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By
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Optimisation of landfill leachates treatment by membrane bioreactor

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ANAMMOX</td>
<td>Anaerobic Ammonia Oxidation</td>
</tr>
<tr>
<td>AOB</td>
<td>Ammonia Oxidizing Bacteria</td>
</tr>
<tr>
<td>ASM</td>
<td>Activated Sludge Model</td>
</tr>
<tr>
<td>ATU</td>
<td>Allylthiourea</td>
</tr>
<tr>
<td>BNR</td>
<td>Biological Nitrogen Removal</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological (or Biochemical) Oxygen Demand</td>
</tr>
<tr>
<td>CAS</td>
<td>Conventional Activated Sludge</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid dynamics</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>DDT</td>
<td>Dichlorodiphenyltrichlorethane</td>
</tr>
<tr>
<td>DIN</td>
<td>Deutsches Institut fur Normung</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved Oxygen</td>
</tr>
<tr>
<td>EDC</td>
<td>Endocrine Disrupting Compounds</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetatic Acid</td>
</tr>
<tr>
<td>EPS</td>
<td>Extra Polymeric Substances</td>
</tr>
<tr>
<td>F/M ratio</td>
<td>Food/Microorganism ratio</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular Activated Carbon</td>
</tr>
<tr>
<td>HRT</td>
<td>Hydraulic Retention Time</td>
</tr>
<tr>
<td>IAWPRC</td>
<td>International Association on Water Pollution Research and Control</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standarization</td>
</tr>
<tr>
<td>IWA</td>
<td>International Water Association</td>
</tr>
<tr>
<td>KN</td>
<td>Kjeldahl Nitrogen</td>
</tr>
<tr>
<td>MBR</td>
<td>Membrane Bioreator</td>
</tr>
<tr>
<td>MCRT</td>
<td>Mean Cell Residence Time</td>
</tr>
<tr>
<td>MDR</td>
<td>Maximum Denitrification Rate</td>
</tr>
<tr>
<td>MLSS</td>
<td>Mixed Liquor Suspended Solids</td>
</tr>
<tr>
<td>MLVSS</td>
<td>Mixed Liquor Volatil Suspended Solids</td>
</tr>
<tr>
<td>MSL</td>
<td>Model Specification Language</td>
</tr>
<tr>
<td>MSW</td>
<td>Municipal Solid Waste</td>
</tr>
<tr>
<td>NF</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>NOB</td>
<td>Nitrite Oxidizing Bacteria</td>
</tr>
<tr>
<td>PAC</td>
<td>Powdered Activated Carbon</td>
</tr>
<tr>
<td>PAH</td>
<td>Poly Aromatic Hydrocarbon</td>
</tr>
<tr>
<td>PBDE</td>
<td>Polybrominated Diphenyl Ethers</td>
</tr>
<tr>
<td>PCB</td>
<td>Polychlorinated Biphenyls</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
</tr>
<tr>
<td>SBR</td>
<td>Sequecing Batch Bioreactor</td>
</tr>
<tr>
<td>SDNR</td>
<td>Specific Denitrification Rate</td>
</tr>
<tr>
<td>SI</td>
<td>International System of units</td>
</tr>
<tr>
<td>SMP</td>
<td>Soluble Microbial Products</td>
</tr>
<tr>
<td>SNR</td>
<td>Specific Nitritification Rate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>--------------</td>
<td>-----------------------------------------</td>
</tr>
<tr>
<td>SOUR</td>
<td>Specific Oxygen Uptake Rate</td>
</tr>
<tr>
<td>SRT</td>
<td>Sludge Retention Time</td>
</tr>
<tr>
<td>SVI</td>
<td>Sludge Volume Index</td>
</tr>
<tr>
<td>TN</td>
<td>Total Nitrogen</td>
</tr>
<tr>
<td>TSS</td>
<td>Total Suspended Solids</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>VFA</td>
<td>Volatil Fatty Acids</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organisation</td>
</tr>
<tr>
<td>WW</td>
<td>Wastewater</td>
</tr>
<tr>
<td>WWTP</td>
<td>Wastewater Treatment Plant</td>
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</table>
Introduction

Context

Apparently inexhaustible, fresh water is an element that takes further and further value in the world. Most of the countries will have to face a lower availability in the short term caused by an increasing demand related to industrial development and population growth. Furthermore, water resources are decreasing in many countries due to climatic changes.

The mobilisation and use of surface water have been a priority for human civilization since a long time ago. Nowadays, water is so familiar to many of us, that often we forget its role, its importance and our absolute neediness. Not only direct human water needs must be considered but the needs of the total environment have to be protected.

To face the growing demand and the impossibility of further exploitation of natural resources, the human civilization is conducted to search for new solutions. Desalination of sea water is an option, for example, but at high energetic costs so water reuse takes more and more importance. We are conducted to economically and technically study and develop water reuse processes, particularly in the warm climate countries [1].

Another issue associated to the industrial and economic development of countries is the increasing production of household and industrial wastes. During the last decade, annual production of garbage is in the range 300 to 800 kilos per person per year in the developed countries and a little less than 200 kilos per person per year in the rest of the world [2]. Sanitary landfill is nowadays a very well accepted method and the most used one thanks to its economic advantages. Comparative studies on the many ways to eliminate wastes like incineration or composting suggest that landfilling is a better option considering initial investments and operational costs [2]. Environmental problems associated are also minimized. Wastes could be degraded under controlled conditions eventually until a transformation into inert and stabilized materials [2]. However, landfills produce effluents: biogas that has to be used to produce energy (otherwise it only contributes to the greenhouse effect) and leachates that have recently gained interest because of their characteristics of highly polluted wastewater [3]. The pollution, particularly the bio-assimilable part, can be treated by
biological processes that minimize the energetic costs and the toxicity of sub-products. These processes are generally composed of complex bacterial ecosystems capable of degrading pollutant matters. They are contained in systems that will allow creating the adequate conditions for the maintenance and multiplication of several strains. Nevertheless, the production of excessive sludge constitutes a sanitary problem as well, because the sludge can contain a concentrate of pollutants and eventually pathogen micro-organisms.

Membrane bioreactors (MBR) are among the several available techniques proposed to treat high pollution loaded wastewater like landfill leachates. They have recently proved their efficacy for treating high concentration of ammonia nitrogen [4]. The principle of this technology relies on a biological process with a membrane filtration step. The traditional settler technique is replaced by the membrane, increasing separation capacities. This new essential feature of MBR systems leads to several advantages like higher biomass concentration and the possibility of functioning at very low Food/Microorganisms ratio (F/M ratio) and high sludge age. The metabolism of the bacterial culture generally used in municipal wastewater treatment plants is changed and is now focused on maintenance, minimizing the cellular synthesis and the sludge production [5].

The membrane bioreactor configuration more generally used to treat nitrogen compounds in landfill leachates is composed essentially of three parts: An anoxic environment for denitrification, an aerated environment for nitrification and the membrane filtration part. A detailed study and the optimisation of the overall process grouping these three interconnected systems, constitutes the objective of this research work.

Objectives

The aim of this research project is to optimise the treatment of landfill leachates using membrane bioreactors. The optimisation will be performed by acting over the aeration that can be applied in excess increasing operational costs.

The treatment´s main objective is to eliminate leachate´s nitrogen compounds combining nitrification and denitrification and other biological processes associated. In order to attain this main objective, several different specific objectives must be accomplished.
- To obtain a complete removal of ammonia nitrogen, meaning a complete nitrification in order to respect the legislation that is becoming to be more and more strict.

- To obtain good removal of total nitrogen, meaning, to enhance the denitrification process using the internal carbon source available and a minimum of external carbon source.

- To obtain good performances in the removal of organic pollution measured as Chemical Oxygen Demand (COD). In the case of old leachates, the aim is to eliminate part of the so called hard COD, also named refractory COD that is mostly composed of humic and fulvic acids. This will lead to an economy of activated carbon in the post treatment.

- To keep the aeration at the lowest feasible level but ensuring the biomass´s dissolved oxygen needs and the membrane fouling control.

- To maintain a minimal sludge production. The costs associated to the remediation of the sludge will be diminished.

- To control membrane fouling.

This project will use leachates of the Muertendall Sanitary Landfill site located in Luxembourg. A real scale MBR is already in operation with good removal performances but with high aeration costs (75% of the bioreactor volume is aerated and only 25% is anoxic).

This work aims at demonstrating that this aerated volume could be diminished not only by using less energy but also ameliorating the removal performances.

A specially designed pilot installed in Arlon, Belgium, was put into operation treating Muertendall´s leachates. At the beginning, equivalent conditions to the real scale station were reached. Then, aeration was decreased. Performances were evaluated by analytical measurement over two campaigns.

Parallel to that, simulations based on the ASM family (activated sludge models) models were performed through the specially conceived simulator WEST®. Initial simulations were made
with ASM1 and ASM3 models but a specific model was introduced to simulate the case of low aeration. A characterization of the leachates based on ASM’s partition of the matter was necessary.

**Outputs of the research project**

Two articles were accepted for publication in the scientific journal “Environmental technology” edited by Taylor & Francis. The chapter 6 in this thesis, named “Lanfill leachates characterization for simulation of biological treatment with activated sludge model nº1 and activated sludge model nº3” was accepted for publication during October 2010. The chapter 7 in this thesis, named “Simulation of a membrane bioreactor pilot treating old landfill leachates with activated sludge models nº1 and nº3” was accepted during February 2011.

The chapter 8 named “Optimization of N removal in landfill leachates treatment with membrane bioreactor; pilot plant and full scale studies” was accepted (abstract) for oral presentation in the thirteenth international waste management and landfill symposium, taking place in Sardinia, Italy during October 2011.

**References**


Chapter 1: Landfill leachates

Abstract: Landfilling is a world-wide spread technique used to control municipal and industrial wastes. Among the problems and cost associated to the operation, the leachate treatment constitutes an important part. Leachates are complex in composition and strongly loaded with ammonia nitrogen and organic matter. Treatment before reintroduction into the water cycle is essential; otherwise the natural environment could be drastically changed. Landfill, leachates characteristics and the environmental problems associated will be described in this chapter as well as some treatment alternatives.
1.1 Landfill

Landfills are specially conceived places for final disposal of wastes. They constitute a valuable alternative to incineration process that is also commonly applied worldwide. In Luxembourg for example, 32.5 % of waste goes to landfills and the rest to an incineration plant [1].

The process principle is that trapped waste will be transformed under controlled conditions into a more or less inert material without negative influence for the surrounding environment. Several layers of isolating materials are placed in the bottom of the landfill, including synthetic liners to avoid underground water pollution [2]. Just over the isolation layers, a collecting system must be placed to recover the leachates produced. Sometimes this system includes pumps or is conceived to function by gravity. The drainage collection and extraction system play an important role in the performance of the landfill [3]. Clogging of this system occur and must be considered as well [4].

![Figure 1-1 Landfill schematics (Based on [5])]({})

During the exploitation period, grind and compacted garbage are placed into the landfill. Several disposal configurations exist like “in cells compartments” or “by zones”. The choice is usually made depending on the site geometry and machinery available but degradation conditions of wastes could also be influenced. When a certain amount of rubbish is placed, good practice suggests to cover it with isolating materials and land, in order to avoid light
garbage surging, odour lost, excessive rain infiltration or biogas lost. Layer by layer the cavity is filled to the top where a final vegetal cover is placed after isolation and land layers.

An adapted network of wells allows recovering the biogas that is produced during the process. Biogas can then be used to generate electricity, hot water or regrettably is just burned.

Decomposing waste material rest trapped into this semi-isolated environment for years. During this time, water trapped in waste but most of all rain infiltration generates leachates that could be defined as highly polluted percolation liquids. Landfill internal hydraulic is very complex because it depends on many parameters specific to each landfill [6]. Internal moisture can be evaluated using electrical resistivity and temperature related hypothesis but results are not technically functional [7]. However, there are calculation tools to estimate the quantity of leachate generated by a landfill [8].

Leachates composition depends on biochemical processes inside the landfill. The complex decomposing microbial community depends on the garbage’s characteristics that constitute microorganism’s food, environmental factors inside the landfill, temperature, the amount of rain, humidity, age of the site, and so on. Preferential flow paths and organic compounds sorption non-equilibrium are important phenomenons to consider as well in percolating water through a landfill [9]. Finally seasonal variations are also influencing the process [10].

Long term behaviour will constitute an important factor to take into account because the landfill (and thus waste materials inside) will evolve through several stages of decomposition. These steps will produce not only different amounts of effluents but also different effluent compositions for long periods of times. For example, the required period to wash out salts in landfillled wastes is very long (up to 20 years) [11]. Landfill municipal solid waste (MSW) will have long term emissions of dissolved organic carbon, chloride and nickel after anaerobic degradation and thus the definition of inert waste is questioned [12]. Furthermore, new regulations encourage waste reduction and recycling strategies that constantly modifies the landfill characteristics and force to adapt the knowledge previously acquired.

Thus, landfill is a complex local issue that must often be considered taking into account neighbourhood groups and university representative opinions [13]. Especially adapted
treatment is mandatory for leachates that until now are sometimes just being treated in a settler and then directly rejected into the natural environment [14].

1.2 Leachates Characteristics

Landfill leachates contains more than 90 organic and metal organic compounds and 50 inorganic elements, including halogenated aliphatic compounds, benzene, alkylated benzenes, phenol, alkylated phenols, ethoxylates, polycyclic aromatic compounds, phthalic esters, chlorinated benzenes, chlorinated phenols, polychlorinated biphenyls (PCBs), chlorinated dioxins and chlorinated furans, bromated flame-retardants, pesticides, organic tin, methyl mercury and heavy metals [15]. Among pharmaceutical residues, naproxene and ibuprofen are present in high concentrations contrasting with other high consumption products such as paracetamol that are not highly detected [16]. Occurrence of Endocrine Disrupting compounds (EDCs) is widely documented. Types and concentrations depend on each landfill. EDCs include estrogens, phytoestrogens and components of massively employed personal care products [17]. The presence of salt is also reported and may influence the biological degradation [18]. Leachates matrix is thus very complex, and composition results may be altered by analyses made following methodology developed for other types of aqueous samples [19].

Despite the presence of an unknown number of different compounds, the dominant removal mechanism in leachate treatment is the removal of ammoniacal nitrogen. Indeed, the ammonification of organically bound forms of nitrogen (such as amino acids and proteins) liberate important amount of ammonia. The critical parameter for consideration in plant design is thus ammoniacal content, but COD values should be considered as well or specifically treated afterwards. Pesticides, other trace organics and trace metals, show a significant reduction in aerobic biological treatment processes as well [20]. Considering the high content of organic waste in landfill (30% of weight in Luxembourg [1]), the hydrolysis rate of organic material and the biokinetics of the system are the dominating processes affecting the waste stabilization rate, and therefore, the leachate quality [21].

Young Landfills contains large amounts of biodegradable organic substances and important moisture. This scenario is ideal for a very fast anaerobic fermentation that produces volatile
fatty acids (VFAs) [22]. This acid fermentation is also called acidogenic phase. Leachates generated during this period contain mostly rapidly biodegradable matter. The compounds of low molecular weight that could be more quickly degraded can be classified as proteins, carbohydrates and lipids and therefore, they should have relatively high degradation kinetics [23].

When landfills get old, methanogenic organisms develop converting VFAs into bio gas. When this occurs, organic content in leachates diminishes and passes from fast biodegradable matters to be very slowly biodegradable compounds like humic and fulvic acids. These compounds are stable organics supposedly derived from cellulose and lignin [24]. Humic substances present smaller molecules and had a tendency to increase as the landfill age increase, meaning that humification take place [25].

Considering the several stages of biodegradation in landfills, three stages in the life of a landfill are commonly considered. They correspond to three classes of leachates according to the different compositions (Table 1-1).

<table>
<thead>
<tr>
<th>Table 1-1 Classes of leachates [26]</th>
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<tbody>
<tr>
<td>Age (years)</td>
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<tr>
<td>pH</td>
</tr>
<tr>
<td>COD (mg L⁻¹)</td>
</tr>
<tr>
<td>BOD₅/COD</td>
</tr>
<tr>
<td>Organic compounds</td>
</tr>
<tr>
<td>Heavy metals</td>
</tr>
<tr>
<td>Biodegradability</td>
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High concentration of ammonia nitrogen is reported in all classes. The COD, Biological Oxygen Demand (BOD), phosphorous and nitrogen, tend to reduce with the increase of the age of cell, evidencing the degradation process [23]. Leachate composition allows thus to estimate the age of the landfill [27]. Despite that leachate quality depends on each landfill characteristic, some authors consider that methanogenic leachates are very similar in composition (Ammoniacal nitrogen: 1000-3000mgN/L, COD: 2000-8000mg/L, BOD₅: below 1000mg/L) whether from sites in temperate northern hemisphere countries, from tropical countries in either hemisphere, and irrespective of economic status of the country [28].
Knowledge acquisition takes time when we are chasing a moving target. It is the case when considering landfill emission behavior, because it is gradually changing during the exploitation period and especially when the operation lifetime of landfill is continuously extended [29].

1.3 Environmental problems associated

The contact between these highly polluted juices called leachates and landfill surrounding ecosystems put in immediate danger the natural equilibrium present leading to numerous negative consequences for the environment. Monitoring groundwater contiguous to sanitary landfills shows very often the presence of pollutants [30]. Furthermore, pollution could escape the area and enter the water cycle (figure 1-2). It must not be forgotten that water is like the blood of our planet and has a circulation cycle that includes rain, soil infiltration, groundwater circulation into rivers and finally to the oceans where evaporation leads again to rain and so on. Pollution of landfills could propagate everywhere including irrigation wells, with leachates as the intermediary, so the treatment of these liquids is indispensable.

