^{-1}$ and $10 \text{ mgTP} \cdot \text{L}^{-1}$ at the influent, would be of around $400 \text{ kgN} \cdot \text{d}^{-1}$ and $70 \text{ kgP} \cdot \text{d}^{-1}$. The production of natural fertilisers also allows reducing the impact on climate change in terms of CO_2 emissions. As based on figures from [30], the production of NPK fertilisers involves an average of 1 kgCO_2 per kg of fertiliser produced (excluding transport).

A nutrient-recovery application, developed over the past years, is the production of struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}_{(s)}$) from post-digestion liquors. The recovery of struvite by crystallisation processes is technically and economically feasible [31] and the main parameters when applied to conventional post-digestion liquors have been identified [32]. Several companies (e.g. Ostara in Canada, SUEZ in France, CNP in Germany, or Paques in the Netherlands) are already commercialising such crystallisation systems for struvite recovery.

Furthermore, the digestate after AD is a potential stream containing valuable nutrients on its matrix. The sludge recycling for agriculture application as fertilizer must be considered (e.g. post-treatment with a mature technology such as composting) as a potential practical way for maximizing sewage resource recovery [33].

1.4. Towards a new wastewater treatment train concept

As previously explained, to carry out enough mineralization of organic matter in sewage, this process demands an extensive use of aeration, leading to huge amount of energy consumption in terms of electricity. In addition, a large volume of sewage sludge and GHG emissions also render problems of sustainability, especially under the circumstances of the global energy crisis and climate change. It is important to highlight the necessity to work in order to find new wastewater treatments which enable the WWTPs to move from being energy consumers and nutrient removal sites to energy producers and nutrient recovery sites. The goal of a better

capture of the full energy and nutrient resource potential present in the wastewater is an increased understanding of the importance of working toward greater sustainability in wastewater treatment systems [5,14,34,35]. Society must consider wastewater as a part of the solution to the problem of natural resources, as wastewater actually is a potential source from which energy and nutrients can and should be recovered in an economical manner [14,36–38]. *Table 1.2* lists the potential recovery of resources from municipal wastewater, not including heat recovery, under the assumption that the chemical energy is recovered in the form of CH₄ through AD and that the remaining organic carbon after such treatment is used as an organic fertilizer [14].

Table 1.2. Potential recovery of resources from municipal wastewater. Prices are based on the market value of comparable products [14].

Potential recovery	Per m ³ sewage	2009 market prices	Total (€)
Water	1 m ³	0.25 €·m ⁻³	0.25
Nitrogen (N)	0.05 kg	0.22 €·kg ⁻¹	0.01
Methane (CH ₄) ^a	0.14 m ³	0.34 €·m ⁻³	0.05
Organic fertiliser ^b	0.10 kg	0.20 €·kg ⁻¹	0.02
Phosphorus (P)	0.01 kg	0.70 €·kg ⁻¹	0.01
		Total	0.35

^a Based on 80% recovery of organic matter in the form of biogas and 0.35 m³·kg⁻¹ COD removed.

^b Based on 20% organic matter remaining after AD. The price is based on the agricultural value of organics.

The WWTP of the future must be going in this direction: to be capable to be a net energy producer and to recover as much of the resource present in wastewater as possible, which mean to be self-sustainable. The feasibility of new sustainable and resource-efficient WWTPs with the purpose of recovering more solids than in a primary settler, as an alternative to conventional systems, has been considered (*Figure 1.3*). This new configuration would allow, on the one hand, producing more biogas as well as reducing the energy required for post-treatment and, on the other hand, the recovery of nutrients would be more feasible. In *Table 1.3*, the ultimate achievement targets for this new flowsheet are compared with the general situation in current WWTPs (based on the average values of CAS systems).

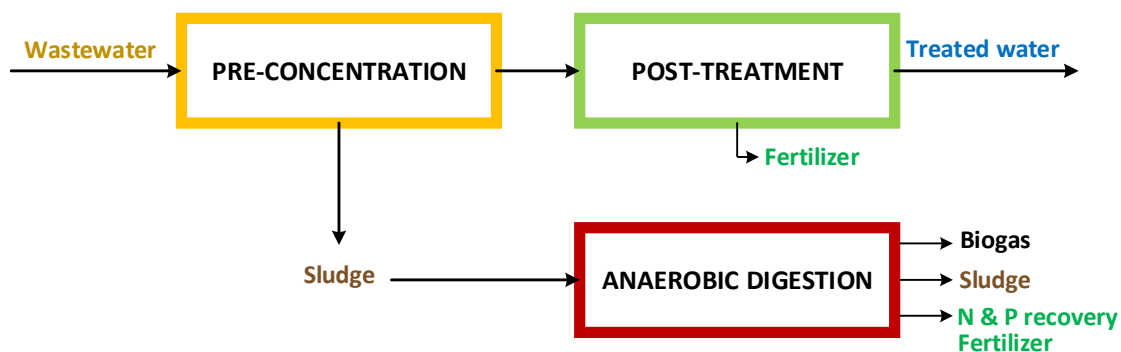


Figure 1.3. New concept of a wastewater treatment plant (WWTP).

Table 1.3. Comparison of the new wastewater treatment plant (WWTP) concept to the conventional system (CAS) targets.

Target	Current situation (CAS system)	New WWTP concept (expectations/targets)
Energy self-sufficiency (electricity requirements)	20–40%	60%
Nutrient recovery	0%	70%
By-products returned to land	40%	80%
Carbon footprint reduction	-	30%

This new vision of the wastewater treatment will have an economic and environmental positive impact on the whole society thanks to decreasing energy demand and increase nitrogen and phosphorus recovery in WWTP.

In economic terms, the OPEX of the plants will be reduced considering energy and nutrients recovery. Moreover, due to the increase of energy costs throughout the whole of Europe, as well as the increase of fertiliser costs, this cradle-to-cradle flowsheet is also expected to be economically-sustainable within the next decade.

From the environmental point of view, the impact to the environment associated to GHG emissions will be lessened thanks to the diminution of them (from 0.43 to 0.28 kgCO₂·m⁻³ of wastewater treated) and the recovery of nutrients will lead to reducing the conventional production of fertilisers [4,5,37]. The global environmental concern leads to a stricter threshold of emission, remarking the necessity to improve the efficiency of processes and start talking about recovery rather than removal to meet discharge requirements.

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CHAPTER 2

Objective and Methodology

2. Objective and Methodology

2.1. Aim and general objective

This PhD thesis aims at evaluating scientifically at pilot scale the feasibility of integrating existing technologies (bio-sorption, anaerobic digestion (AD) and adsorption) to be operated under new conditions in order to: a) recover much more primary sludge than conventional primary settling to maximize energy production, and b) recover nutrients from the bio-sorption effluent and also from the supernatant of the AD by means of both adsorption and precipitation processes. The effectiveness, efficiency and the technical, economic and environmental feasibility of the selected treatment technologies, as well as of the whole system, to achieve their purpose will be particularly targeted in this thesis. As previously commented in *Chapter 1*, it is important to highlight that the paradigm of wastewater treatments plants (WWTPs) must change in the future years. Nowadays, WWTPs are energy consuming and only part is recovered in AD (25% on average) and nutrients are removed. Therefore, this work is focused on studying the prospects and limitations of a real innovative flowchart, as depicted in *Figure 2.1* in a context to recover nutrients (nitrogen, N; phosphorus, P) and maximize energy production from municipal wastewater.

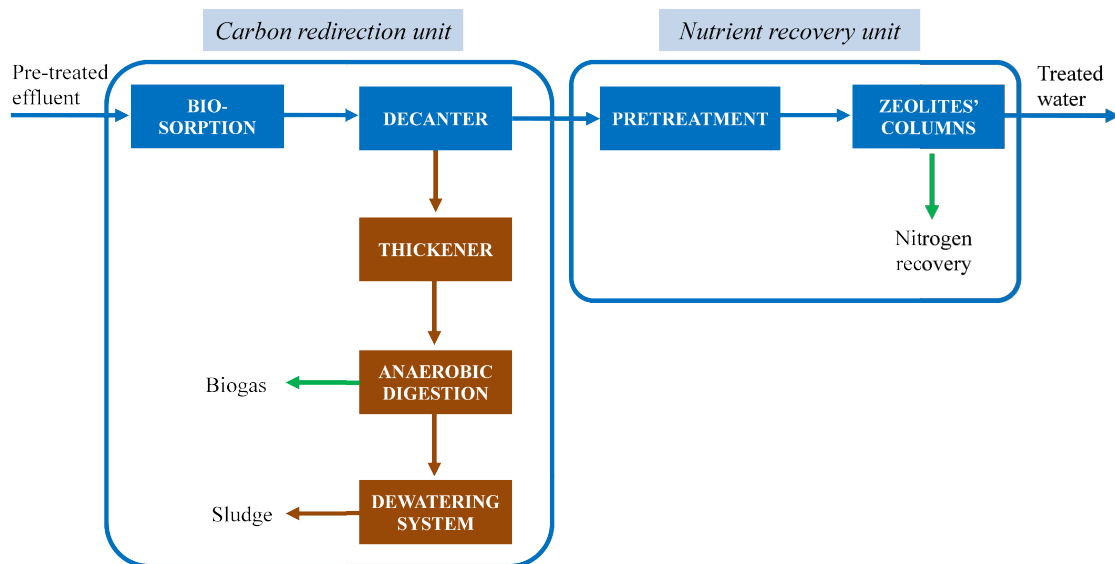


Figure 2.1. Aim of this PhD thesis, addressing the global flowchart.

2.2. Specific objectives

This thesis has been built as an integration of different processes and technologies focused on the recovery of nutrients and energy; namely bio-sorption, AD, ion-exchange by means of zeolites and membrane contactors, and comparison with conventional flowcharts. While some of these processes and technologies have been addressed through experimental activities, others have focused on summarizing and analysing the data generated to achieve the main goal of this work. Therefore, the specific objectives of this PhD thesis are listed below:

- Overview of the new concepts on carbon redirection in wastewater treatment plants. Changes in carbon paradigm: from conventional activated sludge (CAS) processes to new alternative options using high-rate aerated sludge processes (HRAS). Operational principles, technological implementation and process feasibility (*Chapter 3*).
- Assess the performance of biological adsorption for obtaining a concentrated organic primary sludge stream to be used for digestion to produce biogas and an effluent stream rich in ammonium (*Chapter 4*).
- Select the most appropriate zeolite for the removal and recovery of nitrogen by means of ammonium adsorption (*Chapter 5*).
- Assess the performance of adsorption materials for ammonium removal at pilot scale. Understand the basics of the adsorption mechanisms involved (*Chapter 6*).
- Evaluate the integration of a natural zeolite with hollow fibre membrane contactors for the selective extraction of ammonium nitrogen from treated wastewater effluent and subsequent concentration and purification of ammonium (*Chapter 7*).
- Demonstration of the environmental benefits and the economic viability. Quantification of the reduction in terms of environmental impacts using a Life Cycle Analysis (LCA) approach (*Chapter 8*).

2.3. Methodology

A combination of activities was conducted in order to accomplish with the main objective and the specific objectives of this thesis:

- Selection of a WWTP and establish a detailed characterization of the composition of all streams of the selected WWTP for the project based on historical analysis.
- Design, construction and operation of the pilot plant.
- Environmental and economic assessment of the innovative technologies proposed in this thesis by using an LCA.

2.3.1. Wastewater treatment plant selection

The selection of an adequate WWTP is important to ensure the relevance of the results to come. The selected WWTP, Vilanova i la Geltrú WWTP (from now on ‘Vilanova WWTP’), complies with the requirements for the demonstration of the prototype: a medium plant with primary settler, biological reactor and AD.

Vilanova WWTP, depicted in *Figure 2.2*, treats a mix of municipal and industrial wastewater from Vilanova i la Geltrú and Sant Pere de Ribes in the Garraf region (South of Barcelona, Spain) and its global nominal capacity is $25,500 \text{ m}^3 \cdot \text{d}^{-1}$ (130,050 population equivalent, PE). The plant was designed to remove carbon through CAS treatment. Sewage treatment line, preceded by an external unit to the WWTP, consists of pre-treatment (screens, grit and fats), primary sedimentation in circular settling tanks, biological aerated plug-flow reactors and secondary sedimentation in circular settling tanks. A portion of the treated effluent is filtrated and disinfected by chlorination to be used as service water; another part is used as industrial water in the plant, and the rest of the treated wastewater is discharged into the sea. On the other hand, the sludge treatment line consists of sludge thickening (primary sludge by gravity; and secondary sludge by flotation with no coagulant addition), AD at mesophilic conditions (37°C) and sludge dewatering in centrifuges (with the addition of cationic polyelectrolyte). Dewatered sludge is transported to thermal drying installations. The gas line is constituted by a gasometer, an engine cogeneration and heat exchanger boilers. The plant incorporates a cogeneration engine capable to produce energy approximately for the 50% of the WWTP’s needs.



Figure 2.2. Aerial view of Vilanova WWTP, location of the pilot plant.

Throughout a complete year, the plant experiences no significant seasonal differences regarding the influent flow; flowrate fluctuates between 12,500 and 15,000 m³·d⁻¹.

In 2013, the biochemical oxygen demand (BOD₅), the chemical oxygen demand (COD) and the total suspended solids (TSS) inlet concentrations (defined as the influent quality) remained between 200–500 mgBOD₅·L⁻¹, 600–1,700 mgCOD·L⁻¹ and 150–700 mgTSS·L⁻¹, respectively. Organic matter and suspended solids are successfully removed throughout the process. Overall, the process provides an average removal of about 91%, 85% and 84% of BOD₅, COD and TSS, respectively. The maximum COD and BOD₅ values were obtained in the same months in which high concentrations of suspended solids were measured in the raw influent wastewater, which evidences that organic matter is predominantly particulate and slowly biodegradable. Total nitrogen ranged from 55 to 105 mgN·L⁻¹ while phosphorus varied from 8 to 13 mgP·L⁻¹. Nutrients are removed throughout the process with an efficiency of 48% and 66% for N and P, respectively. The detailed monthly data collected over the year 2013 can be consulted in *Appendix A*.

To understand the behaviour of carbon and nitrogen along the whole WWTP process, a mass balance is shown in *Figure 2.3*.

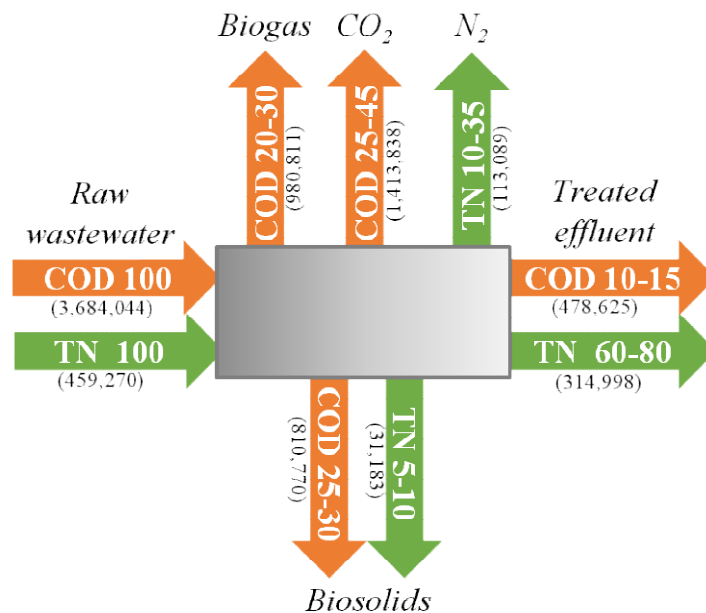


Figure 2.3. Carbon and nitrogen mass balance of Vilanova WWTP based on analytical data for the years 2013 and 2016. Values inside brackets are expressed in kgCOD·year⁻¹ (year 2016).

As it can be seen in *Figure 2.3*, between 20–30% of the influent total COD could be converted to biogas through AD and almost the same percentage remains into sludge. After the biological treatment, only 10–15% of the inlet COD is still present in water. However, a major percentage of the organic matter contained in wastewater (25–45%) is lost out of the system mineralised to CO₂.

The nitrogen mass balance demonstrates that Vilanova WWTP does not remove nitrogen from wastewater via nitrification-denitrification process (or other technology since more than the half of total nitrogen could be measured in the effluent. Only a low percentage not higher than 10% could be recovered contained in biosolids.

From an energetic point of view, the annual energy consumption of the plant is around 0.41 kWh·m³ of treated wastewater, which represents an electrical energy consumption of 2,043,395 kWh·y⁻¹. Taking into account that the plant produces enough electricity to supply about the 50 % of the WWTP's demand (1,026,847 kWh·y⁻¹), it can be concluded that Vilanova WWTP is quite efficient. It is explained by the fact that nitrification process does not take place in the process, therefore, the energy consumption is relatively low in comparison to other plants (which common electricity consumption range between 0.3 to 0.6 kWh·m³ of treated wastewater) [1]. More data related to energy can be consulted in *Appendix B*.

2.3.2. Pilot plant description

Vilanova WWTP's case base enabled to define a configuration for the flowchart to be implemented in the prototype.

It consisted of two different units: a carbon redirection unit (based on pre-concentration unit + AD unit) and a nutrient recovery unit. This configuration would allow, on the one hand, producing more biogas as well as reducing the energy required for post-treatment and, on the other hand, the recovery of nutrients would be more feasible. *Figure 2.4* shows an overview of the whole installation.

The selection of the treatment processes was conducted according to the literature review (see *Chapter 1*) and previous experience in the research group. The different units of the pilot plant are described as follows.

The setting, regulation and control of the operating parameters and the operation of the whole prototype were only possible achieved by means of a programmable logic controller (PLC) program (one for each unit). Each pilot unit is thought to operate automatically due to its high

grade of automation, even though manual mode was also available (but the software was needed).



Figure 2.4. PhD thesis pilot plant.

Carbon redirection unit

The carbon recovery pilot, as shown in *Figures 2.5–2.6*, is based on two consecutive steps: a pre-concentration (1) followed by an AD (2). It was conceived in two separately (one for each step) but connected modular units including: (1) 6 tanks of 1 m³ each (1 buffer tank, 1 mixing tank and 4 aeration tanks) and 1 decanter for separation of sludge and treated water (effluent); and (2) a 0.7 m³ active volume anaerobic reactor for the conversion of the thickened sludge into biogas, a tank of in total 0.8 m³ divided in 2 equal compartments of about 0.4 m³ each for the storage of thickened and digested sludge, respectively.

The pre-concentration unit, based on a HRAS system, was designed for an average incoming flow rate of 0.5 m³·h⁻¹ and a maximum flow rate of 1 m³·h⁻¹. Aerated tanks were designed in a way that they could be operated independently and either in series or parallel and together with its modular design allow: (i) testing completely stirred tank reactor (CSTR) conditions as well as plugging flow conditions and (ii) changing process parameters, such as retention time (HRT), volumetric loading rate (Bv) and sludge loading rate (Bx) by modifying the active reactor volume. Meanwhile, AD was designed as a conventional CSTR since extra equipment required for a more innovative temperature-phased AD (TPAD) configuration would not compensate for the slightly higher COD-to-biogas conversion, about 5%. It was able to manage a flow of at least 35 L·d⁻¹ at a HRT over 20 days and to operate under both mesophilic (overall power

consumption: $3.31 \text{ kWh}\cdot\text{d}^{-1}$) and thermophilic (overall power consumption: $4.13 \text{ kWh}\cdot\text{d}^{-1}$) temperature conditions.

The detailed P&IDs of the pre-concentration and AD units can be consulted in *Appendix C* and *D*, respectively.



Figure 2.5. General view of the modular pre-concentration pilot unit.



Figure 2.6. General view of the anaerobic digestion (AD) pilot unit.

Nutrient recovery unit

Depicted in *Figure 2.7*, the design of the nutrient recovery pilot was based on an ion-exchange unit by means of granular zeolites columns, preceded by a glass filter and an ultrafiltration (UF) unit as a pre-treatment step to protect zeolites and remove the remaining solids and particulate COD of the raw water. It was conceived to treat $1 \text{ m}^3 \cdot \text{h}^{-1}$ raw water. The UF system was provided with 5 columns of hollow fibre membranes (model UF44-12). Two ion-exchange columns (2x200 L, nominal flow rate of $500 \text{ L} \cdot \text{h}^{-1}$; $2\text{--}4 \text{ BV} \cdot \text{h}^{-1}$) packaged with granular clinoptilolite zeolites (100 kg per column; corresponding to the 60% of the active column's volume) were displayed. Columns connection was set individually or in both parallel and series mode. Their design was set to operate in co-current or counter-current. Four tanks (750 L each) were placed to store ultra-filtered water and effluent from the zeolite columns, in twos respectively. These tanks were equipped with an on-line sensor for the measurement of the ammonium concentration. Apart from the water produced by the system itself (ultra-filtered and zeolites' effluent water), chemicals used in this system to wash each device and regenerate zeolites were hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium hypochlorite (NaClO), sodium chloride (NaCl) and sulphuric acid (H_2SO_4).

The detailed P&ID of the nutrient recovery unit can be consulted in *Appendix E*.



Figure 2.7. General view of the nutrient recovery pilot unit.

2.4. PhD thesis organization

The following chapters of this thesis cover the specific topics and results obtained in each proposed prototype unit to the new wastewater treatment concept as depicted in *Figure 2.8*.

- *Chapter 3*: New concepts on carbon redirection in wastewater treatment plants: A review.
- *Chapter 4*: Pre-concentration by bio-sorption and bio-oxidation of urban wastewater: a carbon redirection evaluation.
- *Chapter 5*: Nutrient recovery design to treat pre-concentrated effluent: an overview of the batch and column tests with different types of zeolites.
- *Chapter 6*: Nutrient recovery from urban wastewater by integration of granular natural zeolite as extraction and concentration technology: validation at pilot scale.
- *Chapter 7*: Recovery of ammonia from domestic wastewater effluents as liquid fertilizers by integration of natural zeolites and hollow fibre membrane contactors.
- *Chapter 8*: Environmental and economic assessment: Guidelines for implementation.

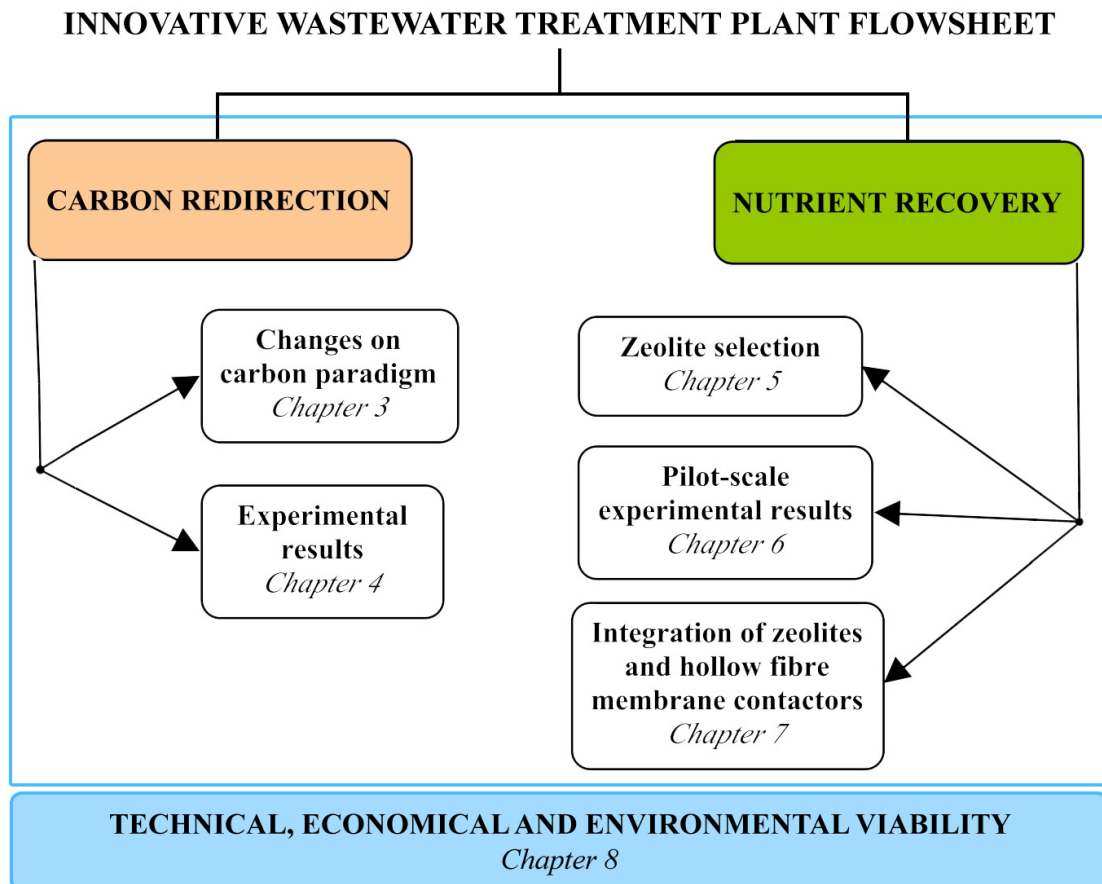


Figure 2.8. Organization of the PhD thesis.

2.5. References

- [1] J. Wan, J. Gu, Q. Zhao, Y. Liu, COD capture: A feasible option towards energy self-sufficient domestic wastewater treatment, *Sci. Rep.* 6 (2016) 1–9. doi:10.1038/srep25054.

CHAPTER 3

*New concepts on carbon redirection in
wastewater treatment plants: A review*

3. New concepts on carbon redirection in wastewater treatment plants: A review

3.1. Introduction

Municipal wastewater is a valuable resource. However, the majority of the world's municipal wastewater treatment plants (WWTPs), which are based on the conventional activated sludge (CAS) process (*Figure 3.1*), remove potential resources from wastewater. When using CAS, carbon (C) present in wastewater ($300\text{--}800\text{ mgCOD}\cdot\text{L}^{-1}$) is not fully recovered as it is partially oxidized into carbon dioxide (CO_2), up to 30% by means of biological processes [1]. This process demands extensive aeration to promote the mineralization of organic matter and the production of an effluent with an organic content below the legal requirements. It is estimated that aeration represents between 30% and 60% of the total energy consumption of a plant ($20\text{--}35\text{ kWh}_e\cdot\text{PE}^{-1}\cdot\text{y}^{-1}$ in Western Europe) [2]. Seventy per cent of the organic load is transformed into biomass that could be valorised for agricultural uses or valorised energetically as biogas. Some studies point out that the chemical energy contained in the organic load of wastewater (about $235\text{ kWh}_{th}\cdot\text{PE}^{-1}\cdot\text{y}^{-1}$) could otherwise be harvested to produce energy and satisfy the energy needs of a CAS system [3]. Anaerobic digestion (AD) is regarded as the core technology for energy recovery and methane production from sludge, but it is only installed in medium and large size plants, where it is economically feasible.

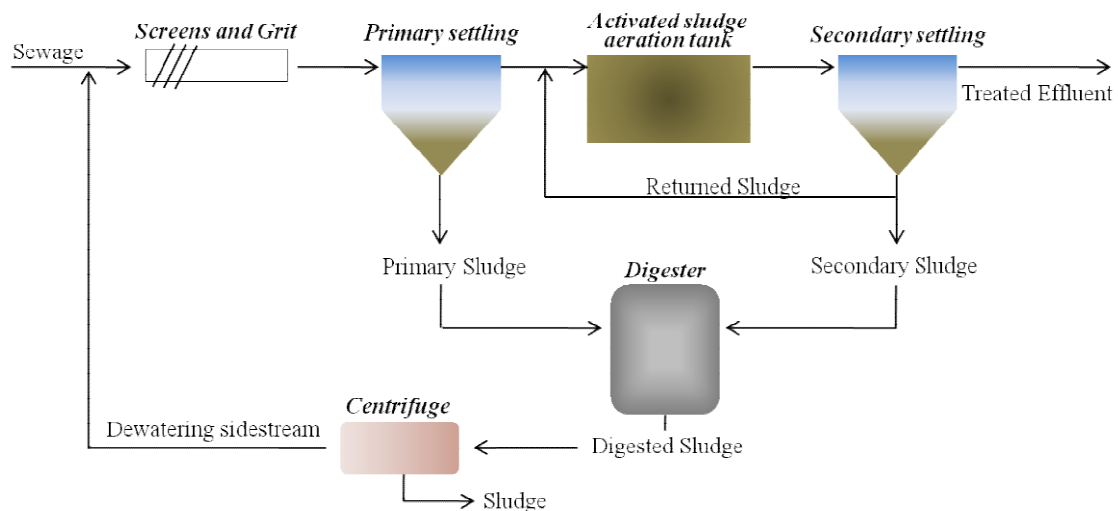


Figure 3.1. Scheme of the configuration of a wastewater treatment plant (WWTP) based on a conventional activated sludge (CAS) system with pre-treatment, primary settling and biogas production.

Additionally, the large volume of excess sludge to be treated or the greenhouse gas (GHG) emission inherent in a CAS process also yields economic and sustainability problems [4]. According to Jin et al. (2016) [4], the annual production of excess sludge in the European Union is over 10 million tons of waste activated sludge (WAS), whose treatment and disposal account for about 30–60% of the total operating cost in a CAS treatment plant [5].

Most of the large WWTPs (above 200,000 population equivalent; PE) in Europe were built in the 1980s/1990s and were therefore built with the aim of removing organic pollution from wastewater. These plants would require refurbishing to achieve the targets of energy self-sufficiency and nutrient recovery. In general, in the last years, worldwide initiatives have promoted the implementation of innovative technologies in WWTPs to reduce energy consumption and recover resources from wastewater [6]. International organizations have promoted an initiative to accelerate, develop, demonstrate and further implement innovative technologies to enhance the recovery of wastewater, nutrients, energy, heat and other valuable products in Water Resource Recovery Facilities (WRRFs) at reduced costs [7].

By implementing C redirection technologies in diluted streams (such as the influent of urban WWTPs), it is possible to obtain a concentrated stream suitable for the waste-to-energy pathway, since the AD of pre-concentrated wastewater can result in self-supporting energy. Indeed, with a chemical oxygen demand (COD) level above $5 \text{ g}\cdot\text{L}^{-1}$, the biogas produced can cover the overall heat input costs [2].

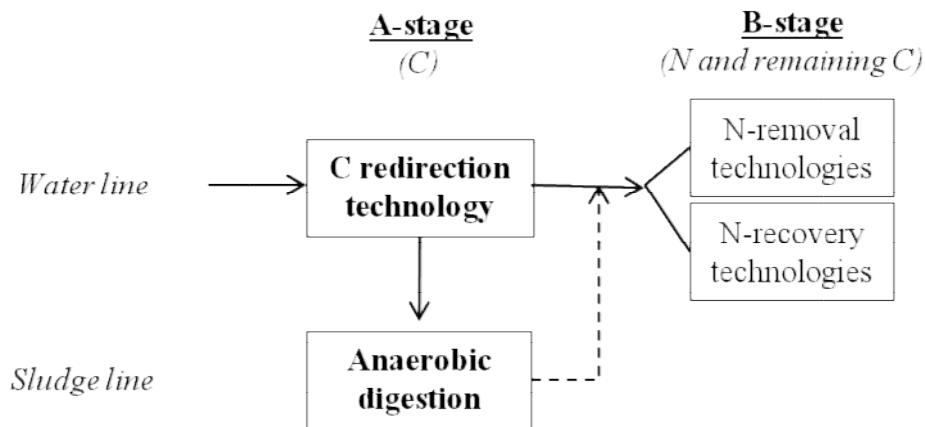


Figure 3.2. Diagram of the scope of this study. In the proposed scheme of wastewater treatment, carbon (C) redirection technologies are placed in water line to treat the mainstream. The treated effluent of the A-stage altogether with centrates of anaerobic digestion are treated in a next stage (B-stage) to be focused on nitrogen (N) and remaining carbon. The impact on nitrogen can be made by either N-removal or N-recovery technologies.

The purpose of this review is to focus on high-rate activated sludge (HRAS) technologies for carbon redirection from the mainstream to the sludge line, followed by AD downstream at the sludge line, as a promising solution to improve the energy efficiency of a WWTP (*Figure 3.2*). The main alternatives to achieve the highest recovery redirection and consequent reduction of the biological oxidation to CO₂ (C mineralization) are reviewed. Preliminary attempts to model and simulate the performance of HRAS, previous research at the laboratory and pilot scales and available references for this process at full scale are also reviewed.

3.2. Changes to the carbon paradigm: alternatives to the conventionally activated sludge system

In recent years, studies have focused on finding alternatives to conventional systems. The challenge is to find a more sustainable, energy- and resource-efficient process [4,8,9]. With the purpose of make the whole system energy positive, efforts are directed towards finding a strategy that, compared with a primary settler, will be able to recover more carbon (called carbon redirection). Carbon redirection technologies (pre-concentration technologies) are capable of removing particulate, colloidal and soluble organic matter from the system to produce a high amount of sludge [10].

Different pre-concentration strategies have been suggested to maximize energy production. *Figure 3.3* depicts a classification of the strategies according to their operational principle: physical, chemical or biological processes. This section provides a brief description of the emergent technologies focused on carbon redirection.

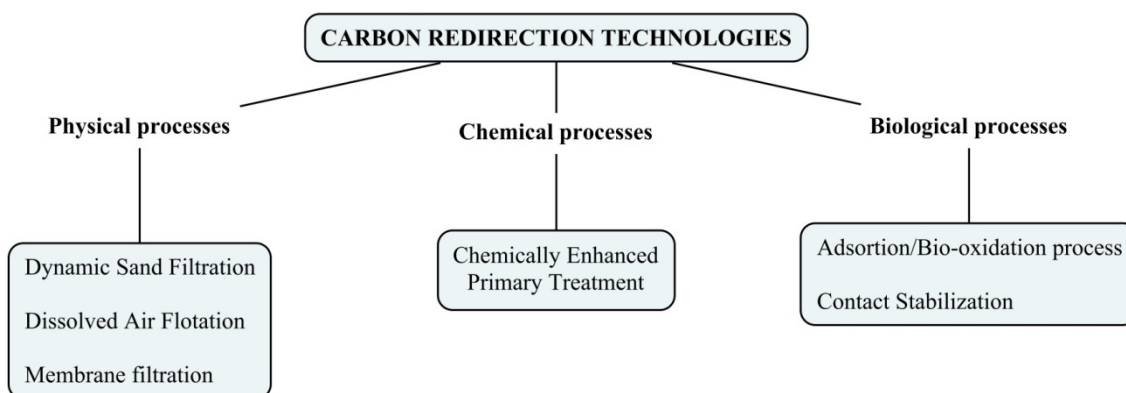


Figure 3.3. Diagram of the different carbon redirection technologies studied, classified according to their operational principle: physical, chemical or biological.

3.2.1. Carbon redirection by physically mediated sorption processes

Carbon redirection by filtration: dynamic sand and other filtration systems

Dynamic sand filtration (DSF) of urban wastewater is an interesting option for wastewater pre-treatment since the majority of suspended solids can be retained. The basic principle of continuous contact filtration is that the sand bed works at the same time as a flocculation reactor and filter, so there is no need for any extra flocculation, sedimentation or flotation step [11]. One commercial example is the DynaSand filter [11].

The efficiency of removal of suspended solids (SS) may vary from 50% to 90% according to the hydraulic loading rate, filter design and medium characteristics. A significant part of the COD may also be removed, but to a lesser extent than the SS. Compared to conventional treatment, DSF has lower capital costs, reduced space requirements (the treatment plant space requirement can be reduced by 70–80%), and smaller sludge production [11]. Moreover, DSF offers significant reductions of coagulant dosages and chemical savings, despite the fact that the use of flocculants can increase filter performance.

Several technologies have been used for wastewater filtration, but the most commonly used filter media are incompressible materials with a fixed porosity of between 35% and 50%, such as sand or anthracite [12]. Some of the primary filtration technologies found at a high readiness level have been identified. Fuzzy Filter® (Schreiber Corporation, AL) is a well-established compressed media filtration technology mainly used in tertiary treatment, but it can be easily adapted for use as C redirection technology. The bio-filtration system (BBF™) of BTK is an up-flow process system using expanded polypropylene as a floating media layer for filtration. The Salsnes Filter™, from Trojan Technologies, removes suspended solids and provides thickening and dewatering up to 30%w/w thanks to a rotating belt filter. ClearCove Systems' commercializes a hybrid process based on enhanced physical clarification (batch settling under different section sizes allowing settling of particles of different sizes) and filtration of settled wastewater using a 50 micron stainless steel screen.

Carbon redirection by dissolved air flotation

Dissolved air flotation (DAF) works as a combined liquid separator and sludge thickener. It is very efficient in the removal of particles and can substantially decrease the particle load to the filters compared to direct filtration. The DAF unit is divided into two zones: the contact zone, where air microbubbles (10–100 µm) are introduced in the influent and aggregate with the flocs; and the separation zone, where the bubble-floc aggregates are separated by floating [13]. This

integration permits designing filters at higher rates. Reported results have shown that the combination of two-stage DAF and dual media filtration leads to SS and COD removal efficiencies of 99% and 75–85%, respectively [14]. This technology is used on a large scale for drinking [14] and industrial wastewaters [15]. It is also applied to increase thickened sludge concentration to 30–60 g·L⁻¹ of SS [16,17]. A well-known system used nowadays at WWTPs to help them in terms of energy neutrality is the Captivator® system, developed by Evoqua Water Technologies LLC [18].

Carbon redirection by solid-liquid separation using membrane filtration

Membrane filtration systems are promising energy-efficient technologies for the concentration of organics from several streams, such as domestic wastewater, high-rate activated A-sludge and secondary sludge [19,20]. On the one hand, porous membrane filtration (micro- and ultra-filtration) can be applied in different ways: a highly loaded membrane bioreactor (MBR) system (considered as a biological treatment), a dynamic membrane system, a submerged aerated or vibrated membrane filtration system [8,9] and a direct membrane filtration system in a dead-end process with chemically enhanced backwash [1]. On the other hand, non-porous membrane filtration, such as forward osmosis, can concentrate the organic load and nutrients in wastewater to a small volume for potential integration with anaerobic treatment to facilitate resource recovery. Both the leak of ions from the draw solution and the physical effect caused by recirculation of the stream and air scouring result in disaggregation of the sludge flocs and lysis of the cells. This fact increases the soluble COD (sCOD) and volatile fatty acids (VFA) production.

Although these processes have demonstrated that they are technologically feasible at the pilot scale, there are limited publications about the use of porous membranes in the primary treatment of wastewater at full scale [21]. Further research mainly focused on the optimization of energy consumption and membrane fouling is required [4] in order to promote the efficient full-scale implementation of the technology.

3.2.2. Carbon redirection by chemically mediated sorption processes

Carbon redirection by integration of coagulation and flocculation processes has been used to improve the settling properties of the primary treatment. Chemically enhanced primary treatment (CEPT) refers to the addition of chemicals to primary sedimentation basins to agglomerate the smaller sludge particles into larger flocs. Thus, combined with carbon

redirection technologies, total SS (TSS) (including some colloidal particles), total biochemical oxygen demand (BOD) and total COD (tCOD) recovery greatly improve. It represents to some 80–90%, 50–80% and 45–80%, respectively [22]. However, this process is not efficient in removing sCOD [22]. In comparison to CAS, CEPT increases the quantity of sludge produced by nearly 45% (33% corresponding to enhanced solid capture). The efficiency of this process depends on the dose: typical coagulant (iron-salts, such as FeCl_3 or FeSO_4) and flocculant (organic polyelectrolytes) doses are around $100 \text{ mg}\cdot\text{L}^{-1}$ and $0.5\text{--}4 \text{ mg}\cdot\text{L}^{-1}$, respectively [23]. Hence, the total costs of a CEPT are determined by the energy requirements for mixing [23] and by the costs of the additives. Based on the fundamentals of chemical addition, several demonstrations of high-rate clarification processes, also known as ballasted flocculation, have been developed to improve the settling properties of SS: DensaDeg®, marketed by Infilco Degremont Inc.; Actiflo®, manufactured by Veolia/US Filter Krüger; CoMag™, developed by Evoqua; and RapiSand™ by WesTech. These processes work through the addition, at different tanks, of (1) a coagulant (such as ferric sulphate, FeSO_4) to destabilize SS; (2) an anionic polymer and (3) a ballast material. The latter, such as micro-sand (Actiflo®, RapiSand™), chemically enhanced sludge (DensaDeg®) or another material, like magnetite (CoMag™), serves as a ‘seed’ for floc formation. Contrary to the other systems, the DensaDeg® process uses injected air rather than flash mixing to disperse the coagulant. The compact size of units, faster floc formation and decreased particle settling time (which allows clarification to occur up to ten times faster than with conventional clarification) make these systems attractive for high-rate applications [17,24,25].