![Figure 1-2 Groundwater pollution by leachates (based on [31])](image)

A large spectrum of negative effects could be produced by leachate pollution. Riverside sensitive species, in particularly macro invertebrates like *Gammarus pulex* and *Asellus aquaticus* present fertility and growth problems exposed to leachates, which may contain inhibiting toxins [32]. Endocrine disrupting compounds like nonylphenol or bisphenol can affect hormone systems in organisms [33]. Estrogenic and androgenic effects are also
Aquatic environment, including fish downstream landfills present high values of PCB, dichlorodiphenyltrichloroethane (DDT) and polybrominated diphenyl ethers (PBDE) [16]. Phytotoxic components are thus present in the leachates [35]. Fat volatile acids and humic acids are toxic for nitrifying biomass, with degrees of inhibition that depends on the rest of leachate composition and the toxin biodegradation kinetics [36]. Chlorides and ammonia are also present at concentrations that are acutely toxic for fresh water aquatic organisms as well as salt water organisms [15]. Toxicity test may be of great help in understanding and preventing environmental problems associated with leachates lost [37]. Efforts in reducing landfilling of hazardous waste are possibly more beneficial for the environment than reducing the concentration of a specific substance in leachate from say 20μg/l to 5μg/l [29]. Indeed, hazardous waste landfills contain very low biological activity and are mostly inorganic [38].

Ground and surface water and sediments may be polluted by landfill leachates with high amounts of heavy metals bounded with organic matter, carbonates and ferric oxides [39]. Metal contamination inhibits nitrifying and heterotrophic bacteria [40], so metals and metalloids are considered as priority pollutants [41]. However, according to some authors, concentrations of heavy metals are widely at levels below those found in domestic sewage except for chromium [42]. It must be noticed that different chemical species of a metal can have different toxicity and behavior but common metal analyses in landfill leachates consist in an elemental determination only [43].

Considering human health, leachates can contain EDCs with uncertain potential risk to the environment and human health [17]. 1,4-Dioxane, a chemical stable molecule suspected to be a human carcinogen is widely used as solvent and as a stabilizer in chlorinated solvents and is often detected in landfill leachates [44]. Furthermore, dioxin could be present in landfill, especially when incineration ashes are accepted [45].

Among the numerous danger substances mentioned before, the high concentration of ammonia nitrogen constitutes the primary problem. Ammonium and ammonia appear to be responsible for most of the acute toxicity over aquatic organisms in leachates [46]. Depending on pH conditions, ammonia nitrogen could be found under the ionized form (NH₄⁺) that has low negatives impacts on aquatic fauna compare to the gas form NH₃ that is very toxic. Even
at low concentrations, ammonia produce burns in bronchioles of fish that diminish their blood oxygen exchange. Fortunately, in most of the surface runoff waters the pH is in a range between 6.5 and 8.5 so most ammonia nitrogen is present under the less toxic ionized form. However, ammonia could be transformed into nitrites and nitrates (nitrogen cycle) consuming oxygen, a phenomenon that contributes to anoxic situations in the aquatic environment. Nitrites formed from ammonia nitrogen by the nitrification process in wastewater treatment stations or in natural ecosystems are very toxic for living organisms. In the human blood, nitrites can be fixed to haemoglobin to form methaemoglobin and block the oxygen transport capacity. The level of blood oxygen drops leading to a disease called methaemoglobinaemia that is very dangerous, particularly to infants. Furthermore, nitrites could combine with proteins into the digestive tube to form nitrosamines that are suspected to produce cancer [47]. Nitrates that are also formed during nitrification have low toxic levels over the aquatic fauna. However, nitrogen in nitrate is one of the major nutrient elements for plants necessary to metabolize proteins, nucleic acids and cell wall polymers. When nitrates are in excess, they constitute an important factor of eutrophication meaning an excessive grow of algae and plants leading to depletion of dissolved oxygen and to a disequilibrium in the aquatic environment leading to biodiversity lost.

1.4 Treatment alternatives

1.4.1 Introduction

Numerous techniques exist to treat landfill leachates and some of them are used often in a complementary way [48]. The choice of the adequate treatment will depend on several factors that correspond principally to the characteristics of each landfill [49]. For each case, a lot of aspects must be considered, for example, the quality and quantity of leachate, country disposal law, process residuals, geographical and climatic characteristics, economic cost, among many others. Each landfill could have thus a specific adapted solution [50]. In addition, seasonal variation must be considered as it will influence not only leachates amount and composition but also bacterial communities present in the overall biodegradation process [51]. Thus, large leachates treatment plants require complex management strategies that must include planning, engineering and development of several interrelated processes [52].
Pretreatment of wastes like mechanical-biological process or in situ aeration exist in order to ameliorate leachates quality. Other operating actions, aim at concentrating in a short period the outflow from landfill (“flushing”) are also used but appears more problematic [53]. In hot climate due to the strong changes in the amount of leachate produced during rainy seasons, equalization tanks previous to treatment are sometimes needed [54].

Taking into account the difference from one site to another, numerous treatment alternatives exist but biological treatment appears to be the most popular because it is an efficient method for nitrogen removal, acute toxicity and estrogenic effects [34]. Anyway high tech treatment technologies are often a combination of different processes [55].

1.4.2 Mix with domestic waste waters

The mixed wastewater is treated in the already in place municipal depuration stations so it is a very economic technique and thus often used. However, recently the method has been questioned because of the negative effects of slowly biodegradable compounds and heavy metals of leachates that diminish removal performances of the global domestic wastewater process [26]. Furthermore, very high concentrations of ammonia nitrogen found in many leachates may represent doubling or greater of the overall nitrogen loading of the domestic wastewater treatment plant (WWTP) [41]. Finally, European directives are focused on the onsite treatment of leachates so the technique should not remain popular [56].

1.4.3 Recirculation into the landfill

There are benefits and problems associated with leachate recirculation [57]. It is an cheaper method but there are opposed opinions of the real effects over the physical-chemical phenomena occurring during the degradation process and beyond. Operation is complex because the regime of leachates recirculation should be adjusted to the phases of landfill stabilization in order to enhance efficiency in the general process [58]. Besides the primary problems found, accumulation of $\text{NH}_4^+$ and VFAs appear to have a highly negative effect on the biodegradation process [59].
The literature is somehow contradictory depending on the landfill case. Some authors found positive effects like a better nutriment distribution into the landfill and even amelioration in leachate quality. No negative effect in the methanogenic phase is reported by [60]. Recirculation could even increase the amount of methane in biogas due to moisture in dry landfill zones liberating organic materials [61] but others suggest very negative effects like methanogenesis inhibition and acidification [26]. Other studies inform that recirculation do not degrade the quality of the bio gas produced [62].

An interesting variant of this technique is a preliminary nitrification of the leachates before their reintroduction into the landfill. Denitrification into the landfill is then possible on the circulated leachate [61]. Nevertheless, others authors reports that nitrate has a negative effect on waste decomposition [63]. Furthermore, nitrate injections into the landfill may delay the beginning of the methanogenic phase [64]. Actually, this technique is forbidden in several countries including Luxembourg, so clearly there is a lot of space for research. Again, each landfill has its own characteristics to consider in the results.

1.4.4 Lagooning

It is an effective method to remove pathogens, organic and inorganic matter with low operation and maintenance costs that made it very popular, particularly in developing countries, since there is a little need for specialized skills to run the system [26]. The treatment is effective to reach standards for discharge in the public sewer system thanks to a marked removal of the most problematic compounds and an attenuation of yearly concentration fluctuations [65]. However, aerated lagoon treatment efficiencies decrease as leachates become old and biological nitrification is limited and occurs only during summer so most of the nitrogen is eliminated by stripping [66].

1.4.5 Conventional activated sludge (CAS)

It is generally used to treat domestic wastewater. It is rarely used to treat landfill leachates alone. Important disadvantages like inadequate sludge settle ability (high Sludge Volume Index SVI), need for longer aeration times, high energy demand and excess sludge production are problems that forces to focus on other technologies [26]. Considering this, CAS process is
often used with a combination of pretreatment and the use of powdered activated carbon (PAC) treatment to ameliorate removal performances [67]. Bentonite addition to enhance settling properties is also possible using CAS [68].

1.4.6 Sequencing batch reactor (SBR)

This process has great flexibility, and many authors have reported COD removals up to 75%, and 99% for ammonia nitrogen [26]. So it is very effective [61]. SBRs can adapt the duration of aerated and anoxic phases so it is well suited for variable leachate quality [69]. Partial nitrification and denitrification processes can be optimized [70]. Considering this, SBR systems have been implemented successfully to treat landfill leachates in real sites [71, 72]. Between the disadvantages, bulking problems are reported [73]. However, the technique is in strong development and could be also coupled with other methods as constructed wetland systems [74].

1.4.7 Biofilms systems

In these processes, microorganisms are attached to a medium, contrary to suspended biomass systems where microorganisms are suspended generally in formations called bioflocs. This characteristic allows evicting the settling step necessary to separate biomass from treated effluent and thus bulking problems are not longer present. Simultaneous nitrification and denitrification are possible in aerobic biofilms systems [75], meaning that they can be used for leachate treatment [76], [77]. Several configurations exist like trickling filters and moving-bed biofilm reactors [26]. Rotating contactor is also a variant using biofilm properties that may be used to treat ammonium rich leachates [78].

1.4.8 Physical-chemical processes

Several physical-chemical processes exist to treat wastewater pollution; they are generally used as pre-treatment, as a last purification step or to treat a specific pollutant [26]. Among numerous technologies employed for leachate treatment the most popular are: coagulation and flocculation processes [79], air stripping [80], adsorption of humic substances on activated carbon [81], adsorption of ammonium into zeolite [82], advanced oxidation processes like
Fenton’s oxidation [83], photocatalytic process [84], photochemical oxidation of humic substances in the presence of hydrogen peroxide [85], filter materials for removal of heavy metals made of byproducts of steel and paper manufacturing industries [86], humic fraction chemical precipitation [87] and co-generation combined with evaporation [88, 89]. Moreover, combinations are possible like coagulation-flocculation with settling, sand filtration and granular activated carbon (GAC) adsorption with good results at least on lab scale [90].

1.4.9 Plant related systems

Soil plant systems constitute a plausible alternative, and good removal results could be obtained [91]. For example, willow will grow very well on a substrate of nitrified leachate [92]. Treatment by evapotranspiration with young willow *Salix amygdalina* has been applied successfully [93]. Short rotation coppice appears to be a good willow plantation method to treat leachate [94]. Other plants like *Eichhornia crassipes* and green alga *Clorella vulgaris* are also used in nitrogen removal of wastewaters [95].

1.4.10 Wetlands

Wetland systems are well adapted to leachate treatment [96]. In particular, removal of heavy metals is possible [97]. However, wetland could have low efficiency [98]. This is why this technique is generally used in combination with other processes [99].

1.4.11 Membrane technologies

During the last 20 years, effective treatments based on membrane technology have emerged as a viable treatment alternative. Nanofiltration (NF), reverse osmosis (RO), microfiltration, and ultrafiltration (UF) are the main membrane processes applied for landfill leachates treatment [26]. NF is a convenient method to remove organic pollutants and heavy metals from leachates [100, 101]. Often coupled with biological systems, it can provide a superior effluent quality with low COD levels suitable for trade effluent disposal, and open up the potential for water reuse on-site [102]. RO is an efficient, reliable and economical technology to treat landfill leachates [103, 104] and also an environmentally friendly way to solve the problems with this kind of liquids proven by more than 20 years of experience according to
Furthermore, it can be used coupled with a previous SBR system to obtain an even better effluent quality [106]. Microfiltration cannot be used alone and is mostly used as a pre-treatment for other membrane or chemical processes [26]. UF could also be used as pre-treatment but these kinds of membranes coupled with biological treatment give birth to the named membrane bioreactor systems that are commonly used nowadays in municipal WWTP and are slowly replacing the traditional CAS. High performances of nitrification-denitrification could be achieved treating landfill leachates with aerated MBR [107]. However biological treating in anaerobic submerged membrane bioreactor is possible, with post-treatment to attain discharges regulations [108]. MBR present better performances than SBR treating landfill leachates according to some authors [109]. Several variants of MBR systems exist, namely floating media biofilter-crossflow microfiltration system, submerged membrane adsorption bioreactor and sponge-submerged membrane bioreactor [110]. Furthermore, MBR can be combined to other MBR, for example, for a final nitrification step [111]. Of course, combined MBR with activated carbon systems are more effective than MBR alone [112, 113].

1.4.12 Others techniques associated

Leachate pollution, particularly ammonia and COD concentration could be attenuated by sand layers and other complex soil mechanisms [114]. Unsaturated sandstone appears to be very effective [115]. Re-utilization of treated leachates in other processes like cooling towers is also possible and constitutes a valuable reuse option [116]. Excess concentrated sludge mixed with biowaste can be used to feed, an anaerobic fermenter and produce bio gas [117]. Bioremediation, Ozone treatment and geo-bed filters are other treatment possibilities [118]. Bio-augmentation of nitrifying organisms in a special reactor connected to return sludge is an effective upgrade to biological processes that could replace most expensive high volume extensions [119]. Other combined process exists including evaporation steps and post treatment of distillate with reverse osmosis [120].

1.5 References


http://science-vocabulary.blogspot.com/


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**Chapter 2: Membrane bioreactor**

Abstract: Membrane bioreactors are conventional activated sludge systems that use a membrane for separation of soluble and particulate matter instead of a settler. This particular coupled system allows improving wastewater biological treatment. In this chapter, the different available types of membranes will be presented, as well as the activated sludge systems. The primary problems associated to the operation, mathematical modelling and control options will be introduced. Finally, the advantages of the MBR over the CAS system will be highlighted.

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2.1 Background

Biological processes like CAS are bioreactors specially designed to treat water pollution. They are called bioreactors because of the microorganism’s community (also called activated sludge that is composed mostly of bacteria) that develops into the confined volume where several transformations of matter or “reactions” will occur. The most common technique used since the beginning of the 20º century to separate microorganisms from treated water is sedimentation by gravity in settlers. However, there are bulking and other problems associated to filamentous bacteria that transform this phase frequently into the operational bottleneck step of the overall process.

Between 1960 and 1970, the first trials to replace settlers by ultrafiltration membranes are reported [1], giving birth to the so called MBR. This new coupled process allows not only to forget bulking problem but also to reach high concentrations of biomass, transforming the ecology of activated sludge used-so far. From 1970 to 1990, the technology moves forward to industrial applications principally in Japan and North America but also in the UK and South Africa. This was made possible by companies like Dorr-Oliver with Sanki Engineering Co. Ltd, Thetford Systems now part of Zenon Environmental and by Kubota [1]. In the early 1990s, external configurations in which membrane modules are outside the bioreactor, were more often used with limited wider application because of highest power consumption compared to submerged MBR that appeared after mid 1990s [2]. By the year 2000, there were over 500 MBRs in operation principally in Japan but also in North America and Europe, with predominance of the aerobic biological process rather than anaerobic bioreactor [1]. By 2006, 2259 MBRs (considering only 4 providers: Zenon, USFilter, Kubota and Mitsubishi-Rayon) were in operation worldwide [2].

Considering research, journal articles involving studies on MBRs were scarce before 1990 and less than 10 per year during the 1991-1995 period but increased notably to more than 80 per year in 2004 [2]. It must be noticed that publications are a good indicator of the number of highly qualified personnel being trained in the area.

Resuming, MBR develops rapidly from an advanced laboratory technology into a commercially feasible process for full scale use with important reductions in operating costs
during the last decade [3]. MBR industry can be considered as mature and stabilized with more industrial applications, for the moment, but with municipal WWTP market increasing fast [4]. In the future, upgrading of existing wastewater treatment plants with MBR technology, will become more and more popular, because of constant increasing demand and high discharge restrictions [5].

2.2 Membranes

2.2.1 Introduction

A membrane could be defined as a barrier that allows the passage of certain elements and retains the others. They exist in nature from the beginnings of life. The most ancient biological cells were in possession of one. They should have been a logical step in wastewater treatment but unfortunately nature is not usually easy to imitate. Fortunately, the manufacture and the use of membranes for filtration of wastewater had known an important development in the last years. Filtration membranes are semi-permeable barriers that allow retaining solutes or particles contained in solvent. RO, NF, UF and microfiltration are different membrane nomenclature associated to the different pore size and thus to the dimension of the retained compounds (figure 2-1).

An ideal membrane must have high permeability associated to high selectivity and must be thermally, chemically and mechanically resistant [6]. Permeability is related to the size and density of membrane pores. However, according to Poisseuille´s law, the thickness of the membrane will influence as well in the flow rate through each pore. The thermal and chemical resistance is associated to the materials which composed the membrane. Mechanical resistance depends on operational aspects but also on membrane structure and geometry.
2.2.2 Types of membranes

Three types of membranes exist (figure 2-2) and can be distinguished by their internal configuration [6]. The first kind called “symmetric membranes” are composed of only one material with uniform thickness composition. The second one is the “asymmetric membranes” that differentiate from the first ones, because of the presence of several layers of different porosity. Finally there are the so called “composite membranes” that are composed of various materials with different porosity.

![Figure 2-2 Types of membranes (based on [6])](image-url)
The materials used for fabrication can be separated into two big families. On one side, there are the organic or polymer membranes and on the other there are the mineral ones. The organic ones represent more of the 80% of the market [6], probably by their low production cost and availability in many pore sizes. The most used organic materials include cellulose derivatives, polyamides, polysulfones, polyolefins and acrylic polymers. The mineral ones are mostly composed of ceramic but there are also made of porous carbon, metals or glass.

2.2.3 Membrane configuration

The membrane geometry is related to the configuration employed. Flat plates, tubular and hollow-fibre are the main configurations used (figure 2-3). In general, manufacturer seeks for characteristics like to have an important filtration area, being easy to clean, high turbulence to enhance mass transfer, low energy consumption, and of course at the lowest price possible. Anyway, the short membrane lifetime is generally reported to be the main disadvantage of the system [8].

![Membrane configurations](image)

Figure 2-3 Membrane configurations (Based on [6] and [9])

The tubular configuration was the first being developed. In this process, the membrane module is placed outside the bioreactor (external configuration, figure 2-4). Membrane tubes have diameters going from 6 to 25 millimetres, and the filtration unit can contain several ones depending on the flux to be treated. They are usually placed in parallel to facilitate replacement. Filtration is carried out from inside to outside the tube through the membrane. Pumps must ensure the necessary over-pressure leading to high operational cost.

Hollow fiber membranes are placed submerged into the bioreactor where mixed liquor will circulate from the outside to the inside of the fibre (submerged configuration, figure 2-4).
Filtration is made by aspiration in this case. Flat plate membranes are also used in a submerged configuration.

When using an external configuration, membrane clogging is somehow diminished by the fact that filtration flux is perpendicular to the mixed liquor flux. However, the phenomenon is still present. In the submerged configuration, air must be injected close to the membranes in order to produce turbulence and a back washing procedure must be established periodically.

![Figure 2-4 External and submerged membrane configurations](image)

2.2.4 Membrane clogging

In order to explain clogging fundamentals, several concepts must be defined:

*Driving force:* It is generally associated to a pressure driven force developed by pumps.

*Flux:* It is the quantity of material which passes through a unit area of membrane per unit of time. For example, in the international system of units (SI) we could say a flux of: 1 m$^3$ of water per m$^2$ of membrane per second (m$^3$/m$^2$-s)). Simplifying, we obtain m/s, this is why sometimes the flux is also called permeability speed. This flux is related to the driving force and to the total resistance offered by the membrane and the interfacial region next to it.

*Factors opposing to the driving force:* Everything that prevents the movement of water, like the membrane or everything that is deposited on.
Polarisation layer: When filtration is on, there is always in contact with the membrane a limited layer where water is continually being expulsed and solutes accumulate at abnormally higher concentrations. This phenomenon is called polarisation.

The membrane clogging, also called hydraulic resistance or fouling, is the augmentation of the resistance offered by the membrane over the driving force. It is generally caused by compounds present in the wastewater or by compounds generated in the activated sludge that will deposit and accumulate over the membrane forming a polarisation layer. The effects will depend on the membrane nature (pore size, material and configuration), hydrodynamic conditions close to the membrane and the trans-membrane pressure difference.

Furthermore, the environmental conditions applied to the biomass will influence as well because of the variations in the amounts of microbial products. Extracellular polymeric substances (EPS) and soluble microbial products (SMP) are the primary compounds accused to enhance membrane fouling [10, 11, 12, 13, 14]. The initial fouling development could be characterized by three layers with different composition and consequences on the overall fouling resistance [15]. The upper cake layer consists of loosely bound biomass flocs and attached SMP. The intermediate one is composed equally by SMP and biomass flocs or EPS cluster, and the last pore fouling layer contains a higher concentration of soluble proteins strongly bound to the membrane.

Filterability is an important factor in MBR systems which depends on suspended EPS that themselves increase with high mechanical stress and high Food/Microorganism ratio [16]. EPS have thus an important role, having a little hydrophobic fraction; they also have often been reported to be involved in floc cohesion and organization [17]. Particularly, it is the irreversible adsorption of soluble EPS (Soluble Polysaccharides that are up to 84% of EPS) that could be the main cause of membrane fouling [13, 10, 18].

Other authors mention that membrane fouling mechanisms are dominated by external fouling, which is closely related to the movement of cell population to the membrane surface and inorganic precipitation that form the strongly attached cake layer [19].
The fouling layer in MBR is mostly governed by deposition of soluble compounds, particularly proteins-like substances (Polypeptides) [19]. However, other studies affirm that the relative contribution to resistance to filtration during fouling of dissolved molecules is very low [21]. Reversible fouling vs irreversible fouling is an also recurrent terminology considering this phenomenon. Clearly, fouling is a complex phenomenon that involves numerous factors that until now are not well described and in the better cases, are well understood in a particular situation but can vary widely from one station to another. For example, a study reports that high salinity which is a common factor to consider, greatly affects the physical and biochemical properties of an activated sludge, by increasing SMP and EPS concentrations and of course, it also affects membrane fouling [22].

2.2.5 Mathematical modelisation of hydraulic resistance

The simplest equation that describes the hydraulic resistance phenomenon is the one proposed by the french engineer Henry Darcy (1803-1858).

\[ J = \frac{\Delta P}{\mu R} \]

With:
\[ J \] = Volumetric flux (m·s\(^{-1}\))
\[ \Delta P \] = Trans-membrane pressure difference (Pa)
\[ \mu \] = Fluid viscosity (Pa·s).
\[ R \] = Resistance (m\(^{-1}\))

Resistance value will depend on factors opposed to the free circulation of flux. For example, considering the membrane and the polarisation layer resistance we have:

\[ R = R_{\text{membrane}} + R_{\text{polarisation layer}} \]

Trans-membrane pressure is used for assessing fouling in a MBR, but long-term behaviour prediction remains unclear [23]. Complete understanding of surface-interaction mechanisms, including particle and soluble material roles, is a key factor in modeling the filtration of
biological suspension [24]. Nowadays, computational fluid dynamics (CFD) are used to study the mass transfer coefficient and permeate flux in MBRs [25].

2.2.6 Filtration operation strategies to control fouling

Several techniques have been developed to control fouling. Direct aeration under the membrane, chemical cleaning and back washing are upon the more used.

**Membrane aeration:** Air is directly pumped under the membranes to create turbulence that will disperse the fouling materials. Aeration applied to membranes in configurations like air-jet, and air-lift allows greater flux and thus membrane fouling could be diminished [26]. Size of bubbles and fluxes are important. Coarse bubbles have weaker effect on dislodging foulants from the membrane surface than fine bubbles at critical aeration velocities [27]. Mixed liquor suspended solids (MLSS) is also a factor to consider because oxygen transfer diminishes at high concentrations. Finally, it must not be forgotten that aeration cost are important as well [28].

**Membrane cleaning:** Off-site chemical cleaning is effective in restoring membrane performances by removing foulants deposited within the membrane or strongly fixed on the membrane surfaces [27]. The most common product used includes citric acid and sodium hydroxide.

**Membrane backwashing:** A periodic backflush allows removing the slow accumulation of sludge inside the hollow fibber lumen, ameliorating membrane permeability, in particular, combined with coarse bubble aeration [29]. Generally, periods of filtering and back washing are established. Relaxation periods are also frequently being used. During relaxation time, no filtration or back washing is made so turbulence and mass movement related to aeration will predominate.
2.3 Activated sludges

2.3.1 Introduction

Biological processes adapted from natural microorganism behavior have been created to treat wastewater, particularly to eliminate soluble and particulate organic matter but also to diminish nutrient content. The aim is to produce optimal environmental conditions for the microorganisms that will develop using the organic compounds present in wastewater as carbon source, often measured as COD. The oxidation of this organic matter could be either aerobic or anaerobic. Anoxic conditions are also usually found in these kinds of processes.

Subsequently, a way to separate microorganism from the water must be found. We seek to obtain on one side a concentrate of microorganisms that could be directly recycled into the process and on the other, the treated water. Gas will be produced, mostly carbon dioxide (CO$_2$) in the aerobic case, and CO$_2$ in combination with methane in the anaerobic case. The mixed liquor is frequently purged in order to maintain a determined MLSS concentration in the systems.

Following a similar logic, these biological processes are also capable of diminishing several problematic compounds present in wastewater like nitrogen derivative, phosphor, heavy metals, xeno-biotic substances, etc. The original microorganism strains but most of all the conditions applied to the biomass will directly have an influence on performances. Feed variations (concentration and volumes) must be considered as conditions applied to biomass as well.

With biological processes, high performances are generally obtained, and the system tolerates variable loads. However, many microorganism colonies are very sensitive to many chemical products present in wastewater, and the process is slow compared with chemical treatment. Finally high energy consumption, particularly in aerated systems is to be signalised as well.
2.3.2 Classification

The biological processes can be classified according to the feed characteristics (continuous or fed-batch), by their redox conditions, and if it is a biofilm or a suspended biomass. In general, continuous regimes are used when large volumes are to be treated. The fed-batch or discontinuous fed, like for example SBR systems, are often used to treat smaller volumes. However, the system is also used industrially using two or more units in parallel. MBRs are generally operated with continuous regime.

The redox conditions are aerobic, anoxic or anaerobic. It must be remembered that in wastewater treatment, the absence of oxygen as electron acceptor is called anoxic condition and the absence of any other electron acceptor (nitrate, sulphate) is called anaerobic. The processes oriented to organic carbon treatment can be aerobic or anaerobic, anoxic systems are generally employed for nitrogen-removal. The configuration applied usually for nitrogen removal includes a denitrification tank followed by a nitrification tank with recirculation. However, other configurations may include many tanks [30].

The fixed biofilm processes are characterized by the presence of an inert support medium on which biomass will develop. In suspended biomass processes, the microorganisms grown suspended into the mixed liquor generally regrouped in biofloc formations.

2.3.3 Microbiology

Biological processes conceived to treat wastewater are composed of micro ecosystems contained in one or several bioreactors in which many kinds of microorganisms cohabit and interact. Most of this so called activated sludge is composed of bacteria that have a fundamental role in the conversion of organic compounds into biomass and gas products. Furthermore, just like in nature, some bacteria can convert ammonia into nitrate and finally into nitrogen gas (nitrification-denitrification). Other trophic levels are also present and include predators, like protozoans and metazoan that are able to consume bacterial organic compounds and predators as well.
Microorganisms can be classified according to the redox conditions of the environment in which they can survive, but also to their carbon needs and finally to the energy resources used. The most common distinction is between heterotroph and autotroph bacteria. Heterotroph bacteria use organic carbon as energy and as a carbon source for the production of new cells. Autotroph bacteria use reactions that involve inorganic compounds to obtain energy and inorganic carbon for cell synthesis. In our case, the first ones are responsible for the consumption of the COD, and denitrification. The second ones are responsible for nitrification.

As a general rule, Autotroph organisms are less efficient in energy recovery, and thus they have a slow growth rate compared to heterotrophs. In wastewater treatment, we generally seek for conditions of neutral pH and ambient temperature but every microorganism or microecosystem could have its own optimal conditions. Temperature preference is also used to classify microorganisms. Psychrophile, mesophile and thermophile are used to refer to an organism that has optimal growing rate at 15°C, 35°C and 55°C respectively.

### 2.3.4 Mathematical modelisation

In order to describe what is happening during a biological process, implicated compounds must be differentiated. Then, biological reactions must be defined according to stoichiometry and the implicated compounds, each one having a characteristic kinetic rate.

Microorganisms growing kinetics are more often described by the so called Monod kinetics [31].

\[
\mu = \frac{\mu_m \times S}{K_S + S}
\]

With:
- \(\mu\) = Specific growth rate coefficient (d\(^{-1}\))
- \(\mu_m\) = Maximum specific growth rate (d\(^{-1}\))
- \(S\) = Limiting substrate concentration (g/l)
- \(K_S\) = Half saturation coefficient (g/l)
This expression is based on the model for enzyme kinetics of Michaelis & Menten (1913) to describe the growth during the exponential phase in dependence of nutrient concentration in a culture medium. Monod’s growth model was proposed as an empirical model to describe the microbial growth. It introduces the concept of a limiting nutrient [32].

Monod kinetics are combined with mass balances that include inlets, outlets, accumulations and transformations in the reactor resulting in a differential equation system. The evolution of the compounds could then be described allowing the simulation of the micro system behavior. It must be noticed that solving this complex differential equations system is not an easy task and generally, adapted software and powerful new-generation computers are needed.

2.3.5 Used parameters to describe activated sludge process

Using a simplified approach, meaning considering all microorganisms present as one activated sludge and the different substrate compounds of the influent as one substrate, allows to define important parameters of the system.

![Figure 2-5 Simplified schematics of the MBR process](image)

*Hydraulic residence time (HRT):* The hydraulic residence time corresponds to the theoretical time of contact between the influent to be treated and the biomass. It represents the relation between reactor volume and influent flow rate.

\[
HRT = \frac{V}{Q}
\]
With:

\[
\begin{align*}
\text{HRT} &= \text{Hydraulic residence time (d)} \\
V &= \text{Reactor volume (l)} \\
Q &= \text{Influent flow rate (l/d)}
\end{align*}
\]

HRT is a very important parameter because it can be associated with the organic charge, often represented by the food-microorganisms ratio (F/M ratio). This parameter is associated with reactor volumes and with exploitation costs. Because MBR gives the opportunity to work under complete retention of biomass (high mixed liquor suspended solids (MLSS) concentration), it is possible to choose between important ranges of F/M ratio. However, there is a tendency to operate MBR under low F/M ratio. For the treatment of industrial wastewater with MBR, even small variations of the HRT influence the COD consumption performances. High HRT allows obtaining better nitrification and COD consumption performances for wastewater that contains low biodegradable compounds and high ammonia concentration [18]. Furthermore, with low HRT, the organic charge is bigger leading to highest biomass production [32].

*Sludge age or mean cell residence time (MCRT):* Sludge age is a relation between the amount of biomass present into the bioreactor and the amount of biomass purged in a period of time.

\[
MCRT = \frac{V}{Q_p}
\]

With:

\[
\begin{align*}
\text{MCRT} &= \text{Mean cell residence time (d)} \\
V &= \text{Reactor volume (l)} \\
Q_p &= \text{Purge flow rate (l/d)}
\end{align*}
\]

MCRT is associated with the organic matter consumption performances. Under long MCRT, SMP concentration is reduced. However, long MCRT is associated to very low F/M ratio. For the industrial wastewater case, there is no consensus over the MCRT to use. The choice will depend on the nature and biodegradability of pollutant compounds to be treated [34]. High sludge age leads to low specific oxygen consumption. Nevertheless, the volumetric oxygen consumption increases [35]. Specific biological activity like specific oxygen uptake rate
(SOUR), specific nitrification rate, (SNR) and specific denitrification rate (SDNR) will be reduced under high MCRT. Fouling rate could also be affected negatively [36]. Other authors suggest no effect on membrane filtration [37]. Under high sludge age, constant MLVSS/MLSS ratios suggest that no accumulation of inorganic compounds in the biomass is observed [38]. The biomass concentration may evolve into an equilibrium concentration proportional to the volumetric load [37, 39]. The overall yield also could be influenced negatively under high MCRT [40].

**Volumetric loading rate:** The volumetric loading rate is a relation between the mass of substrate that goes into the reactor per unit of time and the reactor volume.

\[
\text{Volumetric loading rate} = \frac{Q \times (Se - S)}{V}
\]

With:
- Volumetric loading rate (gCOD/(l·d))
- \(Q\) = Influent flow rate (l/d)
- \(Se\) = Inlet substrate concentration (gCOD/l)
- \(S\) = Reactor substrate concentration (gCOD/l)
- \(V\) = Reactor volume (l)

**Mass loading rate:** The mass loading rate is a relation between the mass of substrate that goes into the reactor per unit of time and the sludge mass present. This value is often referred as the food/microorganism ratio (F/M ratio).

\[
\text{Mass loading rate} = \frac{Q \times (Se - S)}{V \times X}
\]

With:
- Mass loading rate (gCOD/(gMLSS·d))
- \(Q\) = Influent flow rate (l/d)
- \(Se\) = Inlet substrate concentration (gCOD/l)
- \(S\) = Reactor substrate concentration (gCOD/l)
- \(V\) = Reactor volume (l)
- \(X\) = Reactor sludge concentration (gMLSS/l)
Yield: As mentioned before, the Yield or sludge production performance is a relation between the mass of biomass produced by unit of substrate mass consumed. A theoretical value could be found according to the substrate characteristics but the observed value is usually calculated or measured. The assumption that biomass is represented by MLSS could be used (at steady state).

\[ Y_{OBS} = \frac{Q_p \times X}{Q \times (S_e - S)} \]

With:
- \( Y_{OBS} \) = Observed yield (gCOD biomass/gCOD)
- \( Q_p \) = Purge flow rate (l/d)
- \( X \) = Reactor sludge concentration (gCOD biomass/l)
- \( Q \) = Influent flow rate (l/d)
- \( S_e \) = Inlet substrate concentration (gCOD/l)
- \( S \) = Reactor substrate concentration (gCOD/l)

Sludge Volume Index (SVI): The SVI represents the volume occupied by a concentrated sludge that is obtained after allowing it to settle for a period of time (half an hour typically). This index is used primarily to assess the settling ability of particles or other types of suspensions in the activated sludge. Filamentous bacteria, for example, can increase the index value and generates so called filamentous bulking and thus decrease settling velocity. Correlation between the SVI and the growth of filamentous bacteria were found [41].

2.4 MBR advantages

MBR with submerged membranes, allow confining the totality of the biomass into the reactor offering several advantages:

2.4.1 High biomass concentration

MBR technology allows working with very high biomass concentration compared with conventional systems. Concentrations can go from 8 to more than 30g per liter [42, 43].
Anyway, there is a limit because of the influence on fouling and on oxygen transfer [44]. This high concentration allows more compact systems.

2.4.2 Pathogens removal properties

Micro-filtration and ultra-filtration membranes used in MBR retain suspended matter that includes virus and pathogenic organisms [45, 46]. The quality of treated water is therefore superior to the one found with conventional techniques using decantation.

2.4.3 Sludge age control

The MCRT can be controlled independently of the HRT. It is possible to work under very large ranges of sludge age going up to 1000 days [37]. This will allow controlling several parameters like, for example, the mass loading rate.

2.4.4 Development of low growing rate bacteria

The complete retention of biomass combined with the low mass loading rate allows diminishing the growing activity of heterotrophic bacteria. This will lead to the development of low growing rate bacteria like nitrifying autotrophic ones that in general are the limiting step of the system, particularly in CAS [47, 46]. Also bacteria degrading less degradable compounds could have enough time to grow and to develop some activity in the reactor.