3.2.3. Carbon redirection by biologically mediated sorption processes

The ability of activated sludge to rapidly adsorb COD and BOD is exploited in biological carbon redirection processes. Adsorption onto sludge flocs occurs in a significantly shorter timescale than the other biological processes involved in activated sludge systems (i.e. assimilation, storage into the sludge matrix and microbial growth) [26]. The application of short hydraulic and sludge retention times allows selective strengthening of this route in favour of oxidative processes [27]. Therefore, the term ‘bio-sorption’ is commonly used [3].

The concept of biological sorption may be explained by three distinct, fast and non-simultaneous processes [28,29]. Firstly, both particulate and soluble organic compounds physico-chemically adhere to the floc. Then, adsorbed compounds are hydrolysed to smaller soluble compounds by enzymes or extracellular polymeric substances (EPS). Finally, the absorption of the latter into the cell is used for anabolism and catabolism processes. The physico-chemical removal of particulate and colloidal COD is achieved via biological

flocculation (adsorption into the biological floc) and subsequent solids-liquid separation [30] while the soluble fraction gets captured through intracellular storage mechanisms, bio-synthesis or bio-oxidation [31]. Maximizing removal of particulate and colloidal COD while minimizing COD hydrolysis and mineralization of the slowly biodegradable COD is fundamental for carbon redirection. Then, efforts to minimize hydrolysis processes of COD should be based on the benefits provided by HRAS with short sludge age (SRT) and low hydraulic retention time (HRT). Regardless of the size of the pollutants, bio-sorption refers to both the biological adsorption and the biological flocculation of COD onto sludge flocs. The efficiency of bio-sorption is known to be linked to bio-flocculation, sludge characteristics (like type and fraction of EPS), the presence of storage compounds, SRT, HRT and even dissolved oxygen (DO) levels in the reactor [32,33]. Even though it is a controversial subject, some authors point out the poor settling properties of HRAS systems as one of the main operational drawbacks [29,34]. Other studies, however, have reported an excellent settleability and dewaterability of A-sludge, attributed to the low EPS content in the mixed liquor [35]. Jimenez et al. (2007) [36] found that increasing the SRT above three days did not improve bio-flocculation, while Kinyua et al. (2017) [37] pointed out that EPS production did not seem to have a significant influence on bio-flocculation and settling due to the short SRT of HRAS systems. It is clear that more research is needed to explicitly investigate the real effect of the operational parameters that control HRAS in terms of sludge settling properties.

The sludge age in this process is short, which makes this sludge (which is called ‘adsorptive sludge’ or ‘young sludge’) more digestible; consequently, higher energy production is achieved [6,38], while nitrification is limited.

In recent years, HRAS processes have gained attention and demonstrated successful results because of their highly efficient removal of particulate, colloidal and dissolved organic matter [39]. Moreover, biological processes have become the most interesting, competitive, sustainable and cost-effective available alternatives to CAS as part of the consumed energy is recovered and the addition of chemicals is not, at first, required.

HRAS systems can be found in several wastewater treatment processes, which are described below.

Adsorption/bio-oxidation process

The adsorption/bio-oxidation process (A/B process) was firstly developed in the 1950s [40]. Some years later, in the 1970s, it was reintroduced by Dr Botho Böhnke from RWTH Aachen University [41] at the WWTP in Krefeld, Germany. The objective was to develop a cost-

effective configuration. It was focused on maximizing carbon recovery from wastewater (to produce more energy through biogas) while reducing nutrients concentration to conform to the German regulations. The process consists of two consecutive stages (*Figure 3.4-A*): a high loaded activated sludge stage ($2\text{--}10 \text{ gBOD}\cdot\text{gVSS}^{-1}\cdot\text{d}^{-1}$) followed by a clarification step for carbon removal, known as A-stage (scope of this section); and a lower food to microorganisms (F/M) ratio stage ($<0.1 \text{ gBOD}\cdot\text{gVSS}^{-1}\cdot\text{d}^{-1}$), B-stage, for biological oxidation and nutrient removal. A-stage's objective is to maximize the capture of carbon, under colloidal and particulate form, into microbial sludge by biological, physical and chemical methods (such as adsorption, flocculation and coagulation) and to redirect organic carbon towards an AD step for biogas production [10,42–45]. Given the low and dynamic operational conditions in A-stage, microorganisms are better adapted not only to intracellular storage but also to adsorption instead of growth. This dominating storage affinity is characterized by the uptake and conversion of rapidly biodegradable COD to storage polymers.

Under optimum operational conditions, the A-stage may achieve high removal efficiency, typically 70–80% of tCOD, 30% of sCOD and 80–95% of SS, while the nutrients remain unaffected [44]. However, due to the high TSS/COD removal efficiency in A-stage, the bio-oxidation stage does not have sufficient carbon for a conventional denitrification process, so other processes need to retrofit to handling nutrients (e.g. anammox, short-cut nitrogen removal systems) [22].

The above-mentioned advantages of bio-sorption technology over conventional processes (such as smaller reactor volume required, low energy demand and ability to handle shock loads, among others) have promoted its full-scale implementation in several WWTPs (see *Section 3.3.4*).

Contact-stabilization process

The contact-stabilization (CS) approach, initially examined as a low-rate process by Coombs (1922) and Ullrich and Smith (1951), has recently been evaluated as an advanced primary treatment process [26,47] to improve the carbon harvesting from wastewater for high-strength synthetic wastewater [10] and for low strength wastewater [3]. As shown in *Figure 3.4-B*, the CS process uses two tanks. The first is a contact tank, where wastewater is brought into contact with the activated sludge at low HRT ($< 30 \text{ min}$) under moderate DO conditions (around $1 \text{ mgO}_2\cdot\text{L}^{-1}$). The second is a stabilizer, an aerated tank that stabilizes and oxidizes extracellular (particulate and colloidal) and intracellular (soluble) carbon from C-rich returned sludge [3]. The COD removal efficiency of the conventional CS process can reach 85–90% [3]. Removal of

organic load occurs mainly via biological sorption and storage on the activated sludge flocs. Under optimum operating conditions, the removal efficiencies obtained in the CS system were 70–80% of tCOD, 30% of sCOD, 80–95% of SS and 18% total Kjeldahl nitrogen (TKN) [35]. The main advantage of the CS process over other HRAS processes is the production of highly concentrated sludge since the stabilizer ensures that a strong concentration gradient is present between the sludge and the wastewater [29].

To fully exploit the advantages of the CS process, a high-rate contact-stabilization (HiCS) process was developed as a high-load system in a CS configuration [10]. The aeration of recycled sludge before the contact tank allows regenerating biological adsorption and flocculation properties of the flocs through biodegradation of bio-adsorbed organic matter and favours the generation of EPS in the contactor [48]. Sludge that is subjected to an intermittent feeding regime (feast-famine), as used in CS systems, is more likely to show high storage capacity [49]. It has been reported that HiCS lab-scale systems can recover from 55% [39] up to 70–80% [47] of incoming organic matter into sludge.

Comparing all these pre-concentration technologies in terms of electrical energy generated, all present higher benefits than CAS. According to Wan et al. (2016) [22], in typical domestic wastewater, a maximum recoverable electrical energy of about $1.6 \text{ kJ}\cdot\text{g}^{-1}\text{COD}$ is estimated. Calculations of the maximal theoretical electrical energy produced for an A-stage process, a CS process and a CEPT are 3.2, 2.3 and $2.1 \text{ kJ}\cdot\text{g}^{-1}\text{COD}$, respectively.

From the economic point of view, it is reported that the total costs for physical processes are close to $0.05\text{--}0.06 \text{ €}\cdot\text{m}^{-3}$ [21]. Diamantis et al. (2013) [50] calculated an additional cost for CEPT in relation to chemicals of about $0.1 \text{ €}\cdot\text{m}^{-3}$.

In terms of efficiency, among them, the physical or physico-chemical separation technologies have the advantage that they are not as selective as microbially-driven separation. However, they are mostly limited to separate out particulate (settleable and colloidal) components. On the other hand, biological oxidation processes only convert biodegradable compounds to energy, but they are able also to remove also part of the dissolved (biodegradable) substrate, while particulate and colloidal substrate must be hydrolysed and brought into solution before becoming incorporated into biomass or being mineralized.

Therefore, considering all discussed above, a promising separation process should be a combination of both physical and biological separation processes. It has been recognized in the literature as a hybrid process incorporating biological adsorption and bio-flocculation stages [51]. *Section 3.3* focuses on this specific technology concept.

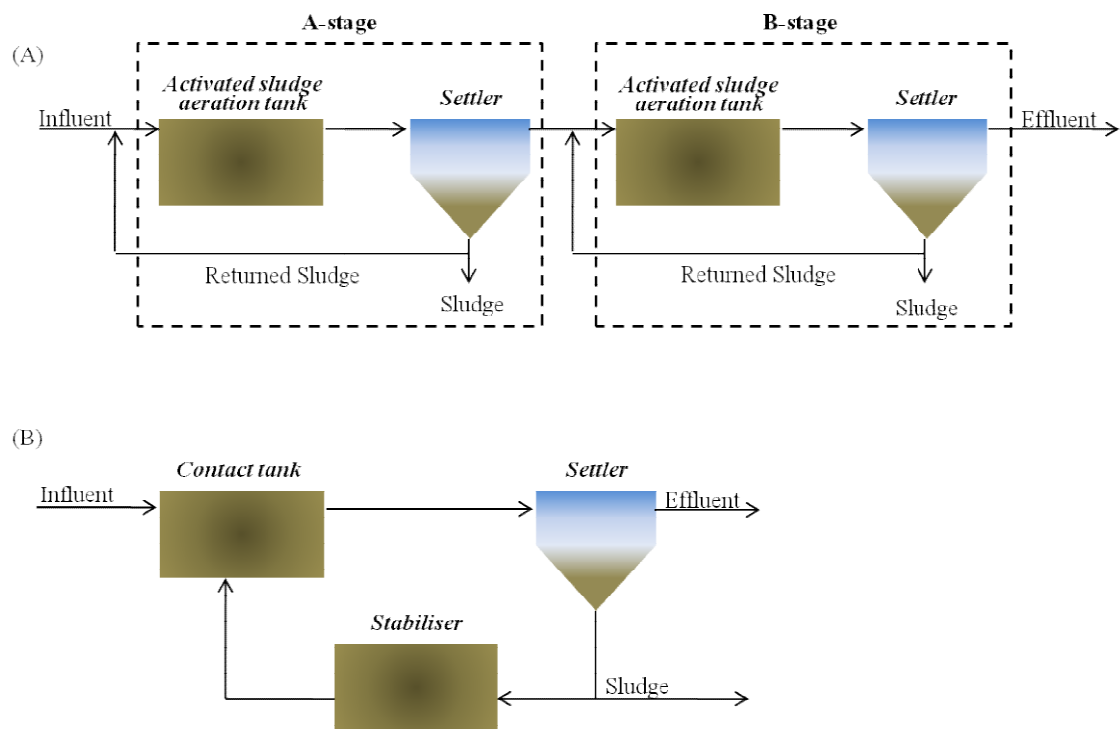


Figure 3.4. (A) Scheme of the process configuration of an A/B process, a biological system comprising a high loaded activated sludge stage for carbon removal (A-stage) followed by a lowly loaded stage (B-stage) for biological oxidation and nutrient removal. Each activated sludge stage has its own settler and sludge recycling system. (B) Scheme of the process configuration of a contact stabilization (CS) process, which consists of two tanks: a contact tank and a stabiliser tank, coupled to a settler for effluent-sludge separation.

3.3. HRAS as proof of the concept of carbon redirection

3.3.1. Operational and design conditions for HRAS

Based on the values reported in the literature, a comparison of the typical operating conditions for a CAS and a HRAS system are shown in *Table 3.1*. HRAS processes operate at significantly lower HRT, SRT and DO to boost the capture of carbon to biomass instead of being mineralized. Consequently, the loading rate of HRAS is notably higher, with a minimal sludge-specific loading rate of $2 \text{ kgBOD} \cdot \text{kg}^{-1} \text{VSS} \cdot \text{d}^{-1}$. However, the loading rate for HRAS can also be lower if HRAS system is applied after CEPT treatment. A summary of the relevant operational parameters in a HRAS system from the reviewed literature is offered below.

Table 3.1. Comparative of the operating conditions applied in CAS and HRAS systems.

	HRT (h)	SRT (days)	COD_{IN} (mg·L ⁻¹)	F/M ratio (gBOD·gVSS ⁻¹ ·d ⁻¹)	DO (mgO ₂ ·L ⁻¹)
CAS	4–9	8–20 ^a	300–800 ^b	0.2–0.6 ^c	2
HRAS¹	≤ 0.5 ^d	0.1–1 ^e		2–10 ^f	0.5–1 ^g

¹ HRAS comprises A-stage of the A/B process (also named as HiCAS) and high-rate contact-stabilisation (HiCS) processes.

^a [52]; ^b Average medium strength wastewater: 500 mg·L⁻¹ [2]; ^c [32,35]; ^d [37,39]. Other authors [48,49] consider HRT < 1 h; ^e Several authors agree on considering 0.5 days as the optimal value for SRT [26,37,48]. Other authors [10,49] consider 2 days as maximum SRT value; ^f [53]; ^g [32,33,37].

The HRT determines the activity of biomass, in terms of being a bio-oxidation or a bio-sorption system. In HRAS systems, the HRT must be set so that it is enough to allow biomass development and a bio-sorption process, but short enough to ensure that carbon mineralization is impeded. From *Table 3.1*, it can be concluded that, in general terms, HRT below 0.5 hours is typical in A-stage configurations. Optimization of HRT can lead to capital and operational expenditure reductions since low retention times are linked to lower operating costs (i.e. energy for aeration) per kg BOD treated, and lower aeration basin size.

In respect of SRT, it has to be set with the aim of optimizing the sludge concentration and biomass yield and the efficiency of the system (in terms of removal) and avoid the development of other processes (e.g. nitrification) [54,55]. As shown in *Table 3.1*, HRAS is characterized by low SRT from 0.1 to 1 day. Lowering the aerobic SRT results in lower energy requirements for aeration and increased organic matter converted into young and fast-growing sludge easily digested in AD [32]. Bolzonella et al. (2005) [56] calculated the relationship between SRT and specific gas production (SGP) (in m³·kgVS_{fed}⁻¹) using the following exponential equation: $SGP = 0.23 \cdot e^{-0.028 \cdot SRT}$. From their study, they determined that AD will achieve higher SGP values if the sludge is younger; then, more biogas can be converted to heat and electrical energy. However, it is possible that SRT may not be greatly reduced without the need for some physical-chemical measures due to the stringent requirements for nutrient removal in the next stage, which results in the production of a large amount of chemical sludge that does not contribute to biogas production.

Most of the successful studies and full-scale implementation of HRAS systems have been focused on urban wastewater (in average 600 mgCOD·L⁻¹, as shown in *Table 3.1*). However, it can be stated that a higher COD concentration in the influent results in higher COD adsorption, even though mixed liquor suspended solids (MLSS) concentration in the process is a key factor

because it is related to the active biomass in the system for carbon and other components' adsorption. Based on previous studies [35,57], it can be concluded that working with MLSS concentration up to approximately $3,000 \text{ mgTSS}\cdot\text{L}^{-1}$ benefits bio-flocculation. It enhances carbon capture without negatively influencing the oxygen transfer rate.

The loading rate, referred to as the F/M ratio, is a critical design parameter in HRAS wastewater treatment, ranging between 2 and $10 \text{ kgBOD}\cdot\text{kgVSS}^{-1}\cdot\text{d}^{-1}$ (*Table 3.1*). An increase in loading rate will lead to an increase in sludge production, as more substrate will become available [55]. The required high F/M ratio is achieved by controlling the amount of waste-activated sludge withdrawals from the system.

As the HRAS aims at minimizing carbon mineralization, DO concentration has been identified as a critical parameter to determine the turning point to promote or inhibit oxidative conditions [58]. Limiting oxygen supply contributes to bio-sorption since biomass has limited oxygen concentration for its metabolisms demand. According to *Table 3.1*, efficient COD removal with low overall aeration requirements (compared to conventional systems) might be achieved by the HRAS process operating with DO concentrations below $1 \text{ mg}\cdot\text{L}^{-1}$ [32,33,58].

Although wastewater treatment is subject to daily and seasonal temperature variations, there is no consistent agreement in the literature on determining the most desirable operational temperature value for HRAS systems. A study carried out by Jimenez at Strass WWTP [59] showed a significant impact of temperature on the COD removal efficiencies in A-stage. It was observed that the overall COD removal from the HRAS increased from approximately 55% at low temperatures (less than $10 \text{ }^{\circ}\text{C}$) to 65% at higher temperatures (higher than $15 \text{ }^{\circ}\text{C}$). In view of the fact that the higher COD removal is attributed to the soluble COD, results obtained concluded that higher temperatures are more desirable. On the other hand, it is also stated in the literature that higher temperatures are less desirable because the biomass growth yield goes down as temperature increases. Moreover, oxygen consumption per unit of substrate removed increases with increasing temperature (from 0.64 to $1.38 \text{ mgO}_2\cdot\text{mg sCOD}^{-1}$ at $4 \text{ }^{\circ}\text{C}$ and $34 \text{ }^{\circ}\text{C}$, respectively). So, a lower temperature is also better from an energy-efficiency point of view [29].

Jimenez et al. (2015) [32] performed a wide study on the impact of the main design and operation parameters (e.g. SRT, HRT and DO) on the HRAS performance in treating urban wastewater at psychrophilic temperatures to understand their effect on the organic carbon redirection. Results indicate that working under low SRT conditions, lower soluble COD mineralization occurred and maximum particulate and colloidal COD content in the sludge was achieved.

It is estimated that under optimal operational conditions, as will be further discussed in *Section 4.4*, HRAS systems are beneficial in terms of a global energy balance: the aeration requirements are reduced by up to 40% and an important proportion of the influent COD (from 50% to 80%) is recovered.

The design guidelines and recommendations for managing influent carbon loads in WWTPs through HRAS treatment from low-strength [3] to normal/high-strength [10,32] wastewaters have been studied to maximize carbon redirection and capture. One main conclusion in the case of the low biodegradable carbon concentration of the CEPT streams involves the need for a relatively higher fraction of substrate for the production of EPS to achieve bio-flocculation. Differently to the conventional application of HRAS systems, which are typically applied on raw wastewater, when HRAS reactors are operated after CEPT or low-strength wastewater, the operational conditions need to be adapted to the decreased particulate and colloidal organic fraction [44,53,60].

With the aim of being energy self-sufficient plants, the goal is to obtain the maximum organic fraction concentration in the sludge to increase energy production from wastewater. Two different dewatering technologies can be coupled to an HRAS system to separate the HRAS-sludge a settler and a membrane. Commonly, the HRAS sludge is separated in a settler. Nevertheless, the poor settling properties of the concentrated sludge reduce the assurance of high VFA production and further valorisation into value products (such as biopolymers, medium and long chain fatty acids, and bio-fuels), since the stream is partially diluted [61].

According to Cagnetta et al. (2016) [61], at least 45% of the COD of an HRAS configuration can be recovered as valuable VFA by using membrane technology.

To date, membrane technologies have not been used for that purpose, but taking into account A-sludge sedimentation properties, it could be a promising strategy in a next future, especially if a high-quality effluent is needed for the B-stage.

3.3.2. Modelling efforts to describe the performance of A-stage as HRAS

Modelling tools for WWTP have been shown to be essential to improve system performance and for design purposes. However, limited efforts have been directed towards describing and evaluating the efficiency of A-stage systems in removing COD and solids as the core of the energy production [62,63]. The main limitation has been focused on the fact that the International Water Association (IWA) activated sludge models (ASM1, ASM2, ASM2d and

ASM3) are not suitable for the A-stage process as they do not include EPS production and bio-flocculation [64–67].

Several modelling efforts have been made over the years, but with limited success. Early models using ASM1 or combining ASM1 and ASM3 were carried out by Henze et al. (1987) [64] and Winkler et al. (2001) [68], but they did not properly fraction the influent COD nor predict COD removal particularly through the intermediate clarifiers. Later on, Haider et al. (2003) [69] accounted for bio-flocculation by including a function that converted a portion of the influent particulate matter into settleable material that was removed by the clarifier model. They also provided general recommendations for the selection of kinetic parameters for heterotrophs in A/B processes, and the use of a higher maximum specific growth rate and the lower half-saturation coefficient for COD compared to those in CAS models. Additionally, soluble COD fractionation criteria were introduced to describe an incomplete conversion of soluble COD in the A-stage due to the use of a higher specific growth. However, the model was focused on describing the removal of soluble COD but not on how to describe and quantify the adsorbed COD fraction in the A-stage. A few years later, Nogaj et al. (2013) developed a new model strategy, including new state variables to the generally accepted CAS model ASM1 [66], to adapt the model to an A-stage. This strategy was negatively associated with the increasing complexity of the mathematical model and the need for a set of measurements that are not usually available in the regular operation of WWTP.

A new approach was postulated by Smitshuijzen et al. (2016) [33] with the purpose of providing a simple modelling tool to describe the main processes in a highly loaded aerobic COD removal reactor. It simultaneously describes the growth and adsorption of COD. This approach has been the scope of study of several research groups in Europe [71] and the USA [35]. The model is based on ASM1, but includes nitrite concentration as an additional state variable as well as different organic compounds concentrations: i) biodegradable organics (S_S); ii) soluble inert non-biodegradable organics (S_I); iii) slowly biodegradable organics (X_S); and; iv) particulate inert non-biodegradable organics (X_I). A large fraction of X_S and X_I would be adsorbed in the A-stage. Heterotrophic bacteria (X_{HET}) were considered the main bacterial population whose decay produces X_S and X_I . Colloidal COD has not been included as a separate variable to avoid unnecessary complexity. Storage COD, a difference between faster or slower biodegradable sCOD, and colloidal COD were not included in this model. To counterbalance it, a fixed percentage of X_S was assumed as adsorbed in the A-stage.

The WWTP in Dokhaven (Rotterdam, The Netherlands) was used as the source of full-scale data for model evaluation [33]. The model outputs for total COD concentration in the effluent are lower than the mean value from the measured data set with less than 10%, and the sum of

the X_S in the excess sludge and that in the outflow A-stage is 60% of total inflow X_S . Forty per cent of the X_S was hydrolysed and approximately 50% of the X_S was adsorbed in the A-stage [33]. The major part of the biodegradable organics was removed according to the steady-state simulation results.

3.3.3. Relevant laboratory and pilot-scale results for HRAS

Different studies at laboratory and pilot scale have been carried out to determine the removal efficiencies of different HRAS configurations. *Table 3.2* gathers some of the studies done recently and reports their main characteristics.

According to HRAS operational values established in the literature (*Table 3.1*), most of the reported studies operate within the ranges defined (with the exception of SRT in CS processes, HRT and DO) and under similar conditions (except for HRT and MLSS).

More than half of the incoming COD (on average, 55–60%) is redirected for energy recovery in both lab- and pilot-scale studies and, as a maximum, up to 80%. Under low HRT conditions, the predominant carbon removal mechanism is physical adsorption instead of biological degradation (it requires higher HRT). This corroborates the results obtained by modelling, which estimated that approximately 50% of the X_S was adsorbed in the A-stage [33]. With decreasing MLSS concentration, lower COD removal efficiencies are observed. This fact is attributed to the deterioration of the floc properties and desorption of organics. On the other hand, some discrepancies are reported in the discussion of the optimal value and the effect of SRT (lower or higher) on the promotion of capturing COD by bio-sorption [32,37]. These differences in conclusions can be justified by different influent characteristics and the consideration of different MLSS concentration in each study. Conversely, in the case of the CS process, it is observed that decreasing the SRT resulted in increasing carbon redirection and the minimization of C mineralization due to enhanced sorption of organics as opposed to heterotrophic biomass growth.

When evaluating the effect of the process on COD, very few references focus on its effect on nitrogen (N). Since operational SRT is relatively short in comparison to the optimal values for ammonia oxidation, nitrogen is slightly affected (< 25%). So, a subsequent stage focused on nitrogen removal (B-stage) must be coupled. As mentioned in *Section 3.2.3* and discussed in *Section 3.3.5*, it is necessary to determine the BOD/N ratio of the HRAS effluent to find the most suitable process for its purpose.

Table 3.2. Comparative of the working conditions and operational results obtained of some of the most recent studies carried out by a HRAS system.

Reference	Configuration and separation system (settler/membrane)	Lab/pilot scale	Inputs ^a						Outputs ^a			
			WW composition ^b COD _{IN} (g·L ⁻¹) N _{IN} (g·L ⁻¹)	HRT (min)	SRT (days)	MLSS (gVSS·L ⁻¹)	DO (mgO ₂ ·L ⁻¹)	T (°C)	COD removal (%)	COD redirected (%)	N removal (%)	Mineralization (%)
[72]	A-stage + Settler	Lab	0.52 0.63	54	0.3–0.5	3.3	2	n.a.	80 ±3	n.a.	24 ±12	n.a.
[73]	A-stage + Settler	Pilot	n.a. n.a.	15–20	0.5	1–2	n.a.	n.a.	55	n.a.	20	n.a.
[32]	A-stage + Settler	Pilot	0.48 n.a.	> 15	> 0.5	n.a.	> 0.3	n.a.	78	n.a.	n.a.	37
[37]	A-stage + Settler	Pilot	0.63 n.a.	60	0.56	3.5	1	n.a.	78	54.4 ±5.5	n.a.	21.5
[47]	BSS (+ settler)	Lab	~ 0.60 ~ 0.90	30	1.5	4	2–4	n.a.	75 ±5	n.a.	18	n.a.
[74]	CS (+ settler)	Pilot	0.41 n.a.	50.4 ^c 246 ^d	6	1.12 ^a 3.17 ^b	n.a.	n.a.	86	n.a.	n.a.	n.a.
[49]	CS (CoSEA)	Lab	~ 0.60 n.a.	n.a.	3	3	n.a.	15	80 ±5	55	n.a.	n.a.
[10]	HiCS + Settler	Lab	0.76 n.a.	0.14 ^e	1.1	2	2	15	60	36	n.a.	0
[39]	HiCS	Lab	0.67 n.a.	15 ^a 40 ^b	1.31	n.a.	1.5	15	64.6 ±3	55.1 ±3.4	n.a.	14
[3,48]	HiCS + Settler	Pilot	0.15 0.02	30 ^a 86 ^b	1.73	0.62 ^a 1.28 ^b	0.36 ^a 3.63 ^b	27	61 ±11	n.a.	n.a.	35

^a The values reported are those corresponding to the best operation results studied in the corresponding paper; ^b All studies were performed using raw municipal wastewater (except [10] and [39], which operated treating synthetic wastewater); ^c Contactor; ^d Stabilizer; ^e t₁/t₂; n.a.: not available

As discussed previously, HRAS are operated at a short HRT and SRT and high sludge-specific loading rate, which results in a higher sludge yield and better degradability than CAS treatments. For both HRAS and CAS, there is reduced knowledge of the biomass community in relation to its dynamics, functional output and sensitivity towards external and/or environmental factors. However, the development of advanced molecular techniques provides new tools for monitoring the community dynamics of activated sludge and exploring the interactions of microbial species with other species, environmental factors and the functional output of the system [75,76]. Meerburg et al. (2016) [77] evaluated, at full scale, a HRAS and a CAS treatment over a period of ten months and identified that microbial communities are distinctly different in terms of richness, evenness and composition. Moreover, the two communities show a similar degree of weekly dynamics, although HRAS treatment dynamics are more variable. HRAS communities are less shaped by deterministic factors (e.g. environmental and operational variables) than CAS communities, and in both systems continuously core and transitional sub-communities are more shaped by deterministic factors than the sub-community of continuously rare members. Finally, it was reported that HRAS ecology shows a co-occurrence pattern similar to that of CAS ecology but is less likely to be correlated to environmental variables.

3.3.4. Relevant full-scale implementations of HRAS in Europe

Wastewater treatment facility managers are highly motivated to develop new energy-efficient processes due to the high rates they pay for electricity operating with the conventional process. These municipal and industrial WWTPs work on innovative treatment concepts (A-stage, HRAS, MBR) to achieve the goal of decreasing energy consumption and increasing energy production until achieving self-sufficiency. Some A/B process plants have been built in Middle Europe in the last decades, mainly in countries such as Germany, Austria and The Netherlands, and a few in the USA. However, information on the A-stage is available but limited, and it mainly has a descriptive content of the process rather than operational and result values [60]. There is no unique design basis for the A-stage process; it has been implemented in existing installations as for the following examples. At Stolberg WWTP (Germany), the design was configured with two A-stage trains between existing aerated grit removal tanks and primary settlers [78]; A-stage in Utrecht WWTP (The Netherlands) takes place in square, complete-mix tanks; in Dokhaven and Nieuweer WWTPs (The Netherlands), A-stage is carried out in rectangular, plug-flow tanks; and in Garmerwolde WWTP (The Netherlands), A-stage is retrofitted into circular tanks [60].

The best known examples of A-stage implementation at WWTPs in Europe are: Strass WWTP and Salzburg WWTP in Austria; Krefeld WWTP, Rheinhausen WWTP, Loerach WWTP,

Pulheim WWTP and Schwarzenbeck WWTP in Germany; Nieuwveer WWTP, Donhaven WWTP, Utrecht WWTP and Garmerwolde WWTP in The Netherlands; Toulouse WWTP in France; and Sjölanda WWTP in Sweden. The main characteristics of the most important WWTPs with HRAS configuration are compiled in *Table 3.3*.

From the results obtained, it can be concluded that the operational conditions under which A-stage performs at WWTPs facilities are in accordance with the values defined at lab- and pilot-scale. On the other hand, from *Table 3.3*, large differences can be observed in the design and performance of the A-stage in the different WWTPs.

A-stage WWTPs have a total COD removal efficiency of 55–96% at SRT of 0.3–0.7 days, within the range discussed in *Section 3.3.3* (however, Nieuwveer WWTP achieves only 5–15% removal efficiency). A large fraction of the removed COD (24–48%) is adsorbed on the sludge, which promotes the recovery of the organic content in the form of energy, capable of satisfying the energy requirements of the plant [44]. For example, in the specific case of the well-known self-sufficient Strass WWTP, it is able to generate all the electricity needed only counting 11% of the total calorific energy available in the wastewater [38].

Notice that the aeration energy requirement per unit of COD removed is between 0.04 and 1.7 kWh·kgCOD_{removed}⁻¹, allowing savings in aeration costs in comparison to a conventional design. Combining it with an energy-efficient process for nutrients removal, an energy-positive wastewater treatment might be feasible in the near future.

No data from the WWTPs in terms of temperature is reported in the literature, but some studies show a relevant impact of temperature on the efficiency of COD removal in A-stage at full-scale operation [38]. There is a possible dependency between COD removal efficiency and the temperature of wastewater. It has been observed that working at a higher wastewater temperature, the overall COD removal increases.

COD removal could also be increased by the addition of chemicals, although there is no need to use chemicals to remove organic matter. The use of chemicals is conceivable for phosphorus (P) removal.

Table 3.3. Comparative of the technical and operational information of the most representative WWTPs in Europe with HRAS (A-stage) configuration treating municipal wastewater.

WWTP	Country	Year	PE	Flow rate capacity (m³·d⁻¹)	SRT (days)	HRT (min)	F/M ratio (kgBOD·kgMLSS⁻¹)	Chemical addition	Organic compounds removal	TN removal	TP removal	Energy content	Aeration energy requirement (kWh·kgCOD⁻¹_{rem})	Reference
Strass im Zillertal WWTP	Austria	1999	250,000	n.a.	0.5	n.a.	n.a.	NO	55–65% of the organic load	n.a.	n.a.	54 Wh·PE ⁻¹ (11%)	0.039	[38,60,79]
Krefeld WWTP	Germany	1985	1,200,000	n.a.	n.a.	n.a.	n.a.	n.a.	96% COD 99.7% BOD	93%	97%	n.a.	n.a.	[80]
Nieuwveer WWTP	The Netherlands	n.a.	400,000	240,000	0.65	15	1.5–3.9	YES	53% COD 61% BOD	29%	44%	24%	0.104	[60]
Dokhaven WWTP	The Netherlands	1987	620,000	n.a.	0.27	n.a.	n.a.	YES	74% COD 82% BOD	38%	68%	48%	0.169	[60,81,82]

n.a.: not available

3.4. Carbon redirection management for achieving self-sustainable energy plants

According to our own data from a pilot study (www.life-necoverly.eu) and literature data from experimental research studies and pilot/full-scale demonstrations incorporating HRAS (see *Table 3.2*; [83]), this paper proposes a simplified carbon and nitrogen mass balance through the different units that form the overall treatment (*Figure 3.5*). It is expected that 65% of carbon will be redirected to the sludge phase during the bio-sorption step [22]. Available results demonstrate that it is not easy to increase this percentage using only bio-sorption, and therefore the liquid effluent from this unit will already contain 40% of the influent COD [22]. Considering 50% COD removal in the AD, it is estimated that approximately 35% of the influent COD will be converted into biogas [22]. Digested sludge will be dewatered and most of the remaining COD will remain in the biosolids, which may be used in agriculture.

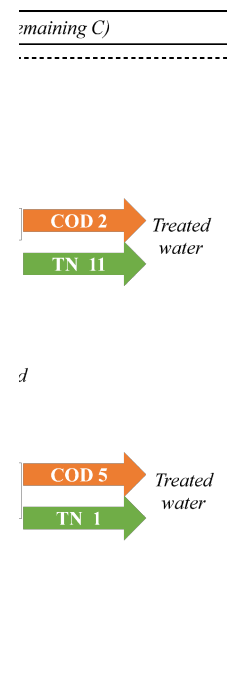


Figure 3.5. Proposed carbon (C) and nitrogen (N) mass balance in a HRAS process with bio-sorption as A-stage and Anammox (as N-removal technology) or ion-exchange (as N-recovery technology) as B-stage. (own data; [22,83]).

On the other hand, Khiewwijit et al. (2015) [84] proposed a full-scheme treatment including carbon redirection stage, by using a HRAS and an AD for energy recovery. An Excel-based simulation tool was built to evaluate different treatment configurations and these were compared to a reference CAS treatment based on several performance indicators reflecting the conditions in The Netherlands/Western Europe. The carbon recovery, expressed as methane yield, increased from 24% in CAS treatments to 39% in the HRAS configuration based on the total organic load in the wastewater influent stream. Differences were associated with wastewater composition and operational parameters used. However, results obtained from its carbon mass balance (3% mineralization, 77% A-sludge to DA; 20% A-stage effluent) are very optimistic in comparison to other similar studies [84].

When analysing the energy balance, a net value of $0.24 \text{ kWh}\cdot\text{m}^{-3}$ of wastewater is estimated, whereas, in the case of CAS treatment, the net energy yield estimated is $-0.08 \text{ kWh}\cdot\text{m}^{-3}$ of wastewater [84].

As expected, this carbon redirection treatment scheme will reduce CO_2 emissions from 0.43 (typical for a CAS system) to $0.28 \text{ kgCO}_2\cdot\text{m}^{-3}$ of wastewater. The main reason is the larger fraction of organic load that is converted to methane (CH_4) rather than aerobically mineralized to CO_2 [84].

3.5. Research needs and issues to be resolved for the promotion of carbon redirection using HRAS

The key operational parameters that define an HRAS system are, as detailed in *Section 3.2.3*, SRT, HRT and DO concentrations. Although a significant number of references are available in the literature, there is no general consensus on the relationship between these parameters and the settling ability of A-sludge. Therefore, as previously stated by Kinyua et al. (2017) [37], it is clear that more research is required. Although prior research has characterized EPS production in CAS sludge and HRAS systems, the relationship between the above-mentioned operational parameters, EPS and settling properties is not clear. Some authors suggest that EPS production increases with increasing SRT [85], while others point out that total EPS is not directly affected by SRT [34,86].

In case of sludge with poor settling properties, it is clear that advanced clarification or even membrane separation (depending on the subsequent B-stage) may be required to ensure a successful solid-liquid separation that allows redirection of the sludge to the anaerobic digestion unit and production of a stream with low solids content, suitable for the B-stage.

Another aspect that needs further discussion and development is the suitability of the effluent obtained from a carbon redirection process. HRAS systems require a subsequent B-stage or an advanced nutrient removal system to meet effluent quality. As highlighted in *Section 3.2.3*, conventional denitrification processes may require a higher BOD/N ratio than that of the effluent from the A-stage. In these cases, the addition of some external carbon source may be required. Alternatively, advanced nitrogen removal processes (such as nitrate shunt followed by denitrification or anammox), which have lower carbon requirements, may be an interesting alternative. In other situations, however, the amount of carbon in the effluent from the bio-sorption unit may be too high for the subsequent B-stage; this is the case reported by Gong et al. (2017) [87] and Sancho et al. (2017) [88], who evaluated a B-stage based on nitrogen recovery through ion-exchange. In these kinds of processes, the presence of carbon represents a limitation for the nitrogen adsorption. In these cases, an intermediate step or a combination of bio-sorption and bio-oxidation may be essential to produce a nitrogen-rich effluent with a minimal concentration of carbon, in line with the Urban Wastewater Treatment Directive (COD <125 mg·L⁻¹) [89]. It is, therefore, necessary to develop and validate global treatment trains that ensure the feasibility of the A-stage and the production of an effluent that meets the requirements of the subsequent B-stage.

Finally, it is important to emphasize the need to improve knowledge on the fundamental mechanism of the bio-sorption stage. During the development stage of HRAS, the most accepted and used method for quantifying the bio-sorption capacity of activated sludge depends on the settling velocity of solids. However, this test is not robust enough to accurately quantify bio-sorption [90], mainly because of the sludge responsible for the HRAS process typically shows different settling properties and characteristics from conventional activated sludge. In addition, influent wastewater streams could contain typically more than 55% settleable organic load, which coincides with the conventional bio-sorption capacity. Similar problems were faced when ex-situ aerobic yield was used as an alternative approach for the determination of bio-sorption in batch systems [3], and the bio-sorption capacity was not sensitive enough to quantify differences between HRAS types, potentially due to enhanced storage mechanisms under the feast-famine approach. To solve such limitations, Rahman et al. (2017) [48] proposed the use of ex-situ oxygen uptake rate (OUR) measurements over long periods (up to 40 h) and the bio-sorption yield was considered as the area underneath the OUR curve normalized for solids concentration. Data were compared with in-situ-based bio-sorption quantification by appropriate quantification of C-mass balances, including the contribution of EPS. A clear relationship between bio-sorption yield and in-situ bio-sorption with C-mass balance, carbon redirection and SRT was observed, suggesting two viable methods for the quantification of bio-sorption. The in-situ bio-sorption quantification is identified as a prediction tool to determine bio-sorption due

to the inclusion of wastewater composition (e.g. organic load), EPS and operational parameters (e.g. SRT).

3.6. Conclusions

Based on existing demonstrations (lab-, pilot- and full- scale), HRAS is demonstrated to be an acceptable technology to redirect carbon in WWTPs (around 60%). In comparison to CAS, it is possible to obtain higher production of sludge rich in carbon to further produce a valuable source of energy. Moreover, thanks to the lower oxygen demand and lower energy consumption, costs are saved.

However, more research is needed to solve the bottlenecks that are still unsolved. Future research should concentrate on HRAS sludge settling properties and on finding a suitable B-stage alternative process to combine them with.