2.4.5 Reduction of sludge production

Thanks to the possibility of working with low mass loading rate, the system could be orientated to a maintenance status. Under these conditions, it is possible to have very low sludge productions, and it is even possible to reach nearly zero net sludge production [37]. This situation allows reducing sludge treatment environmental impact and cost.

Other more specific advantages are also referred in literature. For example, bioreactors with membrane technology are an efficient way to remove endocrine disrupting compounds in wastewater [48]. Phenols can be degraded in membrane bioreactors. Good results were
obtained including organic removal treating synthetic wastewater [49]. High molecular weight compounds contained in wastewater can be degraded in MBR with high effluent quality [45].

Polycyclic aromatic hydrocarbons (PAH) content in leachates could be correctly reduced during treatment with membrane bioreactor [50]. Integrated membrane process, including a MBR and reverse osmosis treating landfill leachates showed stable removal efficiency in spite of the unbalanced carbon to nitrogen ratio (C/N) of 0.16 as BOD₅ and total nitrogen (TN) base [51]. From an economical point of view, lower operating costs were achieved with MBR including reverse osmosis compared to conventional advanced treatments.

More generally, MBRs show better results for nutrient removal than a conventional activated sludge process [52]. The MBR sludge contains a much higher fraction of non-flocculating microorganisms, more dispersed biomass and smaller flocs, which may contribute to better performances than CAS [53]. Excellent performances are obtained treating municipal wastewater with 96% removal for COD and 95% removal for KN using MBR with biomass concentration up to 25gMLSS/l [46]. Biological nitrogen removal (BNR) systems with recycle of the nitrates require less aerobic volume to accomplish complete nitrification than conventional fully aerobic activated sludge systems operating under the same conditions [54].

2.5 References


Chapter 3: MBR for leachates treatment

Abstract: The key aspects of the behavior of a biological bioreactor are influenced by the conditions applied but most of all by the properties of the treated wastewater. When treating landfill leachates, some important microbiological differences are found compared with traditional municipal wastewater treatment. In this chapter, the primary processes present in nitrogen removal are presented, meaning Hydrolysis, COD consumption, nitrification and denitrification. Novel processes like anaerobic ammonia oxidation are briefly announced as well.
3.1 Microbiological aspect

Bioreactors can be considered as artificial ecosystems with complex interactions between biotic, physical and chemical factors. The biological culture is responsible for the removal of pollutant matters in wastewater treatment. Some pollutants are the substrates of certain microorganisms present in the so called activated sludge. It is important to note that the term activated sludge refers to all the components present into sludge, including extracellular polymeric substances, feeding wastewater components and a very large amount of different bacterial species and predators. Considering that about 104 different genomes per gram occur in soils, and the number may be very high in aquatic habitats as well, we are very far from understanding the complexity of bacterial life in any natural habitat [1]. However, in bioreactors some environmental factors can be more or less controlled simplifying the task. Population dynamics in wastewater treatment reactors are governed by the substrate composition and SRT, but other environmental factor are also important like variations as pH values, temperature shifts or substrate concentrations inhibition [2]. In MBRs, most of the bacteria are grouped in biofloc formation but there is always some fraction that is fixed to any kind of support present, like membranes or just the tank walls. Flocs are complex formations that are characterized by their morphology, their physical properties and by their components, including bacterial species.

Comparison of the diversity of activated sludge plants is very complex as there are always some spatial, diurnal and intra sample variations, but some authors suggest that one sample could be representative of biomass diversity in each plant [3]. However, this is only valid considering that the WWTP has reached steady state, which is generally not the case. More often, abiotic parameters are changing permanently, in particular, feed composition and pollutant concentration so the biotic part is adapting constantly living in an evolving environment.

From a trophic point of view, microorganisms can be classified into two groups: decomposers and predators. Predators that develop slowly will be favored in systems like MBR operated with low F/M ratios and high MCRT.
Decomposers constitute the more important fraction of the activated sludge. They are composed primarily of bacteria but also of some osmotic protozoa that can consume soluble substrate as well [4]. As mentioned before, they will be generally associated in flocs, adaptation that optimises substrate recovery and provides protection against predators. The two main bacterial communities present are heterotrophic and autotrophic bacteria. Heterotrophic bacteria found in WWTP are from genus Bacillus, Pseudomonas, Alcaligenes, Moraxella, and Flavobacterium. Denitrifying bacteria from genus Achromobacter, Arthrobacter and Hyphomicrobium are also present [4].

The presence of filamentous biomass is also an important aspect regarding the flocs formation and properties. Filamentous microorganisms have an enormous role in activated sludge settlings [13]. Furthermore, they behaviour can be modelled and can be integrated into ASM1 [14]. Biological nutrient removal process conditions favour these types of bacteria, so they are in competition with other floc forming organisms [15]. Filamentous microorganisms are principally affected by DO concentration and F/M ratio so most of them are typically associated with low F/M and high DO concentration but there are types that may prefer low DO [16]. In MBR, settling properties are not necessary so the organisms responsible for bulking like Microthrix parvicella can be exploited enhancing their high denitrification rate [17].

Other groups that can be found are autotrophic bacteria, like genus Nitrosomonas, Nitrosococcus, Nitrospira and Nitrosocystis. They are responsible for Ammonia oxidation during nitrification. Nitrite oxidation is performed by genus Nitrobacter, Nitrospiras and
Nitrosococcus. Recently, the Anammox bacteria role was enhanced, particularly, for landfill leachates treatment [18].

![Figure 3-2 Denitrifying bacteria](image)

Other Gram positive G-like coccoid bacteria are also present and can represent a large group of microorganisms, which role in treatment plants is not yet clear [22]. Methanogenic organisms that are normally not present significantly can be responsible for up to 85% of organic degradation in immature landfill leachate according to some authors [23].

Predators that consume bacteria can belong to Flagellates, Amoeba and Ciliate groups among Protozoa and also Rotifers and Nematodes [24].

![Figure 3-3 Protozoa, rotifer and nematode](image)

Finally, the micro-organisms associated with activated sludge foams are not deeply understood and they have been recently described [30]. Microorganisms, able to degrade refractory COD compounds such as humic acids, are also present in an MBR operated with high sludge age [31]. White-rot fungi that can degrade Lignin could be present also [32].

Considering the high ammonia concentration present in landfill leachates, it is expected to find more autotrophic bacteria than in municipal WWTPs. Furthermore, the low F/M ratio applied and the use of membrane separation technique will lead to the presence of slow growing organisms, including predators and other bacterial types like anammox.

60
3.2 Hydrolysis

During the hydrolysis process, large molecules are transformed into smaller ones. They can be directly degraded by microorganisms then. Catabolism of organic substrates by bacteria needs large polymers being hydrolysed into smaller molecules that can be transported across the cell membrane. Hydrolysis is generally a slow process compared to the biological growth processes so it can often be a rate limiting step considering the overall biological wastewater process [33].

Hydrolysis of some components may occur including the hydrolysis of dissolved organic matter, particulate organic matter, organic nitrogen, etc. It will depend on the assumption of the overall model used. In fact, the phenomenon is more complex because the number and types of compounds that could be hydrolysed is enormous. Moreover, there is no consensus on the association between hydrolytic enzymes and active biomass, what exactly controls the level of these enzymes remains a mystery [34].

The process rate could be described by a simple first order process concerning hydrolysable material, but it is generally described by a more complex expression of the saturation type. For example, the description used in ASM3 is as follows:

\[
  r_H = k_H \cdot \frac{X_S / X_H}{K_X + X_S / X_H} \cdot X_H
\]

With:
- \( r_H \) = Hydrolysis rate (gCOD/L·d)
- \( k_H \) = Hydrolysis constant (g COD/(gCOD·d))
- \( K_X \) = Hydrolysis saturation constant (gCOD/gCOD)
- \( X_S \) = Hydrolysable matter (gCOD/l)
- \( X_H \) = Biomass involve in hydrolysis (gCOD/l)

In this situation, the heterotrophic biomass has a maximum hydrolysis capacity. When the ratio between hydrolysable matter and biomass corresponds to the hydrolysis saturation constant, the hydrolysis rate is at half of the maximum rate. The hydrolysis constant can have different values depending on the electron acceptor and the hydrolysable matter considered.
For bioreactor modelling, the hydrolysis process is a simplified name for a complex amount of reactions that convert matter into a readily biodegradable substrate for biomass. The incorporation of the hydrolysis in ASM models results in the addition of a time delay for the utilization of oxygen since it is only associated with growth of organisms at the expense of biodegradable substrate. An important difference between hydrolysis in ASM1 and ASM3 is that in the first one, electron donor is considered in the kinetic rate, contrasting with ASM3 approach in which it is of less dominating importance for the rates of oxygen consumption and denitrification [35].

3.3 COD consumption

3.3.1 Introduction

The COD in municipal wastewater can be divided into a soluble (unseattleable-uncoagulable), a colloidal (unseattleable-coagulable) and a particulate (seattleable) fraction. The soluble fraction contains readily biodegradable COD and inerts. The colloidal one is composed of hydrolysable COD and some biomass (up to 24%). Particulate fraction contains biomass (up to 14%) and hydrolysable COD, with a little proportion of inert matter. Hydrolysable matter can be divided into two fractions with different kinetics [36].

In the biological treatment of wastewater, heterotrophic bacteria are the primary consumers of the biodegradable fraction of COD. It was reported that biofilm bacteria can be adapted to the use of humic substances as a carbon source just like any other more easily used carbon source like amino acids or carbohydrates [37]. Considering landfill leachates, a large amount of organic matter present is generally considered as inert by most of the treatment processes. Organic matter is therefore a complex mixture of different components that, according to several properties can be differentiated in fractions of similar behavior.

When entering a bioreactor, the organic matter present in the wastewater can follow several pathways according to the degree of complexity of the description of the process used. In ASM models for example, organic matter can be oxidated to carbon dioxide and different nutrients, can be assimilated in biomass, can be converted into another form of organic matter or can just pass through unchanged. In the last case, it will mean that the organic matter in
question is not biodegradable, at least by the bioreactor concerned. Another classification usually used to characterize organic matter is considering the carbohydrates, fats and proteins. The oxygen consumption associated varies considerably from one group to another.

3.3.2 Stoichiometry and energetic

Organic matter chemical composition can be approximated by expression: $C_{18}H_{19}O_9N$ [33]. In order to obtain the energy resulting from the organic matter oxidation the two half reactions of electron donor and acceptor can be used. For the aerobic case,

$$\frac{1}{70}C_{18}H_{19}O_9N + \frac{28}{70}H_2O \rightarrow \frac{17}{70}HCO_3^- + \frac{1}{70}NH_4^+ + H^+ + e^-$$

With $\Delta G^o = -32$kJ/eq, and

$$\frac{1}{2}H_2O \rightarrow \frac{1}{4}O_2 + H^+ + e^-$$

With $\Delta G^o = 78$kJ/eq

Hence, the combined expression:

$$\frac{1}{70}C_{18}H_{19}O_9N + \frac{1}{4}O_2 \rightarrow \frac{17}{70}CO_2 + \frac{1}{70}HCO_3^- + \frac{1}{70}NH_4^+ + \frac{1}{10}H_2O$$

With $\Delta G^o = -110$kJ/eq

3.3.3 Heterotrophic yield

Heterotrophic bacteria will metabolize organic substrate converting it into biomass. The relationship between the mass of substrate consumed and the mass of biomass produced is called the heterotrophic yield. Typical values of growth yield for heterotrophic biomass are near 60% on a COD-basis [33]. The yield concept could be confusing particularly in wastewater treatment systems in which it is generally expanded to the overall increase of the complete sludge mass.

Another aspect to consider is that the energy efficiency of heterotrophic bacteria is close to 60% meaning that a part of the energy must be used in another phenomenon like storage. Thus the yield of an activated sludge will depend on the amount of carbon used for energy production, for growth, for storage and the amount transformed into extracellular polymeric
substances [33]. The yield will be also influenced by the time in which the transformation takes place. For example, bacteria could have a high yield in a short lapse of time during which they just store organics and grow, but if the time lapse increases, the bacteria will have the time to consume the stored material or just decay and the yield will diminish accordingly.

The maximum yield constant generally used in biological wastewater models for the aerobic growth process in wastewater is around 0.6 to 0.65gCOD/gCOD even if the observed yield is often lower due to maintenance or endogenous respiration [33]. Anyway, the real yield will depend also on the substrate characteristics, biomass species, the amount of substrate for each biomass species and so on. Possibly, the yield value could even change with time.

Heterotrophic bacteria will also need nutrients in order to growth, particularly nitrogen and phosphorus but also sulphur and iron. It is possible to calculate the demand for nutrients by mass balances but the calculation will be based in an estimation of the chemical composition of microorganisms.

3.3.4 Kinetics

Heterotrophic growth kinetics is normally described as a Monod expression:

\[
\mu_H = \frac{\mu_{H_{\text{max}}} [S]}{K_S + [S]}
\]

With:

- \(\mu_H\) = Heterotrophic specific growth rate (1/d)
- \(\mu_{H_{\text{max}}}\) = Heterotrophic maximum specific growth rate (1/d)
- \([S]\) = Substrate concentration into the reactor (gCOD/l)
- \(K_S\) = Saturation constant of ammonia nitrogen (gCOD/l)

3.3.5 Environmental factor influence over heterotrophic conversions

Temperature: It is possible to describe the temperature dependence of biological processes by the exponential expression first derived by Jacobus Henricus van’t Hoff (1852-1911) that corrects the maximum growth rate and thus the process kinetics.

\[
\mu_{\text{max}}(T) = \mu_{\text{max}}(20^\circ\text{C}) \exp(\kappa(T-20))
\]
With:

\[ T = \text{Temperature (°C)} \]
\[ K = \text{Temperature constant} \]

This expression is valid in the temperature range 0–32°C. From 32°C to 40°C the maximum specific growth rate become constant, then it finally declines to zero at around 45°C. In the thermophilic range (50-60°C), the growth process also occurs with a maximum specific growth rate up to 50 per cent higher than at 35°C [33].

**Dissolved oxygen:** the influence of dissolved oxygen over the kinetics could be described by a Monod-type expression.

\[ \mu_H = \mu_{H_{\text{max}}} \times \frac{[O_2]}{K_{S,O2} + [O_2]} \]

With:

\[ \mu_H = \text{Heterotrophic specific growth rate (1/d)} \]
\[ \mu_{H_{\text{max}}} = \text{Heterotrophic maximum specific growth rate (1/d)} \]
\[ [O_2] = \text{Dissolved oxygen concentration into the reactor (gO}_2/l) \]
\[ K_{S,O2} = \text{Dissolved oxygen saturation constant (gO}_2/l) \]

The dissolved oxygen saturation constant reflects diffusional limitations into flocs or biofilms so it will depend on size and thickness respectively.

Considering the substrate and the oxygen, the following double Monod expression is obtained:

\[ \mu_H = \mu_{H_{\text{max}}} \times \frac{[S]}{K_S + [S]} \times \frac{[O_2]}{K_{S,O2} + [O_2]} \]

In the case that organic matter is consumed under anoxic conditions, meaning with nitrate (or nitrite) as electron acceptor, oxygen acts as a non-competitive reversible inhibition. Specific growth expression for the kinetics is as follows:

\[ \mu_H = \mu_{H_{\text{max}}} \times \eta_{NOX} \times \frac{[S]}{K_S + [S]} \times \frac{K_{S,O2}}{K_{S,O2} + [O_2]} \times \frac{[NO_3]}{K_{S,NO} + [NO_3]} \]
Note that a correction factor for the maximum anoxic growth is added. This specific process is also known as denitrification.

\textit{pH}: aerobic heterotrophic conversion is pH dependent with a maximum growth rate between 7 to 8. With lower or upper pH, the growth rate declines to very low values. Low pH is more common in the treatment process. It could be the consequence of low pH in the raw wastewater, nitrification or even with chemical precipitation of phosphorus.

3.4 Nitrification

3.4.1 Introduction

Nitrification is a biological process in which the ammonium is transformed into nitrite and then eventually into nitrate. The process includes two steps, involving two different groups of bacteria, the ammonia oxidizing bacteria (AOB) that oxidizes ammonia to nitrite, and the nitrite oxidizing bacteria (NOB) that oxidizes nitrite to nitrate [1] (figure 3-4).
Nitrogen is part of a complex cycle where numerous oxidation-reduction reactions take place thanks to the nitrogen atom that has six levels of oxidation [39].

The global oxidation reactions are:

\[
NH_4^+ + O_2 + H^+ + 2e^- \leftrightarrow NH_2OH + H_2O
\]

\[
NH_2OH + H_2O \leftrightarrow NO_2^- + 5H^+ + 4e^-\]

\[
NO_2^- + \frac{1}{2}O_2 \leftrightarrow NO_3^-
\]

The first reaction is endothermic so hydroxylamine (NH$_2$OH) will almost never be produced and according to this, hydroxylamine is rarely detected in autotrophic aerobic environments.
3.4.2 Stoichiometry and energetics

The process of nitrification is generally achieved by autotrophic microorganisms, specifically chemolithotrophic ones. They use CO$_2$ as a carbon source and reduced nitrogen as an energy source [39].

The process takes place according to two stages. The ammonia nitrogen generally under the ammonium form is oxidized into nitrite by a bacterial group named Nitrosomonas. Then, nitrites are oxidized into nitrates by another bacterial group called Nitrobacter. Other bacterial groups like Nitrospiras, Nitrococcus and Nitrosocystis could participate as well.

In wastewater treatment, large ranges of bacterial species could be present. However, thanks to genetic investigations, it is generally accepted that the different species performances do not differentiate greatly from performances of Nitrosomonas and Nitrobacter. This is why the conceptual engineer point of view considers that the process is divided into only two bacterial groups and even sometimes only one bacterial group with more or less known stoichiometry and kinetics [33].

The process that describes the energetic consumption of (AOB) is [39]:

$$NH_4^+ + \frac{3}{2}O_2 \rightarrow NO_2^- + H_2O + 2H^+$$

With $\Delta G^o = -240$ to $-350$kJ/mol.

The process that describes the energetic consumption of (NOB) is [39]:

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$$

With $\Delta G^o = -65$ to $-90$kJ/mol.

Nitrifying bacteria have generally a low growth rate that represents one of the major problems to obtain good nitrification performances in wastewater treatment. Most of these kinds of bacteria are autotroph, so they use carbon dioxide as a carbon source. The carbon dioxide must be reduced before becoming part of the biomass. This reduction is made through the oxidation of the nitrogen source of the concerned organism [33].
For the AOBs, meaning for the ammonium oxidation, the growth expression is:

\[
15CO_2 + 13NH_4^+ \rightarrow 10NO_2^- + 3C_5H_7O_2N + 23H^+ + 4H_2O
\]

For the NOBs, meaning for the nitrite oxidation, the growth expression is:

\[
5CO_2 + NH_4^+ + 10NO_2^- + 2H_2O \rightarrow 10NO_2^- + C_5H_7O_2N + H^+
\]

### 3.4.3 Nitritation biomass yield

Nitrosomonas (or AOB) will consume ammonium nitrogen because of energetic needs and because of growth. It is known that the two reactions will occur but the proportion in which each reaction occurs is not known and could vary from an activated sludge to another. In order to obtain a global expression for this part of nitrification called Nitritation the biomass yield \(Y_{AOB}\) must be added.

This parameter could be estimated from bioenergetics [35]. Nevertheless, it must generally be measured. It gives information about the amount of biomass produced per amount of ammonium nitrogen consumed [33]. It could be expressed in different units, but in general it is expressed in gMLVSS/gNH\(_4^+\)−N. Considering the MLVSS equivalent to the amount of biomass expressed as C\(_5\)H\(_7\)O\(_2\)N, \(Y_{AOB}\) grams of C\(_5\)H\(_7\)O\(_2\)N are formed from consumption of 1 gram of nitrogen in the ammonium form.

Adding the expression for energy consumption multiplied by “x” and the expression for growth divided by three (to obtain only one molecule of C\(_5\)H\(_7\)O\(_2\)N instead of three), it is possible to express the nitritation in only one expression:

\[
(x + \frac{13}{3})NH_4^+ + (\frac{3x}{2})O_2 + 5CO_2 \rightarrow C_5H_7O_2N + (x + \frac{4}{3})H_2O + (2x + \frac{23}{3})H^+
\]

Taking into account the molecular weights, it is possible to obtain “x” in function of \(Y_{AOB}\).

Using the value proposed by [33] of \(Y_{AOB}=0.1\)gMLVSS/gNH\(_4^+\)−N we obtain (for the sludge and specific conditions of this author’s experiment):

\[
81NH_4^+ + 115O_2 + 5CO_2 \rightarrow C_5H_7O_2N + 80NO_2^- + 78H_2O + 160H^+
\]
It can be deduced that Nitrosomonas use almost 95% of consumed nitrogen for energetic needs and only a little more than 5% for growth. The oxygen consumption can also be estimated: 3.2 grams of O$_2$ are necessary to oxidise 1 gram of ammonia nitrogen.

Using the value proposed by [38] of $Y_{AOB} = 0.05$ grams of biomass per gram of nitrogen (for the sludge and specific conditions of this author’s experiment):

$$161NH_4^+ + 236O_2 + 5CO_2 \rightarrow C_5H_7O_2N + 160NO_2^- + 158H_2O + 322H^+$$

It can be deduced that Nitrosomonas use more than 97% of consumed nitrogen for energetic needs and less than 3% for growth. The oxygen consumption could also be estimated: 3.3 grams of O$_2$ per gram of ammonia nitrogen oxidized.

The value of biomass yield $Y_{AOB}$, depends on the composition and the conditions applied to the biomass. The measured value obtained by each author will influence the general expression, so it must be used with caution. The values obtained are, however, generally very close or at least of similar magnitude.

3.4.4 Nitratation biomass yield

Nitrobacter (or NOB), will consume nitrites because of energetic needs and because of growing similarly to the AOB case. In order to obtain a global expression for this part of nitrification called Nitratation the biomass yield $Y_{NOB}$ is needed.

This parameter that is generally measured, gives information about the amount of biomass produced per amount of consumed nitrogen under nitrite form [33]. It could be expressed in different units, but in general it is expressed in gMLVSS/gNO$_2^-$-N. Using the same procedure that for AOB (using “y” instead of “x”), it is possible to express the nitratation in only one expression:

$$(y+10)NO_2^- + NH_4^+ + (y/2)O_2 + 5CO_2 + 2H_2O \rightarrow C_5H_7O_2N +(y+10)NO_3^- +H^+$$

Taking into account the molecular weights, it is possible to obtain “y” in function of $Y_{NOB}$. 

Using the value proposed by [33] of \( Y_{NOB} = 0.06 \, g \text{MLVSS}/g \text{NO}_2^-\text{N} \) we obtain (for the sludge and specific conditions of this author’s experiment):

\[
135\text{NO}_2^- + \text{NH}_4^+ + 67\text{O}_2 + 5\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_5\text{H}_7\text{O}_2\text{N} + 135\text{NO}_3^- + \text{H}^+
\]

It can be deduced that nitrobacter use more than 92% of consumed nitrogen for energetic needs and only a bit more than 7% for growing purposes. The oxygen consumption could also be estimated: 1.1 grams of \( \text{O}_2 \) are necessary to oxidise 1 gram of nitrite nitrogen.

Using the value proposed by [38] of \( Y_{NOB} = 0.02 \, g \text{MLVSS}/g \text{N} \) for the sludge and specific conditions of this author’s experiment:

\[
404\text{NO}_2^- + \text{NH}_4^+ + 197\text{O}_2 + 5\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_5\text{H}_7\text{O}_2\text{N} + 404\text{NO}_3^- + \text{H}^+
\]

It can be deduced that Nitrosomonas use more than 97% of consumed nitrogen for energetic needs and less than 3% for growing. The oxygen consumption could also be estimated: 1.1 grams of \( \text{O}_2 \) per gram of nitrite nitrogen oxidized.

Just like for the AOB, the value of biomass yield \( Y_{NOB} \), depends on the composition and the conditions applied to the biomass. The measured value obtained by each author will influence the general expression, so it must be used with caution. Each case will have its own general expressions.

Finally, it is possible to obtain a general expression for the overall nitrification process combining general expressions for nitritation and nitratation. Nitritation expression multiplied by \((y+10)\) and added to nitratation expression multiplied by \((x+10/3)\) allows to eliminate nitrites.

Using values proposed by [33]: \( Y_{AOB} = 0.1 \, g \text{MLVSS}/g \text{NH}_4^+\text{N} \) and \( Y_{NOB} = 0.06 \, g \text{MLVSS}/g \text{NO}_2^-\text{N} \) we obtain the following general expression:

\[
51\text{NH}_4^+ + 95\text{O}_2 + 5\text{CO}_2 \rightarrow \text{C}_5\text{H}_7\text{O}_2\text{N} + 50\text{NO}_3^- + 49\text{H}_2\text{O} + 101\text{H}^+
\]

It can be deduced that during nitrification, 4.3 grams of \( \text{O}_2 \) are necessary to oxidise 1 gram of ammonia nitrogen. Furthermore, using molecular weights, the overall yield for autotrophic biomass \( Y_A \) can be obtained. For this case, \( Y_A = 0.159 \, g \text{MLVSS}/g \text{NH}_4^+\text{N} \).
Using values proposed by [38]: \( Y_{AOB} = 0.05 \text{gMLVSS/gNH}_4^+\text{--N} \) and \( Y_{NOB} = 0.02 \text{gMLVSS/gNO}_2^-\text{--N} \) we obtain the following general expression:

\[
116\text{NH}_4^+ + 225\text{O}_2 + 5\text{CO}_2 \rightarrow \text{C}_3\text{H}_7\text{O}_2\text{N} + 115\text{NO}_3^- + 113\text{H}_2\text{O} + 231\text{H}^+
\]

It can be deduced that during nitrification, 4.4 grams of \( \text{O}_2 \) are necessary to oxidise 1 gram of ammonia nitrogen. Furthermore, using molecular weights, the overall yield for autotrophic biomass \( Y_A \) can be obtained. For this case, \( Y_A = 0.07 \text{gMLVSS/gNH}_4^+\text{--N} \).

Again, results depend in each case on measurement and conditions applied to the biomass.

### 3.4.5 Kinetics

The nitrification kinetics could be described according to a Monod-type relation.

For the nitritation, meaning for the Nitrosomonas bacteria:

\[
\mu_{AOB} = \mu_{AOB}^{\text{max}} \times \frac{[\text{NH}_4^+]}{K_{S,NH4} + [\text{NH}_4^+]} 
\]

With:
- \( \mu_{AOB} \) = Specific growth rate (1/d)
- \( \mu_{AOB}^{\text{max}} \) = Maximum specific growth rate (1/d)
- \([\text{NH}_4^+]\) = Ammonia nitrogen concentration into the reactor (gN/l)
- \( K_{S,NH4} \) = Saturation constant of ammonia nitrogen (gN/l)

For the nitratation, meaning for the Nitrobacter bacteria:

\[
\mu_{NOB} = \mu_{NOB}^{\text{max}} \times \frac{[\text{NO}_2^-]}{K_{S,NO2} + [\text{NO}_2^-]} 
\]

With:
- \( \mu_{NOB} \) = Specific growth rate (1/d)
- \( \mu_{NOB}^{\text{max}} \) = Maximum specific growth rate (1/d)
- \([\text{NO}_2^-]\) = Nitrite nitrogen concentration into the reactor (gN/l)
- \( K_{S,NO2} \) = Nitrite nitrogen saturation constant (gN/l)
For simplifying purposes, nitrification could also be considered as one process. It is the case of the ASM family models.

### 3.4.6 Environmental factor influence over nitrification

In practice, ammonium oxidation is usually the slowest step and thus the limiting stage of the overall nitrification process. Nitrite will be present in important amounts only when the process is accomplished under non-stationary conditions, like for example: a non constant inlet flux, put into operation period, or under operational problems [33].

Temperature: Temperature dependence of biological processes could be described by the exponential expression first derived by Jacobus Henricus van’t Hoff (1852-1911) that corrects the maximum growth rate and thus the process kinetics.

\[
\mu_{\text{max}}(T) = \mu_{\text{max}}(20^\circ\text{C}) \exp(\kappa(T-20))
\]

With:

- \( T \) = Temperature (ºC)
- \( \kappa \) = Temperature constant

This expression can be applied for temperatures between 10 and 22ºC. For highest temperatures (30-35ºC), the maximum growth became constant and then between 35 and 40ºC it starts to diminish. Normally, the nitrification does not occur with thermophilic temperatures, (50-60ºC). For temperatures between 0 and 10 ºC the van’t Hoff expression can be used as well.

Just like any other type of bacteria, nitrifying bacteria are especially sensitive to rapid temperature changes. When the temperature increases rapidly (in few hours) the growth rate is lower than expected, similarly when the temperature drops rapidly the growth rate declines more than if the temperature dropped gradually [33].

**Dissolved oxygen:** the influence of dissolved oxygen over the kinetics could be described by a Monod-type expression.

\[
\mu = \mu_{\text{max}} \times \frac{[O_2]}{K_{S,O_2} + [O_2]}
\]
With:
\[ \mu = \text{Specific growth rate (1/d)} \]
\[ \mu_{\text{max}} = \text{Maximum specific growth rate (1/d)} \]
\[ [O_2] = \text{Dissolved oxygen concentration into the reactor (gO}_2/l) \]
\[ K_{S,O_2} = \text{Dissolved oxygen saturation constant (gO}_2/l) \]

Considering the substrate and the oxygen, for example, for nitritation, the following Monod expression is obtained:

\[
\mu_{\text{AOB}} = \mu_{\text{AOBmax}} \times \frac{[NH_4^+]}{K_{S,NH_4} + [NH_4^+]} \times \frac{[O_2]}{K_{S,O_2} + [O_2]}
\]

With:
\[ \mu_{\text{AOB}} = \text{Specific growth rate (1/d)} \]
\[ \mu_{\text{AOBmax}} = \text{Maximum specific growth rate (1/d)} \]
\[ [NH_4^+] = \text{Ammonia nitrogen concentration into the reactor (gN/l)} \]
\[ K_{S,NH_4} = \text{Saturation constant of ammonia nitrogen (gN/l)} \]
\[ [O_2] = \text{Dissolved oxygen concentration into the reactor (gO}_2/l) \]
\[ K_{S,O_2} = \text{Dissolved oxygen saturation constant (gO}_2/l) \]

Dissolved oxygen saturation constant depends of oxygen diffusion into the media. Oxygen diffusion is a very important parameter. Each station has its own value because it depends on specific conditions applied to the system (floc size, biomass type, biomass concentration, etc.). Nitrifying bacteria are more sensitive to low temperatures that heterotrophic bacteria. However, they are very resistant to high oxygen concentrations [33].

\text{\textbf{pH}}: The nitrification process depends of pH with an optimum located between 8 and 9. Because of the nitrification influence over the pH, the pH value inside the flocs or close to the biofilm will be lower than the one in the liquid phase [33]. Nitrification leads to pH drop that could lead to other chemical mechanisms as an increase of phosphorus solubility [40]. Local pH variations near bacterial flocs are sufficient to produce effects even with the general pH under control.
Inhibiting substances: The nitrification could be inhibited by several substances present in wastewater treatment plants (WWTP). Nitrifying biomass is not more sensitive to toxic substances than others bacteria present in the WWTP. The primary inhibiting substances are metals and some organic substances like sulphured compounds, phenols and cyanides [33]. If microorganisms are exposed to several inhibiting substances at the same time, the effect of individual substances is generally more powerful in a synergy effect [33].

The nitrifying biomass only uses mineralised nitrogen and has a low growth rate. These two reasons make them appear late in the biological process chain of WWTP or even in a natural environment as rivers. The effect of inhibition by other bacteria activities as heterotrophs is possible. It is evident that even the presence of other bacteria will influence at least the transport of nutrients, so they could have negative effects.

3.5 Denitrification

3.5.1 Introduction

Denitrification is a biological process in which bacteria are able of consuming oxidized nitrogen and converting it to N₂ gas through a series of intermediates, which could escape afterwards to the atmosphere (figure 3-4). Denitrifying organisms could be heterotrophic bacteria or autotrophic bacteria. Heterotrophic bacteria are the most common. They use free molecular oxygen if available as electron acceptor. Under anoxic conditions, nitrite and nitrate could serve as electron acceptor as well. Autotrophic bacteria can use H₂ or reduced sulfate compounds as electron donors [39]. Heterotrophic microorganisms are generally represented by the Pseudomonas species [38]. Their needs for organic matter,(in order to perform denitrification) constitutes a problem because normally the effluent of a nitrification reactor contains a low organic concentration.

To face this, two situations are possible. In the first, denitrification is enhanced by addition of an external carbon source that could be methanol or high organic loaded wastewater. Maximum denitrification rate (MDR) obtained in industrial wastewater treatment at 20°C with high ammonium content are 0.64gN/(gMLVSS·d) with ethanol as carbon source and 0.11gN/(gMLVSS·d) with methanol [41]. The other option is to let endogenous
denitrification take place. In this process, bacteria will use their own cell reserves as an internal substrate, and thus they will produce less biomass and at a lower rate [38].

The five nitrogenous compounds implicated in denitrification are nitrate, nitrite, nitric oxide and nitrous oxide besides the already mentioned atmospheric nitrogen. The reduction is carried out by one organism in four steps, which could be inhibited and thus allowed for intermediary products to escape [39]. High nitrate concentration and low organics substrate concentration could lead to this situation. Being very difficult to measure, the kinetics of intermediates reactions are not known in detail. Furthermore, it is very difficult to show how much nitric oxide and nitrous oxide is being produced so there is no exact nitrogen balance [39].

The catabolism of denitrification could be described in the following simplified form using methanol as an energy source [39]:

\[
6\text{NO}_3^- + 2\text{CH}_3\text{OH} \rightarrow 6\text{NO}_2^- + 2\text{CO}_2 + 4\text{H}_2\text{O} \\
6\text{NO}_2^- + 3\text{CH}_3\text{OH} \rightarrow 3\text{N}_2 + 3\text{CO}_2 + 3\text{H}_2\text{O} + 6\text{OH}^- 
\]

The overall reaction:

\[
6\text{NO}_3^- + 5\text{CH}_3\text{OH} \rightarrow 3\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O} + 6\text{OH}^- + \Delta G^o
\]

With \( \Delta G^o = -783 \text{kJ/mol} \)

The energy will be employed for grow and for energy yield steps. It is shown that some alkalinity is produced as well as \( \text{CO}_2 \).

3.5.2 Stoichiometry and energetic

In order to obtain the energy resulting from the organic matter oxidation the two half reaction of electron donor and acceptor could be used [33].

\[
\frac{1}{70} \text{C}_{18}\text{H}_{19}\text{O}_9\text{N} + \frac{28}{70} \text{H}_2\text{O} \rightarrow \frac{17}{70} \text{CO}_2 + \frac{1}{70} \text{HCO}_3^- + \frac{1}{70} \text{NH}_4^+ + \text{H}^+ + e^- 
\]

With \( \Delta G^o = -32 \text{kJ/eeq} \) and

\[
\frac{1}{10} \text{N}_2 + \frac{3}{5} \text{H}_2\text{O} \rightarrow \frac{1}{5} \text{NO}_3^- + \frac{6}{5} \text{H}^+ + e^- 
\]
With $\Delta G^o = 71 \text{kJ/eeq}$

Hence, the combined expression is:

$$\frac{1}{70} C_{18}H_{19}O_9N + \frac{1}{5} NO_3^- + \frac{1}{5} H^+ \rightarrow \frac{1}{10} N_2 + \frac{17}{70} CO_2 + \frac{1}{70} HCO_3^- + \frac{1}{70} NH_4^+ + \frac{1}{5} H_2O$$

With $\Delta G^o = -103 \text{kJ/eeq}$

The organic matter provides the energy and the carbon source for biological growth.