3.7. References

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CHAPTER 4

Pre-concentration by bio-sorption and bio-oxidation of urban wastewater: a carbon redirection evaluation

4. Pre-concentration by bio-sorption and bio-oxidation of urban wastewater: a carbon redirection evaluation

4.1. Introduction

The main objective of a wastewater treatment plant (WWTP) is producing clean water, meeting discharge requirements. In order to achieve this goal, it must be produced an upper diluted effluent and a bottom effluent with a higher quantity of solids. Most of the current WWTPs achieve it by means of conventional activated sludge (CAS) systems, which degrade the biological materials from wastewater [1]. However, a more sustainable alternative to CAS systems can be possible by means of promoting carbon (C) redirection options. There are several processes that are capable of redirecting organic carbon for possible energy generation. Nevertheless, they are generally limited to the removal of settleable particulate matter (e.g., physical processes, such as primary sedimentation or dissolved air flotation), require external chemical addition (e.g., chemically enhanced primary treatment) or mineralise a large fraction of the influent carbon (e.g., activated sludge process) [2]. One process that has been successfully used for carbon redirection is the high-rate activated sludge (HRAS) process [3]. The main purpose of the pre-concentration step (based on bio-sorption) is to maximize the chemical oxygen demand (COD) and the total suspended solids (TSS) removal and to minimize the nitrogen removal [4]. The latter can be obtained by a specific combination of the process parameters: hydraulic retention time (HRT), sludge retention time (SRT) and sludge concentration, which promotes bio-sorption, minimizes bio-oxidation and guaranteeing good effluent quality [5–10]. Moreover, nitrification can be avoided by applying short HRT, low SRT and low dissolved oxygen (DO) levels [5,6]. This way the microorganism community configured a young sludge able to adsorb organic matter to its cell wall rather than degrade it, as it happens in the conventional system. Furthermore, given this residence time, nitrifier organisms cannot grow, this way nitrogen is not removed so it can be later recovered [11].

The objective of this chapter is to test operating conditions for C removal at small scale (4.5 L reactor) to, later on, scaling-up to a pilot unit. In order to test the impact of different process conditions on the pre-concentration of domestic wastewater by means of a combination of bio-sorption and bio-oxidation, a series of specific process conditions were tested at lab-scale. The impacts of the following parameters were tested: HRT, SRT, temperature (T), DO and the addition of an iron-based coagulant.

4.2. Methodology

4.2.1. Laboratory scale experimental device

An experimental design incorporating fourteen different test conditions were examined at lab-scale. All experiments were performed with the same reactor configuration, lasting each one until the scenario operated under steady-state conditions (generally, one week). Reactor performance was evaluated by the measurement of the main characteristics of influent and corresponding effluent and of the mixed liquor suspended solids concentration in the reactor. A schematic illustration of the pre-concentration set-up and the reactor unit are given in *Figure 4.1*. The experimental device consisted of an aerated vessel with an active volume of 4.5 L, connected to a decanter with an active volume of 2.5 L (inner diameter of 8 cm). The settled sludge in the decanter was continuously recycled to the aerated vessel by means of a peristaltic pump, at about the same flow rate as the influent flow rate. The influent was pumped in the aerated vessel by means of a second peristaltic pump. The influent vessel was equipped with a large stirrer in order to prevent settling of influent suspended solids.

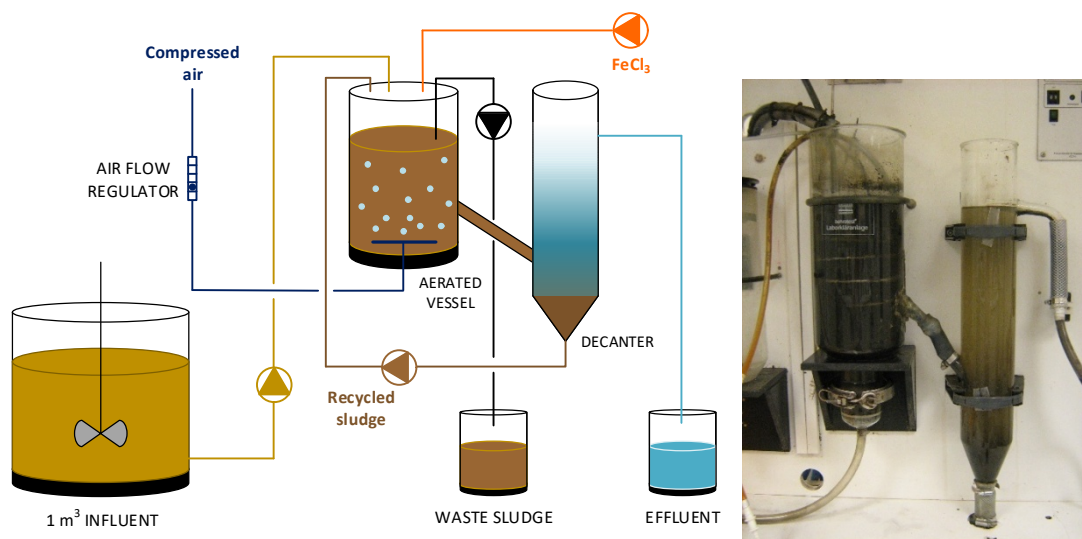


Figure 4.1. Scheme of the lab-scale reactor set-up and device for the pre-concentration tests.

The HRT was directly correlated to the influent flow rate. In case they were changed, the sludge recycle rate was adjusted at the same time. Sludge recycle rate was always equal to the influent flow rate. The regulation of the SRT was obtained by the withdrawal of a certain volume of mixed liquor from the aeration vessel using a peristaltic pump. For the calculation of the SRT,

only the flow rate of the mixed liquor sludge withdrawal pump was considered. The impact of influent and effluent TSS concentrations on the SRT was not taken into account. In this approach, the sludge concentration in the waste sludge equalled the mixed liquor sludge concentration. Because of the relatively low HRT, the Fe-solution was added directly in the aeration vessel in a continuous way by means of a peristaltic pump connected to a time clock (several pulses per hour). Iron (Fe) was dosed (about 1.5 L per day) under the form of a 0.1% iron chloride (FeCl_3) solution ($1 \text{ gFeCl}_3 \cdot \text{L}^{-1}$ or $0.34 \text{ gFe} \cdot \text{L}^{-1}$). The dosage of Fe varied between $3\text{--}5 \text{ mgFe} \cdot \text{L}^{-1}$ influent. The set-up was not equipped with a DO controller. The control of DO was tested by using a different type of aeration pump. Part of the experiments was run at room temperature (around $20 \text{ }^\circ\text{C}$). To examine the effect of lower temperature (around $12 \text{ }^\circ\text{C}$), a cooling device was used. The latter was placed inside the reactor.

4.2.2. Model urban wastewater

Samples of raw municipal wastewater (1 m^3 container) were collected on a weekly basis from the full-scale treatment plant and immediately connected to the reactor at room temperature (about $20 \text{ }^\circ\text{C}$). The minimum, maximum and average values are presented in *Table 4.1*. For seven days, the same raw water was used as feed. The switch from one influent sample to another was normally done during the last days of an experiment (mostly on the 6th day). In that way, two different influent samples were used per test period, but at the time of sampling, the influent was relatively fresh. Important differences occurred in the influent samples.

According to the different analysis performed along analytics, the average values for total COD (tCOD), TSS and total nitrogen (TN) in the influent were 913 , 494 and $54 \text{ mg} \cdot \text{L}^{-1}$, respectively. Consequently, besides the impact of SRT, HRT, DO, temperature and Fe addition, there was also an important effect of unforeseen fluctuations in the influent samples for the final evaluation, especially the suspended solids concentrations varied strongly and resulted in high fluctuations of tCOD and tBOD.

4.2.3. Operational conditions

An overview of the final test scheme, experiments and corresponding experimental conditions is presented in *Table 4.2*. The chronological order of the consecutive experiments was determined to start by examining relatively short HRT and SRT. Each experiment, conducted under specific process conditions of HRT, SRT, DO, temperature and Fe addition, was operated for at least 1 week to ensure that the operational conditions were reaching steady-state conditions when

analysing the sampling of influent and its corresponding effluent. New test conditions were applied the day after sampling and analyses.

Table 4.1. Overview of the minimum, the maximum, the average and standard deviations values of all influent samples (in mg·L⁻¹).

	Minimum value	Maximum value	Average
pH	6.9	8.5	7.5±0.5
Total COD (tCOD)	500	2,955	913±634
Soluble COD (sCOD)	191	944	366±177
Total BOD₅ (tBOD₅)	270	2,100	602±462
Soluble BOD₅ (sBOD₅)	125	530	221±109
Total suspended solids (TSS)	55	2,780	495±664
Volatile suspended solids (VSS)	55	2,170	459±607
Total nitrogen (TN)	27	74	54±13
Ammonium (NH₄⁺-N)	14	42	28±11
Nitrate (NO₃⁻-N)	0.1	4	1±1.5
Total phosphorus (TP)	10	28	14±5
Phosphate (PO₄³⁻-P)	6	15	9±3

4.2.4. Analytical procedures

Reactor performance was evaluated by the measurement of influent and effluent pH, tCOD, sCOD, tBOD, sBOD, TSS, TN, NH₄⁺-N, NO₃⁻-N, TP and PO₄³⁻-P. Total and soluble COD and all nitrogen and phosphorus forms analyses were conducted using the corresponding HACH test kit (Hach Company, Loveland, Colorado). BOD₅ was measured using manometric respirometric BOD OxiTop method. TSS and VSS were analysed according to the Standard Methods [12]. The analyses of the different influent samples were performed about one day after the arrival of the influent container and feeding to the reactor. Besides the influent and effluent detailed characterization (one detailed analysis per experiment performed on the same day because of the short HRT), also the mixed liquor in the reactor was followed on a weekly basis. The results of the analyses of the different experiments are presented in *Table 4.3*.

Table 4.2. Overview of the test periods and corresponding controlled process parameters.

Experiment	HRT h	SRT d	T °C	DO mg·L ⁻¹	Fe addition Y/N
1	1	0.25	20	> 2	N
2	1	0.25	20	< 0.5	N
3	1	0.25	12	> 2	N
4	1	0.25	12	< 0.5	N
5	1	0.25	20	> 2	Y*
6	1	0.25	20	< 0.5	Y*
7	1	0.25	12	> 2	Y*
8	1	0.25	12	< 0.5	Y*
9	1	1	20	> 2	N
10	1	1	20	< 0.5	N
11	2	1	20	< 0.5	N
12	2	1	20	> 2	N
13	2	1	20	> 2	Y**
14	1	1	20	> 2	Y**

*Fe addition as FeCl₃ at a dosage of about 5 mg Fe·L⁻¹ influent; ** Fe addition as FeCl₃ at a dosage of about 3 mg Fe·L⁻¹ influent.

4.3. Results and discussion

4.3.1. Start-up of the pre-concentration lab-scale reactor

Prior to the start of the first experiment, the reactor was seeded with fresh activated sludge originating from the same wastewater treatment plant as the influent samples. The pumps for feeding, sludge recycle and sludge withdrawal and the DO regulation were tested and further adjusted. The influent flow rate and the sludge withdrawal flow rate were gradually increased until the premised process conditions of Experiment 1 were achieved (*Table 4.2*).

Table 4.3. Overview of the experimental conditions and analytical values.

Experiment	Units	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14
<i>Process conditions</i>															
Duration	days	7	7	9	7	9	9	6	6	8	7	7	7	7	6
HRT	hours	0.9	0.9	1.0	0.9	0.9	0.9	1.1	1.0	0.9	1.0	1.9	1.9	1.7	1.0
SRT	days	0.20	0.28	0.26	0.33	0.32	0.3	0.35	0.33	1.06	1.02	1.0	1.0	1.0	1.05
Volumetric loading rate	g tCOD·Lr ⁻¹ ·d ⁻¹	26.2	17.1	22.8	18.7	15.1	75.5	25.1	39.5	19.7	14.4	7.9	9.8	7.1	14.6
	g MLTSS·Lr ⁻¹	0.69	0.30	0.78	0.38	0.71	3.06	0.60	0.49	3.40	1.57	1.73	3.39	2.69	4.02
Sludge concentration	g MLVSS·Lr ⁻¹	0.64	0.23	0.48	0.28	0.52	2.32	0.55	0.48	3.02	1.44	1.49	2.55	2.14	-
	g tCOD·g MLVSS ⁻¹ ·d ⁻¹	17.4	74.2	47.4	66.9	28.9	32.6	45.6	83.2	6.52	10.0	5.3	3.85	3.32	-
DO	mg O ₂ ·L ⁻¹	2.7	0.3	4.6	0.6	5.5	<0.5	5.5	5.4	4.0	0.2	0.2	4.9	6.8	3.3
Temperature	°C	22	24	15	16	26	24.4	24.4	15.7	23.4	23.4	21.9	22.0	20.3	20.6
FeCl ₃	mg Fe · L _{influent} ⁻¹	0	0	0	0	4.5	4.6	6.0	0.7	0	0	0	0	2.8	3.1
<i>Influent characteristics</i>															
pH	-	7.1	7.2	8.4	7.8	8.2	7.0	6.9	7.1	7.4	7.5	8.5	6.9	7.8	7.7
tCOD	mg·L ⁻¹	952	675	931	707	590	2955	1412	1617	703	618	624	788	500	597
sCOD	mg·L ⁻¹	944	339	405	395	447	433	195	465	438	369	299	315	256	215
tBOD	mg·L ⁻¹	570	460	500	485	420	2100	700	920	525	380	310	460	270	330
sBOD	mg·L ⁻¹	530	230	250	260	-	250	150	300	140	165	160	175	125	140
TN	mg·L ⁻¹	59	54	74	48	65	58	66	58	52	64	45	27	43	40
NH ₄ ⁺ -N	mg·L ⁻¹	41	34	19	31	42	34	22	30	34	38	32	14	31	35
NO ₃ ⁻ -N	mg·L ⁻¹	4	0.9	2.5	0.3	0.8	0.1	4	2	0.7	0.7	0.4	0.4	0.3	0.4
TP	mg·L ⁻¹	10	18	23	28	16	13	15	15	14	13	14	10	11	11
PO ₄ ³⁻ -P	mg·L ⁻¹	8	15	13	10	12	7	6	9	12	9	7	7	8	8
TSS	mg·L ⁻¹	55	235	461	300	290	2780	815	665	308	200	360	450	205	220

Experiment	Units	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14
<i>Effluent characteristics</i>															
pH	-	7.8	7.5	8.8	7.7	8.3	7.4	7.4	7.3	7.7	7.8	8.1	7.6	8.1	8.0
tCOD	mg·L ⁻¹	104	178	446	351	160	320	152	173	386	437	276	272	117	187
sCOD	mg·L ⁻¹	84	168	366	236	99	215	113	157	280	330	192	157	68	84
tBOD	mg·L ⁻¹	65	118	290	220	100	160	80	145	80	220	110	120	32	65
sBOD	mg·L ⁻¹	50	115	220	145	-	90	52	135	50	120	80	60	30	20
TN	mg·L ⁻¹	66	43	51	50	53	59	27	46	50	57	42	20	28	38
NH ₄ ⁺ -N	mg·L ⁻¹	45	35	16	31	32	32	18	28	29	36	31	12	22	30
NO ₃ ⁻ -N	mg·L ⁻¹	0.4	0.6	0.6	0.5	0.3	0.5	7	1	0.5	0.6	0.4	0.3	0.5	0.3
TP	mg·L ⁻¹	12	16	10	12	7	8	5	8	13	12	10	8	7	8
PO ₄ ³⁻ -P	mg·L ⁻¹	11	14	7	10	5	6	4	7	10	9	6	5	5	6
TSS	mg·L ⁻¹	85	85	290	290	50	60	50	130	205	175	24	80	56	88
<i>Removal</i>															
tCOD	%	89	74	52	50	73	89	89	89	45	29	56	65	77	69
sCOD	%	91	50	10	40	78	50	42	66	36	11	36	50	73	61
TN	%	0	20	31	0	18	0	59	21	4	11	7	26	35	5
NH ₄ ⁺ -N	%	0	0	15	0	23	6	18	6	15	5	3	14	29	14
TSS	%	0	64	37	3	83	98	94	80	33	13	93	82	73	60

4.3.2. Overview of the process conditions and results of the different experiments at lab-scale

To test the impact of the five process conditions (HRT, SRT, DO, temperature and Fe addition) on the bio-sorption/bio-oxidation process, the latter were deliberately altered one after another in the course of the lab-scale experiments (see *Table 4.2*).

Afterwards, a comparison was made between test periods with very similar test conditions to evaluate the impact of one specific process parameter that was deliberately altered on reactor performance.

Impact of HRT

When mutually comparing the results of the different experiments where only the HRT was changed, a clear positive effect of the prolongation of the HRT from 1 h to 2 h on the COD and TSS removal efficiencies could be observed (56–77% and 73–93% tCOD and TSS removal at 2h HRT, respectively, in comparison to 29–69% and 13–60% tCOD and TSS removal at 1h HRT). Longer HRT allows for a longer contact between wastewater and biomass and, hence, for more bio-sorption and/or bio-oxidation.

The removal of TN it is also increased (26–35%) when working at high HRT operational values. On the other hand, $\text{NH}_4^+\text{-N}$ removal efficiency remains virtually unaltered.

Impact of SRT

No clear positive effect of the prolongation of the SRT (from 0.25 up to 1 day) could be withdrawn from the results presented in *Table 4.3*.

It was observed that at shorter SRT (Experiments 1–8), the TSS in the reactor (MLTSS) was always very low and varied between 0.3 and 0.8 gMLTSS·L⁻¹. Only when an influent with an exceptionally high TSS was fed to the reactor (Experiment 6), a higher MLTSS concentration was measured (3.06 gMLTSS·L⁻¹).

Most probably, the measured MLTSS and MLVSS at this SRT were mainly composed of influent TSS and to a lesser extent of biomass, except for Experiment 1 (0.055 gTSS_{influent}·L⁻¹). In this case, an exceptional influent was used because it contained relatively high sCOD and very low TSS concentrations, compared to all other influent samples. When prolonging the SRT (Experiments 9–14), considerably higher MLTSS (1.57–4.02 gMLTSS·L⁻¹) and MLVSS

(1.44–3.02 gMLVSS·L⁻¹) concentrations were obtained in the reactor. However, the latter was also related to the influent TSS concentrations.

It is expected that a higher biomass in the reactor will result in a more stable process (lower sludge loading rate), with a higher potential for both bio-sorption and bio-oxidation. It must be indicated that the measurements of MLTSS and MLVSS must be considered as the sum of activated sludge and residual TSS/VSS of the influent. On the basis of the TSS/VSS measurements, no distinction can be made between activated sludge and influent TSS. The latter also contained a relatively high organic fraction.

Regarding TN removal, lower SRT reports higher efficiencies (about 20%), but it is at SRT 1 day where more ammonium removal was achieved (10% on average).

Impact of DO

From the results presented in the overview table above, no important effect of the DO level on the COD and TSS removal efficiencies could be withdrawn. Under the process conditions tested, a low DO of about 0.5 mgO₂·L⁻¹ seemed to be enough. It is corroborated by Jimenez et al. (2015) [6], who states that HRAS systems require almost 60% less aeration than conventional processes (about 2 gO₂·L⁻¹). Moreover, working at lower oxygen concentrations, the growth of nitrifiers is avoided [11].

At this range of DO, higher TN and NH₄⁺-N removal efficiencies were obtained: on average, 28% TN and 14% NH₄⁺-N.

Impact of temperature

As observed for the DO, no clear effect of temperature on COD and TSS removal efficiencies was measurable in the different experiments. It should be noted that all comparative experiments in terms of temperature were conducted at short SRT and HRT. Most probably, under these test conditions, bio-sorption and TSS separation played a more important role, compared to bio-oxidation. Hence, for bio-sorption and TSS separation, the temperature was probably of minor importance.

Contrary to TN, ammonium had not a big impact of temperature; it was practically maintained at both temperature values tested. Total nitrogen removal was more efficient at a cooler temperature (average removal of 37%) than at room conditions (10% on average).

Impact of iron-based coagulant addition

In contrast to most of the other process parameters tested, a very clear improvement of reactor performance was always achieved when Fe was supplied to the reactor (mutual comparison of experiments with the same process conditions, except for Fe). As reported by Wett et al. (2015) [13], chemical additions not only resulted in a better separation of suspended solids and, hence, lower effluent concentrations of tCOD and TSS, but in most of the experiments, it also gave rise to higher sCOD conversions. The latter can be explained by a better retention of activated sludge in the reactor. In experiments with Fe addition, especially at higher SRT and HRT, a high sludge blanket was observed in the decanter.

Nitrogen removal was benefited by the addition of chemicals. On average, these percentages correspond to 28% and 16%, TN and $\text{NH}_4^+\text{-N}$ respectively.

Theoretically, the addition of $3 \text{ mgFe}\cdot\text{L}^{-1}$ (Experiments 13 and 14) and $5 \text{ mgFe}\cdot\text{L}^{-1}$ (rest of the experiments with Fe dosage) can have a limited effect on phosphate removal. If a minimum molar ratio Fe/P (MW: 56/31) of 1/1 is taken into account, the addition of $5 \text{ mgFe}\cdot\text{L}^{-1}$ can precipitate about $2 \text{ mgPO}_4^{3-}\text{-P}$. On average, the effluent $\text{PO}_4^{3-}\text{-P}$ concentration was $8 \text{ mgP}\cdot\text{L}^{-1}$ (average removal of 12%) in the test periods without Fe addition. When Fe was added, the average effluent $\text{PO}_4^{3-}\text{-P}$ amounted to $5.5 \text{ mgP}\cdot\text{L}^{-1}$ and corresponded with an average removal efficiency of 32%. So a clear impact of Fe addition on partly removal of phosphate could be measured in these tests.

4.3.3. Evaluation of the performance of the pilot plant

From the results obtained at laboratory scale, a pilot plant unit based on HRAS system for carbon redirection was operated. The equipment employed in this process is rather similar to the one used in the conventional system (see *Chapter 2*). The innovation lies beneath in the modification of key parameters (HRT, SRT, DO, temperature and Fe addition) to configure a young microorganism community able to adsorb organic matter to its cell wall rather than degrade it, as it happens in the conventional system (*Table 4.4*). Furthermore, given this short residence time, nitrifier organisms cannot grow, this way nitrogen is not removed so it can be later recovered (see *Chapters 5–7*).

Table 4.4. Main parameters' settings of the pilot unit as a bio-sorption system: operational values and method of regulation.

HRT (h)	1–2	The modification of the TRH was achieved working at the fixed influent flow and using a determined number of 1m ³ reactors (max. 4 reactors).
SRT (days)	0.5–1	Regulated by the purge of the excess generated sludge.
DO (mgO₂·L⁻¹)	0.5–1	The air stream is generated by a frequency driver blower which is capable of controlling the air flow supplied in order to control de DO level in the first reactor tank.
Temperature	Ambient	Controlled by two sensors: one at the entrance of the system and another at the first reactor tank.
Fe addition	Yes/No	Peristaltic pumps controlled by PLC

The bio-sorption unit has faced several problems during its operational period. During the first months of operation, most of the problems were related with pipe clogging; the particulate material present in pre-treated wastewater from Vilanova WWTP caused clogging of the small pipes installed (to guarantee the achievement of short HRT and low SRT). After several months, finally, it was solved by installing a rotary sieve with a mesh of 5 mm. During the remaining experimental period, the main issue to deal with was the retention of the biomass inside the system; the poor settleability of the sludge made the separation of the sludge and treated effluent very difficult and most of the sludge was discharged with the effluent. Many strategies have been implemented to solve this operational issue (modification of the decanter influent pipes, chemical dosing, installation of a new decanter with a higher retention time and even installation of a column-type reactor to replace the bio-sorption reactor). It is true that the modifications made slightly improve the performance, but it was not possible to obtain a stable effluent. However, with those operational parameters, it was expected that a 6% extra sludge would be formed and about 10 % carbon would be mineralized.

Since no results could be obtained from the carbon redirection unit, a simulation of this pilot unit has been run. *BioWin*, a wastewater treatment process simulator developed by EnviroSim Associates LTD., was used as a modelling tool to provide simulated results. *Figure 4.2* represents a theoretical scenario in which the primary and the secondary treatments are replaced by a pre-concentration unit. The process was simulated by means of an activated sludge reactor

(A1 + A2) with an SRT of only 0.5 days and an HRT of 5 hours followed by an anaerobic digester (HRT = 29 d; T = 35 °C). Under these operational conditions, the effluent fulfils the quality requirements in terms of organic matter. However, simulations indicated that the addition of Fe-based coagulant (around 29 kgFeCl₃·d⁻¹) is needed after the pre-concentration unit if P removal is required (P < 1 mg·L⁻¹ in the effluent). According to *Biowin* simulations, a production of biogas around 1,900 m³·d⁻¹ is expected, which represents an increase of almost 47% respect to the conventional configuration (1,296 m³·d⁻¹). This increase can be attributed to the higher biodegradability of the sludge (lower SRT) and a consequent increase of the volatile material destruction. The addition of FeCl₃ is also recommended in the digester (around 140 kg·d⁻¹) in order to decrease P concentration to 1 mg·L⁻¹ and also to protect the subsequent zeolites column, which would be implemented for nitrogen recovery.

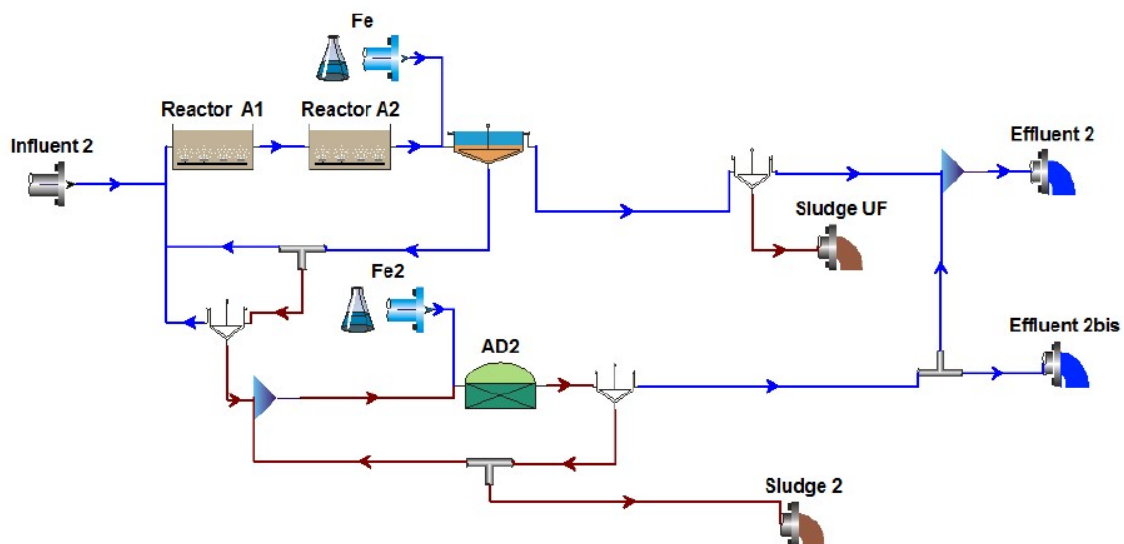


Figure 4.2. Simulated scenario of Vilanova WWTP in which the primary and the secondary treatments are replaced by a pre-concentration unit (reactors A1 and A2).

Consequently to the operational difficulties, the anaerobic digestion unit was fed with mixed sludge from Vilanova WWTP because a stable C-rich sludge was not obtained from bio-sorption during long periods of time. However, a long operational period allows demonstrating that the anaerobic digestion pilot unit was able to reproduce successfully the full-scale AD performance. The efforts with this pilot (while waiting for the C-rich sludge) were directed to make a complete scale-up study.

The COD removal achieved is around 56% which is slightly higher than the typical 40–50% for a conventional WWTP. The amount of bio-methane (CH_4) produced is established by the stoichiometry, which sets the value in $0.345 \text{ kgCH}_4 \cdot \text{kg}^{-1}\text{COD}$. The specific production of bio-methane per kilogram of COD in the influent (it directly relates the sludge fed with the amount of biogas produced and hence the energy associated), achieved values of $0.18 \text{ kgCH}_4 \cdot \text{kg}^{-1}\text{COD}$ in the influent. Based on the works of Smitshuijzen et al. (2016) [14] and Wan et al. (2016) [15], it is expected that 25% extra biogas production could be achieved if it were possible to digest C-rich sludge from bio-sorption.

If a similar analysis to that of the pilot is carried out to the WWTP data, it can be concluded that it shows a slightly inferior COD removal (46%) with specific production of $0.15 \text{ Nm}^3 \cdot \text{kg}^{-1}\text{COD}$ in the influent. Regarding the stoichiometry conditions, WWTP AD is under this reference value of $0.35 \text{ kgCH}_4 \cdot \text{kg}^{-1}\text{COD}$. The difference might be due to a scale and age factor. The anaerobic digester of the plant has many years and is much bigger than the pilot one. This leads to an imperfect development of the anaerobic digestion due to death volumes, foams, and a less efficient heating system.

4.4. Conclusions

The conclusions of the study show that the effect of DO and temperature in carbon and nitrogen removal has not been much appreciated. From the results presented, it is not shown a clear positive effect of the prolongation of the SRT from 0.25 up to 1 day. When prolonging the SRT to about 1 day, considerably higher TSS concentrations were obtained in the reactor. On the other hand, a clear positive effect of the prolongation of the HRT from 1 h to 2 h, on the COD, TSS and TN removal efficiencies could be observed. Longer HRT allows for a longer contact between wastewater and biomass and, hence, for more bio-sorption and/or bio-oxidation. Moreover, a very clear improvement of reactor performance was always achieved when a Fe-based coagulant was supplied to the reactor. Chemical addition not only resulted in lower effluent concentrations of tCOD and TSS but in most of the test cases, it also gave rise to higher sCOD conversions. Moreover, a clear impact of Fe addition on partly removal of $\text{PO}_4^{3-}\text{-P}$ (about 32%) could be measured in the experiments.

There was an important effect of unforeseen fluctuations in the influent samples, especially, the suspended solids concentrations varied strongly and resulted in high fluctuations of tCOD and tBOD.

The scaling-up from laboratory to pilot scale has not been possible in our study since several operational and technical problems have had to overcome. It is believed that the site chosen to install the pilots were not the most appropriated. This is due to the bad settling properties of the WWTP sludge, which was not so bad in the first trials of the evaluation of the sites. Furthermore, there were other problems that were not possible to forecast, such as uncontrolled discharges in the WWTP incurring in a huge variable load. Nevertheless, this technology has been widely studied and results demonstrated that bio-sorption is a promising technology. Moreover, a new bioreactor was designed. It was expected to obtain a 6% extra sludge while about 10 % carbon would be inevitable mineralized as CO₂. Modelling simulations of the carbon redirection pilot unit reported that almost the half biogas production in conventional WWTP (604 m³·d⁻¹) could be extra generated in this new configuration.

Although it has not been possible to digest the sludge produced in the bio-sorption, it has been possible to assess the correct operation of the AD unit and the scale factor between pilot scale and full scale. This scale factor study demonstrates that the AD unit operates in a similar way to that of WWTP but slightly more efficiently. According to the results obtained in the AD, if it were possible to digest this carbon-rich sludge, 25% extra biogas production would be expected.

4.5. References

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CHAPTER 5

Nutrient recovery design to treat pre-concentrated effluent: an overview of the batch and column tests with different types of zeolites

5. Nutrient recovery design to treat pre-concentrated effluent: an overview of the batch and column tests with different types of zeolites

5.1. Introduction

Nitrogen is an essential nutrient for all living forms and, moreover, it is a key component for fertilizer production and indeed, it is critical to agricultural uses. However, the presence of nitrogen in water can lead to an excessive growth of algae and the consequent depletion of the dissolved oxygen is an effect of the nutrient overloading in surface water receiving bodies [1]. Therefore, the removal of ammonium from wastewater to avoid the consequences of eutrophication processes has become a challenge. In order to reach the required low levels of ammonium nitrogen ($\text{NH}_4^+\text{-N}$) in the discharged effluents, which can be as low as $1 \text{ mgNH}_4^+\text{-N}\cdot\text{L}^{-1}$ [2], a nitrogen treatment step is essential as part of the wastewater treatment process.

In conventional wastewater treatment plants (WWTPs), nitrogen removal is commonly achieved by means of a biological nitrification-denitrification process, where ammonium is transformed into nitrogen gas [3]. Anaerobic ammonium oxidation (Anammox) appears as a promising alternative to the conventional process due to the low energy consumption and the suppression of the necessity of an external carbon source (typically methanol) to denitrify [4,5]. However, the Anammox technology still presents relevant limitations such as long start-up periods, strong sensitivity to operation conditions variation and a high susceptibility to reactor threats [6,7]. Additionally, it is expected that in the future these biological processes may not be able to sustain the nitrogen removal ratios required to meet the regulated discharge values. Moreover, ammonium is at present increasingly considered a resource, and not only a compound that has to be removed from wastewater [8]. Consequently, there has been a renewed interest to recover nutrients from waste streams as a synergy of economic, energy and environmental considerations.

Physicochemical methods have been widely used for the removal and recovery of ammonium species from waste streams in a usable form to supplement existing ammonia production. The most commonly used cation exchange materials are inorganic materials (zeolites) and organic resins, all of them suitable for the selective removal of ammonium. Apart from natural zeolites (from mineral mining), a variety of synthetic zeolites synthesised from fly ash (ZFA) is commercially produced and can be used for wastewater treatment. Among other synthetic cation exchange materials, the most used are strong acid cation (SAC) and weak acid cation (WAC) exchange resins, mainly co-polymers of di-vinyl benzene and styrene with functional groups attached to them. Many authors [9–12] have investigated the ion-exchange potential of these

materials with respect to ammonium removal. In comparison to ion-exchange resins, zeolites exhibit higher selectivity to ammonium ions in the presence of common competing cations (e.g., sodium, potassium, calcium and magnesium) [13,14], they are cheaper ($< 0.2 \text{ €}\cdot\text{kg}^{-1}$ compared to $3\text{--}25 \text{ €}\cdot\text{kg}^{-1}$ of organic resins), technology based on zeolites column are compact in size, and they allow easy operation and maintenance, low treatment costs in the full-scale applications [15–17].

The aim of this chapter is to evaluate different types and sizes of zeolites to select the most appropriate zeolites for the recovery of $\text{NH}_4^+\text{-N}$ in the main line (around $50 \text{ mgNH}_4^+\text{-N}\cdot\text{L}^{-1}$), as well as the maximization of side-streams ($500\text{--}2,000 \text{ mgNH}_4^+\text{-N}\cdot\text{L}^{-1}$ found in digester supernatant or the liquid return streams of sludge dewatering facilities such as centrifuges and belt filter presses; up to 25% of the total nitrogen load) by means of ammonium adsorption (Figure 5.1) to its further design and implementation at pilot scale. With this ion-exchange technique, ammonium is adsorbed temporarily to zeolites adsorbent by filtering the nitrogen-rich (N-rich) water through a zeolite packed to later on be recovered by regenerating the ion-exchange material. Also, it is studied the impact of ionic strength and competition of other ions and components, such as total suspended solids (TSS).

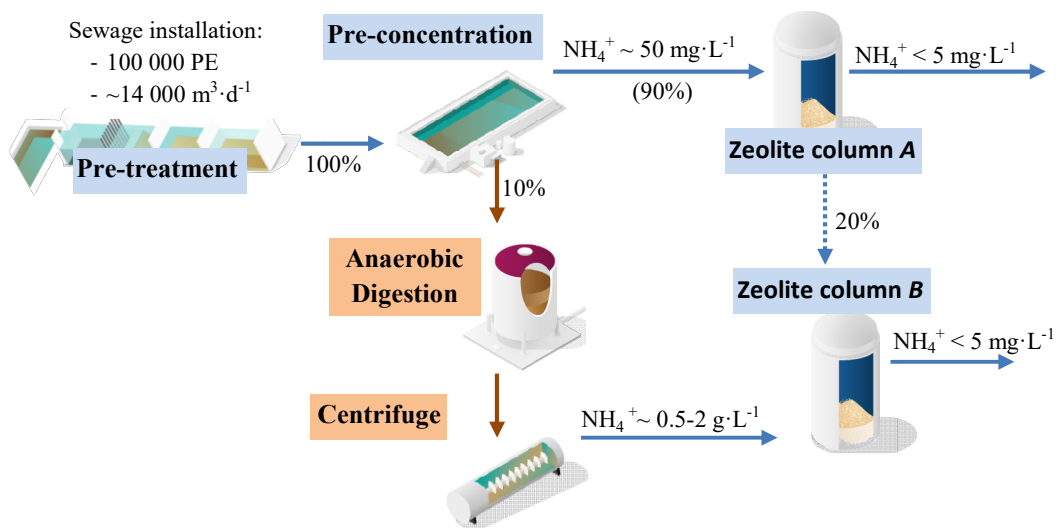


Figure 5.1. Schematic diagram of the two main implementation options of zeolites for ammonium (NH_4^+) recovery on the wastewater water line.

5.2. Experimental methodology

5.2.1. Ion-exchange materials

Two different commercial granular natural zeolites were selected: Zeocem and Rota Mining (RM). For first period tests, a smaller (2.5 to 5 mm) and a larger (8 to 16 mm) grain size were tested (*Figure 5.2*). For the second series of tests, smaller grain sizes (0.5 to 1 mm) of the same two types of zeolites were tested. Besides natural zeolites types, also a small grain size sodium modified zeolite (Na-modified) from Zeocem was included in this latter series to corroborate that activated zeolite reports better results than the natural ones.

An overview of the main characteristics of the two zeolite types is presented in *Table 5.1*.

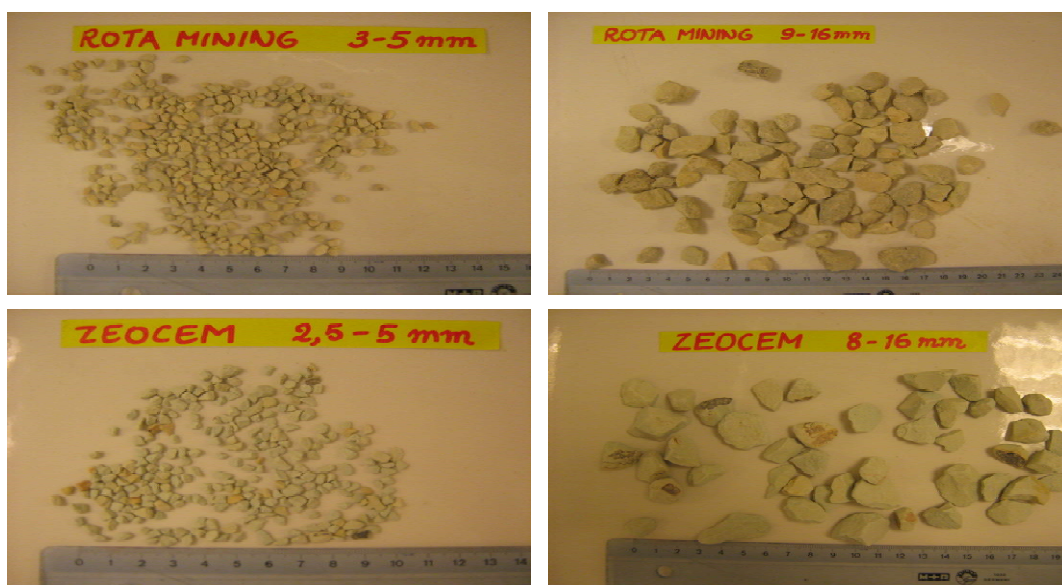


Figure 5.2. View of the different zeolite grain sizes that were used for the batch experiments and column tests.

5.2.2. Composition of model wastewater

The N-rich water used in tests was synthetic water consisting of ammonium chloride (NH_4Cl) in tap-water. N-influent concentrations of $50 \text{ mg}\cdot\text{L}^{-1}$ (or $0.19 \text{ gNH}_4\text{Cl}\cdot\text{L}^{-1}$), simulating the effluent of the bio-sorption/bio-oxidation step in mainline; and $1,000 \text{ mg}\cdot\text{L}^{-1}$ (or $3.8 \text{ gNH}_4\text{Cl}\cdot\text{L}^{-1}$), simulating the concentrates stream, were prepared. They were named as diluted and concentrated synthetic wastewaters, respectively.

In order to determine the effect of the presence of other ions on the $\text{NH}_4^+\text{-N}$ adsorption, minerals and phosphorus (P) were extra dosed to tap-water to obtain an influent that simulated the composition of a real wastewater (based on Vilanova WWTP influent composition; *Table 5.2*). Also, domestic wastewater was performed in order to examine the effect of other components such as chemical oxygen demand (COD) and TSS on the $\text{NH}_4^+\text{-N}$ adsorption.

Table 5.1. Overview of the main characteristics of the two selected zeolite types: Rota Mining and Zeocem.

	Rota Mining	Zeocem
Zeolite	Clinoptilolite (90–95%)	Clinoptilolite (84%)
Selectivity	$\text{Cs}^+ > \text{NH}_4^+ > \text{Pb}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Ba}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$	
Cation exchange capacity (CEC) ($\text{gNH}_4^+\text{-N}\cdot\text{kg}_{\text{zeolite}}^{-1}$)	25.5–35.7	20.4–25.5
Price ($\text{€}\cdot\text{ton}^{-1}$)	108–122	98–130

Table 5.2. Overview of mineral composition of tap-water used, the addition of components to simulate Vilanova WWTP influent wastewater and simulated final water composition.

Component	Tap-water ($\text{mg}\cdot\text{L}^{-1}$)	Extra addition in tap-water ($\text{mg}\cdot\text{L}^{-1}$)	Tap-water + minerals ($\text{mg}\cdot\text{L}^{-1}$)
Ca^{2+}	79	11 (as CaCl_2)	83
Mg^{2+}	9	36 (as MgCl_2)	54
K^+	3	24.5 (as KCl) 12.5 (as KH_2PO_4)	51
Na^+	27	237 (as NaCl)	270
PO_4^{3-}P	0.05	10 (as KH_2PO_4)	9

5.2.3. Batch tests description

Batch tests were run to generate adsorption isotherms and to mutually compare the ion-exchange capacity of selected zeolites at the different $\text{NH}_4^+\text{-N}$ concentrations wastewaters. In each series of batch experiments, 200 mL of N-rich synthetic water (per test) were brought in contact with different concentrations of the zeolite to be tested. An Erlenmeyer with an active volume of 200 mL were placed on a shaker for continuous mixing. After a relatively long

contact time of 2.5 h, samples were taken and filtered to determine the residual $\text{NH}_4^+\text{-N}$ concentrations. All tests were performed at room temperature.

5.2.4. Column tests description

Column tests were conducted to observe breakthrough behaviour and to determine operating conditions.

Two similar set-ups were run in parallel (*Figure 5.3*), each one consisting of an influent pump and a relatively small cylindrical column, partly filled with zeolite. Because of the difference in particle size of the zeolites, the dimensions of the columns were not identical for the larger particle sizes (diameter of 6 cm and height of 35 cm) compared to the dimensions of the columns for the smaller particle sizes (diameter of 2.5 cm and height of 95 cm). The N-rich water was added in a continuous way by means of a peristaltic pump. The columns were operated in upstream or downstream mode. In all the column tests, the zeolite was completely submerged. Variable hydraulic retention times (HRTs) were applied in columns, from 9 to 60 minutes, depending on the grain size. There was no internal recycle. All tests were performed at room temperature.



Figure 5.3. Two similar column set-ups for zeolite tests with larger particle grain size.

5.2.5. Sampling and analysis

On a regular basis, sub-samples of the effluents were taken for the follow-up of the residual $\text{NH}_4^+\text{-N}$ concentrations in function of running time and the treated bedvolumes (BV). The

analyses were carried out according to the Hach method (LCK 304, LCK303 and LCK 302; Hach Company, Loveland, Colorado). Total COD and phosphate ($\text{PO}_4^{3-}\text{-P}$) were conducted using the corresponding HACH test kit. TSS was analysed according to the Standard Methods [18].

5.3. Results and discussion

5.3.1. Batch tests

Table 5.3 summarizes the process conditions and results of the batch experiments in diluted synthetic wastewater, in diluted synthetic water with extra addition of minerals and P and in sewage for a zeolite concentration of $5 \text{ g}\cdot\text{L}^{-1}$. In Table 5.4, the results of the corresponding batch experiments at concentrated synthetic water for a zeolite concentration of $100 \text{ g}\cdot\text{L}^{-1}$ are shown.

Table 5.3. Overview of the process conditions and results of the zeolite batch experiments with a low $\text{NH}_4^+\text{-N}$ concentration of $50 \text{ mg}\cdot\text{L}^{-1}$ and a zeolite concentration of $5 \text{ g}\cdot\text{L}^{-1}$ (contact time of 2.5 h).

Type zeolite	$\text{NH}_4^+\text{-N}$ adsorption ($\text{mgNH}_4^+\text{-N}\cdot\text{g}_{\text{zeolite}}^{-1}$)		
	Synthetic water	Synthetic water + minerals and P	Wastewater
Zeocem (0.5–1 mm)	2.2	2.2	1.8
Zeocem (2.5–5 mm)	1.7	0.6	<i>Not tested</i>
Zeocem (8–16 mm)	0.7	0.6	<i>Not tested</i>
RM (0.6–1.5 mm)	<i>Not tested</i>	2.2	2.4
RM (1.5–3 mm)	0.9	0.4	<i>Not tested</i>
RM (3–5 mm)	1.7	1.2	<i>Not tested</i>

Table 5.4. Overview of the process conditions and results of the zeolite batch experiments with a high $\text{NH}_4^+\text{-N}$ concentration of $1 \text{ g}\cdot\text{L}^{-1}$ and a zeolite concentration of $100 \text{ g}\cdot\text{L}^{-1}$ (contact time of 2.5 h).

Type zeolite	$\text{NH}_4^+\text{-N}$ adsorption ($\text{mgNH}_4^+\text{-N}\cdot\text{g}_{\text{zeolite}}^{-1}$)		
	Synthetic water	Synthetic water + minerals and P	Wastewater
Zeocem (2.5–5 mm)	5.8	4.8	<i>Not tested</i>
Zeocem (8–16 mm)	1.9	2.0	<i>Not tested</i>
RM (1.5–3 mm)	4.3	3.1	<i>Not tested</i>
RM (3–5 mm)	5.1	4.9	<i>Not tested</i>

In most of the tests, the $\text{NH}_4^+\text{-N}$ adsorption was below $3 \text{ gNH}_4^+\text{-N}\cdot\text{kg}^{-1}_{\text{zeolite}}$. The maximum $\text{NH}_4^+\text{-N}$ adsorption in the batch experiments was about 5 to $6 \text{ gNH}_4^+\text{-N}\cdot\text{kg}^{-1}_{\text{zeolite}}$. In general, the measured $\text{NH}_4^+\text{-N}$ adsorption in all the batch experiments was considerably lower than the theoretical CEC values, given by the suppliers (*Table 5.1*): for the Zeocem type, the CEC ranges between 20.4 and $25.5 \text{ gNH}_4^+\text{-N}\cdot\text{kg}^{-1}_{\text{zeolite}}$ and for the Rota Mining zeolite, the CEC varies between 25.5 and $35.7 \text{ gNH}_4^+\text{-N}\cdot\text{kg}^{-1}_{\text{zeolite}}$.

When comparing the $\text{NH}_4^+\text{-N}$ adsorption of more or less similar grain sizes of the two zeolites, Zeocem versus Rota Mining, no important differences were measured between these two zeolite types. The same test conditions gave about the same $\text{NH}_4^+\text{-N}$ adsorption. On the other hand, comparing the results of the batch experiments with the small zeolite grain sizes versus the corresponding tests with the larger zeolite grain sizes, it can be concluded that CEC is drastically decreased for larger grain sizes. Under comparable test conditions, the smaller zeolite particle sizes always gave a higher $\text{NH}_4^+\text{-N}$ adsorption due to the greater available surface area.

The highest $\text{NH}_4^+\text{-N}$ adsorption in the batch tests with diluted water was obtained with the Na-modified zeolite. At the lowest concentrations of zeolite tested ($5 \text{ g}\cdot\text{L}^{-1}$), the $\text{NH}_4^+\text{-N}$ adsorption for the Na-modified zeolite ranged between 3.6 and $5.0 \text{ gNH}_4^+\text{-N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ and was almost double of the corresponding $\text{NH}_4^+\text{-N}$ adsorption of the other zeolite types with relatively small grain sizes (test series 2). The Zeocem (0.5–1 mm) zeolite gave considerably lower $\text{NH}_4^+\text{-N}$ adsorption than the Na-modified zeolite when tested under similar conditions. For the zeolite concentration of $5 \text{ g}\cdot\text{L}^{-1}$, the $\text{NH}_4^+\text{-N}$ adsorption capacity of the Zeocem (0.5–1 mm) zeolite varied between 1.8 and $2.2 \text{ gNH}_4^+\text{-N}\cdot\text{kg}_{\text{zeolite}}^{-1}$. These results confirm the fact that modification of the zeolite increases the $\text{NH}_4^+\text{-N}$ adsorption capacity.

For each of the zeolites tested, the tests carried out with synthetic water gave the highest $\text{NH}_4^+\text{-N}$ adsorption. As could be expected, the addition of minerals and P to the N-rich water resulted in lower $\text{NH}_4^+\text{-N}$ adsorption. However, the decrease in $\text{NH}_4^+\text{-N}$ adsorption remained limited both at the diluted and concentrated synthetic waters. No important differences in $\text{NH}_4^+\text{-N}$ adsorption were obtained in experiments with wastewater. In most of the tests, the $\text{NH}_4^+\text{-N}$ adsorption was even higher in the tests with wastewater, indicating that the $\text{NH}_4^+\text{-N}$ adsorption in batch experiments was mainly influenced by the presence of minerals.

In conclusion, all results of the lab-scale studies indicate that the best $\text{NH}_4^+\text{-N}$ adsorption capacity was obtained with 0.5–1 mm Na-modified zeolite. However, because of the risk for clogging problems, even in the absence of suspended solids in the influent, a compromise must be made between a satisfying $\text{NH}_4^+\text{-N}$ adsorption capacities as well as a low risk for clogging problems. More extended tests on pilot-scale are therefore required.

5.3.2. Column tests at relatively low ammonium influent concentration in synthetic media

In the first series of column experiments, six different zeolite samples (it concerns the four zeolites of batch test series 1 and the two best zeolites of batch test series 2) were tested to determine the ammonium adsorption capacity at relatively low $\text{NH}_4^+\text{-N}$ influent concentration. Tests were performed in diluted synthetic water. The effect of the presence of other residual compounds (such as COD, TSS, P), present in the effluent of the bio-sorption/bio-oxidation process, was not investigated in these column tests. A summary of the most important process conditions and results of the zeolite column tests, when treating a diluted synthetic influent, is given in *Table 5.5*.

Table 5.5. Summary of the column tests with zeolites in diluted synthetic wastewater.

INFLUENT: ca. 50 mgNH₄⁺-N·L⁻¹	RM (0.6–1.5)	RM (3–5)	RM (9–16)	Zeocem (2.5–5)	Zeocem (8–16)	Zeocem modified (0.5–1)
Process conditions tested						
Mass zeolite (g·column ⁻¹)	280	280	826	323	836	280
BV (mL·column ⁻¹)	170	110	460	130	530	170
(mL·kg _{zeolite} ⁻¹)	607	390	560	400	630	607
Contact time (min)	14	20	52	16	65	15
NH ₄ ⁺ -N inf. concentration (mg·L ⁻¹)	52	50	60	50	62	52
Total inf. volume (BV)	321	166	62	189	30	343
Total inf. volume (L)	54.6	18.2	28.4	25.7	15.9	58.4
Total N added (g·column ⁻¹)	2.84	0.91	1.70	1.29	0.99	3.04
Results						
Total NH₄⁺-N sorption						
gNH ₄ ⁺ -N·kg _{zeolite} ⁻¹	6.5	3.0	1.4	3.1	0.7	8.2
gNH ₄ ⁺ -N _{sorbed} ·column ⁻¹	1.8	0.8	1.2	1.0	0.6	2.3
% NH ₄ ⁺ -N adsorption	63	91	68	79	61	76
Total NH₄⁺-N sorption (gNH₄⁺-N·kg_{zeolite}⁻¹)						
with eff. < 5 mgNH ₄ ⁺ -N·L ⁻¹	3.3	1.8	0.1	1.4	0.06	6.2
with eff. < 15 mgNH ₄ ⁺ -N·L ⁻¹	4.8	3.0	0.5	2.9	0.1	6.8
Total BV treated						
with eff. < 5 mgNH ₄ ⁺ -N·L ⁻¹	125	ca. 100	< 4	ca. 75	ca. 1	198
with eff. < 15 mgNH ₄ ⁺ -N·L ⁻¹	203	166	19	167	2.9	223

ca.: circa; approximately

Since the total influent volume and the total amount of $\text{NH}_4^+\text{-N}$ added were not the same in the 6 tests, the mutual comparison was made on the basis of the amount of $\text{NH}_4^+\text{-N}$ adsorbed to the zeolite. As already clearly observed in the batch experiments, the larger grain sizes of the zeolites drastically decreased the $\text{NH}_4^+\text{-N}$ adsorption capacity for the low $\text{NH}_4^+\text{-N}$ influent concentrations. Considerably higher $\text{NH}_4^+\text{-N}$ sorption was measured in the column tests with the smaller zeolite grain sizes. The results of the column tests with a similar grain size of the zeolite types, Rota Mining and Zeocem, under similar process conditions were very well comparable. Slightly better results were achieved for the Rota Mining zeolite type.

The zeolites with the smallest grain sizes tested (range of 0.5–1.5 mm) clearly had considerably higher $\text{NH}_4^+\text{-N}$ adsorption capacities, compared to the other zeolites. The best results were achieved with the Na-modified zeolite: a total $\text{NH}_4^+\text{-N}$ adsorption of more than $8 \text{ gNH}_4^+\text{-N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ could be obtained. Also, Rota Mining (0.6–1.5 mm) gave satisfying results: a total $\text{NH}_4^+\text{-N}$ adsorption of about $6.5 \text{ gNH}_4^+\text{-N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ could be achieved in the test. However, the filterability of this zeolite column decreased in the course of the test, treating only synthetic water. This observation indicates that the zeolites with very small grain sizes can cause clogging problems of the columns, even in the absence of suspended solids in the influent.

When the required effluent quality of maximum $15 \text{ mgNH}_4^+\text{-N}\cdot\text{L}^{-1}$ was taken into account, the highest $\text{NH}_4^+\text{-N}$ adsorption amounted to about $6.8 \text{ gNH}_4^+\text{-N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ for the Na-modified zeolite and to $4.8 \text{ gNH}_4^+\text{-N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ for Rota Mining (0.6–1.5 mm). The latter corresponded with the treatment of respectively 223 and 203 BV.

5.3.3. Column tests at relatively low ammonium influent concentration in domestic wastewater containing different solids concentration

In order to examine the impact of other components present in wastewater, especially the presence of suspended solids, extra column tests treating low $\text{NH}_4^+\text{-N}$ concentration domestic wastewaters containing different TSS concentrations (32, 132 and $250 \text{ mgTSS}\cdot\text{L}^{-1}$, considered as relatively low, medium and high concentration, respectively) were performed. An overview of the main characteristics of the three wastewaters tested is given in *Table 5.6*.

Three similar column tests were carried out with the Na-modified zeolite (280 g per column). The same procedure, as described for the previous column tests, was applied. In order to prevent sedimentation of the suspended solids in the influent vessels, the latter was placed on a magnetic stirrer. An overview of the process conditions and the results of the three adsorption

tests are presented in *Table 5.7*. All adsorption tests had to be stopped because of severe clogging problems that already occurred after some hours.

Table 5.6. Overview of the main characteristics of the domestic wastewaters (WW) containing TSS used for the zeolite column tests.

	WW 1	WW 2	WW 3
Total COD (mg·L ⁻¹)	372	271	190
TSS (mg·L ⁻¹)	250	132	32
NH₄⁺-N * (mg·L ⁻¹)	45	45	49
PO₄³⁻-P (mg·L ⁻¹)	8	8	8

**Extra NH₄Cl was added to obtain an ammonium concentration of about 50 mgNH₄⁺-N·L⁻¹.*

In general, the results of the three column tests showed that the presence of suspended solids in the influent gave rise to severe clogging problems far below the total adsorption capacity was reached. Experiments ran with relatively medium and high TSS concentration wastewater (132 to 250 mgTSS·L⁻¹) resulted in a fast clogging of the columns. After the treatment of less than 10 BV, the zeolite with a fine granular size was clogged and no more water could be filtered through the columns. When a wastewater with a relatively low TSS concentration of 32 mg·L⁻¹ was pumped into the zeolite column, a higher volume of water could be treated (about 41 BV). However, also in this case, severe clogging problems occurred before saturation of the zeolite. Until the end of this experiment, no NH₄⁺-N could be measured in the effluent. In these tests, a maximum of 41 BV could be treated compared to 343 BV in the corresponding test with synthetic water.

It was observed that the higher the TSS concentration, the more rapidly clogging occurred. Hence, the results of these experiments indicate that prior to the NH₄⁺-N recovery by means of zeolite columns, the effluent of the pre-concentration step should be submitted to a pre-treatment for almost complete TSS removal.

Table 5.7. Process conditions and results of the sorption test with Na-modified zeolite in wastewater containing 32, 132 and 250 mgTSS·L⁻¹.

	Wastewater TSS concentration		
	Low (32 mg·L ⁻¹)	Medium (132 mg·L ⁻¹)	High (250 mg·L ⁻¹)
Process conditions tested			
Type and Size range	Zeocem modified 0.5–1 mm		
Mass zeolite in column	280 g		
Bedvolume (BV)	170 mL		
Water flow	Constant and downstream		
HRT or contact time (min)*	29	23	25
Influent NH ₄ ⁺ -N concentration	45 mg·L ⁻¹		
Results			
Cumulative NH₄⁺-N sorption total test (gNH ₄ ⁺ -N _{sorbed} ·kg _{zeolite} ⁻¹)	1.23	0.26	0.24
Effluent** (mgN·L ⁻¹)	0	0	0
Total bedvolumes treated*** (BV)	41.4	9.8	9.1

* Average value; ** Average residual TAN concentration in the effluent of a specific interval; *** Before clogging

5.3.4. Column tests at relatively high ammonium influent concentration with synthetic solutions

In the second series of column experiments, five different zeolite samples (it concerns the four zeolites of batch test series 1 and the best zeolite of batch test series 2) were tested to determine the NH₄⁺-N adsorption capacity at relatively high NH₄⁺-N influent concentration. Tests were performed in concentrated synthetic wastewater. The effect of the presence of other residual compounds (such as COD, TSS, P), present in the effluent of the bio-sorption/bio-oxidation process, was not investigated in these column tests. In *Table 5.8*, a summary of the most important process conditions and results of the zeolite column tests when treating a concentrated synthetic influent is given.

Table 5.8. Summary of the column tests with zeolites in concentrated synthetic water.

INFLUENT: ca. 1,000 mgNH₄⁺-N·L⁻¹	RM (3–5)	RM (9–16)	Zeocem (2.5–5)	Zeocem (8–16)	Zeocem modified (0.5–1)
Process conditions tested					
Mass zeolite (g·column ⁻¹)	284	824	287	891	280
BV (mL·column ⁻¹)	150	500	110	530	170
(mL·kg _{zeolite} ⁻¹)	530	600	380	600	607
Contact time (min)	45	56	35	70	23
NH ₄ ⁺ -N inf. concentration (mg·L ⁻¹)	922	922	938	938	990
Total inf. volume (BV)	40.5	5.0	52.3	4.0	40.4
Total inf. volume (L)	6.1	2.5	5.8	2.1	6.9
Total N added (g·column ⁻¹)	5.62	2.31	5.44	1.97	6.80
Results					
Total NH₄⁺-N sorption					
gNH ₄ ⁺ -N·kg _{zeolite} ⁻¹	12.7	1.6	12.5	1.7	16.3
gN _{sorbed} ·column ⁻¹	3.6	1.3	3.6	1.5	4.55
% NH ₄ ⁺ -N adsorption	64	57	66	78	67
Total NH₄⁺-N sorption (gNH ₄ ⁺ -N·kg _{zeolite} ⁻¹)					
with eff. < 150 mgNH ₄ ⁺ -N·L ⁻¹	6.5	0.7	8.0	0.8	13.8
Total BV treated					
with eff. < 150 mgNH ₄ ⁺ -N·L ⁻¹	14	1.5	23	1.4	23

ca.: circa; approximately

Since the total influent volume and the total amount of NH₄⁺-N added were not the same in the five column tests, the mutual comparison was made on the basis of the amount of NH₄⁺-N adsorbed to the zeolite. As already clearly observed in the batch experiments, a higher NH₄⁺-N influent loading resulted in a higher NH₄⁺-N exchange capacity of all zeolites tested in case an effluent quality of 150 mgNH₄⁺-N·L⁻¹ (10 times higher than in the column tests with the lower influent NH₄⁺-N concentrations) was focused on. As also reported in batch tests, the larger grain sizes of the zeolites drastically decreased the NH₄⁺-N adsorption capacity for the high NH₄⁺-N influent concentrations. Considerably higher NH₄⁺-N sorption was measured in the column tests with the smaller zeolite grain sizes. Yet, slightly better results were achieved for the Zeocem zeolite type.

Both zeolite samples with relatively small grain sizes of 2.5–5 mm gave about the same NH₄⁺-N adsorption capacity. When the required effluent quality of maximum 150 mgNH₄⁺-N·L⁻¹ was taken into account, the NH₄⁺-N adsorption varied between 6.5 gNH₄⁺-N·kg_{zeolite}⁻¹ (Rota Mining)

and $8 \text{ gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ (Zeocem). The latter corresponded with the treatment of 14 to 23 BV, which is equivalent to 8 to 14 L N-rich water $\cdot\text{kg}_{\text{zeolite}}^{-1}$, respectively. For the column tests with the larger zeolite grain size, a very fast breakthrough was measured for both zeolite samples: already after the treatment of about 1.6 BV, the effluent NH_4^+-N concentration reached the level of $150 \text{ mgNH}_4^+-\text{N}\cdot\text{L}^{-1}$.

The best results were achieved with the Na-modified zeolite. Its total NH_4^+-N adsorption amounted to $16.3 \text{ gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ and, taking a threshold effluent value of $150 \text{ mgNH}_4^+-\text{N}\cdot\text{L}^{-1}$, the maximum NH_4^+-N adsorption amounted to $13.8 \text{ gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$, corresponding with the treatment of about 23 BV. At the end of the lab-scale test, the columns were not yet completely saturated, so higher NH_4^+-N adsorptions can be expected in case higher effluent NH_4^+-N concentrations were allowed or several zeolite columns were operated in series.

5.3.5. Zeolites regeneration test

After a previous phase of zeolite selection, Rota Mining (3–5 mm) and Na-modified zeolites were preliminarily tested in order to evaluate their adsorption and regeneration capacity under different ammonium concentration conditions to select the zeolite that will be used and tested in the pilot unit. The selected zeolite regeneration method is based on a chemical regeneration, using sodium hydroxide (NaOH) and a mixture of NaOH and sodium chloride (NaCl). For the regeneration of almost complete saturated zeolites, tests were performed in batch mode with 1 M sodium hydroxide (NaOH). Prior to the addition of NaOH, zeolite columns were rinsed with tap-water. Therefore, the influent flow rate was decreased with a factor of about 10 and about 4 BV were pumped over the zeolite columns. An overview of the regeneration test is presented in *Table 5.9* for Na-modified zeolite and in for Rota Mining zeolite.

Table 5.9. Overview of the column regeneration test of the Na-modified and Rota Mining 3–5 mm zeolites with 1 M NaOH followed by a mixture of 1 M NaOH and 1 M NaCl.

		Cumulative Time (h)	Cumulative Influent Volume (ml)	Cumulative N recovery (mg)
Na-modified	1 M NaOH	32.5	1323	59
	1 M NaOH + 1 M NaCl	6.0	1633	60
	TOTAL	38.5	1633	60
Rota Mining 3–5 mm	1 M NaOH	32.6	2289	44
	1 M NaOH + 1 M NaCl	6.0	2749	44
	TOTAL	38.6	2749	44

As can be derived from the results of the two regeneration tests with 1 M NaOH, followed by a mixture of 1 M NaOH and 1 M NaCl, very low amounts of $\text{NH}_4^+\text{-N}$ was recovered in both regeneration tests after the addition of relatively high volumes of regeneration liquid. Moreover, clogging of both columns occurred after an intermediate stop during the weekend (zeolite columns remained submerged in water over the weekend); afterwards, there was a gradual restart of filtering through the zeolite columns.

Because of the poor results of the regeneration tests, both zeolites were taken out of the column reactors and were divided into different parts to perform extra batch regeneration tests with different regeneration solutions (NaOH and/or NaCl at different concentrations). To determine the required volume of the regeneration liquid per test, a regeneration factor of 40 was taken into account. After a reaction time of 2.5 hours, the regeneration liquid was analyzed ($\text{NH}_4^+\text{-N}$), separated from the zeolite and replaced by the same volume of fresh regeneration liquid. This step was repeated 3 successive times. After the performance of the regeneration trials, some analytical and measurement errors were detected and that fact could entail obtaining non-representative data for this phase. At pilot scale, it would be necessary to test and optimize the regeneration of zeolites (see *Chapter 7*).

In order to compare the impact of the regeneration liquid on the $\text{NH}_4^+\text{-N}$ recovery from the saturated zeolite, the Na-modified zeolite was taken out of the column reactor and was divided into five equal parts (on wet weight). Three of these parts were used for three different regeneration tests:

- *Test 1*: 1 M NaOH.
- *Test 2*: a mixture of 1 M NaOH and 1 M NaCl.
- *Test 3*: a mixture of 2 M NaCl and 0.1 M NaOH.

To calculate the required amount of regeneration liquid, it was the intention to take a regeneration factor of 40. In total, 6.9 L of N-rich water was treated in the column test. The corresponding regeneration volume would be 170 mL for the total amount of zeolite in the column. This volume is very low for the regeneration of 280 g of zeolite. Most probably, the regeneration factor of 40 is not applicable for highly loaded $\text{NH}_4^+\text{-N}$ waters. In the batch regeneration tests, higher volumes of regeneration liquid were taken.

For the treatment of about 56 g of zeolite (20% of the initial total dry weight of 280 g), 200 mL of regeneration liquid was applied. After two hours of equilibration, the liquid phase was separated by centrifugation and analysed. Then, the same volume of fresh regeneration liquid

was added. This step was repeated four successive times. In *Table 5.10*, an overview is presented of the three batch regeneration tests.

When extrapolating the results of each batch regeneration test to the total amount of zeolite in the column test (regeneration factor of 5), the total amount of $\text{NH}_4^+\text{-N}$ recovered by the three regeneration liquids was:

- *Test 1*: 1.64 g $\text{NH}_4^+\text{-N}$ by means of 1 M NaOH or 36% of the adsorbed $\text{NH}_4^+\text{-N}$ (in total 4.55 g of nitrogen in the column test with 280 g of zeolite);
- *Test 2*: 1.86 g $\text{NH}_4^+\text{-N}$ by means of 1 M NaOH + 1 M NaCl or 41% of the adsorbed $\text{NH}_4^+\text{-N}$;
- *Test 3*: 3.11 g $\text{NH}_4^+\text{-N}$ by means of 2 M NaCl + 0.1 M NaOH or 68% of the adsorbed $\text{NH}_4^+\text{-N}$.

From the results of the regeneration tests, it could be derived that the best regeneration solution tested was the mixture of 2 M NaCl + 0.1 M NaOH. Treatment of the saturated zeolite with this regeneration solution resulted in the recovery of 68% of the $\text{NH}_4^+\text{-N}$. Considerably lower $\text{NH}_4^+\text{-N}$ recoveries were achieved in the regeneration tests with 1 M NaOH and with the mixture of 1 M NaOH + 1 M NaCl.

Table 5.10. Overview of the results of the batch regeneration tests with Na-modified zeolite after adsorption test in concentrated synthetic water.

(mg $\text{NH}_4^+\text{-N}\cdot\text{L}^{-1}$)	Regeneration solution*		
	1 M NaOH	1 M NaOH + 1 M NaCl	2 M NaCl + 0.1 M NaOH
Start with 200 mL	696	942	840
After 2 h	690	764	752
Replacement 200 mL			
Start	146	163	106
After 2 h	750	858	1,373
Replacement 200 mL			
Start	191	202	348
After 2 h	196	232	846
Replacement 200 mL			
After 2 h	5	7	143

*Each batch test was performed with 20% of the saturated zeolite from the column test (i.e. with 56 g of dry zeolite) and with 200 mL of regeneration solution.

It should be indicated that relatively high volumes of regeneration liquid were applied in these batch experiments. To regenerate 20% of the saturated zeolite from the column test, in total 800 mL of regeneration liquid was applied. This would mean 4 L of regeneration liquid for the total column or 58% of the 6.9 L of N-rich water that was previously treated in the column test. Hence, this would correspond with a very low regeneration factor of 1.7.

5.3.6. Adsorption test after regeneration

The regenerated Na-modified zeolite from the three batch tests was returned into the column (60% of the initial amount) and a new adsorption test was started with concentrated synthetic water. The same procedure as in the first adsorption test was applied. An overview of the process conditions and the results of this column test is presented in *Table 5.11*. In *Figure 5.4*, the evolution of C/C_0 in function of treated BV (cumulative values) is graphically presented, both for the first adsorption test and for the second adsorption test after batch-wise regeneration of the saturated zeolite. C_0 is the influent NH_4^+ -N concentration and C is the measured effluent ammonium concentration for the tested interval.

Table 5.11. Process conditions and results of the sorption test with Na-modified zeolite in concentrated synthetic water – Test with 60% of initial zeolite amount, after batch-wise regeneration.

Process parameters	
Type and Size range	Zeocem modified 0.5–1 mm
Mass zeolite in column	168 g
Bedvolume (BV)	102 mL
Water flow	Constant and downstream
HRT or contact time	Average of 14 minutes
Influent NH_4^+ -N concentration	990 $\text{mg}\cdot\text{L}^{-1}$
Results sorption	
Cumulative NH_4^+-N sorption total test	17.4 $\text{gNH}_4^+-\text{N}_{\text{sorbed}}\cdot\text{kg}_{\text{zeolite}}^{-1}$
Cumulative NH_4^+-N sorption < 150 $\text{mg}\cdot\text{L}^{-1}$	15.5 $\text{gNH}_4^+-\text{N}_{\text{sorbed}}\cdot\text{kg}_{\text{zeolite}}^{-1}$
Treated water volume	50 BV or 5.0 L (60% of the initial amount of zeolite)

Although the batch regeneration tests with the saturated zeolite from the first adsorption test did not result in a complete recovery of the nitrogen (based on the $\text{NH}_4^+\text{-N}$ analyses), the second adsorption test gave more or less the same total $\text{NH}_4^+\text{-N}$ adsorption ($17.4 \text{ gNH}_4^+\text{-N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ versus $16.3 \text{ gNH}_4^+\text{-N}\cdot\text{kg}_{\text{zeolite}}^{-1}$). The difference in $\text{NH}_4^+\text{-N}$ adsorption between the first and second adsorption test can be related to the small scale of the experiments and the extrapolation of all measurements. Nevertheless, the second adsorption test clearly demonstrated that, under the tested conditions, the zeolite Na-modified zeolite could maintain its total $\text{NH}_4^+\text{-N}$ adsorption capacity after regeneration.

Taking into account an effluent $\text{NH}_4^+\text{-N}$ concentration of $150 \text{ mg}\cdot\text{L}^{-1}$ as a threshold value, the breakthrough occurred after the treatment of 23 BV (first test) and 30 BV (second test). The latter corresponded with the total adsorption of respectively about $13.8 \text{ gNH}_4^+\text{-N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ (first test) and $15.5 \text{ gNH}_4^+\text{-N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ (second test). In both tests, a very fast increase of the effluent $\text{NH}_4^+\text{-N}$ concentrations were measured after the treatment of 25 and 35 BV, respectively.

In the first adsorption test, the effluent $\text{NH}_4^+\text{-N}$ concentrations were almost not detectable in the first part of the adsorption test. After regeneration, effluent $\text{NH}_4^+\text{-N}$ concentrations ranging between $22 \text{ mg}\cdot\text{L}^{-1}$ and $102 \text{ mg}\cdot\text{L}^{-1}$ were measured from the start on.

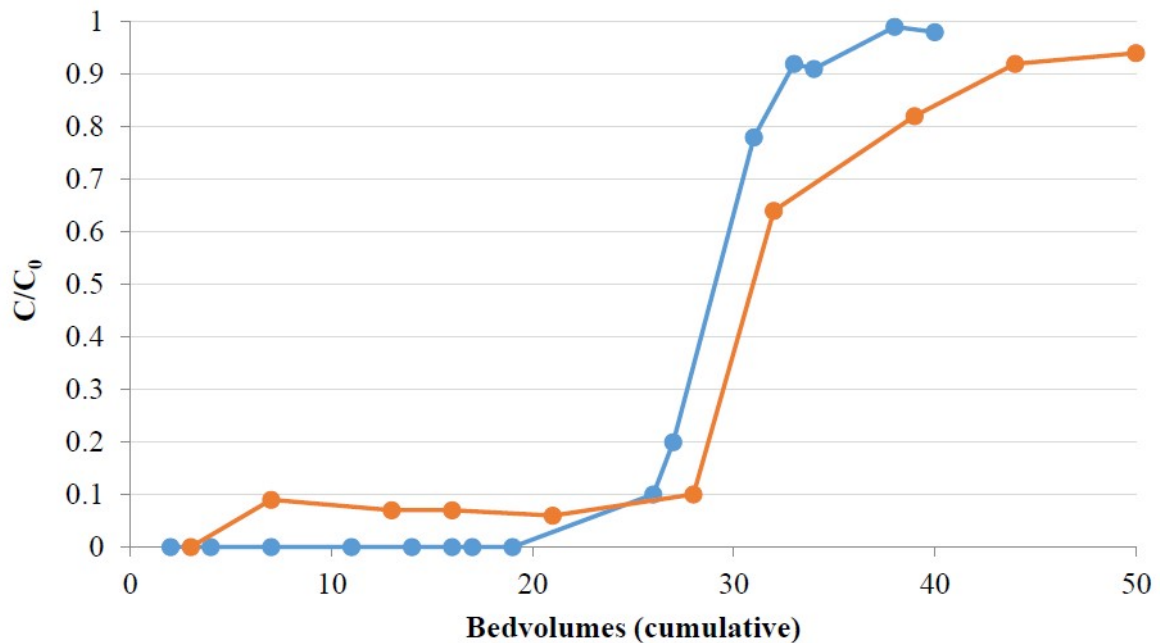


Figure 5.4. Evolution of C/C_0 as a function of cumulative treated effluent (bedvolumes; BV) for the zeolite column test with Na-modified zeolite in concentrated synthetic wastewater. First adsorption test (blue line) and second adsorption test (red line) after batch-wise regeneration of the saturated zeolite.

5.4. Conclusions

Batch tests were run to generate adsorption isotherms and to mutually compare the ion-exchange capacity of different zeolites. Column tests were conducted to observe breakthrough behaviour and to determine operating conditions.

In general, with both diluted and concentrated effluents, the measured NH_4^+-N adsorption in all the batch experiments was considerably lower than the corresponding values given by the suppliers: obtained around $5-6 \text{ gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ in comparison to the theoretical CEC of $20-35 \text{ gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$. No important differences were measured between the two zeolite types. The results showed that higher NH_4^+-N influent loading ($1,000 \text{ mgNH}_4^+-\text{N}\cdot\text{L}^{-1}$) resulted in a higher NH_4^+-N CEC of the zeolites tested, but zeolites sooner became saturated. Moreover, under comparable test conditions, the smaller zeolite particle sizes always gave a higher NH_4^+-N adsorption due to the greater available surface area.

Considerably higher NH_4^+-N sorption was measured in the column tests with the smaller zeolite grain sizes. The best NH_4^+-N adsorption capacity was obtained with Na-modified zeolite for both influent concentrations: a total NH_4^+-N adsorption of more than $8 \text{ gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ (at $50 \text{ mgNH}_4^+-\text{N}\cdot\text{L}^{-1}$) and $16.3 \text{ gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ (at $1,000 \text{ mgNH}_4^+-\text{N}\cdot\text{L}^{-1}$) could be obtained. When the required effluent quality of maximum $15 \text{ mgNH}_4^+-\text{N}\cdot\text{L}^{-1}$ was taken into account, the highest NH_4^+-N adsorption amounted to about $6.8 \text{ gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ for the Na-modified zeolite.

The results of the column tests containing different concentrations of TSS showed that the presence of TSS in the influent gave rise to severe clogging problems. Prior to the NH_4^+-N recovery by means of zeolite columns, the wastewater should be submitted to a pre-treatment for almost complete TSS removal and also the remaining COD. According to these results obtained, a sand filter and an ultrafiltration unit will be considered as a pre-treatment system in the pilot plant design to protect zeolites unit.

From the results of the regeneration tests, it could be derived that the best regeneration liquid tested was the mixture of $2 \text{ M NaCl} + 0.1 \text{ M NaOH}$. Treatment of the saturated zeolite with this regeneration liquid resulted in the recovery of 68% of the NH_4^+-N . However, a very low regeneration factor of 1.7 was obtained. It was concluded that at pilot scale it would be necessary to test and optimize the regeneration of zeolites. It will involve testing different regeneration agents (NaOH, NaCl), modes of regeneration (co-current versus counter-current), optimise the adsorption time and flow in the adsorption phase, among others.

In general, all results of the lab-scale studies indicate that, by preference, a modified zeolite type with a small grain size ($\leq 1 \text{ mm}$) should be chosen for the NH_4^+-N -recovery pilot-scale tests.

However, because of the risk for clogging problems, even in the absence of suspended solids in the influent, a compromise must be made between a satisfying NH_4^+ -N adsorption capacity on the one hand and a low risk for clogging problems on the other hand. It was concluded that all these points will be verified and complemented by the tests on pilot-scale (see *Chapter 6*).

5.5. References

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CHAPTER 6

*Nutrient recovery from urban wastewater by
integration of granular natural zeolite as
extraction and concentration technology:
validation at pilot scale*

6. Nutrient recovery from urban wastewater by integration of granular natural zeolite as extraction and concentration technology: validation at pilot scale

6.1. Introduction

As it has been discussed in *Chapter 5*, zeolites are a promising ion-exchange material to be used in wastewaters treatment due to its high affinity towards ammonium (NH_4^+). The recovery of nutrients avoids environmental impact in the treatment train, which is directly related to the reduction of the eutrophication potential [1]. By using zeolites, a quality effluent is produced regarding ammonium concentration as well as zeolites charged with ammonium can be used as ‘green’ solid fertilizer [2]. However, for practical reasons, zeolites could not be removed out of the system once saturated and being chemically regenerated in order to start the process once again and, thus, to maximize its use and profitable its costs [3].

In the field of ion-exchange, the results are not only measured in terms of quality effluent but also the properties of the ion-exchange material, such as the maximum capacity of the material to adsorb ammonium ions (CEC), the amount of ammonium recovered, the factor of concentration (CF) of this recovered ammonium over the ammonium in the influent, its lifetime and the interference of other ions.

Within this thesis, the objective of this chapter is to assess the technical viability of the zeolites in the proposed scheme. This chapter includes the results obtained from the operation of the nitrogen recovery unit.

6.2. Methodology

6.2.1. Wastewater

The wastewater used was the effluent from Vilanova WWTP, whose ammonium concentration was similar than the one expected in the effluent from the carbon redirection unit (about $50 \text{ mg}\cdot\text{L}^{-1}$). This assimilation was possible since Vilanova WWTP is a coastal wastewater treatment plant (WWTP) without nitrogen (N) removal.

6.2.2. Zeolitic ion-exchanger

Derived from the results of lab-scale experiments, a granular natural clinoptilolite was selected as the ion-exchange material to be used at pilot scale zeolite columns. Although activated zeolite reported better results at lab-scale (see *Chapter 5*), Zeocem 0.5–1 mm natural (inactivated) zeolite was chosen since it will be activated after the first regeneration stage with sodium hydroxide (NaOH) solution.