The following equation of reaction can be used for representing biological growth using methanol as organic matter and nitrate as electron acceptor [39]:

$$0.926NO_3^- + CH_3OH + 0.22H_2CO_3 \rightarrow 0.051C_5H_7O_2N + 0.435N_2 + 0.926HCO_3^- + 1.56H_2O$$

Using nitrite as electron acceptor:

$$1.49NO_2^- + CH_3OH + 0.79H_2CO_3 \rightarrow 0.059C_5H_7O_2N + 0.72N_2 + 1.49HCO_3^- + 1.84H_2O$$

Other similar expressions, but using generic organic matter instead, can be found in literature [33]:

$$0.57C_{18}H_{19}O_9N + 3.73NO_3^- + 3.73H^+ \rightarrow C_5H_7O_2N + 1.65N_2 + 5.26CO_2 + 3.8H_2O$$

If considering that the organisms assimilate ammonium, which is mostly the case in wastewater treatment we obtain:

$$0.52C_{18}H_{19}O_9N + 3.28NO_3^- + 0.48NH_4^+ + 2.80H^+ \rightarrow C_5H_7O_2N + 1.64N_2 + 4.36CO_2 + 3.8H_2O$$

3.5.3 Denitrification yields

Two yields are generally used to describe denitrification, the first being the amount of biomass produced per gram of nitrate removed, and the second being the amount of biomass formed per gram of organic matter (as COD) consumed. The first is generally expressed in gMLVSS/gNO_3^- The value is variable in literature because it depends of the particular conditions applied to each experiment. Furthermore, the process will depend on the substrate used. Some authors present values of 0.454gMLVSS/gNO_3^- [39]. Considering the yield of
biomass formed per organic matter formed, values close to 0.4gCOD/gCOD are generally presented [33].

3.5.4 Kinetics

The concentrations of NO$_2^-$, NO$_3^-$ and organic substrate will influence the specific growth rate. Kinetics can be described using Monod kinetics, particularly a double Monod kinetic model [39].

$$\mu_{HNO3} = \mu_{HNO3\text{max}} \times \frac{[S]}{K_{S,S} + [S]} \times \frac{[NO_3^-]}{K_{S,NO3} + [NO_3^-]}$$

With:

- $\mu_{HNO3}$ = Anoxic heterotrophic specific growth rate (1/d)
- $\mu_{HNO3\text{max}}$ = Maximum anoxic heterotrophic specific growth rate (1/d)
- [S] = Substrate concentration into the reactor (gCOD/l)
- $K_{S,S}$ = Saturation constant of substrate (gCOD/l)
- [NO$_3^-$] = Nitrate concentration into the reactor (gN/l)
- $K_{S,NO3}$ = Saturation constant of nitrate (gN/l)

Or similarly for the nitrite case,

$$\mu_{HNO2} = \mu_{HNO2\text{max}} \times \frac{[S]}{K_{S,S} + [S]} \times \frac{[NO_2^-]}{K_{S,NO2} + [NO_2^-]}$$

With:

- $\mu_{HNO2}$ = Anoxic heterotrophic specific growth rate (1/d)
- $\mu_{HNO2\text{max}}$ = Maximum anoxic heterotrophic specific growth rate (1/d)
- [S] = Organic substrate concentration into the reactor (gCOD/l)
- $K_{S,S}$ = Saturation constant of organic substrate (gCOD/l)
- [NO$_2^-$] = Nitrite concentration into the reactor (gN/l)
- $K_{S,NO2}$ = Saturation constant of nitrite (gN/l)
3.5.5 **Parameters influencing denitrification**

Organic substrate, low dissolved oxygen concentration, correct pH and appropriate temperature are needed to obtain denitrification. Therefore, these parameters are the most influential.

*Organic substrate:* Several carbon sources can be used to obtain good denitrification rates so the choice is often based on costs [42]. Acetone, ethanol, acetic acid, glucose and methanol are common examples but most kinds of organics could be used including a cherry juice, olive oil, raw syrup, sawdust, marmalade and of course organic matter in wastewater. The amount of mixed organic substances present, for example in landfill leachates, will complicate the phenomena because the type of energy source used affects denitrification rate. Higher denitrification rates are found with methanol or other easily degradable substrates. Slower rates are found with more humified organics or by using endogenous carbon. Sometimes an external carbon addition is necessary. To optimize the nitrate elimination with an external carbon source process means to minimise the simultaneous exposure of the biomass to oxygen and the carbon source [43].

*Temperature:* Just like for the aerobic heterotrophic growth, temperature dependence of the biological process could be described by the exponential expression first derived by Jacobus Henricus van’t Hoff (1852-1911) that corrects the maximum growth rate and thus the process kinetics.

\[
\mu_{\text{max}} (T) = \mu_{\text{max}} (20^\circ\text{C})\exp(\kappa(T-20))
\]

With:

- \(T\) = Temperature (°C)
- \(\kappa\) = Temperature constant

Growth rate and removal rate of nitrate are both affected by temperature being completely inhibited below 5°C [39]. The process can occur at thermophilic temperatures of 50-60°C with higher removal rate [33].
**pH:** Optimum pH for the denitrification process are around 7 and 9. Low pH must be evicted; otherwise nitric oxides are produced [33].

**Dissolved oxygen:** Dissolved oxygen inhibits the denitrification process. Considering this the effect can still be described using a non-competitive reversible inhibition Monod expression:

\[
\mu_{HNO3} = \mu_{HNO3max} \times \frac{[S]}{K_{S,S} + [S]} \times \frac{[NO_3^-]}{K_{S,NO3} + [NO_3^-]} \times \frac{K_O}{[O_2]}
\]

With:
- \([O_2]\) = Dissolved oxygen concentration into the reactor (gO₂/l)
- \(K_O\) = Saturation constant for oxygen inhibition (gO₂/l)

It must be noticed that denitrification occurs in anoxic zones of aerated activated sludge flocs. The amount of anoxic zones present will depend on the air injection rates and floc structure [44].

### 3.6 Other paths: anammox

Anaerobic ammonia oxidation (ANAMMOX) is the conversion of ammonium directly into di-nitrogen gas under anaerobic conditions with nitrite as electron acceptor (figure 3-4). Being a fully autotrophic method, CO₂ is used as a carbon source. The bacteria responsible of this process were only discovered in the 1980’s with application to wastewater by 1990 [45]. The recent discovery of these bacteria is somehow surprising because they are present everywhere in nature in a non depreciable quantity. Furthermore, their roles in the N cycle are being enhanced by novel studies. Applications to leachate treatment are more recent, and generally combined with nitritation [46, 47]. Anammox bacteria could be present in activated sludge treating landfill leachates, with up to 14% of active biomass and would be responsible for 15% of ammonia removal [18].

When comparing conventional nitrogen removal by nitrification-denitrification with nitritation-anammox, some advantages appear [45]:

Nitrification:
\[ \text{Denitrification:} \quad NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \]

\[ NO_3^- + 4g \text{COD} + H^+ \rightarrow \frac{1}{2} N_2 + \frac{3}{2} g \text{sludge} \]

\text{Nitrification-denitrification:}
\[ NH_4^+ + 2O_2 + 4g \text{COD} \rightarrow \frac{1}{2} N_2 + H_2O + H^+ + \frac{3}{2} g \text{sludge} \]

\text{Nitritation:}
\[ NH_4^+ + \frac{3}{2} O_2 \rightarrow NO_2^- + H_2O + 2H^+ \]

\text{Anammox:}
\[ NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \]

\text{Nitrification-anammox:}
\[ NH_4^+ + \frac{3}{4} O_2 \rightarrow \frac{1}{2} N_2 + \frac{3}{2} H_2O + H^+ \]

As shown, no COD will be needed so the cost associated to the external carbon source will be reduced. Furthermore, the sludge production will be low. The overall process will need less oxygen which increases the sustainability of the operation and lowers the cost. Another advantage is that nitrous oxide N\(_2\)O is not an intermediate because it is absent in Anammox physiology.

The growth rate of Anammox bacteria is very low so special concern must be taken in order to avoid wash-out. Required sludge retention time increases so measures like immobilisation of sludges in compact biofilms or granules are generally undertaken. Nowadays, membrane separation techniques are useful as well.

Several kinds of reactors that contain Anammox bacteria were put into operation for N removal with acronyms according to the particularities of each process. Amongst them, the most cited are the SHARON\textsuperscript{®} process (Single-reactor High rate Ammonium Removal Over
Nitrate), the OLAND process (Oxygen Limited Autotrophic Nitrification Denitrification), CANON process (Completely Autotrophic Nitrogen removal Over Nitrate), and SNAP (Single-stage Nitrogen removal using Anammox and Partial nitritation) [48, 49, 50].

As mentioned before, it is necessary to obtain nitrites by nitritation in order to feed Anammox bacteria. To obtain the partial nitrification, meaning a triumph of Nitrosomonas over Nitrobacter, a strong selective pressure must be applied. For example, keeping oxygen concentration low or applying suboptimal pH could enhance AOB over NOB. Other characteristics of each group can be useful as well like temperature higher rate of AOB over NOB at temperatures higher than 20°C [45].

3.7 References


[29] http://kentsimmons.uwinnipeg.ca/16cm05/16labman05/lb5pg8.htm


Chapter 4: Bioreactor modelisation and simulation

Abstract: Bioreactor modelisation and simulation are important tools for wastewater treatment plants. Modelling the biological treatment allows a better understanding of the processes involved. Simulations could be used to test different scenarios and find cost reduction opportunities. In this chapter, the models used to describe bioreactors are presented starting by their matrix notation. The state-of-the-art Activated sludge models Nº1 and Nº3 are presented in detail.
4.1 Introduction

Mechanistic models are used for simulation and modelling of wastewater treatment plants. These models incorporate mathematical expressions that represent the biological interactions based on hypotheses proposed for the biological processes occurring within a system [1]. ASM1 and ASM3 are examples of these types of biological models. They represent what happen in a particular bioreactor unit of a wastewater treatment plant. However, other units are also present in the real facility and must also be modelled and linked between them through flows. Secondary clarifiers, membranes and recirculation between tanks could be incorporated to the overall treatment process. Simulation platforms like WEST® are tools that allow dealing with all these units at the same time.

A calibration procedure, that can have different levels of information requirements, is necessary in order to obtain good model predictions. Physical configuration (reactor volumes), operating conditions and influent loading patterns must be incorporated as well as the biological model information (wastewater composition and model stoichiometric and kinetic parameters). Different calibration protocols were developed by researchers and could be used but the particularity of each plant must be considered. Furthermore, calibration protocols are very difficult to compare them because each one was developed for a different objective and therefore, they have different focus [2].

4.2 Activated sludge models

The use of models for the simulation of the biological processes has become a very useful tool for design, control and operation of wastewater treatment plants. In addition, models allow a better understanding of processes occurring in the activated sludge, and the relation between them. They are an ideal tool for teaching and research [3]. The ASM development starts no long before 1970, but it was very limited by computer capacities and by the complexity of the written model presentation. It was not until 1982 that this changed, when the IAWPRC (International Association on Water Pollution Research and Control) established a task group on mathematical modeling for design and operation of activated sludge processes [3]. Five years later the result was the nitrogen removal ASM1 model also known as IAWPRC model.
or IAWQ model. Besides the model itself, guidelines for wastewater characterization and development of computer codes were presented constituting a strong platform for development until these days. The simple matrix representation used when presenting ASM1 was a key step towards a common language between researchers. With the rapid development of computers, models became more complex, and recent advances in the understanding of the activated sludge processes have been incorporated. The task group first of the IAWPRC, then called IAWQ, and finally IWA (International Water Association) developed other models as ASM2b, (that includes phosphorus removal) and ASM3 (that include internal storage). All of these models can be modified for each particular case in order to describe more accurately the reality of each bioreactor.

4.3 Matrix notation

A simple example will be used to explain the matrix notation [3]. Consider a situation in which soluble organic substrate is put together with heterotrophic bacteria in water under aerobic conditions. Three components are present besides the water: Heterotrophic biomass (Xb), soluble substrate (Ss) and dissolved oxygen (So). Two main processes occur: biomass growth and decay. Aeration is not considered, but it can. As shown in table 4-1, the components must be placed in the first row of the matrix, the processes on the first column and the process rates in the last column. The elements within the matrix are the stoichiometric coefficients which set up the mass relationships between the components in each process. As shown in the example, for the growth process, (+1) biomass is produced using (-1/Y) substrate and (-(-1-Y)/Y) of oxygen. During decay, biomass is consumed using oxygen. Stoichiometric and kinetic parameters are present in the matrix and can be defined in the lower corners.

<table>
<thead>
<tr>
<th>Process rate (gCOD/(L·d))</th>
<th>Ss</th>
<th>So</th>
<th>Xb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth</td>
<td>$\frac{-1}{Y}$</td>
<td>$\frac{-1-Y}{Y}$</td>
<td>1</td>
</tr>
<tr>
<td>Decay</td>
<td>-1</td>
<td>-1</td>
<td>$b \cdot Xb$</td>
</tr>
<tr>
<td>gCOD/L</td>
<td>-gCOD/L</td>
<td>gCOD/L</td>
<td></td>
</tr>
</tbody>
</table>

With: Y: biomass yield, \(\mu\): specific growth rate, \(K_s\): substrate saturation constant and \(b\): decay coefficient.
With the matrix notation, it is easy to check which processes are affecting the concentration of a single component. In the example, biomass is augmented by growth and diminished by decay. Substrate is diminished by growth and dissolved oxygen is diminished both by growth and by decay.

It is also possible to obtain an expression for the variation of a component in time (conversion rate) by adding the products of stoichiometric coefficient and process rate for each process that influences the component (bioreactor inlet and outlet concentration are not considered).

For example the conversion rate for the biomass is:

\[
\frac{dX_b}{dt} = (+1) \cdot \mu \cdot \frac{S_s}{K_s + S_s} \cdot X_b + (-1) \cdot b \cdot X_b = \mu \cdot \frac{S_s}{K_s + S_s} \cdot X_b - b \cdot X_b
\]

Similarly for the oxygen:

\[
\frac{dS_o}{dt} = (-1 - \frac{Y}{Y}) \cdot \mu \cdot \frac{S_s}{K_s + S_s} \cdot X_b + (-1) \cdot b \cdot X_b = (\frac{Y - 1}{Y}) \cdot \mu \cdot \frac{S_s}{K_s + S_s} \cdot X_b - b \cdot X_b
\]

And for the substrate:

\[
\frac{dS_s}{dt} = \frac{1}{Y} \cdot \mu \cdot \frac{S_s}{K_s + S_s} \cdot X_b
\]

### 4.4 Activated sludge model number 1 (ASM1)

[4]

#### 4.4.1 Introduction

The aim of models is to describe the events occurring within a system. Several processes could be incorporated according to the actual knowledge and to the particularities of a system. Each new process adds complexity, which will involve extra-parameters or variables and accordingly, supplementary efforts. Rates of the process also must be as simple as possible but with the capability of describing correctly an event. The modeller should keep in mind the complexity and time consuming task of estimation of the parameters.
The ASM1 model, one of the simplest ones, includes 13 components as shown in table 4-2. Seven components correspond to the organic matter measured as COD and four others correspond to nitrogen compounds.

<table>
<thead>
<tr>
<th>Si</th>
<th>Soluble inert</th>
<th>Organic matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ss</td>
<td>Readily biodegradable</td>
<td></td>
</tr>
<tr>
<td>Xi</td>
<td>Particulate inert</td>
<td></td>
</tr>
<tr>
<td>Xp</td>
<td>Particulate inert produced in the system</td>
<td></td>
</tr>
<tr>
<td>Xs</td>
<td>Slowly biodegradable</td>
<td></td>
</tr>
<tr>
<td>Xbh</td>
<td>Heterotrophic bacteria</td>
<td></td>
</tr>
<tr>
<td>Xba</td>
<td>Autotrophic bacteria</td>
<td></td>
</tr>
<tr>
<td>Sno</td>
<td>Nitrate</td>
<td>Nitrogen compounds</td>
</tr>
<tr>
<td>Snh</td>
<td>Ammonia</td>
<td></td>
</tr>
<tr>
<td>Snd</td>
<td>Soluble biodegradable organic nitrogen</td>
<td></td>
</tr>
<tr>
<td>Xnd</td>
<td>Particulate biodegradable organic nitrogen</td>
<td></td>
</tr>
<tr>
<td>So</td>
<td>Dissolved oxygen</td>
<td></td>
</tr>
<tr>
<td>Salk</td>
<td>Alkalinity</td>
<td></td>
</tr>
</tbody>
</table>

Si and Xi are not involved in any conversion process but they are present in the system. It is associated to the non biodegradable organic matter that corresponds generally to the effluent organics. Xi is present in the influent wastewater and contributes to volatile suspended solids in the activated sludge system. The processes involved are the growth of biomass, decay of biomass, ammonification and hydrolysis. With the two kinds of biomass present and the possibility of a different electron acceptor for the heterotrophic ones, there are a total of eight processes (nine processes, including aeration, figure 4-1).
4.4.2 Aerobic growth of heterotrophs

During the aerobic growth of heterotrophs, Ss is consumed with oxygen as the electron acceptor. Some ammonia nitrogen is incorporated into the biomass during cell synthesis. During the conversion of ammonia into amino acids, alkalinity decreases.