6.2.3. Nutrient recovery pilot plant description

The design of the pilot plant consisted on a pre-treatment step, by means of a sand filter and ultrafiltration stage. The objective of the pre-treatment was to protect the zeolites columns and remove the remaining solids and particulate COD of the treated influents. Two ion-exchange columns packaged with granular zeolites were incorporated (*Figure 6.1*). Columns connection was set in both parallel and series mode and they operated in downflow. The regeneration of the column was carried out cross-current. Detailed information will be found in *Chapter 2*.

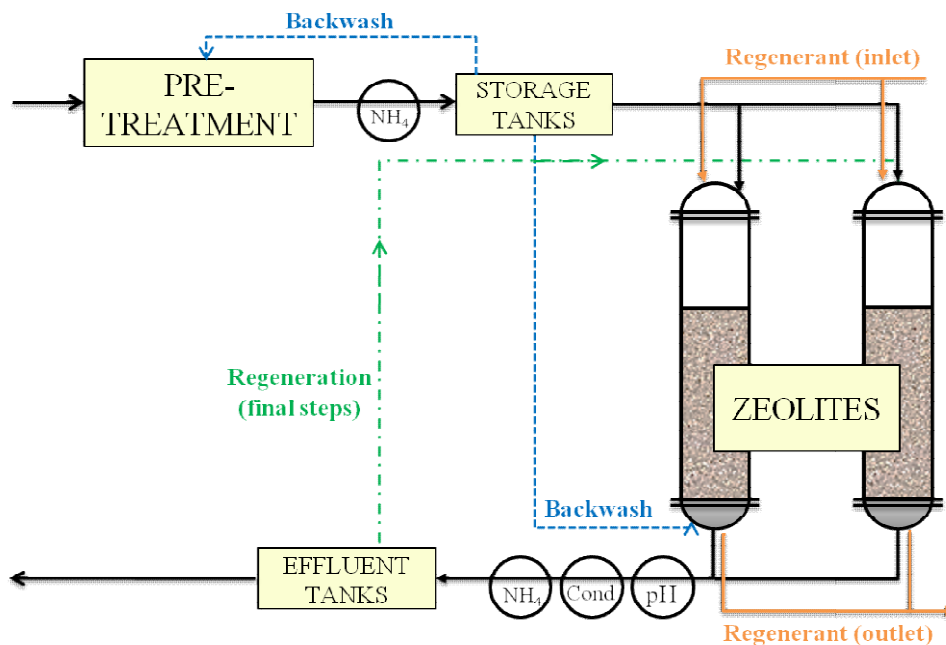


Figure 6.1. General scheme of the nutrient recovery unit (main elements and sensors included) in a co-current mode of operation.

6.2.4. Principle of operation

Columns performance was calculated as a function of the treated effluent volumes expressed as bedvolume (BV). The latter can be defined as the free volume in a packed bed column, as described by *Equation 6.1*.

$$BV = \frac{Q \cdot t}{V_b} \quad [\text{Eq. 6.1}]$$

where BV is the bedvolume, Q is the flow rate ($\text{mL} \cdot \text{min}^{-1}$), t is the elapsed time (min) and V_b is the volume of the reactive bed (m^3).

The volume of the reactive bed (V_b) is defined in *Equation 6.2*:

$$V_b = \pi \cdot r^2 \cdot h_b \cdot \varepsilon \quad [\text{Eq. 6.2}]$$

where r is the internal radius of the column (m), h_b is the length of the zeolite bed (m) and ε is the porosity (%). Experimentally, porosity can be determined by to measure the conductivity of a brine (NaCl) solution passing through the zeolite column.

Notice that BV is a non-dimensional magnitude which mainly depends on the column dimensions. This parameter allows relating breakthrough curves of different columns. Consequently, it is a key magnitude when scaling up or down systems.

Breakthrough curves are sigmoidal curves as illustrated in *Figure 6.2*. The shape of the breakthrough curve can be explained as follows: when the stream enters into the column, target ions (NH_4^+) are captured by fresh zeolite by ion-exchange. At this first moment, zeolite extraction capacity is maximal. As solution keeps passing, the zeolite bed starts saturating. This phenomenon is reflected by the sigmoidal increase, also known as the Mass Transfer Zone (MTZ) [4]. The breakthrough point is defined as the point where the output effluent reaches a target concentration. This point determines the maximum admitted loss of capacity. The column capacity is obtained by integration of the breakthrough curve and the breakthrough point. Knowing the amount of ammonium adsorbed, it is possible to determine the ammonium adsorption capacity (q_{ads}) of the zeolite as given by *Equation 6.3*.

$$q_{ads} = \frac{(C_0 - C)V}{W} \quad [\text{Eq. 6.3}]$$

where C_0 and C are respectively the amounts of initial and final ammonium concentration; V is the amount of aqueous solution and W is the amount of used zeolite expressed as grams.

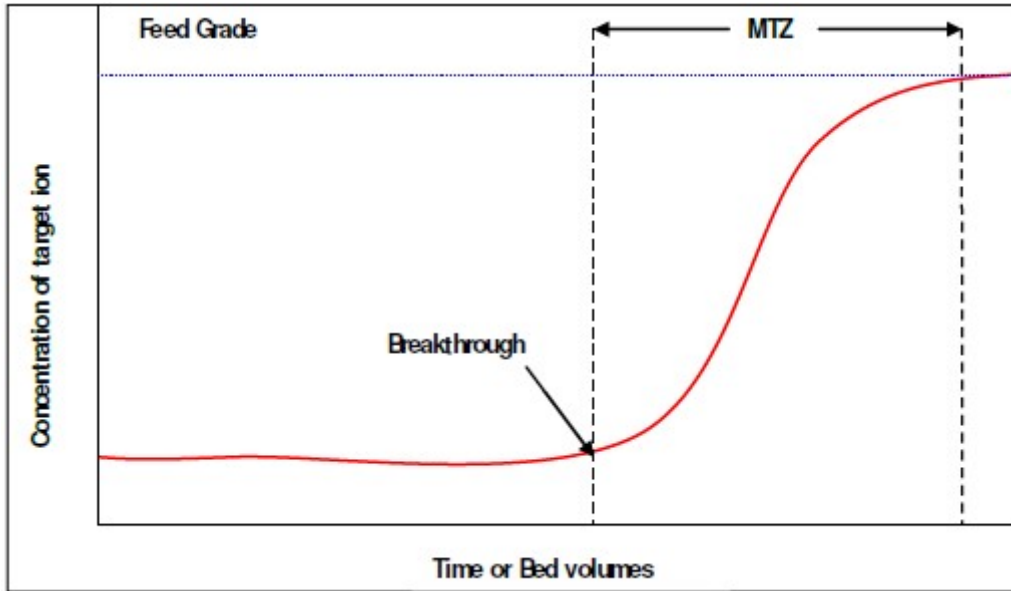


Figure 6.2. Generic breakthrough curve for ion-exchange systems.

Once the maximum established capacity is reached, the system operation is stopped and the column is regenerated by alkaline solution (e.g. NaOH) to promote eluting target ammonium ions from zeolite into the regeneration stream. The removal efficiency (%R) and the concentration factor (CF) are calculated by *Equations 6.4–6.5*:

$$\%R = \frac{C_0 - C}{C_0} \times 100 \quad [\text{Eq. 6.4}]$$

$$CF = \frac{C}{C_0} \quad [\text{Eq. 6.5}]$$

where C_0 and C are respectively the amounts of initial and final ammonium concentration.

In the present study, the selected value was the discharge limit fixed by the regulation of urban wastewater ($10 \text{ mgNH}_4^+ \cdot \text{L}^{-1}$) [5,6]. Ammonium extraction experiments were developed at linear

velocities around $4 \text{ BV}\cdot\text{h}^{-1}$ (between $450\text{--}500 \text{ L}\cdot\text{h}^{-1}$). Linear velocity was fixed according to preliminary column laboratory experiments to assure a nominal HRT of 10 minutes.

Ammonium recovery efficiency from the loaded zeolites beds was evaluated by using 1 M NaOH solutions, using linear velocities of about $6 \text{ BV}\cdot\text{h}^{-1}$ (about $800 \text{ L}\cdot\text{h}^{-1}$; decreased up to $450 \text{ L}\cdot\text{h}^{-1}$ in the last two cycles). Samples were collected along each regeneration cycle and analyzed to determine the ammonium content as well other major cations present. The elution curves were constructed by representing the concentration of ammonium as a function of the regeneration bed volumes. The integration of the elution curve allows determining the amount of ammonium recovery, and it was used to determine the regeneration efficiency by comparison with the ammonium capacity determined from the breakthrough curves.

6.2.5. Analytical procedure

Two ammonium sensors (SC200 AN-ISE, HACH Co.), one at the entrance of ultra-filtered water storage tanks and another at the entrance of the storage tanks of water without ammonium, monitored at real time the ammonium concentration in water. The pilot unit was also provided by conductivity (CTK.1, Injecta S.r.l.) and pH (EGA 133/BNC, Xylem Inc.) sensors at the outlet of zeolites in order to verify that all the chemicals have been removed from the columns after the washing process.

Total chemical oxygen demand (COD), ammonium, nitrate (NO_3^-) and orthophosphate (PO_4^{3-}) concentrations were measured on-site by using the corresponding HACH test kits. In addition, total COD, ammonium, calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+) were also determined by an external laboratory according to Standard Methods. pH and turbidity were analysed by Eutech pH 6+ sensor (EUTECH Instruments Pte Ltd.) and Hi93703 sensor (Hanna Instruments), respectively. Metals were determined by inductively coupled plasma optical emission spectroscopy. Organic compounds were analysed by ultra performance liquid chromatography mass spectrometer (UPLC-MS/MS).

On the completion of the column experiments, samples of the NH_4^+ -saturated zeolites were examined by the field scanning electron microscope (FSEM-EDX) and mineral phases were identified by X-Ray Diffractometry (XRD).

6.3. Results and discussion

6.3.1. Nitrogen recovery

A total of fourteen consecutive cycles have been carried out using the same zeolite sample. Different operational conditions have been tested in order to determine the best characteristics. A summary of the tests is gathered in *Table 6.1*. The zeolite performance in each trial expressed in the form of breakthrough curves (C/C_0 as a function of treated BV) is depicted in *Figure 6.3*.

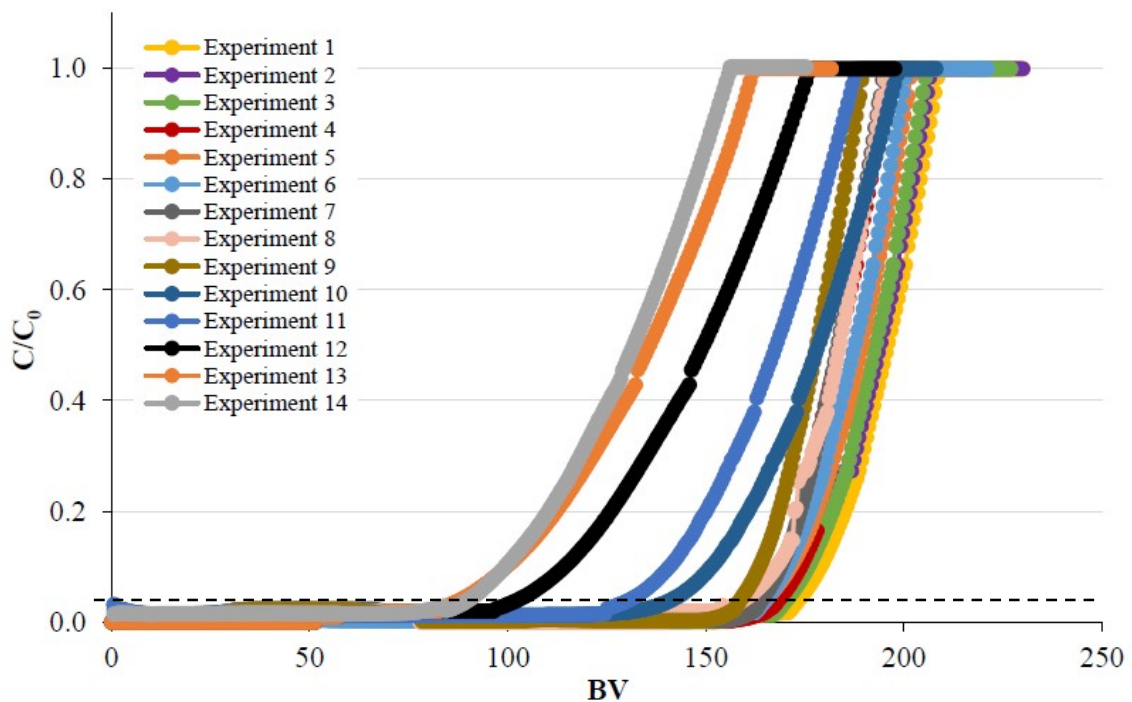


Figure 6.3. Granular zeolite performance expressed as C/C_0 as a function of the cumulative treated effluent bedvolumes (BV). The dashed line represents the operational breakthrough point selected ($C/C_0 = 0.05$).

In the conditions of operation of Vilanova WWTP and the characteristics of its wastewater, zeolites can produce at pilot scale a quality effluent regarding ammonium concentration ($<1 \text{ mgNH}_4^+-\text{N}\cdot\text{L}^{-1}$). Moreover, it has been demonstrated that zeolites could maintain its adsorptive capacity along different experiments, achieving a lifespan of at least 10 cycles (*Figure 6.3*). As it could be seen in *Figure 6.3*, breakthrough points move from initial values above 175 BV until values around 160 BV along the first 10 cycles. Only after more than 10 cycles, breakthrough points diminished to values below 100 BV.

Table 6.1. Summary of the results obtained during fourteen consecutive cycles.

Trial	ADSORPTION			REGENERATION				
	Average NH_4^+ IN ($\text{mg}\cdot\text{L}^{-1}$)	CEC ($\text{g}\cdot\text{kg}^{-1}$)	Total NH_4^+ adsorbed (g)	Regenerating reagent	Regeneration mode	NH_4^+ recovered (g)	NH_4^+ recovered (%)	Concentration factor
1	33.5	n.a.	n.a.	NaOH 0.4% + NaCl 1%	Co-current	n.a.	n.a.	n.a.
2	35.8	7.5	746	NaOH 0.4% + NaCl 1%	Co-current	n.a.	n.a.	n.a.
3	51.4	6,1	609	NaOH 4%	Co-current	548	90	40
4	34.1	4.6	455	NaOH 4%	Co-current	398	87.4	38
5	53.6	6.2	642	NaOH 4%	Co-current	515	80.2	34
6	61.9	13.6	1131	NaOH 4%	Co-current	927	82	53
7	42.2	9.1	914	NaOH 4%	Co-current	744	81.5	67
8	46.4	9.0	898	NaOH 8%	Co-current	552	91.4	55
9	45.8	6.05	605	NaOH 4%	Counter-current	552	91.4	40
10	44.3	6.3	626	NaOH 4% + NaCl 1%	Counter-current	540	86.2	34
11	45.3	6.46	646	NaOH 4% + NaCl 1%	Counter-current	489	76	37
12	51.9	3.95	396	NaOH 4%	Co-current	n.a.	n.a.	n.a.
13	55.4	5,3	531	NaOH 4%	Co-current	447	84.3	24
14	35.6	4.0	403	NaOH 4%	Co-current	433	94	34
Total	637.2	-	8,602*	-	-	6,145*	-	-

*n.a. : not available; *Total amount considering data reported (available data).*

On average, zeolites achieve a cation exchange capacity (CEC) about $7 \text{ gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$, with a maximum CEC of 13.6 in the 6th cycle. However, these values are far from the maximum CEC values reported by the zeolite supplier: 20.4–25.5 $\text{gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ (www.zeocem.com/en/). This is due to fact that the zeolite supplier used NH_4^+ -concentrated synthetic water solutions for the determination of the maximum adsorption capacity of the material whereas reported values correspond to the wastewater considered. Value of exchange capacity for the Zeocem zeolite ($6\text{--}14 \text{ gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$) is in accordance with those reported in the literature when actual values of ammonium in the treated effluent are considered [7]. As it could be seen in *Figure 6.4*, influents with ammonium concentration values from 35 to 55 $\text{mgNH}_4^+\cdot\text{L}^{-1}$, CEC values reported ranged from 7.5 to 15 $\text{gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$ for clinoptilolite zeolites and only a natural modernite (NZ3) reported values close to 20 $\text{gNH}_4^+-\text{N}\cdot\text{kg}_{\text{zeolite}}^{-1}$.

Reported values in this study indicate a good selectivity of the zeolite. However, the potential interference of other cations and components present in wastewater is assessed (see *Section 7.3.2*).

Generally, the performance of zeolites has reported successful results at pilot scale. Nitrogen recovered in the regeneration represents, on average, about 85% of the total nitrogen adsorbed. To improve the percentage of regeneration, each step involved in the process (regeneration mode, regeneration reagent) was studied and trials were carried out to enhance them.

Regeneration mode

Both co-current (cycles 1–8 and 12–14) and counter-current (cycles 9–11) operational modes were tested (*Table 6.1*). Most of the experiments were carried out in co-current mode, as it was recommended by the zeolite supplier. Only three counter-current experiments were carried out towards the end of the life cycle of zeolites. Analysis of data in terms of regeneration performance quantified as ammonium recovered did not provide significant differences. Then, it can be concluded that the regeneration mode has no significant effect on regeneration efficiency for the set of experiments carried out. It should be mentioned that differences measured could be biased because of the fact that counter-current experiments were carried out when a reduction of the zeolite capacity started to be reduced.

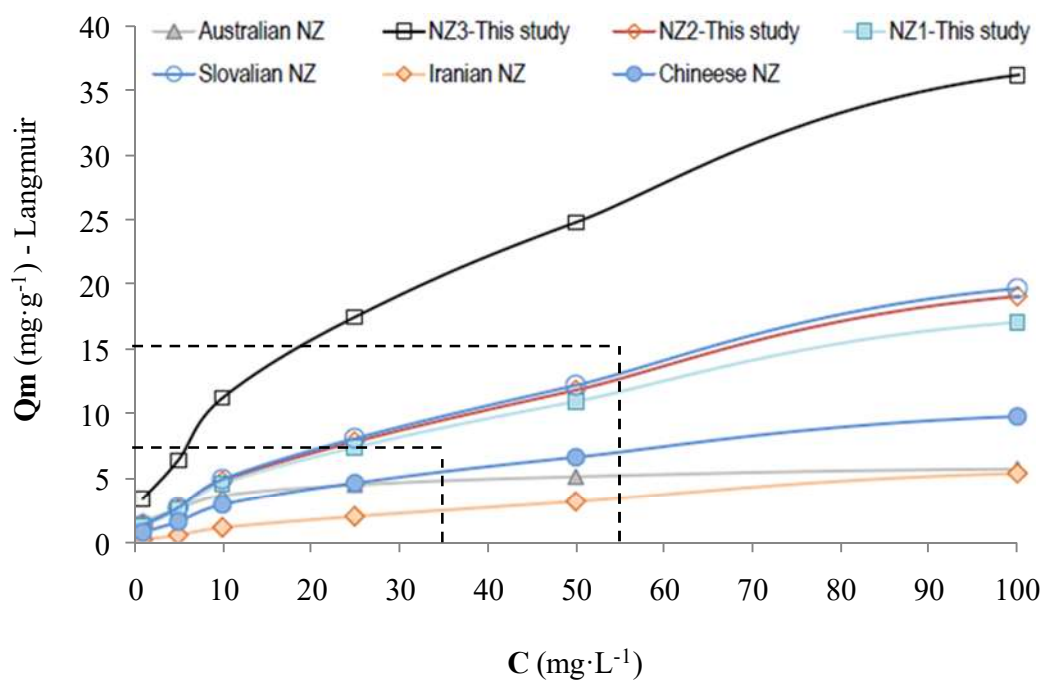


Figure 6.4. Comparison of isotherms for different Yemenian natural zeolites (NZ1, NZ2 and NZ3) and for natural zeolites from Australia, China, Iran and Slovakia (adapted from [7]). Solid lines were calculated using the Langmuir constant collected in the reference. Dashed lines delimit the area under experimental values are comparable with reported values in terms of ammonium influent concentrations ($35\text{--}55\text{ mgNH}_4^+\cdot\text{L}^{-1}$) and CEC ($7.5\text{--}15\text{ gNH}_4^+\text{-N}\cdot\text{kg}_{\text{zeolite}}^{-1}$).

Regeneration solutions efficiency

The natural zeolite (Z-N) used at the pilot scale experimental unit was on-site activated to Na-form using NaOH solutions (Z-Na). The FSEM-EDX analysis revealed the presence of oxygen (O), sodium (Na), magnesium, aluminium (Al), silicon (Si), potassium (K), calcium (Ca) and iron (Fe) as the main elements on the zeolites composition (*Table 6.2*). In Z-Na, the sodium content increase from 0.4 % to 1.5 % and a decrease of potassium and calcium content was observed due to the exchange with sodium ions.

So, regeneration solutions used were sodium based to re-establish zeolites after regeneration step for a new cycle of operation (adsorption). In this case, NaOH and NaCl were chosen as regeneration reagents. To evaluate the effect of each reagent, different trials were done using a solution of NaOH (cycles 3–9 and 12–14), or a combination of NaOH+NaCl (cycles 1–2 and 10–11). Under the same operational conditions, trials that used a solution of NaOH reported higher NH_4^+ recovery (91% – 9th cycle) than the ones using a mixture of both reagents (81%, – an average of 10th and 11th cycles) (*Table 6.1*). Hence, it is concluded that the use of NaOH (without NaCl) as a regenerating agent shows better efficiency.

Table 6.2. Chemical composition (wt. %) of the zeolitic materials: natural zeolite (Z-N), and sodium zeolite form (Z-Na) (table adapted from [8]).

Element	Z-N	Z-Na
O	57.4±2.6	60.3±1.4
Na	0.3±0.0	1.5±0.1
Mg	0.4±0.1	0.4±0.0
Al	5.3±0.2	5.3±0.0
Si	29.7±1.7	29.1±1.5
K	2.9±0.5	1.8±0.2
Ca	1.9±0.3	1.1±0.1
Ti	0.2±0.2	<loq [*]
Fe	1.6±0.4	0.5±0.0

**loq: limit of quantification*

After the determination of the best regeneration agent, the assessment of any diffusion problem was carried out. It was done by performing an experiment doubling the concentration of the reagent: NaOH 8% (8th cycle). Comparing to consecutive cycles working at different concentration of reagent (cycles 7 and 8), it can be concluded that a solution of 8% NaOH (8th cycle) shows better performances on N-recovery (91%) than at 4% NaOH (82%) (*Table 6.1*). Nevertheless, these similar values discarded any diffusion problems and further trials were assessed using 4% NaOH taking into account closely efficiency recovery percentage values and the economic cost of working at higher reagent concentration.

Another parameter to take into consideration is the concentration factor (understood as the concentration of nitrogen in the eluate from regenerations divided by the nitrogen concentration in the influent; *Equation 6.4*). As shown in *Table 6.1*, the eluate from regeneration was 30 to 60 times more concentrated in nitrogen than the influent, reaching a nitrogen concentration between 1 and 2 gN·L⁻¹. *Figure 6.5* depicts the typical profile of the ammonium concentration in the eluate during the regeneration phase of the material inside the column.

After the study of all step involved in regeneration, *Figure 6.6* sums up the results obtained in each regeneration test condition. From this, it is proved that better results in terms of recovery efficiency are obtained regenerating with NaOH 4% solution (both co- and counter-current modes).

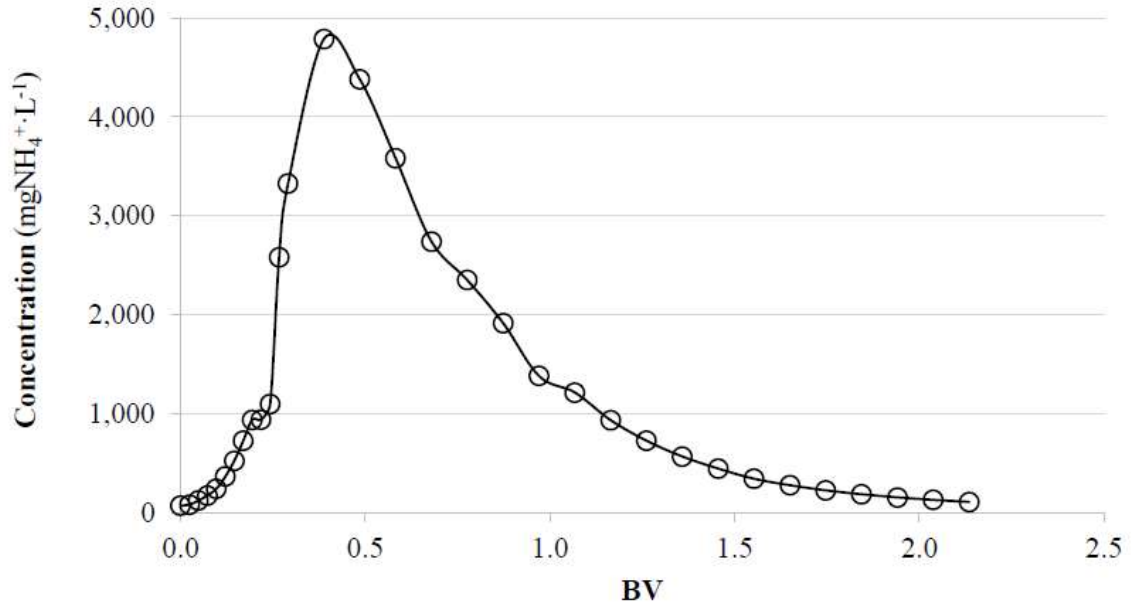


Figure 6.5. Typical profile of the ammonium concentration in the eluate during the regeneration phase (data from the 7th cycle of the experimentation).

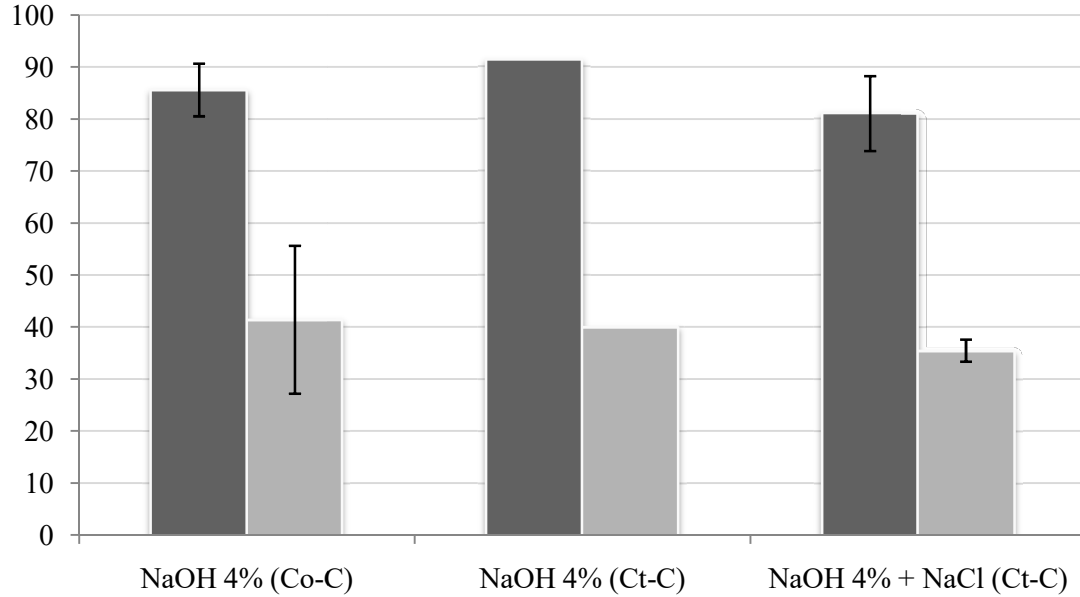


Figure 6.6. Bar graph representing the average value of nitrogen recovered (%) (dark grey) and concentration factor (light grey) of each regeneration experimental conditions. Standard deviation is shown (vertical error bars).

6.3.2. Influence of wastewater composition: the effect of macro and micro pollutants

The composition of a wastewater presents several components (macro and micro pollutants) and ions which may interfere negatively on the adsorptive capacity of zeolites. Hence, part of the pilot-scale study investigates the role of different pollutants as limiting and/or competing components to ammonium adsorption.

On the one hand, macro pollutants are taken into consideration and their evolution along the process is depicted in *Figure 6.7*.

Regarding the obtained data, it is concluded that up to 60% tCOD and 93% SS (represented by turbidity) can be removed from the systems after pre-treatment thanks to the high effectiveness of this step. Half of the present phosphorus in wastewater is retained by zeolites, reducing the adsorptive capacity of this material for ammonium. Contrary, nitrate remains unaffected.

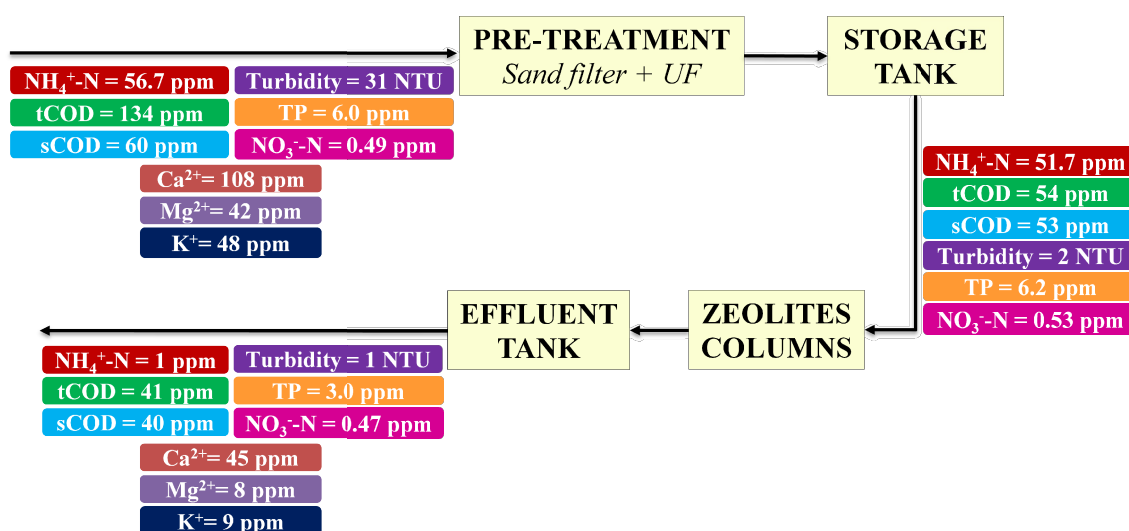


Figure 6.7. General scheme of the composition changes on macro pollutants and competing ions.

Zeolites have a specific affinity for ammonium, but this does not mean that other cations present in wastewater will not be adsorbed. It has been observed that 60% Ca²⁺ is retained in the process (most probably adsorbed into zeolites as exchangeable ions since, because of its particle size, it is thought that these ions will not be affected by the pre-treatment unit). Furthermore, this number grows up to 80 % for Mg²⁺ and K⁺. So, it has been proving that the presence of Ca²⁺, Mg²⁺ and K⁺ could reduce the uptake of ammonium onto zeolites. *Table 6.3* shows the composition of the zeolites used in the pilot plant at the following states: new zeolite (activated

at the laboratory using NaOH), saturated after the first three consecutive cycles and before and after regeneration at the 7th cycle of operation.

Table 6.3. Chemical composition (wt. %) of Zeocem zeolite samples at different stages of operation (values obtained by EDX).

Element	New Na-activated zeolite	Saturated after 3 rd cycle	Saturated after 7 th cycle	Regenerated after 7 th cycle
C	0.0	-	10.4	9.2
O	60.4	54.1	53.0	52.5
Na	1.5	0.8	0.4	1.1
Mg	0.4	0.6	1.4	2.1
Al	5.3	5.1	3.9	4.5
Si	29.1	32.1	17.1	21.2
P	-	0.1	0.6	0.4
S	-	<loq*	-	-
K	1.8	2.5	1.7	1.7
Ca	1.1	3.5	9.8	5.2
Fe	0.5	1.1	1.2	1.4
Cu	-	-	0.6	0.5
Zn	-	-	0.3	0.4

*loq: limit of quantification

From results obtained in *Table 6.3*, the ion-exchange properties of the material are demonstrated by the reduction, on the composition of zeolites, of the exchangeable sodium cations after the period of saturation and its re-establishment after regeneration (due to zeolites are regenerated using NaOH as a reagent). The greatest affinity to exchange ions is between Na⁺ and NH₄⁺ but, as discussed above, other ions present in wastewater can also be exchangeable by Na⁺, becoming competing ions. The presence of other exchangeable cations in wastewater composition (Ca²⁺, Mg²⁺) reduces the affinity capability of zeolites to adsorb ammonium on its framework structure. The adsorption of these competitive cations on zeolites implies a faster saturation of the material, reduction of the total ammonium adsorbed (lower CEC value) and, thus, less total nitrogen amount recovered due to fewer pores are available for ammonium. Nevertheless, the ion-exchange capacity of zeolites is not only affected by competing ions since they are removed from the surface during the regeneration step. Contrary, the accumulation of organic matter, which represents 10% of the zeolites weight, reduces the effective surface for adsorption (7th cycle) and, then, decreases CEC value of the material.

On the other hand, the impact of several micro pollutants, both organic and inorganic, has been assessed (*Table 6.4*). Only chromium, typically as Cr(III) species, and nickel, as Ni(II), seem to be retained in the zeolites and partially desorbed after regeneration step. Nevertheless, concentration values achieved in the effluent and eluate streams are lower than the allowed values for drinking waters (Ni <20 $\mu\text{g}\cdot\text{L}^{-1}$, Cr <50 $\mu\text{g}\cdot\text{L}^{-1}$) [5,6]. Eluate stream is of great importance for agriculture for its potential use as liquid fertiliser after a previous step of a technology of concentration, such as membrane contactors (see *Chapter 7*). So, its metal content concentration must be low (at least as limiting values for drinking waters).

Table 6.4. Metallic and organic micro pollutants concentration: analysis of its influence along the ion-exchange process by means of zeolites.

	Influent ($\text{mg}\cdot\text{L}^{-1}$)	Effluent ($\text{mg}\cdot\text{L}^{-1}$)	Eluate ($\text{mg}\cdot\text{L}^{-1}$)
Metallic micro pollutants			
Chromium (Cr)	< 0.005	< 0.005	0.019
Nickel (Ni)	<0.055	<0.055	0.071
Copper (Cu)	<0.052	<0.052	<0.052
Zinc (Zn)	<0.052	<0.052	<0.052
Arsenic (As)	< 0.005	< 0.005	< 0.005
Silver (Ag)	< 0.005	< 0.005	< 0.005
Cadmium (Cd)	< 0.005	< 0.005	< 0.005
Mercury (Hg)	<0.030	<0.030	<0.030
Lead (Pb)	< 0.005	< 0.005	< 0.005
Organic micro pollutants			
Diclofenac	754	659	767
Triclosan	<LQC*	<LQC*	10.6
Carbamazepine	153	149	373
Trimethoprim	3.16	1.72	6.96
Caffeine	4132	2443	610

* *LQC: Line Quality Control*

On the other hand, caffeine is the organic micro pollutant that is most adsorbed in the material, almost 41% of the inlet caffeine. Caffeine can attach to the surface of zeolites by hydrogen bonds which imply that the regeneration is not able to extract a major part of caffeine [9], limiting the adsorptive capacity of zeolites. Diclofenac, Triclosan, Carbamazepine, Trimethoprim are adsorbed and eluted in different percentages, but all them have not remain retained in the zeolites surface interfering on its adsorptive efficiency capacity.

6.3.3. Microstructure analysis

The composition of zeolites has been analysed at four different stages of its operation to determine any variability in its structure over the operational time. Morphological analysis of zeolite particles, using FSEM (*Figure 6.8*), identified after several cycles of operation the presence of new mineral phases formed during the operation cycles. However, these mineral phases were almost completely removed during the regeneration step, but the zeolite was never able to return to its initial state, involving to a problem of scaling of this unit.

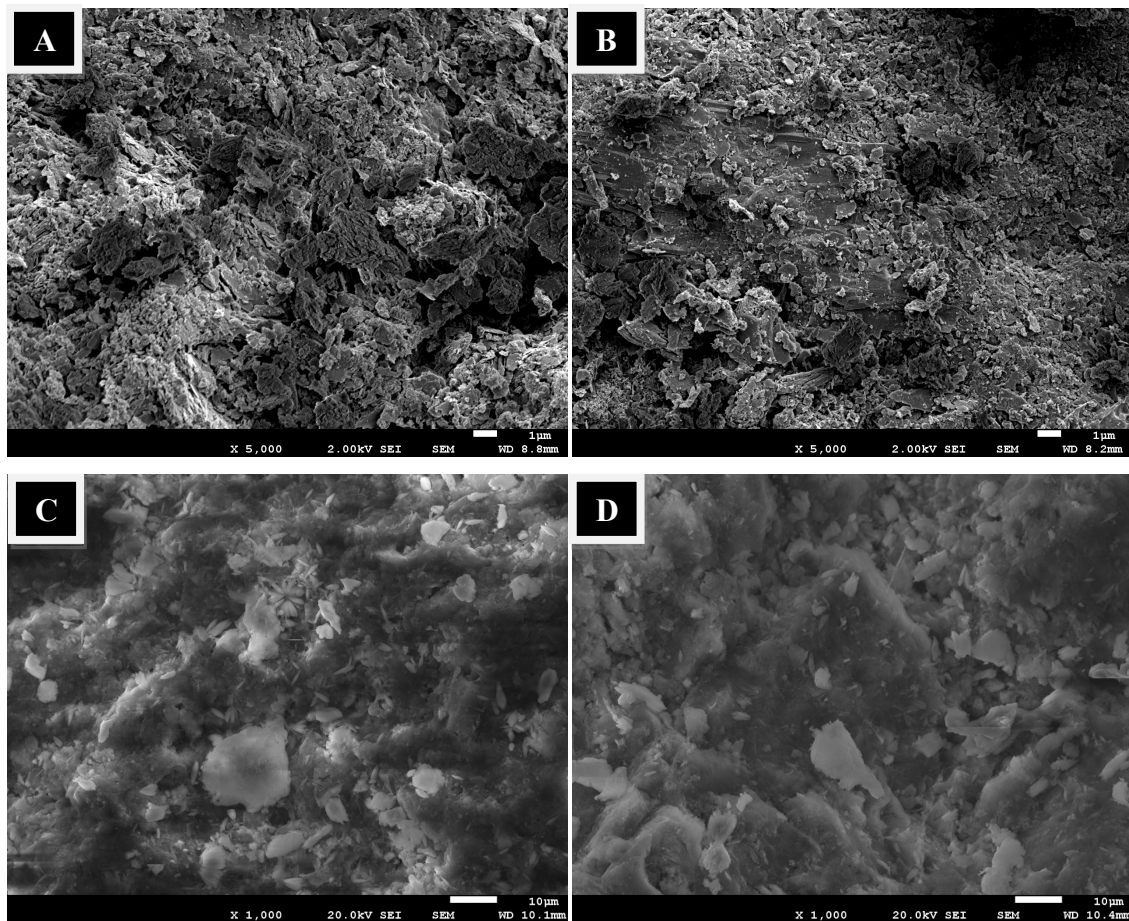


Figure 6.8. FSEM images of zeolites: (A) new zeolite (at magnification $\times 5,000$), (B) saturated after three cycles (at magnification $\times 5,000$), (C) saturated after seven cycles (at magnification $\times 1,000$) and (D) regenerated after seven cycles (at magnification $\times 1,000$). The formation and presence of mineral phases during the same operation cycle can be observed and compared in images C and

D.

FSEM-EDX analysis of the formed minerals phases identified the presence of Ca^{2+} and Mg^{2+} , indicating the formation of its corresponding carbonates forms. The formation of carbonate-rich mineral phase was identified by the addition of hydrochloric acid (HCl) and the release of carbon dioxide ($\text{CO}_{2(g)}$). It was further confirmed by XRD the presence of calcite ($\text{CaCO}_{(s)}$) and magnesium carbonate ($\text{MgCO}_{3(s)}$). The presence of such minerals on the zeolite surface particles supports the high level of compactness of the column bed material once it was removed out of the column to replace them with the new adsorptive material at the end of cycle 14th (*Figure 6.9*). The compactness of zeolites has been also assessed using SEM-EDAX technology. The images obtained are shown in *Figure 6.10*. The formation of calcium carbonate (CaCO_3) crystals, confirmed by EDAX analysis where O and Ca were found, gives evidence to the compactness of zeolite inside columns after some cycles of operation, affecting negatively on the regeneration efficiency.

FSEM-EDX analysis showed also neo-formed mineral phases rich on P, O and Ca indicating the formation of calcium phosphates such as hydroxyapatite. Its content is smaller than calcium and magnesium carbonates and it was not detected by XRD, as they were below of the limit of detection on the size of the mineral phase was approaching values below <10 nm.



Figure 6.9. Sample of new zeolitic material used in this study (left), top view of the zeolite column after fourteen cycles (middle) and sample of a portion of the compacted column bed material after fourteen cycles of operation (right).

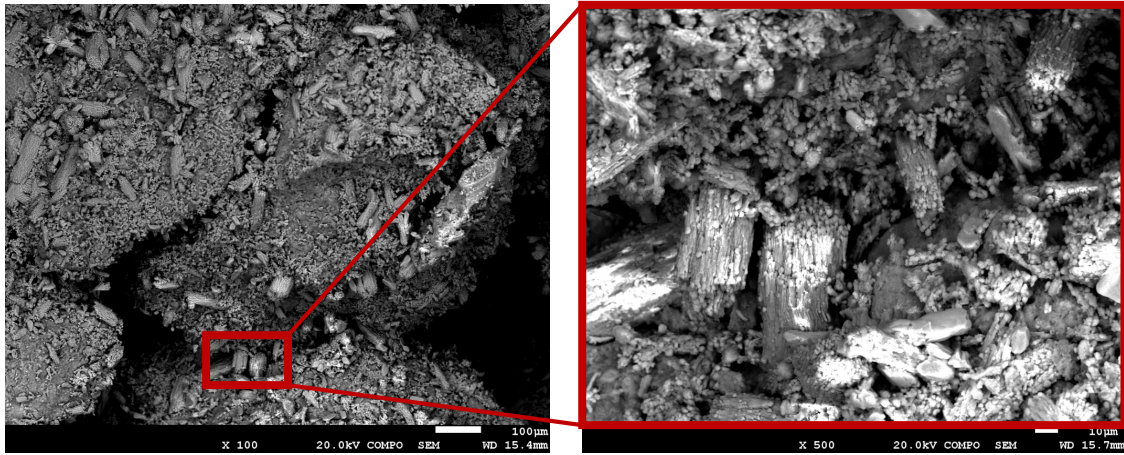


Figure 6.10. FSEM analysis of used zeolite after fourteen cycles of operation at magnification $\times 100$ (left) and $\times 500$ (right).

6.4. Conclusions

It has been assessed that is technically feasible to use zeolites to recover ammonium from wastewater. Zeolites were able to produce a clean effluent in terms of ammonium ($<1 \text{ mgNH}_4^+ \text{ N}\cdot\text{L}^{-1}$), which represents a significant environmental benefit compared to conventional processes, which produce effluents with higher nitrogen concentrations ($<10 \text{ mg}\cdot\text{L}^{-1}$). However, to guarantee its correct performance, a pre-treatment is needed to remove COD and SS from wastewater.

Under the conditions tested at the pilot plant, zeolites showed a CEC of $10 \text{ gNH}_4^+ \text{ N}\cdot\text{kg}_{\text{zeolite}}^{-1}$, reproducible during at least 10 consecutive cycles of operation. It was also demonstrated that zeolites capacity for nitrogen adsorption may be affected by the presence of particulate material and carbon, competitive ions present in wastewater (mainly K^+ , Ca^{2+} and Mg^{2+}), and also by some micro pollutants, such as caffeine, in water composition.

The protocol for regeneration of the zeolites has been optimized during the operation, achieving a maximum regeneration efficiency regenerating with NaOH 4% solution in both co- and counter-current modes ($\%R = 90\text{--}95\%$). Higher ammonium recovery percentage could be achieved if the presence of competing ions and micro pollutants were reduced and the characteristics of the zeolitic material were maintained throughout the cycles. Further research in this sense is required to increase the percentage of nitrogen recovery. Despite this, the concentration factor has achieved high levels ($CF = 30\text{--}60$).

6.5. References

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CHAPTER 7

Recovery of ammonia from domestic wastewater effluents as liquid fertilizers by integration of natural zeolites and hollow fibre liquid-liquid membrane contactors

7. Recovery of ammonia from domestic wastewater effluents as liquid fertilizers by integration of natural zeolites and hollow fibre liquid-liquid membrane contactors

7.1. Introduction

As discussed in previous chapters, the implementation of pre-concentration techniques (e.g. bio-flocculation) generates a high-load organic stream thus promoting the biogas production enhancement [1]. However, its implementation as a mainstream sewage treatment process requires further post-treatment, due to the missing ammonium/ammonia ($\text{NH}_4^+/\text{NH}_3$) removal approach and the relatively lower effluent quality. Most of the post-treatment solutions for the novel pre-concentration processes are focused on autotrophic nitrogen removal [2,3] or on membrane processes to ensure effluent discharged standards [4] (see *Chapter 5*), thus, the possibility to introduce $\text{NH}_4^+/\text{NH}_3$ recovery solutions, such as ion-exchange, is a recently postulated alternative that needs further development [5]. Take into consideration that the regeneration of loaded ammonium zeolites generates rich $\text{NH}_4^+/\text{NH}_3$ concentrates ($2\text{--}6 \text{ gNH}_3 \cdot \text{L}^{-1}$) in sodium chloride (NaCl), sodium hydroxide (NaOH) or NaOH/NaCl solutions. As the ion-exchange concentration step involves pre-treatment for particulate matter removal by sand filters or ultrafiltration, the ammonia concentrates quality is suitable for the integration of hollow fibre liquid-liquid membrane contactors (HFLLMCs) [6] as separation and concentration step.

This process has been used as a polishing step to remove low levels of $\text{NH}_4^+/\text{NH}_3$ from industrial effluents (up to $200 \text{ mgNH}_4^+ \cdot \text{L}^{-1}$) [7–10]. HFLLMCs using polyvinylidene fluoride (PVDF) and polypropylene (PP) have shown high ammonia removal efficiencies dependent on the feed pH and independent on the feed ammonia concentration using strong acids as stripping phase (e.g., sulphuric and hydrochloric acids) [11]. Compared to conventional scrubbers, HFLLMC has a much larger specific surface area, thus space requirements and capital costs are reduced [9,12].

With the aim of finding new technologies to recover nitrogen from wastewater, this chapter evaluates the integration of a natural zeolite for the selective extraction of $\text{NH}_4^+/\text{NH}_3$ from treated wastewater simulating pre-concentration effluents and the subsequent $\text{NH}_4^+/\text{NH}_3$ concentration and purification step using HFLLMCs by producing ammonium nitrate (NH_4NO_3) and di-ammonium phosphate [$(\text{NH}_4)_2\text{HPO}_4$] for its potential use as a liquid fertilizer.

7.2. Methodology

7.2.1. Zeolitic ion-exchanger

A natural zeolite (Z-N) from Slovakian Republic (Zeocem Company) was used. Before using zeolites, samples were washed with deionised water and dried. Zeolites particles below 200 μm were used for batch experiments and 800–1,200 μm particles were used for column experiments. To obtain its sodium form (Z-Na), a dried zeolite sample (30 g) was treated with 250 mL of NaCl ($6 \text{ g}\cdot\text{L}^{-1}$) under reflux conditions for 4 h in two consecutive cycles, which was later washed with deionised water.

7.2.2. Equilibrium and kinetic evaluation of ammonium removal by using batch experiments

To determine the ammonium sorption equilibrium, Z-Na samples (0.2 g) were equilibrated with 15 mL of solutions containing $25 \text{ mgNH}_4^+-\text{N}\cdot\text{L}^{-1}$, with pH ranging from 2 to 11. Ammonium solutions were prepared by using ammonium chloride (NH_4Cl). Experiments were replicated with the effluent stream from the secondary treatment of Sant Feliu Wastewater Treatment Plant (WWTP; Barcelona, Spain) at pH 7.7 ± 0.4 . The average chemical composition of the treated wastewater samples used in this study is shown in *Table 7.1*.

On the other hand, weighted amounts of impregnated samples (10 g of Z-Na) were equilibrated in 1 L of the treated effluent (*Table 7.1*) to evaluate the ammonium sorption kinetics. Assays were performed in triplicate for each sample at room temperature ($22\pm 1 \text{ }^\circ\text{C}$). Samples, filtered at 0.45 μm before analysis, were collected at given times to quantify the ammonium concentration in the initial and remaining solutions.

Table 7.1. Chemical composition of Sant Feliu WWTP (Barcelona, Spain) treated water used for equilibrium and kinetic studies (reported data are average values).

	Na^+	Ca^{2+}	NH_4^+	K^+	Mg^{2+}	Al (III)	Fe (III)
Cationic species ($\text{mg}\cdot\text{L}^{-1}$)	260	130	35	41	39	0.12	0.06
		SO_4^{2-}	HPO_4^{2-}		NO_3^-	Cl ⁻	
Anionic species ($\text{mg}\cdot\text{L}^{-1}$)		95	12		47	541	

7.2.3. Ammonium removal by using column experiments

Samples of Z-Na (800–1,200 μm particles) were packed in a glass column (15 mm inner diameter and 100 mm length). Initially, the column was equilibrated with deionised water. The feed composition was defined as taking as reference the characterization of the treated effluent of a HRAS treatment. The test solution with competing ions was supplied in counter-current through the column. Samples were collected from the outlet of the column by a fraction collector (Gilson FC204) at given time intervals. After column saturation, the sorbent material was washed with deionised water and then the Z-Na was regenerated with a $2 \text{ g}\cdot\text{L}^{-1}$ NaOH solution.

7.2.4. Ammonium recovery as ammonium nitrate and di-ammonium phosphate using liquid-liquid hollow fibre membrane contactors

Synthetic feed solution of NH_3/NaOH simulating the composition of the zeolites regeneration concentrates were used. Additionally, ammonia solutions generated during the regeneration of ammonium loaded zeolite columns ($2 \text{ g}\cdot\text{L}^{-1}$ NaOH; $\text{pH}>12$) were used. Stripping solutions were prepared from 65% (w/w) nitric (HNO_3) or 98% (w/w) phosphoric (H_3PO_4) commercial acid solutions. The experimental setup consisted of a HFLLMC module, a Liquid-Cel 2.5x8" Extra Flow X30HF from Membrane-Charlotte (3M, USA) (Figure 7.1). Two polypropylene tanks, one for the NH_3/NaOH feed solution and other for HNO_3 or H_3PO_4 acid strip solution, were used.

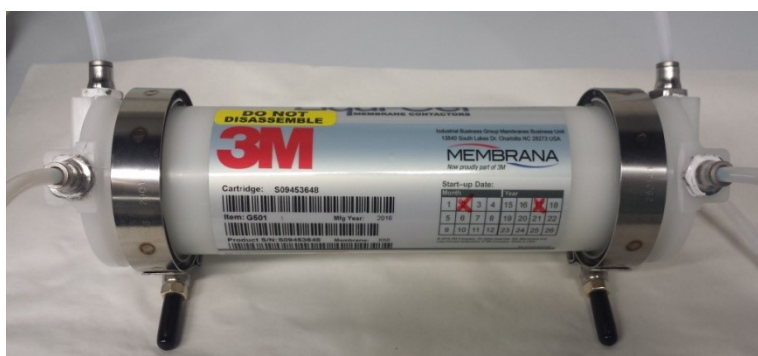


Figure 7.1. Hollow fibre liquid-liquid membrane contactor (HFLLMC) module used in the study.

Between experiments, deionised water was passed through the module to flush out solutions from previous tests. The NH_3/NaOH feed solution was pumped through the HFLLMC lumen

side at different flow rates, while the stripping acid solution was circulated into the shell side in a counter-current mode by using two peristaltic pumps. Both solutions were recirculated to their respective reservoirs. The feed and stripping volumes were 20 and 2 L, respectively. At given times, samples were taken from the feed tank for pH and total ammonia concentration analysis. The solution pH (between 2 to 12) and the acid (HNO_3 or HPO_4) concentration of the stripping tank were monitored. The lumen and shell flows were stopped and membrane pores stability was tested when finishing the experiment. The system was properly cleaned by passing deionised water through both sides in order to remove the remaining solution. All tests were carried out at room temperature (22 ± 1 °C).

7.2.5. Analytical methodologies

Ammonium analyses were carried-out by ion-selective electrode method (4500-NH₃ D) and ions species concentration were determined by Ionic Chromatograph (Dionex ICS-1100 and ICS-1000). The non-purgeable organic carbon (NPOC), total carbon (TC), total organic carbon (TOC), inorganic carbon (IC) and total nitrogen (TN) were determined in a total organic carbon analyzer (Shimadzu, TOC-V_{CPH}). An elemental analysis (including traces) of the treated effluent was performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

7.2.6. Physicochemical characterization of sodium zeolites (Z-Na)

Zeolite samples from sorption and desorption experiments were washed with deionised water to remove the interstitial solution and then oven-dried at 60°C for structural and textural analysis. The chemical composition and morphology of dried samples were determined by a Field Emission Scanning Electron Microscope (FSEM; JEOL JSM-7001F) coupled to an Energy Dispersive Spectroscopy system (Oxford Instruments X-Max). The infrared absorption spectra ($4,000\text{--}550\text{ cm}^{-1}$) were recorded with a Fourier Transform FTIR 4100 (Jasco) spectrometer. The nitrogen gas ($\text{N}_{2(\text{g})}$) adsorption method was used to measure the specific surface area of Z-Na samples (Micrometrics analyzer). A powder X-ray Diffractometer (D8 Advance A25 Bruker) was used for X-ray diffraction (XRD) characterization of Z-Na sample. Tests were replicated at least three times for each sample and the average values are reported.

Samples of Z-Na zeolite were equilibrated in three different ionic strengths (25 mL of deionised water; 0.01, 0.05 and 0.1 M NaCl) at 21 ± 1 °C. The pH drift method was used for the point of zero charge (PZC) determination in the range of pH 2 to 11 [13]. Experiments were performed in triplicate for each sample and the average values are reported.

7.2.7. Data treatment methodologies: ammonium extraction equilibrium and kinetic evaluation and ammonia transport in hollow fibre liquid contactors

The removal of ammonium, q_e , from aqueous solutions was calculated by *Equation 7.1*:

$$q_e = (C_o - C_e) \times \frac{v}{w} \quad [\text{Eq. 7.1}]$$

where C_o ($\text{mg}\cdot\text{L}^{-1}$) and C_e ($\text{mg}\cdot\text{L}^{-1}$) represent the initial and the equilibrium ammonium concentrations, respectively; v (L) is the aqueous solution volume, and w (g) is the mass of zeolite.

The ammonium sorption by Z-Na was evaluated according to Langmuir isotherm (*Equation 7.2*):

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad [\text{Eq. 7.2}]$$

where q_m ($\text{mg}\cdot\text{g}^{-1}$) is the maximum ammonium sorption capacity and K_L ($\text{L}\cdot\text{mg}^{-1}$) is the Langmuir sorption equilibrium constant.

The fractional attainment of equilibrium at time t , $X(t)$, was calculated by using *Equation 7.3*:

$$X(t) = \frac{q_t}{q_e} \quad [\text{Eq. 7.3}]$$

where q_t and q_e are ammonium loading on the particle phase at time t and when equilibrium is achieved ($\text{mg}\cdot\text{g}^{-1}$), respectively.

The Shell Progressive Model (SPM) was selected to describe the ammonium removal kinetics. The SPM describes the sorption process by a concentration profile of the solution containing ammonium ions advancing into a partially saturated spherical particle [14]. The extraction mechanism involves diffusion of ammonium from the solution to the zeolite phase through a number of possible resistances. Ammonium originally present in solution must diffuse across the liquid film surrounding the zeolite particle, transfer across the solution particle interface, diffuse into the zeolite particle bulk and possibly interact with negative charged sites on the zeolite particles. The ammonium removal rate controlling the different steps on the Z-Na particles leads to *Equations 7.4–7.6*:

$$\text{a) Liquid film diffusion control: } X(t) = \frac{3C_{N(s)}K_F}{a_s C_{N(z)}} t \quad [\text{Eq. 7.4}]$$

$$\text{b) Particle diffusion control: } \left[3 - 3(1 - X(t))^{\frac{2}{3}} - 2X(t) \right] = \frac{6D_e C_{N(a)}}{a_s^2 C_{N(z)}} t \quad [\text{Eq. 7.5}]$$

$$\text{c) Ion-exchange reaction control: } \left[1 - (1 - X(t))^{1/3} \right] = \frac{K_s C_{N(s)}}{r} t \quad [\text{Eq. 7.6}]$$

where D_e is the effective diffusion coefficient of ammonium ions in the Z-Na ($\text{m}^2 \cdot \text{s}^{-1}$); r is the radius of the Z-Na particle assumed to be spherical (m); $C_{N(s)}$ and $C_{N(z)}$ are the ammonium concentrations in the bulk solution and in the zeolite unreacted core, respectively ($\text{mg} \cdot \text{L}^{-1}$); a_s is the stoichiometric coefficient, and k_s ($\text{m}^2 \cdot \text{s}^{-1}$) is the chemical reaction constant.

Extraction kinetic data were analysed graphically by using the fractional attainment of equilibrium equations [$F(X) = f(t)$] (Equations 7.4–7.6) and the kinetic parameters were estimated by regression analysis.

7.3. Results and discussion

7.3.1. Ammonium removal capacity of the sodium-zeolite: equilibrium characterisation

Chemical composition of the tested zeolite sample (wt.%) is shown in *Table 7.2*. Energy Dispersive X-ray Spectroscopy (EDX) analyses of natural and the zeolite in the sodium form revealed the presence of aluminium (Al), silicon (Si), oxygen (O), iron (Fe), sodium (Na), magnesium (Mg), potassium (K) and calcium (Ca) as the main elements (*Table 7.2*). In raw zeolite, K^+ and Ca^{2+} are the principal exchangeable cations. The conversion into the Na-form is an effective process as the Na^+ increases up to 1.6%, while K^+ and Ca^{2+} content were reduced up to a 50%.

Mineralogical analysis showed that clinoptilolite is the main mineral phase for both natural and Na-activated zeolites and small percentages of quartz and albite were also detected. The zeolite specific surface area was slightly reduced from 20 ± 0.5 to $19 \pm 0.5 \text{ m}^2 \cdot \text{g}^{-1}$ after conversion to the Na-form as reported by Sprynskyy et al. (2005) [15] for a natural zeolite (Transcarpathia clinoptilolite). FSEM showed crystal clusters with homogeneous crystal size distribution and characteristics plate-like crystals and large entries and cavities to the zeolite framework channels for both zeolites. The presence of small particles covering the surface and lamellar-like crystals in the activated Na-form confirms the partial surface modification of clinoptilolite.

Table 7.2. Chemical composition of tested zeolite samples: raw natural zeolite (Z-N) and sodium zeolite form (Z-Na).

Element	Z-N	Z-Na
Si	29.4±1.9	29.3±1.8
O	56.9±2.4	59.2±1.7
Al	5.2±0.2	5.4±0.3
Fe	1.7±0.3	0.8±0.2
Na	0.3±0.1	1.6±0.3
K	3.0±0.6	1.7±0.4
Ca	2.0±0.4	1.1±0.2

The ammonium sorption capacity on Z-Na zeolite showed pH dependence in solutions of ammonium with competing ions (*Figure 7.2*) simulating the expected conditions of treated domestic wastewater effluent incorporating a high rate activated sludge stage (pH 7 to 8.5) and during regeneration cycles (acid and basic pH values).

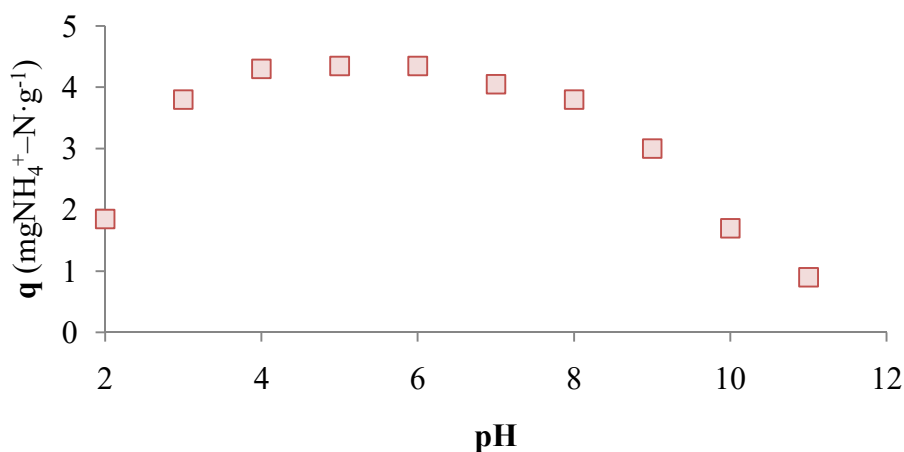
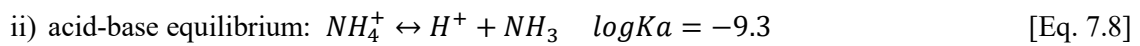
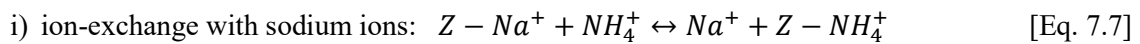


Figure 7.2. Effect of the pH on ammonium removal for the sodium-zeolite form (Z-Na) using batch experiments.

The $\text{NH}_4^+/\text{Na}^+$ exchange process reaches its maximum at the pH range between 4 and 6. According to the zeolite acid-base properties with a pH_{PZC} of 4.9 ± 0.3 (Z-Na), repulsion of ammonium ions with the surface protonated ion-exchange sites was observed below the pH_{PZC} (e.g. in the acid range from pH 2 to pH 3). Sprynskyy et al. (2005) [15] studied the effect of

acidic conditions (e.g., in hydrochloric acid) on a natural clinoptilolite. Na^+ , Ca^{2+} and K^+ were removed from the zeolite by exchange with protons (H^+ ions) and subsequent zeolite analysis shown the destruction of the clinoptilolite structure by mineral dissolution processes as demonstrated the presence of aluminium and silicon in solution.

Then, the maximum ammonium sorption capacity values were measured in the pH range of 4 to 7 and a progressive reduction of sorption capacity was observed at pH above 7 due to the decrease of the ammonium concentration and the conversion to the neutral form (NH_3) [16]. Then, the acid-base equilibria play a major role and the ammonium sorption can be described by the combination of two reactions (*Equations 7.7–7.8*):



where Z^- represents the inorganic groups of the zeolite structure.

According to *Equation 7.8*, ammonium sorption is pH-dependent and it stands that only ions can be removed from solution by ion-exchange with sodium ions. At pH 8 and below, ammonium is present in the cationic form (NH_4^+); therefore, these acidity conditions favour the removal process. Above pH 8 the equilibrium shifts towards the ammonia form and more basic conditions become increasingly less favourable. Thornton et al. (2007) [17] described a reduction of ammonium capacity of mesolite from $49 \text{ mgNH}_4^+ - \text{N} \cdot \text{g}^{-1}$ at pH 6–7 to $37 \text{ mgNH}_4^+ - \text{N} \cdot \text{g}^{-1}$ at pH 8.3 and to $29 \text{ mgNH}_4^+ - \text{N} \cdot \text{g}^{-1}$ at pH 10. This reduction of ammonium removal is used to promote zeolite regeneration and the increase of pH above 11 by using NaOH solutions is adequate to displace reaction 7 to the conversion to the sodium form.

The FTIR spectra showed peaks between 798 and 547 cm^{-1} assigned to deformation vibration modes of O–H, Al–O–Si and Si–O–Si groups. A band at $1,100 \text{ cm}^{-1}$ is attributed to the stretching vibration mode of Si–O groups and the band at $1,630 \text{ cm}^{-1}$ was assigned to the deformation vibration mode of O–H groups of water molecules. Bands in the range from $3,700$ to $3,100 \text{ cm}^{-1}$ have been associated with the O–H groups of the zeolitic structure [18]. The small differences in the spectra of both zeolites are consistent with the exchange between cations of the same valence.

Ammonium sorption isotherms (in single ammonium solutions and in solutions simulating treated wastewater effluents) at constant pH of 8.0 ± 0.2 are shown in *Figure 7.3*. The Langmuir isotherm provided a good description of the ammonium sorption ($R^2 \geq 0.99$) at pH 8, where over 95% of the total ammonium is present as ammonium (e.g. 5% as ammonia). Results

indicated that the sorption process although mainly driven by an ion-exchange, can be described by a solid with a homogeneous monolayer with ion-exchange of equal availability affinity. The maximum ammonium sorption capacity was $23.4 \pm 0.8 \text{ mgNH}_4^+-\text{N} \cdot \text{g}^{-1}$ in single ammonium solutions, compared with $18.7 \pm 0.9 \text{ mgNH}_4^+-\text{N} \cdot \text{g}^{-1}$ for solutions simulating treated wastewater effluents. Higher values were reported by Guaya et al. (2015) [13;19] working with solutions at pH range from 5 to 6, with over 99% of the total ammonium present as NH_4^+ .

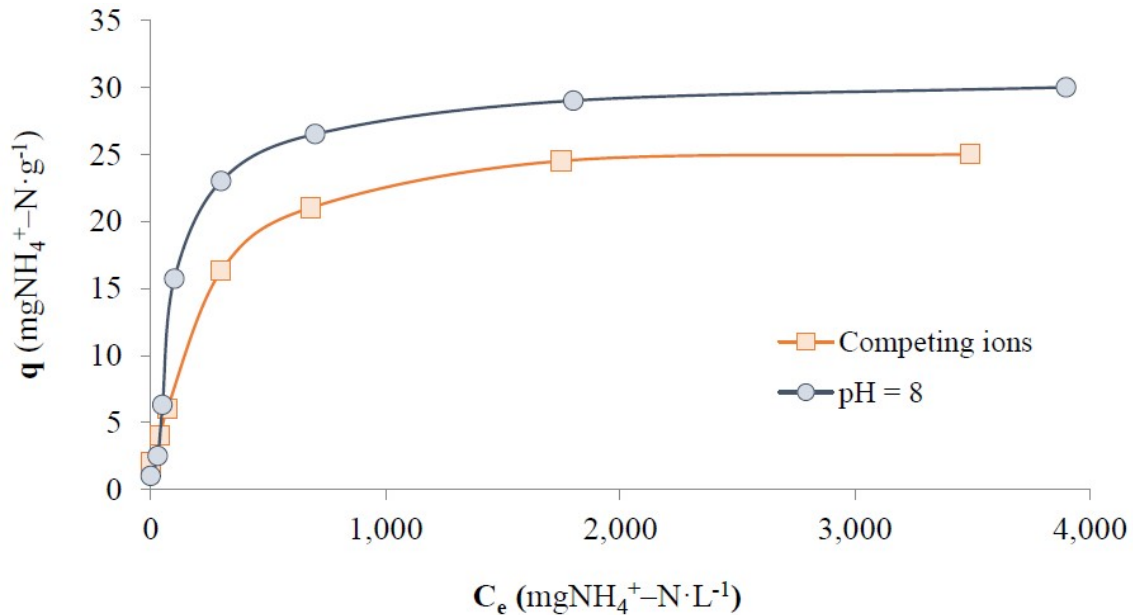


Figure 7.3. Ammonium loading isotherms on Z-Na zeolite in single ammonium solutions and in wastewater effluents containing competing cations at pH 8.

The ion-exchange selectivity of the exchange process is considered mainly affected by the ionic radius and the ionic charge. The sodium ion Stokes hydration ionic radius is higher than ammonium ion providing selectivity differences for the exchange of $\text{Na}^+/\text{NH}_4^+$ that ensure high ammonium removal efficiency [20,21].

Measured ammonium sorption capacities are comparable to those reported by Thornton et al. (2007) [22], using mesolite for the removal of ammonium from digested sludge dewatering liquors (e.g. $200\text{--}700 \text{ mgNH}_4^+-\text{N} \cdot \text{L}^{-1}$) with values between 27 and $36 \text{ mgNH}_4^+-\text{N} \cdot \text{g}^{-1}$. Similar, capacity was reported for a large number of studies using clinoptilolite-rich natural zeolites. Farkas et al. (2005) [23], using a Croatian clinoptilolite measured the total maximum capacity of $7 \text{ mgNH}_4^+-\text{N} \cdot \text{g}^{-1}$ and an operational capacity at the breakthrough of $4 \text{ mgNH}_4^+-\text{N} \cdot \text{g}^{-1}$. Guaya et al. (2015) [13,19] reported capacities of $30 \text{ mgNH}_4^+-\text{N} \cdot \text{g}^{-1}$ also for metal hydrated oxide modified clinoptilolite. Thornton et al. (2007) [17] described higher operational capacities of 39

$\text{mgNH}_4^+-\text{N}\cdot\text{g}^{-1}$ of mesolite in experiments carried out under optimal conditions (e.g. during the first operation cycles). Wang and Peng (2010) [24], in a comprehensive review on ammonium removal by natural zeolites, concluded that the adsorption capacity of clinoptilolite ranges between 2 and 30 $\text{mgNH}_4^+-\text{N}\cdot\text{g}^{-1}$. Some chemical pre-treatments of clinoptilolite may increase its sorption capacity. The ion-exchange order for ammonium, alkali and alkaline earth metals follows: $\text{K}^+ > \text{NH}_4^+ > \text{Ba}^{2+} > \text{Na}^+ > \text{Ca}^{2+}$. However, other ionic species such as transition metal ions and organic solutes could decrease ammonium sorption capacity due to competitive sorption.

7.3.2. Ammonium sorption kinetics by sodium activated zeolites (Z-Na)

Ammonium sorption of sodium activated zeolites (Z-Na) (q_t) over time is shown in *Figure 7.4*. The ammonium sorption rates are comparable with other natural and synthetic zeolites reaching the equilibrium in below 10 min [7,25]. These sorption rates are much faster than the sorption kinetics of ammonium using polymeric ion-exchange resins. This behaviour is attributed to the fact that the ion-exchange reaction ($\text{NH}_4^+/\text{Na}^+$) is favoured due to the higher affinity of ammonium ions to the negative sites than sodium ions as has been described by Ashrafizadeh et al. (2008) [26] using an Iranian natural clinoptilolite.

Analysis of the fractional equilibrium attainment functions [$F(X)=f(t)$] (*Equations 7.4–7.6*) indicated that sorption rate control of ammonium ions is particle diffusion. The first stage of ammonium diffusion from the solution to the external zeolite surface is followed by a sorption stage along the zeolite internal surface. The linear regression coefficients (R^2) values are closer to 1 for *Equation 5* considering particle diffusion as the rate determining step and the diffusion coefficients calculated ranged from 1.1 to $3.4\times 10^{-12} \text{ m}^2\cdot\text{s}^{-1}$. These values are consistent with the results reported for ammonium sorption on natural clinoptilolite impregnated with metal hydrated oxides [13,19] at low initial ammonium concentrations and with diffusion coefficients determined on the removal of heavy metals by natural zeolites [23,25]. Measured kinetic parameters were also comparable with synthetic powder zeolites produced from coal combustion fly ash [27].

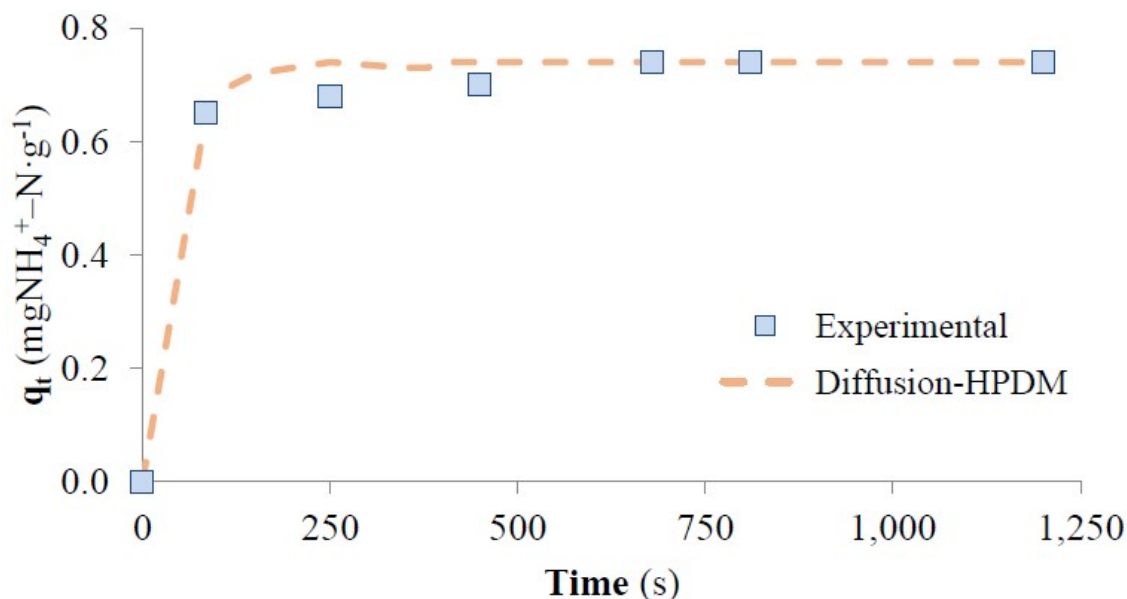


Figure 7.4. Variation of ammonium removal as a function of contact time for single ammonium solutions at pH 8. Points represent experimental data and the trend line is the predicted values assuming particle diffusion control for the sodium-activated zeolite (Z-Na).

7.3.3. Removal of ammonium in fixed bed column tests

The ammonium breakthrough curves for two consecutive cycles are shown in *Figure 7.5*. The ammonium sorption capacity at 120 BV was 21 mgNH₄⁺-N·g⁻¹ in the first cycle compared with 20 mgNH₄⁺-N·g⁻¹ in the second cycle. Dynamic ammonium sorption capacity is comparable with the effect reported for other zeolites [7,25]. More limited capacity (below 2 mgNH₄⁺-N·g⁻¹) was measured for the raw zeolite without being converted to the sodium form (data not shown) and only when zeolites are regenerated by concentrated NaOH solutions, the sorption capacity was improved in the following cycles when values of approximately 20 mgNH₄⁺-N·g⁻¹ were reached.

Sprynskyy et al. (2005) [15] studied ammonium removal from synthetic solutions onto natural and pre-treated forms of a natural clinoptilolite under dynamic conditions. Sodium ions were easily exchanged with ammonium, however, the role of calcium increased with zeolite saturation by ammonium. The maximum ammonium sorption capacity estimated under dynamic conditions was significantly higher than that measured under static conditions. Thermal or chemical (e.g. acid, base and sodium salts) pre-treatment of the raw zeolite confirmed the importance of the ion-exchange mechanism. NaCl pre-treatments showed the most efficient improvement of ammonium removal over other treatments.

Ammonium desorption from loaded Z-Na was performed using 0.05 NaOH solution, as shown in *Figure 7.6*. The highest ammonium concentration achieved in the regeneration solution was

2,900 mgNH₄⁺-N·L⁻¹. The 95% of the eluted ammonium was found at 3 BV representing an enrichment factor of 30.

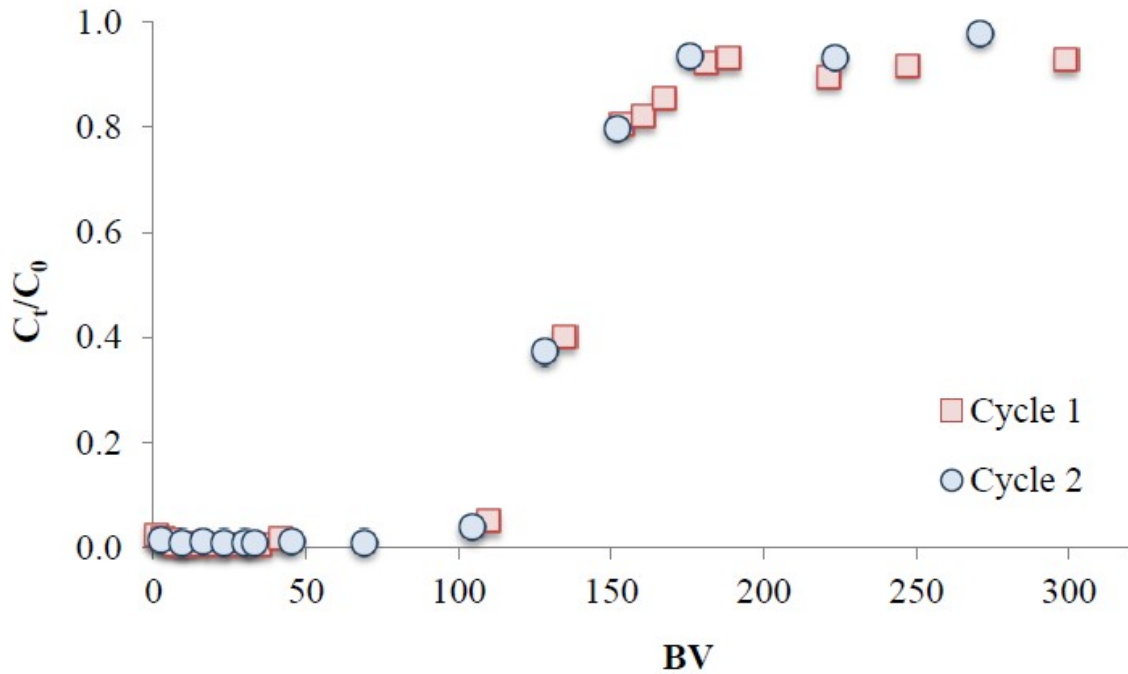


Figure 7.5. Breakthrough curves of ammonium sorption by the granular zeolite in the sodium form (Z-Na). Treated solution contained 115±3 mgNH₄⁺-N·g⁻¹ pumped at a flow rate of 1.5 mL·min⁻¹.

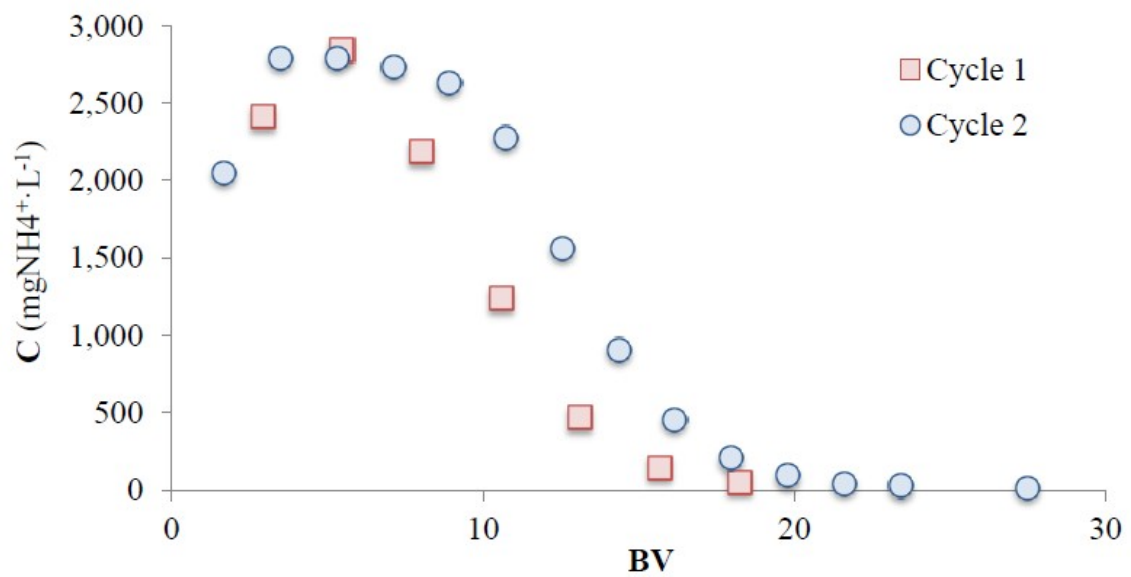


Figure 7.6. Column desorption profile of ammonium from granular loaded Z-Na (breakthrough curves of Figure 7.5) using 2 gNaOH·L⁻¹.