The process rate considered is:

$$\mu_H \cdot \frac{Ss}{K_S + Ss} \cdot \frac{So}{K_{O,H} + So} \cdot Xbh$$

With:

- $\mu_H$ = Maximum specific growth rate for heterotrophic biomass (1/d)
- $K_S$ = Substrate Half-Saturation coefficient for heterotrophic biomass (gCOD/l)
- $K_{O,H}$ = Oxygen half-saturation coefficient for heterotrophic biomass (gO$_2$/l)
A double nutrient limitation of Monod type expression is used to describe the kinetics with dissolved oxygen and soluble biodegradable organics being the rate determining factors. Storage is not considered and therefore removal of substrate will be proportional to growth. The situation in which substrate is removed without biomass growth is associated to the entrapment of Xs in this model.

4.4.3 Anoxic growth of heterotrophs

During the anoxic growth of heterotrophs, Ss are consumed with nitrate as electron acceptor. Just like for the aerobic case, some ammonia is incorporated during growth lowering the alkalinity. However, in this case nitrate acts as electron acceptor leading to a net uptake of a proton and increasing alkalinity.

The process rate considered is:

\[
\mu_H \cdot \frac{S_S}{K_S + S_S} \cdot \frac{K_{O,H}}{K_{O,H} + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot \eta_g \cdot Xbh
\]

With:

- \( \eta_g \) = Correction factor for \( \mu_H \) under anoxic conditions
- \( K_{NO} \) = Nitrate half-saturation coefficient for heterotrophic biomass (gN/l)

The correction factor is included to compensate the reduction of \( \mu_H \) during anoxic growth. Another argument concerning this factor role is that it is possible that only a part of heterotrophic bacteria is capable to denitrify. Otherwise, the process rate is very similar to the aerobic one except that in this case it is nitrate instead of oxygen used in the double nutrient limitation Monod kind expression. The other important difference is the switch-off function used to change from an aerobic to an anoxic situation. It can be noticed that the model does not include a kinetic expression to deal with alkalinity or nitrogen limitations.

4.4.4 Growth of autotrophs

During the growth of autotrophs, dissolved oxygen and ammonia nitrogen are consumed. Nitrate is produced. Alkalinity is decreased because during ammonium oxidation two protons are released. pH influence is not included.
The process rate considered is:

\[
\mu_A \cdot \frac{Snh}{K_{NH} + Snh} \cdot \frac{So}{K_{O,A} + So} \cdot Xba
\]

With:
- \( \mu_A \) = Maximum specific growth rate for autotrophic biomass (1/d)
- \( K_{NH} \) = Ammonia half-Saturation coefficient for autotrophic biomass (gN/l)
- \( K_{O,A} \) = Oxygen half-saturation coefficient for autotrophic biomass (gO\(_2\)/l)

A double nutrient limitation Monod kind expression is used to describe the kinetics with dissolved oxygen and ammonia nitrogen being the rate determining factors.

4.4.5 Decay of heterotrophs

During decay of heterotrophs, particulate substrate, inert organics and organic nitrogen are released. The approach used corresponds to the death-regeneration concept [5] that allows simplifying the model compared to the case in which an electron acceptor is used. It is possible that the real mechanisms involved are not reflected in this model, particularly because of environmental conditions having no participation in decay. Furthermore, decay involves mechanisms and processes such as maintenance, lysis, internal and external decay, predation and death regeneration [6].

The process rate considered is:

\[
b_h \cdot Xbh
\]

With:
- \( b_h \) = Decay coefficient for heterotrophic biomass (1/d)

The magnitude of the decay coefficient must be differentiated from the cases in which the recycling of substrate didn’t occur. In this case, the decay coefficient must be larger in order to give the same amount of oxygen utilization per time-lapse.

4.4.6 Decay of autotrophs

During the decay of autotrophs, particulate substrate, inert organics and organic nitrogen are released just like the heterotrophic case.
The process rate considered is:

\[ b_A \cdot Xba \]

With:

\[ b_A = \text{Decay coefficient for autotrophic biomass} \ (1/d) \]

### 4.4.7 Ammonification

During the ammonification process, soluble biodegradable organic nitrogen is transformed into ammonia nitrogen with a first order equation rate.

The process rate considered is:

\[ k_a \cdot SnO \cdot Xbh \]

With:

\[ k_a = \text{Ammonification rate} \ (l/(gCOD\cdot d)) \]

### 4.4.8 Hydrolisis of Xs

During the hydrolysis process, entrapped organic Xs are hydrolyzed to soluble directly biodegradable substrates.

The process rate considered is:

\[ k_h \cdot \frac{Xs}{Xbh} \cdot \left[ \frac{So}{K_{O,H} + So} + \eta_b \cdot \frac{K_{O,H}}{K_{O,H} + So} \cdot \frac{SnO}{K_{NO} + SnO} \right] \cdot Xbh \]

With:

\[ k_h = \text{Maximum specific hydrolysis rate} \ (gCOD/(gCOD\_biomass\cdot d)) \]
\[ \eta_b = \text{Correction factor for hydrolysis under anoxic conditions} \]
\[ K_X = \text{Hydrolysis half-saturation coefficient} \ (gCOD/gCOD\_biomass) \]

The rate is a first order expression regarding active heterotrophic biomass present. It saturates as the amount of entrapped substrate becomes large in proportion to the biomass, and it is dependent on the concentration of an electron acceptor.
4.4.9 Hydrolisis of Xnd

During this process, soluble biodegradable organic nitrogen is liberated.

The process rate considered is:

\[
k_h \cdot \frac{Xs/Xbh}{K_x + (Xs/Xbh)} \cdot \frac{Xnd}{Xs} \cdot \left[ \frac{So}{K_{o,H} + So} + \eta_b \cdot \frac{K_{o,H}}{K_{o,H} + So} \cdot \frac{Sno}{K_{so} + Sno} \right] \cdot Xbh
\]

It is assumed that the hydrolysis of entrapped nitrogen will be proportional to the rate of hydrolysis of Xs because the organic nitrogen is supposed to be uniformly distributed throughout the Xs.

All this information is present in the matrix representation (table 4-3). For more details about the model, the reader is referred to the original publication.
Table 4-3 ASM1 matrix (soluble and particulate inert organic matters are not included because they are not involved in any conversion processes)

<table>
<thead>
<tr>
<th>Process rate</th>
<th>Ss</th>
<th>So</th>
<th>Sno</th>
<th>Snh</th>
<th>Snd</th>
<th>Salk</th>
<th>Xs</th>
<th>Xbh</th>
<th>Xba</th>
<th>Xp</th>
<th>Xnd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic growth of Heterotrophs</td>
<td>-1/14</td>
<td>-1 + Xbh/14</td>
<td>-Xbh</td>
<td>-Xbh</td>
<td>1/14</td>
<td>-Xbh</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Anoxic growth of Heterotrophs</td>
<td>-1/14</td>
<td>1 + Xbh/14</td>
<td>-Xbh</td>
<td>-Xbh</td>
<td>1/14</td>
<td>-Xbh</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Growth of Autotrophs</td>
<td>-1 + 4.57 - 3a</td>
<td>1/14</td>
<td>-Xbh</td>
<td>1/14</td>
<td>-Xbh</td>
<td>1/14</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Decay of Heterotrophs</td>
<td>1 - f_p</td>
<td>-1</td>
<td>f_p</td>
<td>ΔiXb - f_p ΔiXp</td>
<td>b_h</td>
<td>Xbh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decay of Autotrophs</td>
<td>1 - f_p</td>
<td>-1</td>
<td>f_p</td>
<td>ΔiXb - f_p ΔiXp</td>
<td>b_h</td>
<td>Xba</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonification of Snd</td>
<td>1</td>
<td>-1</td>
<td>1/14</td>
<td>1/14</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Hydrolysis of Xs</td>
<td>1</td>
<td>-1</td>
<td>1/14</td>
<td>1/14</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Hydrolysis of Xnd</td>
<td>1</td>
<td>-1</td>
<td>1/14</td>
<td>1/14</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Stoichiometric parameters (5):

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Default value (20ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heterotrophic yield</td>
<td>$Y_H$ 0.67</td>
</tr>
<tr>
<td>Autotrophic yield</td>
<td>$Y_A$ 0.24</td>
</tr>
<tr>
<td>Fraction of biomass yielding particulate products</td>
<td>$f_P$ 0.08</td>
</tr>
<tr>
<td>Mass of N per mass of COD in biomass</td>
<td>$\alpha_b$ 0.086</td>
</tr>
<tr>
<td>Mass of N per mass of COD in part. products</td>
<td>$\alpha_P$ 0.06</td>
</tr>
</tbody>
</table>

Kinetic parameters (14):

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Default value 20ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum specific growth rate</td>
<td>$\mu_H$ 6</td>
</tr>
<tr>
<td>Substrate half-saturation coefficient</td>
<td>$K_S$ 20</td>
</tr>
<tr>
<td>Oxygen half-saturation coefficient</td>
<td>$K_{D,O}$ 0.2</td>
</tr>
<tr>
<td>Nitrile half-saturation coefficient</td>
<td>$K_{NO}$ 0.5</td>
</tr>
<tr>
<td>Decay coefficient</td>
<td>$b_H$ 0.62</td>
</tr>
<tr>
<td>Correction factor for anoxic growth</td>
<td>$\eta_s$ 0.8</td>
</tr>
<tr>
<td>Maximum specific growth rate</td>
<td>$\mu_A$ 0.8</td>
</tr>
<tr>
<td>Ammonia half-saturation coefficient</td>
<td>$K_{NH}$ 1</td>
</tr>
<tr>
<td>Oxygen half-saturation coefficient</td>
<td>$K_{O_A}$ 0.4</td>
</tr>
<tr>
<td>Decay coefficient</td>
<td>$b_A$ 0.1</td>
</tr>
<tr>
<td>Ammonification</td>
<td>$k_a$ 0.08</td>
</tr>
<tr>
<td>Maximum specific hydrolisis rate</td>
<td>$k_h$ 3</td>
</tr>
<tr>
<td>Hydrolysis half-saturation coefficient</td>
<td>$K_X$ 0.03</td>
</tr>
<tr>
<td>Correction factor for anoxic hydrolysis</td>
<td>$\eta_h$ 0.4</td>
</tr>
</tbody>
</table>
4.5 Activated sludge model number 3 (ASM3) [7]

The ASM3 model arrives more than ten years after the ASM1 model, introducing the storage concept and replacing some not essential characteristics that are not used or that makes difficult the kinetic interpretation. For example, in ASM1 the hydrolysis process has a dominating effect over heterotrophic organism growth, which makes difficult the identification of kinetic parameters.

Furthermore, the simplified decay concept used in ASM 1 was upgraded to the endogenous respiration concept that allows including environmental conditions (aerobic, anoxic).

<table>
<thead>
<tr>
<th>Table 4-4 Components in the ASM3 model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
</tr>
<tr>
<td>Ss</td>
</tr>
<tr>
<td>Xi</td>
</tr>
<tr>
<td>Xs</td>
</tr>
<tr>
<td>Xbh</td>
</tr>
<tr>
<td>Xsto</td>
</tr>
<tr>
<td>Xba</td>
</tr>
<tr>
<td>Sno</td>
</tr>
<tr>
<td>Snh</td>
</tr>
<tr>
<td>Sn2</td>
</tr>
<tr>
<td>Xss</td>
</tr>
<tr>
<td>So</td>
</tr>
<tr>
<td>Salk</td>
</tr>
</tbody>
</table>

The ASM3 model includes 13 components as shown in table 4-4. Seven components correspond to the organic matter measured as COD and three components correspond to nitrogen compounds. The primary phenomena described as processes are the same: oxygen consumption, sludge production, nitrification and denitrification. However, this time 12 processes are present.
4.5.1 Hydrolysis

During the hydrolysis process, slowly biodegradable substrates are mostly transformed into a soluble substrate but also a fraction is transformed into a soluble inert matter. Some ammonia is liberated according to the difference in nitrogen content in particulate and soluble organics. Consequently, alkalinity will be slightly augmented. The process is active independently of aerobic or anoxic conditions. Suspended solids are diminished by this process accordingly to the SS/COD ratio of particulate organics.

The process rate considered is:

\[
k_h \cdot \frac{X_s}{K_X + \left( \frac{X_s}{X_{bh}} \right)} \cdot X_{bh}
\]

With:

- \( k_h \) = Maximum specific hydrolysis rate (gCOD/(gCOD_biomass∙d))
- \( K_X \) = Hydrolysis half-saturation coefficient (gCOD/gCOD_biomass)
Kinetics are simplified in ASM3, compared to the ASM1, because in the first one, hydrolysis takes place at the same rate under anoxic and under aerobic conditions.

4.5.2 Aerobic storage of heterotrophs

In this process, soluble substrate that is rapidly biodegraded produces storage products using oxygen as electron acceptor. Some ammonia is liberated increasing alkalinity. It is assumed that all the substrate is assimilated into a cell internal storage product before being transformed into biomass. Suspended solids will augment in a proportion of 0.6.

The process rate considered is:

$$k_{STO} \cdot \frac{So}{K_{O,H} + So} \cdot \frac{Ss}{K_s + Ss} \cdot Xbh$$

With:

- $k_{STO}$ = Storage rate constant (gCOD/gCOD_biomass∙d)
- $K_s$ = Substrate Half-Saturation coefficient (gCOD/l)
- $K_{O,H}$ = Oxygen half-saturation coefficient (gO$_2$/l)

A double nutrient limitation Monod kind expression is used to describe the kinetics with dissolved oxygen and soluble biodegradable organics being the rate determining. The description of this process is analogue to the one used in ASM1 for growth. The only difference is the replacement of the maximum specific growth rate by the storage rate constant.

4.5.3 Anoxic storage of heterotrophs

In this process, soluble substrate is assimilated into stockage products under anoxic conditions. Nitrate is thus consumed with production of dinitrogen gas. The proportion of nitrogen contained in the soluble substrate is released as ammonia. In addition nitrate is consumed so alkalinity is augmented. Just like in the aerobic case, suspended solids will augment in a proportion of 0.6.

The process rate considered is:

$$k_{STO} \cdot \eta_{NOX} \cdot \frac{K_{O,H}}{K_{O,H} + So} \cdot \frac{Sno}{K_{NOX} + Sno} \cdot \frac{Ss}{K_s + Ss} \cdot Xbh$$
With:

\[ \eta_{\text{NOX}} = \text{Correction factor under anoxic conditions} \]
\[ K_{\text{NOX}} = \text{Nitrate half-saturation coefficient for heterotrophic biomass (gN/l)} \]

The correction factor is added to compensate the reduction of \( k_{\text{STO}} \) during anoxic growth. Another argument concerning this factor role is that it is possible that only a part of heterotrophic bacteria is capable to denitrify. Otherwise, the process rate is very similar to the aerobic one except that in this case it is nitrate instead of oxygen used in the double nutrient limitation Monod kind expression. The other important difference is the switch-off function used to change from aerobic to an anoxic situation. It can be noticed that the model does not include kinetic expressions that can deal with alkalinity or nitrogen limitations.

### 4.5.4 Aerobic growth of heterotrophs

During this process, storage products are consumed producing heterotrophs biomass with the energy obtained from the aerobic respiration. In order to create a heterotrophic organism, some nitrogen in the form ammonia is needed. This ammonia utilization diminishes alkalinity. The suspended solids augment accordingly, both to the augmentation of heterotrophic biomass and to the storage product consumption.

The process rate considered is:

\[
\mu_H \cdot \frac{S_o}{K_{O,H} + S_o} \cdot \frac{S_{Nh}}{K_{NH,H} + S_{Nh}} \cdot \frac{S_{alk}}{K_{ALK,H} + S_{alk}} \cdot \frac{X_{sto}/X_{bh}}{K_{STO} + X_{sto}/X_{bh}} \cdot \frac{X_{bh}}{} 
\]

With:

\( \mu_H \) = Maximum growth rate (1/d)
\( K_{NH,H} \) = Saturation constant for ammonium (gN/l)
\( K_{ALK,H} \) = Saturation constant for alkalinity (mole HCO\(_3\)-/l)
\( K_{STO} \) = Saturation constant for Storage products (gCOD/gCOD)

The kinetic is ruled by a Monod type expression with four nutrient limitations. Rate is determined by the oxygen presence, ammonia, alkalinity and a ratio between stored products and heterotrophic biomass. Alkalinity and nitrogen limitations are novel as they were not considered in ASM1.
4.5.5 Anoxic growth of heterotrophs

In this process, heterotrophic organisms are produced from storage products, using the energy obtained from anoxic respiration. Just like in the aerobic case, an amount of nitrogen in the form of ammonia will be necessary to form the new cells.

However, ammonia consumption effect upon alkalinity will be lower compared to the alkalinity augmentation due to nitrate consumption. The suspended solids will augment accordingly to the augmentation in heterotrophic biomass considering the storage product's consumption.

The process rate considered is:

\[ \mu_H \cdot \eta_{\text{NOX}} \cdot \frac{K_{O_H}}{K_{O_H} + S_O} \cdot \frac{S_{\text{NOX}}}{K_{\text{NOX}} + S_{\text{NOX}}} \cdot \frac{S_{\text{NH}}}{K_{\text{NH,H}} + S_{\text{NH}}} \cdot \frac{S_{\text{ALK}}}{K_{\text{ALK,H}} + S_{\text{ALK}}} \cdot \frac{X_{\text{sto}}}{X_{\text{sto}} + X_{\text{bh}}} \cdot X_{\text{bh}} \]

The kinetic expression includes this time a switch-off function in order to change from anoxic to aerated conditions. The rest is very similar to the aerobic case except for the correction factor added in order to take into consideration the part of the biomass that doesn’t denitrify.