NaCl or NaOH solutions are the most commonly used regeneration solutions for loaded zeolites. Rahmani et al. (2004) [28] described constant regeneration ratios of 95–98% after three loading-regeneration cycles of natural Chinese clinoptilolite, by using a solution of NaCl and without loss of ammonium sorption capacity. Hlavay et al. (1982) [29] also reported regeneration ratios of 98–99% of a Chinese clinoptilolite using a $20 \text{ g}\cdot\text{L}^{-1}$ NaCl solution at $\text{pH}=12.3$. Malovanyy et al. (2011) [30] evaluated the concentration of ammonium from domestic WWTP mainstream before biological treatment with an ion-exchange process. The two-stage treatment line, referred as Ion Exchange assisted CANON (IE–CANON) process showed that using strong-acid cation (SAC) resin and NaCl as regenerant leads to the best results in terms of ammonium concentration and regeneration. However, it should be noted that this study was performed using synthetic wastewater solutions and it is unknown if the ammonium concentration step from real wastewater streams will proceed the same as when synthetic wastewater is used since the content of other ions and pH can influence the process. Moreover, since not only ammonium but also other cations are concentrated, it is unknown if these ions will not inhibit the biological process.

7.3.4. Ammonium recovery from zeolites regeneration concentrates by using hollow fibre membrane contactors

The ammonium zeolite regeneration concentrates were used as the input stream to a liquid-liquid membrane contactor unit to recover and concentrate ammonium solutions. The influence of operation parameters (flow rate, initial ammonia concentration and stripping acid concentration) was evaluated using a closed-loop configuration. The reduction of the ammonia concentration ratio (C/C_0) in the feed tank as a function of time for feed solutions of 0.5 and 1.5 $\text{gNH}_3\cdot\text{L}^{-1}$ is shown in *Figure 7.7*.

The closed-loop set-up allowed ammonia recovery ratios higher than 98%, and ammonia residual concentration values below $150 \text{ mg}\cdot\text{L}^{-1}$ if the required free acid concentration in the stripping phase is maintained constant along the filtration experiment.

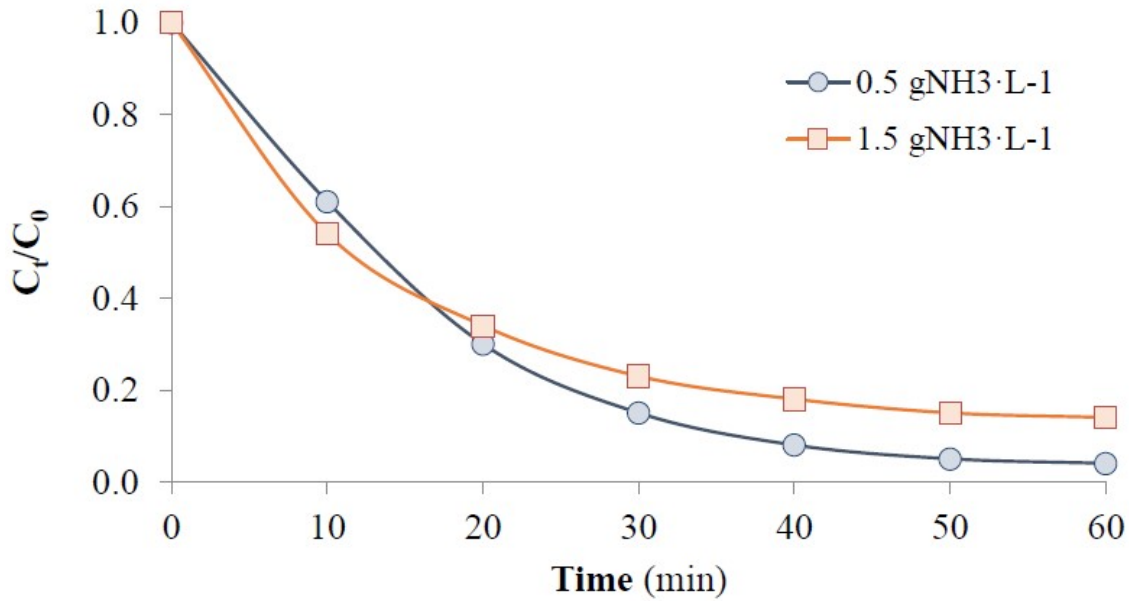


Figure 7.7. Variation of the ammonia concentration ratio (C_t/C_0) as a function of time for experiments at $1.2 \text{ g}\cdot\text{L}^{-1}$ NaOH concentrations at flow rates of 9 and $11 \text{ cm}^3\cdot\text{s}^{-1}$ and using nitric acid (0.5%) as stripping solution.

The ammonia mechanism transport from the feed stream (zeolites regeneration concentrates at pH 11–12) in a HFLLMC involves the transfer from the feed to the stripping phase driven by the differences of ammonia partial pressure between both sides and conversion to NH_4NO_3 and $(\text{NH}_4)_2\text{HPO}_4$ as described by *Equations 7.9–7.13*:



where the subscript index f represents feed stream and s represents stripping stream.

Reactions 7.12 or 7.13, depending on the acid used as stripping solution, ensure the highest difference in ammonia partial pressure between both sides of the membrane and thus provides the chemical potential which drives the separation process.

The ammonia transport process (*Equations 7.9–7.12*) is a very fast step and, in less than 30 minutes, more than 80% was removed. The ammonia flux decreases as membrane filtration time increases due to the reduction in the ammonia concentration in the feed side, and accordingly

the ammonia partial pressure. The total ammonia removal efficiency was 85% for $1.5 \text{ g}\cdot\text{L}^{-1}$ and 98% for $0.5 \text{ g}\cdot\text{L}^{-1}$ within 60 minutes, respectively. *Figure 7.7* shows the ammonia concentration ratio (C/C_0) decrease with typical exponential decay behaviour. In the first step of the removal process, the ammonia gas form ($\text{NH}_{3(\text{g})}$) diffuses from the bulk of the feed stream to the feed-membrane interface (*Equation 7.9*). Then, $\text{NH}_{3(\text{g})}$ volatilizes through the feed-membrane interface and diffuses across the air-filled pore of the polypropylene membrane (*Equations 7.10–7.11*). Finally, it reacts at the membrane-strip interface of the shell side with HNO_3 or H_3PO_4 (*Equations 7.12–7.13*). This reaction is thermodynamically favoured as it involves the neutralization of ammonia with a strong acid.

A critical point of the operational mode for HFLLMC is the presence of $\text{NH}_{3(\text{g})}$, which can traverse the pores in the polypropylene hydrophobic membrane. Consequently, the application of this HFLLMC technology for wastewater can only be feasible if the treated aqueous stream is alkaline. In principle, the pH should be above the $\text{pK}_a (\text{NH}_4^+/\text{NH}_3) = 9.3$. Under basic conditions (pH 11 to 12), where over 99.9% of ammonium is present as ammonia, mass transfer of NH_{3f} is only controlled by the free acid concentration in the stripping side and controlled by the neutralization reactions (*Equations 7.12–7.13*). Thus, free acid concentration in the stripping compartment is the main driving force enhancing ammonia extraction from the feed solution.

The pH (12.2 ± 0.3) of the feed stream (data not shown) was kept constant along the experiment as the buffer capacity of the background NaOH solution ($1.2 \text{ g}\cdot\text{L}^{-1}$ NaOH) is buffering any potential change of pH due to the transfer of ammonia from the feed to the stripping side. Measured values along the extraction tests were below 0.2 pH units. The treated solutions containing residual ammonia concentrations, between 15 and $150 \text{ mgNH}_3\cdot\text{L}^{-1}$, could be suitable for re-use as regeneration solutions of zeolites columns.

The membrane contactors performance for ammonia recovery using H_3PO_4 was evaluated ensuring an excess of acid in the stripping side. Solutions were obtained from elution of ammonium-saturated zeolites loaded using treated effluents from Sant Feliu WWTP and using $2 \text{ g}\cdot\text{L}^{-1}$ NaOH solutions. Concentrated solutions of ammonia from four cycles ranged from 2.1 to $2.7 \text{ gNH}_3\cdot\text{L}^{-1}$ were fed in the closed loop configuration reporting recoveries between 95 and 98% as could be seen in *Figure 7.8*. The transported ammonia was converted to $(\text{NH}_4)_2\text{HPO}_4$ solution in the stripping phase reaching concentrations up to $11 \text{ gNH}_4^+\cdot\text{L}^{-1}$.

Similar results were obtained using a 0.4 M HNO_3 as stripping stream (data not shown). After four cycles, a solution of $17 \text{ g}\cdot\text{L}^{-1}$ of NH_4NO_3 was obtained. The quality of the by-products (incorporated in the zeolites adsorption-elution step) is high as the transport of metal ions on the HFLLMC is restricted by the hydrophobic membrane properties.

The exhausted NH_3/NaOH streams, once ammonia is removed, can be re-used for regeneration of the ammonium-loaded zeolites. The quality of the ammonium phosphate product obtained and its market analysis needs to be also evaluated. Garcia-González and Vanotti (2015) [31] reported that hydrophobic membranes reject undesirable species to fertilizer product stream, but other considerations as the fertilizer concentration range which is useful and achievable must be considered. In relation to the value proposition for the fertilizer product, factors such as the risks associated with losses of fertilizer by evaporation and the transport costs should also be incorporated in the economic assessment.

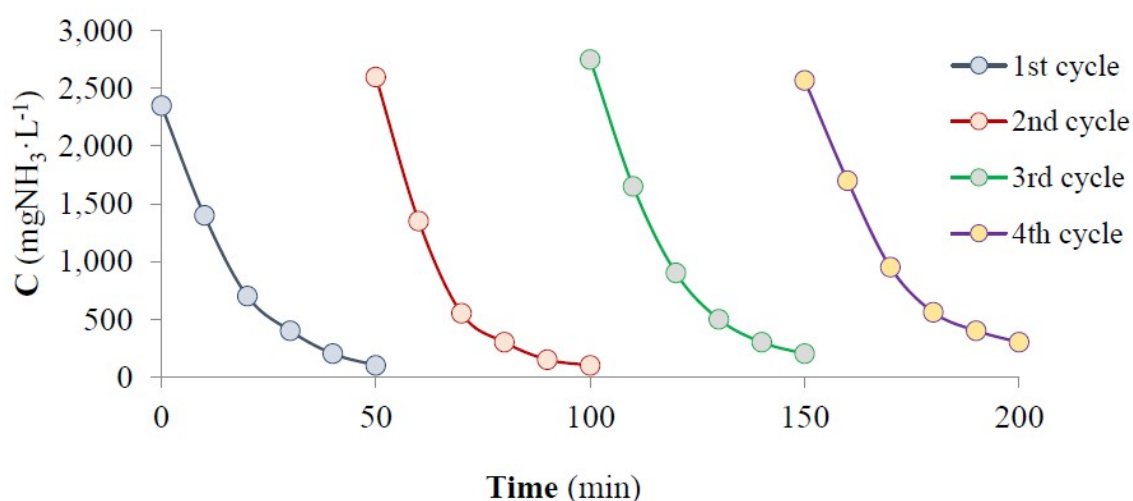


Figure 7.8. Ammonia (NH_3) concentration profile in the feed phase as a function of time for four consecutive cycles using concentrates ($2.1\text{--}2.7 \text{ gNH}_3\cdot\text{L}^{-1}$ and $2 \text{ gNaOH}\cdot\text{L}^{-1}$) at flow rates of $0.5 \text{ L}\cdot\text{min}^{-1}$ with an initial phosphoric acid concentration of 0.4 M as stripping phase.

7.4. Conclusions

The implementation of pre-concentration techniques for achieving energy neutral sewage treatments increases the efficiency of primary sedimentation; however, its implementation as a mainstream sewage treatment requires further post-treatment, due to the missing ammonium removal. This study evaluated the use of zeolite sorption process as a post-treatment for the novel pre-concentration processes. The use of natural zeolites as a precursor of a selective sorbent of ammonium from treated effluents was evaluated in batch and fixed bed experiments. Equilibrium and kinetic parameters were improved after the conversion of the natural zeolite to the sodium form. Results obtained shown promising performance when compared with

available data in the literature for natural clinoptilolite zeolite in terms of selectivity, regeneration and reusability.

Higher enrichment factors allowed obtaining NH_3/NaOH concentrates that can be used to produce potential liquid fertilizers by using HFLLMC.

Trials with HNO_3 and H_3PO_4 acids in HFLLMCs demonstrated a total nitrogen recovery capacity above 95% if an excess of free acid is present in the stripping stream. This solution avoids the use of low-cost common acids (e.g. H_2SO_4 and HCl) as ammonia collectors, providing rich NH_4NO_3 and $(\text{NH}_4)_2\text{HPO}_4$ with high added value as fertilizers. The quality of these by-products, in terms of the absence of transition metal and non-metal ions or organic micro pollutants (e.g. potentially incorporated in the zeolites sorption-elution step), is high as their transport on the hydrophobic HFLLMC is restricted by the membrane properties only supporting solutes in gas phases. The exhausted NH_3/NaOH streams once ammonia is removed can be re-used for regeneration of the ammonium exhausted zeolites filters.

Taking into account the results obtained in the present work, the use of conventional stripping process (e.g. air-stripping) for the regeneration of zeolites is seen as a waste of energy and chemicals and moreover, the process involves the generation of a secondary pollution that requires further treatment. Then, the validated solution integrating a HFLLMC provides an environmentally friendly (less energy intensive) alternative solution.

7.5. References

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CHAPTER 8

*Environmental and economic assessment:
Guidelines for implementation*

8. Environmental and economic assessment: Guidelines for implementation

8.1. Introduction

Wastewater treatment plants (WWTPs) have been designed and operated to reduce pollution on environmental ecosystems. However, WWTPs bring many adverse environmental impacts related to chemicals and energy consumption, gas emissions, as well as the generated sludge, which requires additional treatment [1]. Thus, to reach the equilibrium of sustainability (or even a positive balance), these impacts should not exceed the benefits of its operation.

On the other hand, some research studies have shown that a conventional WWTP has an overall cost (capital and operational expenditure) of about 17–30 € per inhabitant equivalent (IE) per year for large plants (>100,000 IE) and 30–40 €·IE⁻¹·year⁻¹ for smaller plants (10,000–50,000 IE) [2]. About 30–38% of these amounts correspond to operational costs, of which sludge treatment and disposal account for up to 40%.

Under this paradigm, we are forced to rethink and redesign the way we deal with water resources in the future. This thesis has evaluated a new wastewater treatment train focused on carbon (C) redirection and nitrogen (N) recovery. It is an example of an A/B process, a cost-effective configuration able to maximise the carbon recovery of organic compounds from wastewater and its conversion to biogas (A-stage) while reducing nutrients concentration to accomplish with the discharge regulations (B-stage). In the case of proposed innovative WWTP configuration, A-stage consists of carbon redirection, a high loaded biological process operated under specific operational conditions that promote the adsorption of carbon into the sludge and minimize its mineralization (see *Chapters 2 and 4*). The liquid effluent from this A-stage, once treated and adapted to the required quality, is fed to the B-stage, a physico-chemical process based on ion-exchange, in which nitrogen is adsorbed into zeolites, a natural occurring material with high affinity for ammonium, that could provide an ammonia-rich solution suitable for ammonium salts production (see *Chapters 2 and 7*).

This chapter provides a comparative environmental and economic assessment between the innovative technologies proposed in this thesis (carbon and nutrients recovery) and a conventional scenario based on an activated sludge (CAS) process with carbon and nitrogen removal. Additionally, some strategies or guidelines for the further implementation of the innovative technologies considering both greenfield (new construction plants) and brownfield (update existent plants) scenarios are provided.

8.2. Methodology

8.2.1. Case studies

The environmental and economic assessments included in this chapter are based on the comparison between the reference scenario and the innovative WWTP flowsheet on which this thesis is based. A more detailed description of both of them is given in *Chapters 2, 4 and 6*.

- *Reference scenario: CAS system with carbon and nitrogen removal.* Real operational data from Vilanova WWTP has been obtained to do the calculations of the reference scenario. However, this is a coastal plant and therefore nitrogen is not removed from wastewater but discharged into the sea with the effluent. In order to make this reference scenario comparable to the innovative flowsheet (in terms of effluent quality), some hypothesis and estimated calculations (based on bibliography references and Vilanova operational data) have been considered:
 - The increase of 19.4% of the electricity consumption in the biological reactor for higher aeration required for nitrification-denitrification.
 - Direct emissions of nitrous oxide (N₂O) during denitrification processes. It represents 0.05% of the nitrogen removed from wastewater [3].
 - Effluent quality would meet the environmental standards for sensitive areas: 10 mgN·L⁻¹ [4].
- *Innovative WWTP flowsheet.* The assessment of the innovative scheme is based on the scaling-up of the prototypes operated to treat the same flow rate than the reference scenario (25,500 m³·day⁻¹). Results from the operation of the pilot plant (such as electricity and chemicals consumption, regeneration capacity, pollutants removal, etc) have been used to assess the operational costs, together with some assumptions and estimations (see *Sections 8.2.5 and 8.2.6*), based on previous literature research or networking activities with similar projects. The local assumptions can have an important effect on further evaluations. For example, the electricity mix is very country-dependent and can significantly affect the results when assessing processes with high electricity consumption. In this case, the emission factor and the cost considered are 0.34 kgCO₂·kWh⁻¹ and 0.1 €·kWh⁻¹, respectively [5].

8.2.2. Life Cycle Assessment (LCA)

The environmental analysis was performed using Life Cycle Assessment (LCA), a standardized methodology used for the estimation of environmental impacts of a product or system throughout its life cycle, considering the extraction of resources, transportation, production, use, recycling and discarding of products [6]. LCA has been proved to act as a desirable tool to evaluate the environmental effects of WWTPs in both design and operation phases [7]. The leading standards for LCA are ISO 14040 and ISO 14044 [8]. These international standards focus mainly on the process of performing an LCA, an iterative process consisting of four steps:

- *Step 1: Definition of goal and scope of the study.* Definition of the LCA purpose, a functional unit to allow for comparisons, system boundaries, criteria on how allocation problems will be solved, data quality requirements and limitations and hypothesis took.
- *Step 2: Life Cycle Inventory (LCI).* Experimental and operational data from the prototypes operation and also real data from the reference scenario (energy and raw materials consumed, emissions to air, water, soil and solid waste produced by the system under study) are split up into several subsystems and unit processes. The data obtained are grouped into different categories in a LCI table relating them to the functional unit of the study to create a database (*Table 8.1*). Commercial databases that include inventories of many processes will also be used for processes (e.g. the energy generation in Spain) to apply the LCA methodology.
- *Step 3: Life Cycle Impact Assessment (LCIA).* The LCIA phase involves sorting together all substances of the LCI table that contribute to a particular type of environmental impact, consisting of the three following steps: (1) Classification (mandatory), (2) Characterization (mandatory), and (3) Normalization, aggregation and weighting (optional). There are different methods to assess the environmental impact. The characterization method chosen has been the ReCiPe method [9], which determines indicators at two aggregation levels, which can be selected by the user in the LCA software (*Simapro*), allowing the user to choose between environmental impact indicators (robust indicators, but difficult to interpret) or damage indicators (more uncertain indicators, but easier to interpret). *Table 8.1* shows the impact categories used for the characterisation method selected.
- *Step 4: Results interpretation.* In this last phase of LCA, it is necessary to outline conclusions, explain the limitations that have occurred, and provide recommendations.

Table 8.1. Environmental impact categories considered during the dissertation.

LCA impact category	Unit	Definition
Climate Change	kg CO ₂ -eq	Related to emissions of GHG into air expressed as for time horizon of 100 years.
Ozone depletion potential	kg CFC-11-eq	Relative measure for the potency to form Equivalent Effective Stratospheric chlorine.
Terrestrial Acidification	kg SO ₂ -eq·m ⁻³	Changes in soil chemical properties following the deposition of nutrients in acidifying form.
Marine Eutrophication	kg P-eq·m ⁻³	Environmental persistence (fate) of the emission of phosphorus (P) containing nutrients.
Human Toxicity	kg 1,4-DB	Accounts for the accumulation in the human food chain (exposure) and toxicity (effect) of a chemical.
Terrestrial Ecotoxicity	kg 1,4-DB	Impacts of toxic substances on terrestrial ecosystems.
Fossil Depletion	kg oil-eq·m ⁻³	Amount of extracted fossil fuel extracted, based on the lower heating value.

8.2.3. Life Cycle Costing (LCC)

An economic evaluation was carried out through the Life Cycle Costing (LCC) methodology. LCC is an approach to assess all the costs that will be incurred by an asset or service over its entire life cycle: purchase price and all associated costs (delivery, installation, insurance, etc.); operating and maintenance costs (including electricity, fuel and chemicals, waste generation, expected benefits, repositions, and labour force); and end-of-life costs (such as decommissioning or disposal). This iterative process consists of five steps:

- *Step 1: Alternatives assessed.* Definition of the LCA purpose (aim and scope), a functional unit to allow for comparisons, discount rate and costs allocation.
- *Step 2: Life Cycle Costing Inventory (LCCI).* It refers to construction, operation and maintenance and end disposal. Economic and operational data of both scenarios are gathered as LCCI input data (e.g. construction cost, electricity consumption, chemicals construction, sludge management, etc.). In case of purchase, data are not available, official statistics and providers databases are used.

- *Step 3: Aggregation costs.* The aggregation of the following elements (annual values) by stages and by categories gives as result the life cycle costing.

Construction costs (CAPEX): capital expenditures related to investment (materials and equipment). Since investment in assets is done in punctual moments but its benefits last for many years, LCC has a temporal component. To quantify investment costs annually, the Annual Equivalent Cost (AEC) of construction costs is obtained according to *Equation 8.1*.

$$AEC = \frac{CAPEX}{\frac{1 - (1 + i)^{-n}}{i}} \quad [\text{Eq. 8.1}]$$

where, n = time horizon or life span; i = discount rate.

Operation and maintenance cost (OPEX): it includes the expenses needed to operate and maintain the system assets annually: materials and reagents, energy consumption (electricity, gasoil), waste and sludge final disposition, replacement and maintenance of the assets and labour force.

- *Step 4: Monetization of environmental impacts.* According to European Commission [10], several methodologies for monetizing environmental impacts can be applied depending on the characteristics of the good to be valorised (e.g. nutrients recovery is valorised by the market price of ammonium salts).
- *Step 5: Results interpretation.* The economic assessment is based on LCC results analysis and monetization of impacts.

8.2.4. Functional unit (FU)

The primary purpose of a FU is to provide a reference to which the inputs and outputs of the systems are related to ensure that such comparisons are made on a common basis. Thus, FU chosen is the treatment of 1 m³ of wastewater.

8.2.5. Boundaries

Based on a literature review of LCA boundaries in wastewater treatment plants the system boundaries have been defined.

- Electricity consumption. Pumping to submarine emissary, deodorization and general electricity consumption (illumination, air conditioning, control panel, sensors...) are out of the scope of the present LCA.
- Chemicals consumption. The consumption of chemicals in the conventional scenario is associated with the use of polymers for sludge dewatering and iron-salts (iron trichloride; FeCl_3) for removal of hydrogen sulphide in the anaerobic digester. In the innovative scheme, chemicals are also consumed in the solids separation unit considered before the zeolites unit and for zeolites regeneration.
- Transports. The distances calculation (between chemical suppliers and the plant as well as between the plant and the final destiny of sludge (agriculture) has been done using tonne-kilometre factor, which takes into account the total (yearly) consumption of the chemical or the yearly sludge production, the capacity of the lorry or the vehicle used for its transport, and the distance to be travelled. Regarding vehicles, it has been considered the applicable Euro 4 regulation (defined in Directive 98/69/EC and 2002/80/EC).
- Infrastructure. Differences between the equipment in both scenarios have taken into account. On the other hand, the dismantling phase together with the manufacturing process of the different units has not been considered, as literature studies have shown that it is not relevant for the total results [11].
- Sewage sludge. The use of sludge in agriculture considers an avoidance of chemical fertilizers based on a substitutability of 70% for phosphorus and 50% for nitrogen. Moreover, the metal content in the dewatered sludge was assumed to be introduced to agricultural soil. Emissions to air (methane, CH_4 ; ammonia, NH_3 ; and N_2O) and to water (nitrate, NO_3^- , to groundwater; phosphate, PO_4^{3-} , and NO_3^- to surface water bodies) from sludge application were also taken into account based on the experimental results from Bruun et al. (2016) [12] and the work of Yoshida et al. (2018) [13].
- Fugitive emissions. An average value of 2% of CH_4 losses has been considered [14–16].
- Carbon monoxide (CO) and nitrogen oxide (NOx) emissions of the combined heat and power (CHP) unit. The following emissions of greenhouse gases (GHGs) from the biogas combustion have been considered for the cogeneration unit: carbon dioxide (CO_2) = 0 (C neutral); $\text{CO} = 1.99 \cdot 10^{-5} \text{ kg} \cdot \text{MJ}^{-1}$; $\text{NO}_x = 2.67 \cdot 10^{-4} \text{ kg} \cdot \text{MJ}^{-1}$ [17].

- Direct emissions. Overall emissions of N₂O are included for the reference scenario. They are not considered in the innovative flowsheet because they are not expected to occur.

8.2.6. Considerations for implementation

The key parameters that have to be taken into account when considering replication of the innovative treatment configuration are:

- Wastewater composition. The concentration of the target components (carbon and nitrogen) in wastewater will be essential for the economic feasibility of the technology. In countries with high annual precipitation, wastewater is more diluted and therefore the potential revenue obtained from them is lower, which may represent a drawback for the global economic feasibility of a configuration based on resources recovery.
- WWTP size. The first unit of the innovative flowsheet based on carbon and nitrogen recovery configuration focused on carbon redirection has sense only in medium to large WWTP with anaerobic digestion processes (>30,000 population equivalent; PE). Moreover, the payback period is expected to be reduced in large plants, thanks to the optimization of the operational costs, as well as the increase in the potential revenues from the resources recovered.
- Legal framework. The lack of a common legislation at a European level for the use of fertilizers derived from waste represents a relevant barrier for the replication of the innovative WWTP configuration in other sites and regions. However, it is expected that discharge requirements will be every day more stringent, and therefore it is important to develop methodologies and technologies able to reach these requirements.
- Customer acceptance. Apart from policy makers, it is also essential to increase awareness among the end-users of the “new fertilizers” (including farmers, fertilizer industry and also important supermarket chains) about their efficiency and the benefits they represent for the environment.

8.3. Results and discussion

8.3.1. Environmental assessment based on the life cycle impact assessment (LCIA)

Figure 8.1 depicts the influence of each unit of the treatment on the overall impact during the operational and maintenance (O&M) phase for the reference scenario with carbon and nitrogen removal and for the proposed alternative configuration, respectively. On the other hand, the results of the LCIA for the different impact categories at both O&M and construction of the different scenarios are presented in Tables 8.2 and 8.3. A comparison and discussion of the impact in both scenarios on each LCA impact category are provided below.

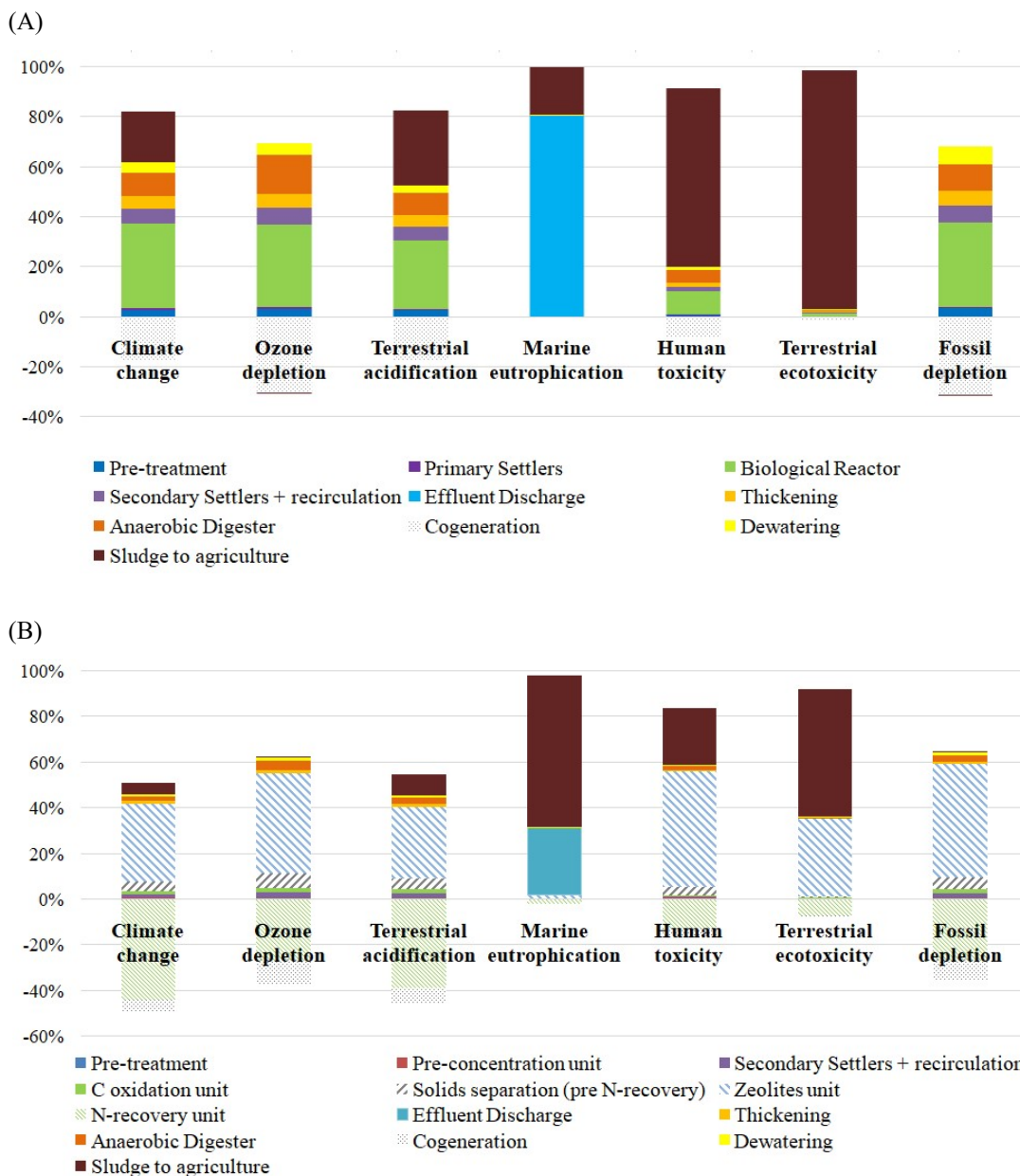


Figure 8.1. LCIA at the operational and maintenance phase of the (A) reference scenario (CAS with carbon and nitrogen removal) and (B) innovative wastewater treatment plant configuration.

Table 8.2. Summary of the LCIA for the reference scenario (CAS with carbon and nitrogen removal).

Impact category	Units	O&M	Construction	Total
Climate Change	kg CO ₂ -eq	$1.32 \cdot 10^{-1}$	$1.65 \cdot 10^{-2}$	$1.48 \cdot 10^{-1}$
Ozone Depletion	kg CFC-11-eq	$1.12 \cdot 10^{-8}$	$9.11 \cdot 10^{-10}$	$1.21 \cdot 10^{-8}$
Terrestrial Acidification	kg SO ₂ -eq	$8.11 \cdot 10^{-4}$	$6.59 \cdot 10^{-5}$	$8.76 \cdot 10^{-4}$
Marine Eutrophication	kg N-eq	$1.77 \cdot 10^{-2}$	$2.79 \cdot 10^{-6}$	$1.77 \cdot 10^{-2}$
Human Toxicity	kg 1,4-DB-eq	$1.13 \cdot 10^{-1}$	$6.03 \cdot 10^{-3}$	$1.20 \cdot 10^{-1}$
Terrestrial Ecotoxicity	kg 1,4-DB-eq	$2.40 \cdot 10^{-4}$	$1.73 \cdot 10^{-6}$	$2.41 \cdot 10^{-4}$
Fossil Depletion	kg oil-eq	$1.79 \cdot 10^{-2}$	$3.46 \cdot 10^{-3}$	$2.13 \cdot 10^{-2}$

Table 8.3. Summary of the LCIA for the prototype.

Impact category	Units	O&M	Construction	Total
Climate Change	kg CO ₂ -eq	$1.04 \cdot 10^{-2}$	$1.20 \cdot 10^{-2}$	$2.24 \cdot 10^{-2}$
Ozone Depletion	kg CFC-11-eq	$2.56 \cdot 10^{-8}$	$7.28 \cdot 10^{-10}$	$2.64 \cdot 10^{-8}$
Terrestrial Acidification	kg SO ₂ -eq	$3.90 \cdot 10^{-4}$	$4.43 \cdot 10^{-5}$	$4.35 \cdot 10^{-4}$
Marine Eutrophication	kg N-eq	$5.16 \cdot 10^{-3}$	$2.86 \cdot 10^{-6}$	$5.16 \cdot 10^{-3}$
Human Toxicity	kg 1,4-DB-eq	$2.81 \cdot 10^{-1}$	$3.59 \cdot 10^{-3}$	$2.85 \cdot 10^{-1}$
Terrestrial Ecotoxicity	kg 1,4-DB-eq	$3.74 \cdot 10^{-4}$	$9.97 \cdot 10^{-7}$	$3.75 \cdot 10^{-4}$
Fossil Depletion	kg oil-eq	$6.32 \cdot 10^{-2}$	$2.61 \cdot 10^{-3}$	$6.59 \cdot 10^{-2}$

In terms of *Climate Change*, the innovative configuration presents a lower impact (85% reduction) compared to a conventional WWTP ($0.022 \text{ kgCO}_2\text{eq}\cdot\text{m}^{-3}$ versus $0.148 \text{ kgCO}_2\text{eq}\cdot\text{m}^{-3}$). Although the consumption of chemicals for zeolites washing and the transport of the zeolites have a significant contribution to this category, avoided emissions are greatly increased. These avoided emissions are related to electricity production in the cogeneration unit, which is increased by the carbon redirection and, mainly, to the avoided emissions of fertilizers production by the fact that ammonium salts could be recovered in the process.

Similar distribution between the different sources of impact is found for *Ozone Depletion*. However, for this category, transport of zeolites has even a higher relevance. In this case, avoided impacts associated to fertilizers production are not enough to offset the impacts of the new process, having, therefore, a higher impact (+117%) than the conventional scenario ($2.64 \cdot 10^{-8}$ and $1.21 \cdot 10^{-8} \text{ kgCFC-11eq}\cdot\text{m}^{-3}$, respectively).

Regarding *Terrestrial Acidification* category, the distribution between the different sources of impact is also relatively similar to the one found for the *Climate Change* category. In this case, the waste category has a higher impact. This is caused by the final use of the sludge produced (agriculture in both scenarios). Although direct impacts of the innovative configuration are higher, avoided impacts by electricity production and fertilizers production offset them, having the latter a lower impact (-50%) on *Terrestrial Acidification*: $4.35 \cdot 10^{-4}$ kgSO₂eq·m⁻³ against $8.76 \cdot 10^{-4}$ kgSO₂eq·m⁻³ of the conventional WWTP.

Impact on *Marine Eutrophication* is mainly caused by the sludge spread in agriculture. Since the innovative scenario is able to produce a zeolites effluent with an ultra-low nitrogen content (NH₄⁺-N = 1 mg·L⁻¹; NO₃⁻-N = 0.47 mg·L⁻¹), a clear benefit in comparison to the conventional plant (-71%) is found: $5.16 \cdot 10^{-3}$ kgNeq·m⁻³ versus $1.77 \cdot 10^{-2}$ kgNeq·m⁻³ in the conventional WWTP.

With regard to *Human Toxicity* category, in the conventional WWTP, the main source of impact is the waste generated. In the innovative scenario, the impact caused by the sludge is similar (since similar amounts of sludge are produced) but the consumption of chemicals and the transport of the zeolites result in a higher impact on this category (0.285 kg1,4-DBeq·m⁻³ in the prototype against 0.120 kg1,4-DBeq·m⁻³ in the conventional WWTP).

In both scenarios, the main source of the impact of *Terrestrial Ecotoxicity* is the digested sludge spread in agriculture, whose content in heavy metals contributes to this category. Additionally, the transport of zeolites in the innovative scenario has a significant impact. This, together with the consumption of chemicals are responsible that the new configuration has a higher impact on *Terrestrial Ecotoxicity* (+55%) than the conventional scenario ($3.75 \cdot 10^{-4}$ kg1,4-DBeq·m⁻³ and $2.41 \cdot 10^{-4}$ kg1,4-DBeq·m⁻³, respectively).

The impact of the two assessed scenarios on *Fossil Depletion* category, in terms of distribution between the different sources, is very similar to the above described for *Ozone Depletion*. Similarly, benefits related to higher energy recovery and to fertilizers production are not enough to offset impacts related to zeolites transport and chemicals consumption.

It can be conclude that, in a conventional WWTP, biological reactor, which requires high electricity consumption for aeration, represents the highest impact of the plant (especially for *Climate Change*, *Ozone Depletion* and *Fossil Depletion* categories) whereas the zeolite unit, which includes chemical regeneration of the column as well as the impact related to the zeolites production and their transport, causes the highest impact in the innovative configuration (except for *Marine Eutrophication* and *Terrestrial Ecotoxicity*). A remarkable benefit is obtained in the cogeneration unit, which presents avoided impacts related to the electricity produced. Moreover,

the produced dewatered digested sludge final use (transport and spread in agriculture) presents some benefits in terms of avoided fertilizers production but at the same time emissions to air, soil and water must be considered.

As it was expected, the impact of construction phase at the conventional WWTP scenario is relatively low (between 0.02–16% depending on the impact category) since it is distributed along the lifespan of each unit. Contrary to this scenario, the impact of construction is more relevant to the alternative configuration proposed. For example, for the *Climate Change* category, the contribution of construction is 54% of the total impact. Lower contributions result for the other impact categories: construction represents the 10% of the total impact for *Terrestrial Acidification*, whilst, for the rest, this phase accounts only for 0.3–4% of the total impact.

8.3.2. Economic analysis

As it will be discussed in detail below with the analysis of CAPEX and OPEX, the economic assessment of conventional alternative ($0.2 \text{ €}\cdot\text{m}^{-3}$) results in today more favourable than innovative configuration ($0.37 \text{ €}\cdot\text{m}^{-3}$) in terms of costs per 1 m^3 treated.

8.3.2.1. Construction costs

According to the economic assessment, the CAPEX of a WWTP with nutrients recovery ($0.109 \text{ €}\cdot\text{m}^{-3}$) doubles CAPEX of WWTP based on nitrogen removal ($0.059 \text{ €}\cdot\text{m}^{-3}$). CAPEX distribution in the percentage of both scenarios is presented in *Figure 8.2*. In the reference scenario (*Figure 8.2–A*), half of the investment is allocated to the bioreactor (biological carbon and nitrogen removal) and secondary settler phase. 35% of construction costs are allocated to sludge line (thickener, anaerobic digestion and dewatering), followed by the cogeneration unit (10%).

However, as it is shown in *Figure 8.2–B*, the most relevant investment costs in the innovative configuration are associated with the nutrient recovery unit. More specifically, solids separation unit based on ultrafiltration technology represents the 25% of the total CAPEX amount. This unit is necessary to avoid that suspended solids (SS) reach the ion-exchange unit (18% of CAPEX), which could significantly reduce the nitrogen exchange capacity of zeolites. However, one of the recommendations is to evaluate if some lower-cost alternative, such as sand filters, could be also implemented as a pre-treatment step reducing the construction costs and

enhancing the economic feasibility of the treatment train. Sixteen per cent of CAPEX is allocated to the carbon recovery unit, composed by a pre-concentration unit, settlers and a carbon oxidation unit to reach the optimal concentration for nitrogen recovery. Sludge line investment costs on this scenario amount to 25% of CAPEX.

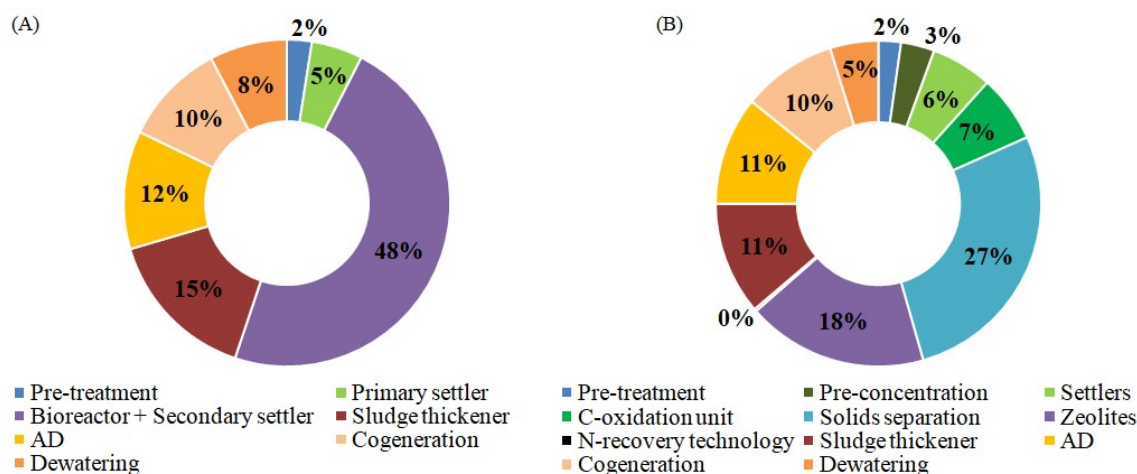


Figure 8.2. CAPEX distribution in (A) reference scenario (CAS with carbon and nitrogen removal) and (B) innovative flowsheet based on carbon and nitrogen recovery.

8.3.2.2. Operation and maintenance costs

Similar to CAPEX analysis, OPEX of the innovative WWTP configuration ($0.259 \text{ €} \cdot \text{m}^{-3}$) almost doubles OPEX of the reference scenario ($0.138 \text{ €} \cdot \text{m}^{-3}$). Of the latter (Figure 8.3–A), labour cost is the main amount of the OPEX (nearly 50%), followed by electricity (nearly 25%). On the other hand, chemicals amount to only 4% of annual costs, followed by sludge and waste management (14%) and maintenance costs (16%). In the case of the configuration based on resources recovery from wastewater (Figure 8.3–B), even though labour cost remains as one of the main costs (25%), the expenditures related to chemicals consumption (27%) and zeolites (20%) amount to nearly half of annual OPEX. The main reason is the high consumption and costs of sodium hydroxide (NaOH) used to regenerate zeolites, the high quantity of zeolites used as a solid material for the ion-exchange process and high costs of phosphoric acid used in N-recovery technology. Regarding zeolites consumption, according to experience from pilot test, zeolites can be reused up to 10 times. Efforts have to be put on making zeolites replacement as well as enlarge operational cycles, by enhancing the cation exchange capacity. Regarding chemicals consumption, NaOH and phosphoric acid, it is for sure an issue to

improve; literature review allows being optimistic since several authors report lower consumption and lower chemicals concentration.

However, these high operational costs associated with nitrogen recovery may be balanced by the selling of a high market value fertilizer. It is essential to increase acceptance of recovered products in order to ensure its market in the future.

Despite the higher OPEX of the nitrogen recovery technology, the economic analysis contributes to point out the strength of the alternative WWTP configuration. This configuration will produce more biogas and, at the end, more electricity will be produced. For each 1 m³ of wastewater treated, 0.02 € of electricity will be obtained. The increasing of electricity production will reduce electricity consumption to 12% of OPEX. Moreover, potential benefits from the selling of the produced fertilisers have been considered, at market price. According to LCC inventory, for each 1 m³ of wastewater treated, fertilizers produced will have a market value of 0.04 €. Fertilizers and electricity production will contribute to reducing its OPEX by around 25%.

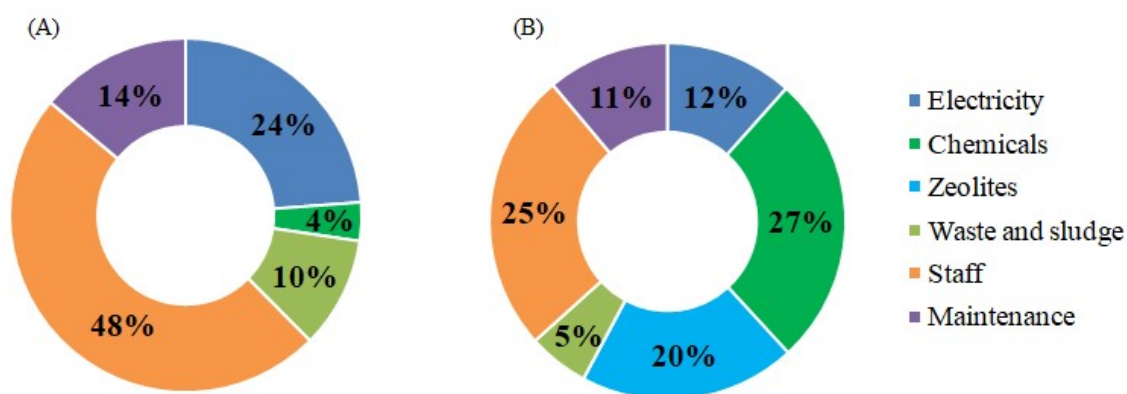


Figure 8.3. Operation and maintenance costs allocation, in %, on (A) conventional wastewater treatment plant (WWTP) scenario and (B) innovative flowsheet based on carbon and nitrogen recovery.

8.3.3. Viability of the innovative flowsheet based on carbon and nitrogen recovery

8.3.3.1. SWOT analysis

The SWOT matrix is a strategic planning technique useful to identify the Strengths, Weaknesses, Opportunities, and Threats related to a project or a technology. The main objective is to identify the internal and external factors that are favourable and unfavourable to achieve

the objectives or, in this case, to further develop and implement the process. Strengths and Weakness are frequently internally-related, while Opportunities and Threats commonly focus on environmental placement. *Table 8.4* shows the SWOT analysis of the innovative configuration. As summarised in *Table 8.4*, these technologies present some strengths when compared with conventional processes, focused on “pollutants removal”, especially from an environmental point of view. It is a clear example of a circular economy that promotes the valorisation of compounds present in wastewater that are lost in a conventional scenario.

Table 8.4. SWOT analysis of the innovative flowsheet based on carbon and nitrogen recovery.

INTERNAL FACTORS	
Strengths (+)	Weaknesses (-)
<ul style="list-style-type: none"> - Improve the energy balance in WWTP: 25% less consumption and 20% extra recovery. - Possibility to recover 90% of nitrogen from wastewater and valorise it. - Nitrogen can be concentrated up to 40 times with ion-exchange process with zeolites. - The effluent generated contains ultra-low nitrogen levels ($<1 \text{ mg}\cdot\text{L}^{-1}$) \rightarrow 71% reduction of impact on <i>Marine Eutrophication</i>. - No N_2O emissions - Compact technology 	<ul style="list-style-type: none"> - CAPEX process is almost twice higher than the CAPEX of a conventional WWTP. - OPEX almost doubles OPEX of conventional WWTP Zeolites and chemical consumption for its regeneration represents 50% of the total OPEX. - Nitrogen recovery requires a previous step able to produce an effluent with a very low content of carbon and particulate material. - Poor settleability of sludge in the bio-sorption process makes solid-liquid separation an issue. - Carbon redirection step is limited to medium and large WWTPs that count with anaerobic digestion processes.
EXTERNAL FACTORS	
Opportunities (+)	Threats (-)
<ul style="list-style-type: none"> - Potential income from the sale of nutrients recovered from wastewater to the fertilizer industry - To reduce dependence on non-renewable resources. - The two technologies demonstrated in the project may be implemented independently. 	<ul style="list-style-type: none"> - Lack of a common legislation at a European level for the use of fertilizers derived from waste. - There is social concern about products obtained from waste.

8.3.3.2. Evaluation of case studies of the implementation feasibility of the innovative flowsheet based on carbon and nitrogen recovery

The implementation of the overall configuration or the combination of the technologies demonstrated in this thesis with conventional ones may be an interesting option, both for new construction and existing plants. However, as it has been mentioned before, its feasibility will depend on each specific site, and also on the wastewater composition and environmental conditions. Three specific scenarios have been defined and the implementation of the innovative WWTP configuration (complete or partial) has been discussed in any case.

1. Greenfield scenario: Full implementation for new construction plants

As it has been mentioned above, the two technologies demonstrated in this thesis, carbon redirection (A-stage) and nitrogen recovery (B-stage) may be implemented together, but always taking into account the necessity to adapt the effluent from the A-stage to the requirements of the zeolites (additional oxidation step, advanced clarification and/or membranes for solid separation).

As demonstrated in *Section 8.3.2*, this configuration is today not economically favourable if compared with a conventional WWTP, but many opportunities for improvement have been identified, which means that it can become feasible in a near future. For example, an alternative would be a single bio-sorption/bio-oxidation stage, after adjusting the operating conditions so that both processes were optimized. Another potential improvement could be the possibility to suppress the physical separation unit installed between carbon and nitrogen units in the case of sludge with good settling properties in the decanter. As mentioned above, the pre-treatment installed to ensure low suspended solids (SS) concentrations in the influent to the zeolites columns was based on ultrafiltration (preceded by a glass filter). The CAPEX of this pre-treatment represents almost 25% of the total CAPEX of the nitrogen recovery unit. The possibility to implement an alternative lower-cost option (such as a sand filter) or even to suppress this unit if a successful separation could be obtained in the decanter would clearly enhance the economic feasibility of the validated configuration.

It is important to mention that anaerobic digestion (AD) is essential to valorise the redirected carbon in the A-stage, and therefore, the flowsheet would be only feasible in medium and large plants (>30,000 PE), which is considered the size of the plant from which a digestion can be implemented in a cost-effective way [18].

2. Brownfield scenario 1: carbon redirection followed by nitrogen conventional biological removal

The possibility to implement a carbon redirection step in an existing plant could be an option to maximize the amount of carbon redirected to the sludge phase and converted into biogas. The effluent for the carbon redirection unit would be fed to the conventional biological process for carbon and nitrogen removal, whose operational conditions should be adapted to a lower carbon load.

The investment costs associated with this modification would depend on each specific case. CAPEX are not expected to be relevant, because part of the current bioreactor (maybe one line in case of different lines available) or any tank of the plant out of operation may be used as a bio-sorption reactor, after adapting and adjusting its operational conditions to a bio-sorption reactor (limited aeration is required to enhance biomass development while minimizing mineralization processes, lower odour emissions thanks to the reduction of the biological opened units, biogas composition should be monitored in order to be sure that the existing treatment is able to remove the undesired compounds, such as hydrogen sulphide: H_2S). For solid-liquid separation, sludge poor settleability is one of the main operational drawbacks identified. It has to be evaluated if the existing primary settler could be used to separate C-rich sludge from the treated effluent or, on the contrary, it would be necessary to implement an alternative or additional device to thicken the sludge before AD.

As commented in previously chapters, a higher organic loading rate (OLR) in the AD is expected. It is important to evaluate if the current anaerobic digester will be able to maintain a satisfactory chemical oxygen demand (COD) removal efficiency, and it will be required to adapt the digester to the new sludge progressively in order to avoid inhibition. Moreover, it is essential to evaluate if the existing engine is able to cope with the larger flowrate or if it should be enlarged (for example with micro-turbines).

From the bio-sorption unit, it is expected that less than 30% of the initial COD is available in the effluent. It is also important to evaluate if this amount is enough to cover the COD requirements of denitrifying bacteria in conventional biological processes. An alternative should be the implementation of a low carbon requirement technology for nitrogen removal, such as Partial Nitrification–Anammox [19]. The operational benefit of this combination compared to the complete implementation is that the amount of carbon remaining in the effluent from bio-sorption does not represent a limitation for the B-stage, but a necessity to cover the organic carbon needs of the bacteria in charge of denitrification.

In this scenario, 25% increase of the energy recovered as biogas is expected, when compared with the previous scenario. However, it is important to highlight that this variation could be only implemented in those plants that count on AD.

3. Brownfield scenario 2: carbon removal followed by nitrogen recovery

Another possibility could be to implement the nitrogen recovery unit after the conventional treatment for carbon removal in those plants that are not removing nitrogen from wastewater. It is the reality for most of the coastal WWTP, such as Vilanova WWTP. Since the effluent is discharged into the sea, they have no limitations related to nutrients concentration.

In the case that discharge regulations get tighter, many wastewater treatment facilities will look to either upgrade or retrofit new equipment at existing treatment process with minimal alterations to achieve these targets. For wastewater treatment facilities already achieving biological nitrogen removal (i.e. effluent 8–10 mgTN·L⁻¹) further reducing effluent TN to levels of <3 mgTN·L⁻¹ can be achieved by adding an ion-exchange process to reach these ultra-low nitrogen levels. Thus, the nitrogen recovery technology could be also implemented as a polishing step.

The investment cost for this retrofitting would depend, as mentioned above, on the specific site. The plant should count on available space for the implementation of the nitrogen recovery unit, but in this case, no effects neither on the existing water line nor in the sludge line are expected.

From an operational point of view, the innovative flowsheet has demonstrated that ion-exchange process with zeolites is effective to recover nitrogen from an effluent complying with discharge requirements in terms of carbon and total SS. Moreover, this configuration could be effective for any WWTP size, since AD is not a requirement in this case.

8.4. Conclusions

The LCA showed that the main environmental impacts of a WWTP take place during the O&M phase. In a conventional WWTP with carbon and nitrogen removal, highest impact (0.148 kgCO₂eq·m⁻³ on *Climate Change*) is a consequence of the electricity consumption in the plant (60%). Between the different stages of the water and sludge line, the highest impact was found in the biological reactor (41%), due to the electricity required for aeration. This is also applicable to *Ozone Depletion*, *Terrestrial Acidification* and *Fossil Depletion*. In these categories, the cogeneration unit represents a benefit since avoids impacts related to

conventional electricity production were higher than the impacts related to the cogeneration unit itself. On the other side, for most of the LCA impact categories analysed in the innovative flowsheet based on carbon and nitrogen recovery, the transport of the zeolites and the consumption of chemicals bear a considerable share of the total impact, especially relevant for *Ozone Depletion*, *Human Toxicity*, *Terrestrial Ecotoxicity* and *Fossil Depletion*. However, this proposal presents 85% lower impact on *Climate Change* compared to the reference scenario thanks to the avoided impacts from electricity production and the obtaining of an N-rich stream suitable for ammonium salts production. Besides the reduction of impact on *Climate Change*, this process provides a 71% reduction of impact on *Marine Eutrophication* in comparison to the reference WWTP thanks to the low nitrogen content achieved in the effluent ($<1 \text{ mgNH}_4^+ \text{-N}\cdot\text{L}^{-1}$) and *Terrestrial Acidification* was reduced by 50%.

Results from the economic assessment shown that the conventional scenario presents lower life cycle costing ($0.2 \text{ €}\cdot\text{m}^{-3}$) than the innovative scheme (estimated at $0.37 \text{ €}\cdot\text{m}^{-3}$). Although carbon redirection improves the energy balance in the innovative configuration (25% less consumption and 20% extra recovery) and the production of fertilisers reduce costs, its higher CAPEX ($0.11 \text{ €}\cdot\text{m}^{-3}$ versus $0.06 \text{ €}\cdot\text{m}^{-3}$, due to the costs of zeolites unit and its pre-treatment) and the high OPEX (regarding zeolites and chemical consumption) make the overall process still not economically competitive nowadays.

Even though the energy balance of the overall process is favoured compared to a conventional WWTP (20% less demand and 25% more recovery), the process is not economically favourable at present, mainly due to the high CAPEX (almost twice higher than the CAPEX of a conventional plant) and OPEX of the nitrogen recovery unit. 50% of these OPEX are associated with the zeolites used for nitrogen adsorption and chemicals consumed for their regeneration.

The innovative WWTP configuration offers a promising alternative to conventional WWTPs to recover and valorise resources from wastewater and the possibility to implement only part of the process, combined with conventional technologies, makes the application range broader. But there is still room for improvement. From the LCA and LCC assessments, some improvements on the new scenario are pointed out to make it more feasible and recommendations for next steps (or research needs) are established with the aim of enhancing the economic feasibility of the process:

- Substitution of separation solids unit based on ultrafiltration technology by other technology available on the market.
- Regarding zeolites, increase the number of use cycles. The increase of the lifetime of the zeolites before regeneration would decrease both specific consumptions of chemicals and

zeolites and chemicals transport. The latter could be also optimised finding a provider closer to the WWTP.

In summary, there is still a long way ahead to convert WWTP in resources recovery facilities, but it is clear that research is required to enhance every day the technical and environmental feasibility of the process, while the legal framework develops new regulations that promote this circular economy concept in wastewater treatment.

8.5. References

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CHAPTER 9

Conclusions

9. Conclusions

It is well accepted that a more sustainable wastewater treatment is required, where energy consumers and nutrients removal plants should be replaced by self-sufficiency, resources (energy and nutrients) recovery systems and environmentally friendly plants. Accordingly, policymakers and governments are progressively implementing measures aimed at reducing the negative impact on the environment, restricting nutrients discharge limits and promoting energy self-sufficiency. Making this real requires a compromise between technological, economic and social challenges, which show the necessity for the transversal technology available.

In this PhD thesis, the potential for a new wastewater treatment train configuration in accordance with the new paradigm has been studied. Over the following pages the most relevant findings raised in the previous chapters, first on carbon redirection and afterwards on nutrient recovery, are summarized. Moreover, the recommendations are also overviewed.

9.1. Key findings regarding carbon redirection

Innovation in wastewater treatment has been tailored towards a promising technology for achieving maximal energy recovery from wastewaters with minimum energy expenditure. The efficiency of bio-sorption is known to be linked to bio-flocculation, sludge characteristics (like type and fraction of extracellular polymeric substances; EPS), the presence of storage compounds, sludge retention time (SRT), hydraulic retention time (HRT) and even dissolved oxygen (DO) levels in the reactor.

Thanks to its operational conditions (low retention times – $HRT \leq 0.5$ h and $SRT < 1$ day – and low oxygen demand – $DO < 1 \text{ mgO}_2 \cdot \text{L}^{-1}$ –), the A-stage treatment promote that around the 60% of carbon present in wastewater is redirected to the sludge phase while limiting the mineralization of carbon to carbon dioxide (CO_2). The entrapped organics (chemical energy) can then be recovered through an anaerobic digestion process by the conversion to biogas without significant energy losses. Therefore, an increase around the 25% of the energy recovered is expected. Moreover, aeration energy requirements per unit of chemical oxygen demand (COD) removed is between 0.04 and 1.7 $\text{kWh} \cdot \text{kgCOD}_{\text{removed}}^{-1}$, allowing saving in aeration costs in comparison to conventional design (representing 20–40% fewer energy requirements).

Several current WWTPs operate under a high-rate activated sludge (HRAS) system, achieving a total COD removal efficiency of 55–96% (at SRT of 0.3–0.7 days). In terms of energy

production, the Strass WWTP, as an example, it is able to generate all electricity needed only counting with the 11% of the total calorific energy available in the wastewater.

The short sludge age in this process makes this sludge better digestible and, consequently, higher energy production is achieved. However, and in contrast to the primary sludge of a conventional wastewater treatment, which has better dewaterability than secondary sludge, A-sludge dewatering property is inferior due to the abundance of extracellular organic materials in the liquor, which are mostly present in colloidal forms.

9.2. Key findings regarding nutrient recovery

The main value of the nitrogen recovery unit is the possibility to extract ammonium (NH_4^+) from the water line and valorise it as a fertilizer.

Zeolites showed high-affinity ammonium, which allows producing an eluate with ammonium concentration up to 40 times higher than the influent, which is essential to make the subsequent processes of ammonium salts production feasible from an economic point of view. A natural clinoptilolite, widely found on most of the European mineral deposit of zeolites, was used successfully in terms of chemical stability. It has been determined that the granular zeolite has an operational cation exchange capacity (CEC) of $9 \pm 2 \text{ gNH}_4^+ \cdot \text{kg}_{\text{zeolite}}^{-1}$ during at least 10 cycles of operation for treated effluents having total ammonium concentration value of $45 \pm 17 \text{ mgNH}_4^+ - \text{N} \cdot \text{L}^{-1}$. Operational CEC values determined are aligned with CEC values reported on batch scale laboratory experiments when working in the range of ammonium concentrations from 30 to 60 $\text{mgNH}_4^+ - \text{N} \cdot \text{L}^{-1}$.

The nutrient recovery unit has demonstrated the viability of zeolites to produce a clean effluent with ultra-low nitrogen concentration ($< 1 \text{ mgNH}_4^+ - \text{N} \cdot \text{L}^{-1}$; 90–95% $\text{NH}_4^+ - \text{N}$ recovery efficiency), which is a relevant environmental benefit, related with the decrease of the effluent eutrophication potential (71% reduction in comparison to the reference WWTP). At the same time, this physico-chemical process avoids dinitrogen monoxide (N_2O) emissions, typical from conventional biological processes based on nitrification-denitrification. However, a pre-treatment that ensures a low concentration of solids in the entrance of the ion-exchange columns is essential to guarantee a high efficiency. It was also assessed that zeolites may be influenced by some macro pollutants (particles, phosphorus, and competitive ions) and micro pollutants (caffeine).

Trials with nitric and phosphoric acids in hollow fibre membrane contactors demonstrated a total nitrogen recovery capacity above 95% if an excess of free acid is present in the stripping

stream. This solution avoids the use of low-cost common acids (e.g. H_2SO_4 and HCl) as ammonia collectors, providing rich ammonium nitrate (NH_4NO_3) and di-ammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$) with high added value as fertilizers.

The quality of NH_4NO_3 and $(\text{NH}_4)_2\text{HPO}_4$ by-products, in terms of absence of transition metal and non-metal ions or organic micro pollutants (e.g. potentially incorporated in the zeolites sorption-elution step), is high as their transport on the hydrophobic hollow fibre membrane contactors is restricted by the membrane properties only supporting solutes in gas phase. The exhausted $\text{NH}_4^+/\text{NaOH}$ streams once ammonium is removed can be re-used for the regeneration of the ammonium exhausted zeolites filters.

9.3. Key findings regarding the proposed scheme

The two different stages that form the innovative treatment train (carbon redirection and nitrogen recovery) may be implemented together (one after the other), but it is essential that the effluent obtained from the A-stage is suitable for the B-stage (especially regarding carbon and particulate matter content). Alternatively, both processes may be implemented independently and combined with other conventional processes, which makes the application range of this technology broader.

The main point towards energy recovery is to capture COD from wastewater for direct anaerobic digestion as much as possible as followed by the proposing of a bio-sorption step previous to bio-oxidation of this organic content to redirect carbon from mineralisation to biogas generation. As it is shown in *Figure 9.1*, as a result of enhancing COD capture, more biogas production can be obtained (5–15%) whereas organic matter converted to CO_2 can be reduced up to 25% in comparison with the reference scenario. It implies producing more energy than in a conventional scenario and, hence, becoming a higher self-sufficient plant (about 60% of the energy demand of the plant can be covered by the energy generated by the treatment itself). Globally, up to 95% of the total COD entering in a WWTP can be removed from the system employing this innovative flowsheet.

Regarding nitrogen recovery, the implementation of a recovery process is essential to promote the recovery of nutrients while reduction its losses to the atmosphere as well as its discharge into the environment. Thanks to the application of an ion-exchange technology, almost 99% of the nitrogen present in wastewater composition can be recovered in the form of fertilisers (90%) or contained into sludge (9%) (*Figure 9.1*).

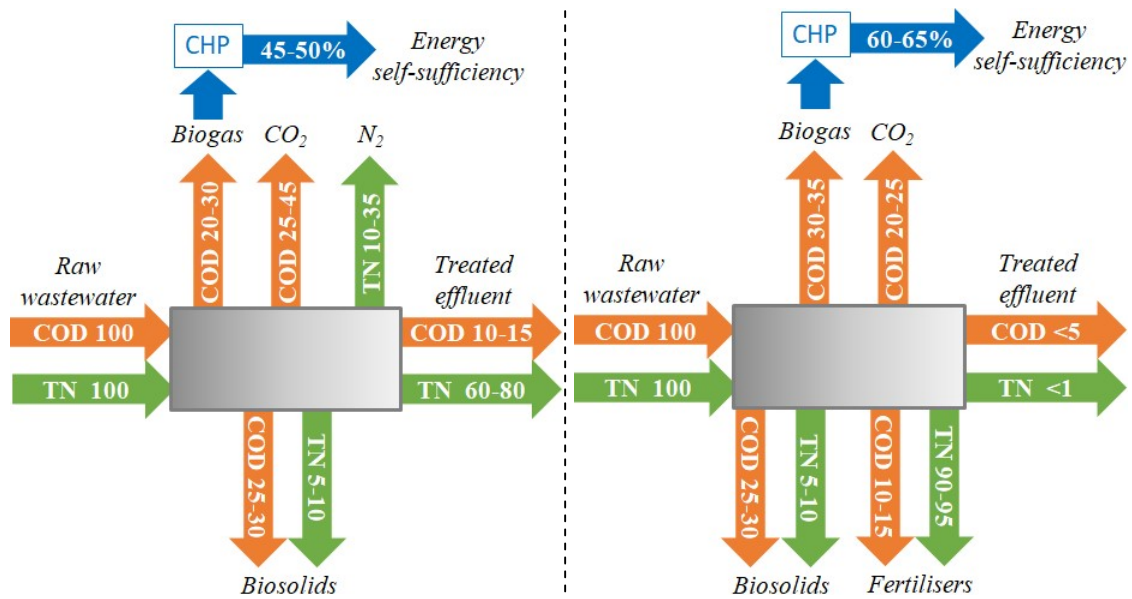


Figure 9.1. Carbon and nitrogen mass balance of the reference scenario (Vilanova WWTP based on analytical data for the years 2013 and 2016; left) and the innovative flowsheet proposed in this PhD thesis (right). Values are expressed in percentage.

Although this innovative flowsheet supposes a better nitrogen paradigm change than for carbon, in conclusion, this proposed scheme represents an opportunity to reduce dependence on non-renewable resources. The possibility to recover more energy may contribute to an energy self-sufficient plant, while the production of fertilizers from wastewater reduces the requirements of conventional products, whose production process is characterized by a high energy demand. The sale of these nutrients to the fertilizer industry may represent an income for the plant operators. Moreover, the implementation of this innovative WWTP flowsheet, presents a lower impact on carbon footprint (85% reduction) compared to a conventional WWTP (0.022 kgCO₂eq·m⁻³ versus 0.148 kgCO₂eq·m⁻³). However, the economic assessment of the technology has demonstrated that today the innovative process is not economically favourable, especially due to the nitrogen recovery unit, which shows higher construction costs (CAPEX) (0.11 €·m⁻³) than the conventional plant (0.06 €·m⁻³) and also high operational costs (OPEX) (0.14 and 0.26 €·m⁻³ for reference scenario and innovative WWTP flowsheet, respectively), mainly related to the zeolites replacement and the chemical consumption for their regeneration. Nevertheless, it is expected that both the zeolites adsorption capacity and the regeneration efficiency may be significantly optimized, which would represent a significant reduction of these operational costs. In addition, it is true that some legal and social barriers represent today a threat to the process development. The lack of a common legislation at a European level for the use of fertilizers derived from waste, as well as the social concern about products obtained from waste, make the process replication an issue. For this reason, the necessity to communicate to the

general public and to the Administration the positive results of research projects in this scientific field is relevant in order to push for the change of paradigm.

9.4. Recommendations suggested for future work

9.4.1. Carbon redirection

As it has been discussed along this thesis, the main operational drawback of high-rate biological processes such as bio-sorption is the poor settling properties of the sludge, mainly linked to the low sludge retention time (SRT <1 day) set in these processes. Lower SRT leads to a worse sludge flocculation (higher sludge volume index, SVI) and poorer effluent clarification. Under these operational conditions and due to the larger surface-to-volume ratio of the filamentous bacteria, they will outcompete floc-forming bacteria, as they have a greater accessibility to the substrate. In some cases, advanced clarification or even membrane separation (depending on the subsequent B-stage) may be required to ensure a successful solid-liquid separation, that allows the redirection of the sludge to the anaerobic digestion unit, and the production of a stream with low solids content, suitable for the B-stage.

Another aspect that needs further efforts development is the suitability of the effluent obtained from this A-stage for the subsequent B-stage. As previously highlighted, the presence of carbon and suspended material is a relevant limitation for nitrogen adsorption, since they decrease the ammonium retention capacity of the adsorbent, worsening the technical and economic feasibility of this technology. In these cases, an intermediate step or a combination between bio-sorption and bio-oxidation may be essential to produce N-rich effluent with very low carbon content ($\text{COD} < 125 \text{ mg} \cdot \text{L}^{-1}$).

Research efforts in the field of the treatment of the A-sludge produced must focus on the optimization of the digestibility of the A-sludge in order to obtain as much as possible energy and a lower biosolids generation. The biosolids management system is considered cost-intensive as it typically accounts for 25–60% of the total operational costs of conventional activated sludge (CAS) WWTPs. Furthermore, its lower production will have a positive impact over the global warming impacts as a driver towards the establishment of energy-efficient WWTPs.

9.4.2. Nutrient recovery

For a good performance of an ion-exchange technology based on zeolites on nitrogen recovery, it is important to ensure that the influent of the zeolites columns contain low carbon and

particulate material. However, this pretreatment could represent almost the 50% of the total CAPEX of this technology and therefore it is essential to focus efforts on the identification of low-cost alternatives, such as for example, a sand filter.

Another issue to work on is the performance of the ion-exchange process itself. A cation exchange capacity (CEC) of zeolites around $10 \text{ gNH}_4^+ \cdot \text{kg}_{\text{zeolite}}^{-1}$ (for ammonium streams with 30 to $60 \text{ gNH}_4^+ \cdot \text{m}^{-3}$) has been observed in the experiments carried out in this thesis, with a lifetime of 10 consecutive cycles. These values are in line with most of the relevant references. Other natural zeolites (e.g. mordenite) or synthetic zeolites, however, could provide higher capacities. On the other hand, they are less abundant and in many cases, they are commercialized in powder form since the cost to produce granular forms is still very expensive. As detailed in *Chapter 6*, some clogging of zeolites was observed when the columns were opened for zeolites maintenance or replacement. Zeolites column bed show partial aggregation during operation basically due to precipitation of calcium carbonates and calcium phosphates, decreasing its active surface and its regeneration efficiency. Then, operational protocols should include along sorption and desorption cycles an acid-washing step to dissolve formed calcium and magnesium precipitates characterized for having cementation properties. The experimentation with transparent columns would allow to visually control the process (i.e. total expansion of the zeolites bed during backwash and regeneration steps), which will be really helpful to control this kind of operational issues.

The regeneration sequence has been improved, but efforts on the improvement of the regeneration protocol will be also an important point to be focused on further research in this field to optimize the efficient yield of the zeolitic material.

Appendices

A: Monthly average wastewater quality characteristics of Vilanova WWTP (2013)

B: Energy data of Vilanova WWTP (2013)

C: P&ID Carbon redirection unit (pre-concentration step)

D: P&ID Carbon redirection unit (anaerobic digestion step)

E: P&ID Nutrient recovery unit

Appendices

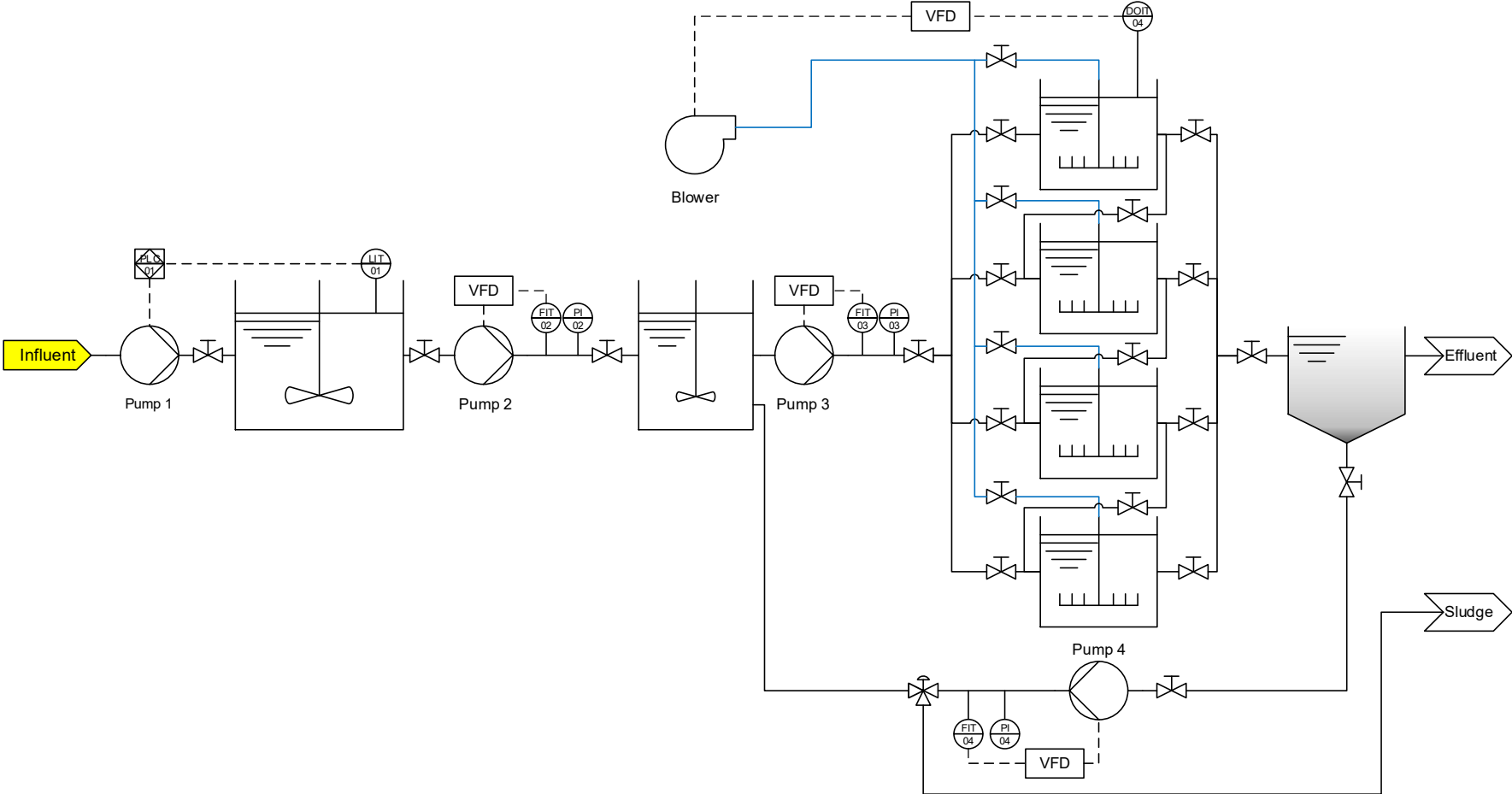
Appendix A: Monthly average wastewater quality characteristics of Vilanova WWTP (2013)

Month	Flow (m ³ ·d ⁻¹)	COD (mg·L ⁻¹)		BOD ₅ (mg·L ⁻¹)		TSS (mg·L ⁻¹)		TN (mg·L ⁻¹)		TP (mg·L ⁻¹)	
		Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
J	12,767	900	194	320	71	239	72	88.7	45.1	10.6	4.1
F	13,113	785	126	314	50	241	56	101	44.1	9.7	3.2
M	14,693	702	86	233	17	312	39	67.2	34.2	8.4	2.8
A	14,991	719	96	445	28	360	39	85.8	45.2	12.3	4.3
M	13,538	643	66	322	9	350	17	75.7	38.9	13.1	3.3
J	13,137	1,342	71	459	18	477	21	82.4	38.7	11.3	3.8
J	13,287	1,685	85	516	21	683	33	66.7	31.3	11.4	3.3
A	13,543	927	67	368	12	435	23	59.1	33.1	11	4.4
S	12,872	782	71	338	12	297	17	60.5	35	8.9	4.8
O	13,460	652	115	279	24	236	49	61.9	39	9.1	5.3
N	15,050	596	126	242	16	154	51	57	33.1	10.8	1.8
D	12,898	643	158	198	30	196	66	91.1	44.2	10.4	2.1
AVG	13,612	865	105	336	26	332	40	74.8	38.5	10.6	3.6

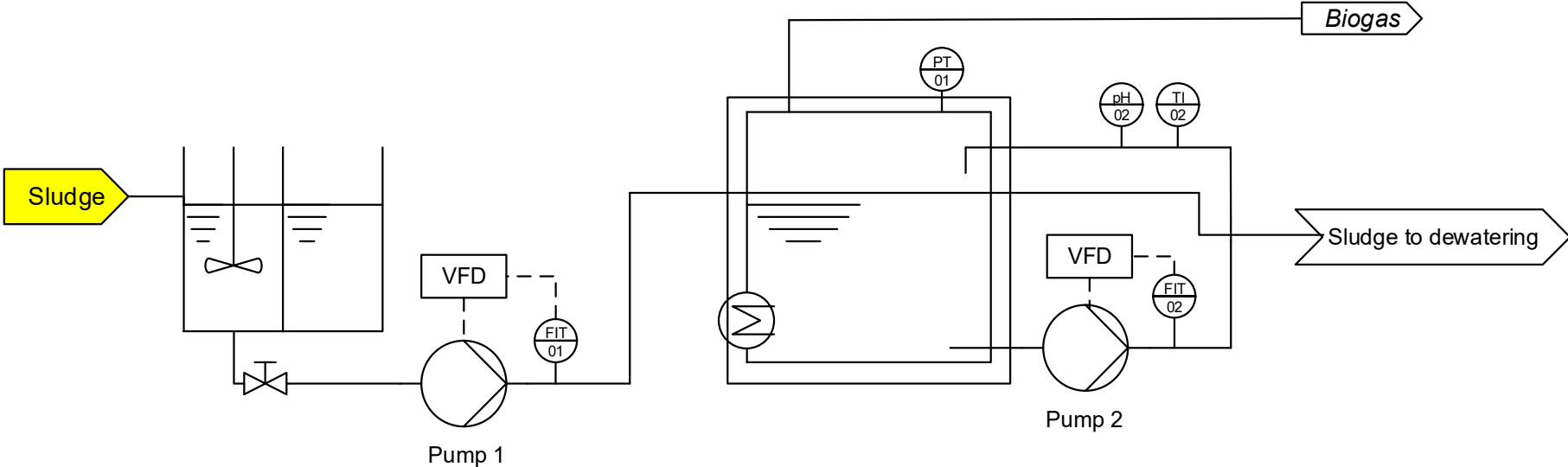
Appendix B: Energy data of Vilanova WWTP (2013)

Volume wastewater (WW) treated in Vilanova WWTP	
Total treated WW (Nm ³ ·y ⁻¹)	4,984,000
COD_{removed} (kg·y ⁻¹)	3,882,007
BOD_{removed} (kg·y ⁻¹)	1,608,591
Biogas production	
Biogas generated (Nm ³ ·y ⁻¹)	471,956
Ratio	
Nm ³ ·m ⁻³ _{water treated}	0.09
Nm ³ ·kg ⁻¹ COD	0.12
Nm ³ ·kg ⁻¹ BOD	0.29
Energy	
Energy from cogeneration (kWh)	1,026,847
Energy bought (kWh)	994,328
Energy consumption (kWh)	2,021,175
Ratios	
kWh consumed·m ⁻³ _{treated WW}	0.41
kWh consumed·kg ⁻¹ _{COD removed}	0.52
kWh consumed·kg ⁻¹ _{BOD removed}	1.26

Appendix C: P&ID Carbon redirection unit (pre-concentration step)



Appendix D: P&ID Carbon redirection unit (anaerobic digestion step)



Appendix E: P&ID Nutrient recovery unit