4.5.6 Aerobic endogenous respiration of heterotrophs

During this process, heterotrophic biomass is transformed into inert particulate organics thanks to the energy obtained from aerobic respiration. A part of the nitrogen contained in the cell will be released in the form of ammonia, as a consequence alkalinity rises. Even if some inert particulate is formed, suspended solids will be decreased because of the lost of biomass. This process is assumed to consider all sorts of biomass loss and energy requirements not associated to growth. It aims at describing decay, maintenance, endogenous respiration, lysis, predation, motility, death and possibly many other processes [3].

The process rate considered is:

\[ b_{H,O} \cdot \frac{S_O}{K_{O_H} + S_O} \cdot X_{\text{bh}} \]

With:

\[ b_{H,O} = \text{Aerobic endogenous respiration rate (1/d)} \]

The kinetic is simple and only takes in to account the oxygen limitations.
4.5.7 Anoxic endogenous respiration of heterotrophs

This process is similar to the aerobic one. Heterotrophic biomass is transformed into inert particulate organics. This time, the energy is obtained from the anoxic respiration. Some ammonia nitrogen will be liberated and nitrate will be consumed increasing alkalinity.

The process rate considered is:

\[ b_{H,NOX} \cdot \frac{K_{d,H}}{K_{d,H} + So} \cdot \frac{Snox}{K_{NOX} + Snox} \cdot Xbh \]

With:

\[ b_{H,NOX} = \text{Anoxic endogenous respiration rate (1/d)} \]

The kinetic is similar to the aerobic case except for the inclusion of the switch–off function for the aerobic/anoxic conditions.

4.5.8 Aerobic respiration of storage products

This process takes into account the fact that storage products are part of heterotrophic biomass, so they also respire aerobically, which consumes oxygen and diminishes suspended solids.

The process rate considered is:

\[ b_{STO,O} \cdot \frac{So}{K_{d,H} + So} \cdot Xsto \]

With:

\[ b_{STO,O} = \text{Aerobic respiration rate for storage products (1/d)} \]

The kinetic is simple and similar to the aerobic endogenous respiration case. The only difference is that this time the kinetic is ruled by the storage product concentration instead of the heterotrophic bacteria concentration.

4.5.9 Anoxic respiration of storage products

Just like in the aerobic case, this process takes into account the anoxic endogenous respiration of storage products because they are part of the heterotrophic biomass. A slightly augmentation of alkalinity is observed accordingly to the nitrate consumption.
The process rate considered is:

\[ b_{STO,NOX} \cdot \frac{K_{O,H}}{K_{O,H} + So} \cdot \frac{Snox}{K_{NOX} + Snox} \cdot Xsto \]

With:

\[ b_{STO,NOX} \] = Anoxic respiration rate for storage products (1/d)

The kinetic is similar to the aerobic expression but with the addition of the switch-off function for aerobic/anoxic conditions.

4.5.10 Aerobic growth of autotrophs (nitrification)

Autotrophic organisms are formed using ammonia nitrogen in the presence of oxygen. They produce nitrate and in addition, alkalinity is reduced. Suspended solids are augmented.

The process rate considered is:

\[ \mu_A \cdot \frac{So}{K_{O,A} + So} \cdot \frac{Snh}{K_{NH,A} + Snh} \cdot \frac{Salk}{K_{ALK,A} + Salk} \cdot Xba \]

With:

\[ \mu_A \] = Maximum growth rate of autotrophic biomass (1/d)
\[ K_{O,A} \] = Oxygen saturation constant for autotrophs (gO₂/l)
\[ K_{NH,A} \] = Ammonium substrate saturation constant (gN/l)
\[ K_{ALK,A} \] = Bicarbonate saturation constant (mole HCO₃⁻/l)

4.5.11 Aerobic endogenous respiration of autotrophs

Autotrophic organisms are transformed into inert particulates through aerobic respiration. Ammonia nitrogen is liberated accordingly to the proportion of N in autotrophic biomass and to the part that is lost with the inert particulate. Alkalinity is slightly augmented and suspended solids are reduced.

The process rate considered is:

\[ b_{A,O} \cdot \frac{So}{K_{O,A} + So} \cdot Xba \]

With:

\[ b_{A,O} \] = Aerobic endogenous respiration rate (1/d)
4.5.12 Anoxic endogenous respiration of autotrophs

Like the aerobic case, autotrophs are transformed into inert particulate but this time under anoxic conditions, meaning with nitrate consumption as the energy source. Ammonia is liberated and nitrate is consumed, which augments alkalinity. Suspended solids are reduced.

The process rate considered is:

\[ b_{A,NOX} = \frac{K_{o,A}}{K_{o,A} + S_o} \cdot \frac{S_{nox}}{K_{NOX} + S_{nox}} \cdot X_{ba} \]

With:

- \( b_{A,NOX} \) = Anoxic endogenous respiration rate (1/d)
- \( K_{NOX} \) = Nitrate saturation constant (gN/l)
### 4-5 ASM 3 matrix representation

<table>
<thead>
<tr>
<th>Process</th>
<th>Stoichiometry</th>
<th>Kinetic parameters</th>
<th>Stochastic / composition parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrolysis</strong></td>
<td>$f_S$</td>
<td></td>
<td><strong>Production of Ss in hydrolysis</strong> $f_S$ $0$</td>
</tr>
<tr>
<td><strong>Aerobic storage of Heterotrophs</strong></td>
<td>$1 - Y_{S_{SS1}}$</td>
<td></td>
<td><strong>Aerobic yield of Xs per Ss</strong> $Y_{S_{SS1}}$ $0.85$</td>
</tr>
<tr>
<td><strong>Anoxic storage of Heterotrophs</strong></td>
<td>$-1$</td>
<td></td>
<td><strong>Yield of Xs per Ss</strong> $Y_S$ $0.24$</td>
</tr>
<tr>
<td><strong>Aerobic growth of Heterotrophs</strong></td>
<td>$-1$</td>
<td></td>
<td><strong>Production of Xs during endogenous respiration</strong> $f_X$ $0.2$</td>
</tr>
<tr>
<td><strong>Aerobic endogenous respiration</strong></td>
<td>$- (1 - f_S)$</td>
<td></td>
<td><strong>N content of Ss</strong> $s_{S_{SS}}$ $0.03$</td>
</tr>
<tr>
<td><strong>Anoxic endogenous respiration</strong></td>
<td>$1 - f_S$</td>
<td></td>
<td><strong>N content of Xs</strong> $s_{X_{BM}}$ $0.02$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>N content of biomass</strong> $s_{X_{SS}}$ $0.07$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>SS to COD ratio for Ss</strong> $i_{S_{SS}}$ $0.75$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>SS to COD ratio for Xs</strong> $i_{X_{BM}}$ $0.75$</td>
</tr>
</tbody>
</table>

**Default values (20°C):**

- **Hydrolysis:** $f_S$ = 0
- **Aerobic storage of Heterotrophs:** $1 - Y_{S_{SS1}} = 0.85$
- **Anoxic storage of Heterotrophs:** $-1$
- **Aerobic growth of Heterotrophs:** $-1$
- **Aerobic endogenous respiration:** $- (1 - f_S)$
- **Anoxic endogenous respiration:** $1 - f_S$
- **Aerobic endogenous respiration of Autotrophs:** $1 - (4.57 / Y_X)$
- **Anoxic endogenous respiration of Autotrophs:** $- (1 - f_S)$
- **Yield of Xs per Ss:** $Y_S = 0.24$
- **Production of Xs during endogenous respiration:** $f_X = 0.2$
- **N content of Ss:** $s_{S_{SS}} = 0.03$
- **N content of Xs:** $s_{X_{BM}} = 0.02$
- **N content of biomass:** $s_{X_{SS}} = 0.07$
- **SS to COD ratio for Ss:** $i_{S_{SS}} = 0.75$
- **SS to COD ratio for Xs:** $i_{X_{BM}} = 0.75$
- **SS to COD ratio for biomass:** $i_{X_{SS}} = 0.9 (0.75 if VSS)$

| Storage rate constant | $k_{sto}$ | Default values (20°C) | **Hydrolysis rate constant** $k_{sto}$ | $1$ |
| Storage rate constant | $k_{sto}$ | **Ammonium substrate saturation** $K_{A_{NM}}$ | $1$ |
| Saturation constant for Fo | $K_{F_{o}}$ | **Oxygen saturation** $K_{O_{2}}$ | $0.5$ |
| Saturation constant for Ss | $K_{S_{SS}}$ | **Bicarbonate saturation** $K_{HCO_3}$ | $0.5$ |
| Saturation constant for substrate | $K_s$ | **Aerobic endogenous respiration rate** $b_{A_{endo}}$ | $0.15$ |
| Saturation constant for Xs | $K_{X_{BM}}$ | **Anoxic endogenous respiration rate** $b_{X_{endo}}$ | $0.05$ |
| Maximum growth rate | $\mu_X$ | **Hydrolysis rate constant** $k_{sto}$ | $3$ |
| Saturation constant for ammonia | $K_{NM}$ | **Hydrolysis saturation constant** $K_{S}$ | $1$ |
| Saturation constant for alkalinity | $K_{NM}$ | **Aerobic endogenous respiration rate** $b_{A_{endo}}$ | $0.2$ |
| Aerobic endogenous respiration rate | $b_{A_{endo}}$ | **Anoxic endogenous respiration rate** $b_{X_{endo}}$ | $0.1$ |
| Aerobic respiration rate for Xs | $b_{X_{sto}}$ | **Anoxic respiration rate for Xs** $b_{X_{SS}}$ | $0.2$ |
| Anoxic respiration rate for Xs | $b_{X_{SS}}$ | **Anoxic respiration rate for Xs** $b_{X_{SS}}$ | $0.1$ |
4.6 West simulator

4.6.1 Introduction

Wastewater treatment techniques allow nowadays to perform removal of organic matter and nutrients in a single system. However, the biological processes are not always well defined. Due to the high complexity of the phenomenon taking place in an activated sludge, models generally stands on a conceptual base. The engineer approach is thus, to reduce this complex group of processes into a conceptual image of how it functions [8]. In order to test whether the conceptual model responds to what is really happening in fact and also to test the model design, engineers build laboratory-scale reactors. Nevertheless, it is not economically feasible to explore all the plausible solutions with this time-consuming method, so simulation appears as a valuable technique for further exploration. Empirical models with statistical approaches were usually used to mimic pilot plant behavior, but the possibilities are reduced. Mechanistic models based on an expanded understanding of the implicated processes like the ASM family models are more powerful, allowing to test new designs beyond the conditions experienced in a physical model.

In order to perform a simulation of a wastewater treatment plant based on ASM models, it is necessary to have a simulator platform. Several packages are available with different versatility and user-friendliness. Examples are Biowin, EFOR, STOAT, Aquasim, GPS-X, SIMBA and WEST® [1]. The tools for dynamic simulation of modern nutrient removal activated sludge systems dates back to 15 years. An example is the ASIM tool [9].

For our case, the WEST® simulator platform will be used because it allows the user to work with specific models and allows to modify existing ones as well. Furthermore, WEST® appears to be more suitable to our academic purposes [1].

4.6.2 General description

The modeling and simulation package WEST® (Wastewater treatment plant Engine for Simulation and Training [8], renamed World wide engine for simulation, Training and Automation [10] is a user-friendly platform for modeling. Existing models like the ones from the ASM family could be used. The possibility to implement and simulate new models is
available as well. In practice, any kind of process that could be described by a system of differential algebraic equations could be simulated with WEST but the application of this software is generally reduced to wastewater treatment plants [8].

WEST is divided into two environments: the configuration builder and the experimentation environment.

In the first one, the user has the possibility of graphically implement the treatment process to be simulated. The software provides different units representing the different parts of a real treatment facility (or pilot). For example activated sludge units are available as well as the anaerobic digesters, sequential batch systems, clarifiers, membranes, flux splitter and combiners amongst many others (figure 4-5). These parts are represented in the software by nodes that are divided in several classes representing the individual components of a system. Finally the nodes must be linked allowing data to flow between nodes. The model will communicate with the external environment through input and output nodes. When the configuration is ready, a runtime model is created. A MSL model (Model Specification Language) is generated, parsed and translated to an executable runtime model that can then be used in the experimental environment.

Within the experimentation environment, the user may access to simulate the previously configured MSL model. Scenario analysis, parameter estimations, sensitivity analysis and optimal experimental design calculations can also be performed [10]. Simulations input,
particularly wastewater characterization must be incorporated through the inlet node. Simulation outputs can then be checked graphically or an export file can be generated.

Another important section of this software is the model base and model editor. In this section, ASM family models that are used by the software to simulate, for example activated sludge units, are incorporated through the easy reading matrix notation. The user has the possibility also to modify these models or to propose new ones. For more details about the software the lector is referred to [8].

4.7 References


Chapter 5: Materials and methods

Abstract: Analytical measurements of determined parameters are very important in the comprehension of water. In wastewater for example, the amount of nitrogen and organic compounds will be crucial to apply the correct treatment. In this chapter, the laboratory analysis measurements made during this research project are presented, meaning ammonium, nitrates, nitrites, chemical oxygen demand, Biological oxygen demand, total suspended solids, Kjeldahl nitrogen, dissolved oxygen, pH, Conductivity and temperature. The method employed in each case is briefly explained as well as some generalities about the parameter measured. In a second part, the membrane bioreactor pilot used in this study is presented. A brief description of the full scale facility of Muertendall is presented as well.

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5.1 Analytical measurements

5.1.1 Ammonium [1, 2, 3, 4]

Introduction: Ammonia nitrogen generally refers to the ionised form (NH$_4^+$) and to the non-ionised (NH$_3$). Its presence is commonly associated to an incomplete degradation of organic matter. Ammonia presence in superficial water could be explained by degradation of vegetal matter in rivers, animal or human organic matter (human expels 15 to 30g of urea daily), industrial effluents, from fertilizer derivatives, etc. Ammonium could be also found in meteoric waters and in deep waters. Ammonia oxidation could lead to anaerobic zones in the water distribution network resulting in water bad flavour and in the corrosion of pipes, particularly the ones made in non chromated copper. Ammonia reacts with chlorine producing organochlorine compounds that can be toxic. Furthermore, the chlorine needed for disinfection is decreased.

Ammonium maximal concentration recommended by the World Health Organization (WHO) for human consumption is 1.5mgN/l. In France, legislation is more restrictive with 0.1mgN/l as the limit. In ground waters, 0.5mg/l is the norm fixed but higher values are tolerated when natural sources are involved. Toxicity for aquatic life is associated with the non ionised form which amount depends on pH and temperature. 0.3mgN/l is the sensitivity threshold, 0.6 to 1.5mgN-NH$_3$/l becomes rapidly acute toxic. Security's threshold is generally situated at 0.03mgN-NH$_3$/l.

Summary of method employed: Ammonia was determined with a potentiometric method using a ammonia ion selective electrode. The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. In the sample, ammonia diffuses through the membrane and modifies the pH of the internal solution, which is sensed by a pH-probe. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode. It must be noticed that dissolved ammonia in the sample (NH$_3$(aq) and NH$_4^+$) is completely converted to NH$_3$(aq) (which diffuses through the membrane) by raising pH to above 11 with a strong base. Potentiometric measurements are carried out with a pH meter having an expanded millivolt scale or with a specific ion meter.
Scope and application: This method is applicable in drinking, surface and saline waters, domestic and industrial wastes. The range covered goes from 0.03 to 1400mg NH$_3$-N/l.

Interferences: High concentrations of dissolved ions affect the measurement, but colour or turbidity do not, which is important in the case of leachates as they are usually colored. Volatile amines act as a positive interference that may be enhanced by acidification. Mercury and silver interfere by complexing ammonia, unless NaOH/EDTA solution is used as a strong base.

Apparatus: - Electrometer (pH meter) with expanded mV scale or specific ion meter (WTW inoLab pH/ION 735)
- Ammonia selective electrode (WTW NH$_4^+$ 500 Series)
- Magnetic stirrer, thermally insulated, and Teflon-Coated stirring bar
- 150ml beakers

Reagents: - Distilled water
- Sodium hydroxide 10N or Sodium hydroxide/EDTA solution10N
- Stock of ammonium chloride solution: 1ml =1mgNH$_3$-N (Dissolves 3.819 grams of NH$_4$CL in 1 liter of distilled water)
- Standard ammonium chloride solutions: Dilute the stock solution

Procedure: - Preparation of standards: Prepare a series of standard solutions covering the concentration range of samples by diluting either the stock or standard solutions of ammonia chloride. Generally, standard solutions are made for concentrations of 1, 10, 100 and 1000mgNH$_3$-N/l.

- Electrometer calibration: Place 100ml of the lowest concentration standard solution in a 150ml beaker and mix with the magnetic stirrer. Stirring speed should be low in order to minimize loss of ammonia. Add sufficient volume of the strong base (NaOH solution or NaOH/EDTA solution) to raise pH above 11. 1ml usually is enough but in the cases when more is needed, don’t forget to note the volume because it is required for subsequent calculations. Wait until a stable reading is obtained. Repeat procedure with the remaining standards, from lowest to highest concentrations.
-Sample measurement: Follow the same procedure that for standards. Modern equipment directly transforms the potential reading to the ammonia concentration. However, this could be done manually.

*Precision and accuracy:* Considering surface water, samples at concentrations below 1mgNH$_3$-N/l presents standard deviations going up to ±0.038. Other results suggest recoveries of 91-96% for concentrations near 0.1mgNH$_3$-N/l. Stirring rate and temperature of 25°C should be maintained during calibration and testing procedures.

5.1.2 Nitrates and nitrites with ion chromatography
[1, 5, 6]

*Introduction:* All forms of nitrogen could lead to nitrates by biological oxidation processes. In natural waters nitrate concentrations could reach 15mgN/l but values close to 2.5mgN/l could be considered as normal. A slightly but constant augmentation of nitrate concentration in surface runoffs and groundwater is observed and could be explained by excessive fertilization in agriculture among other sources related to human industry.

In France, 2% of the population consume water with nitrate concentration over 50mgN/l, in England 100mgN/l are tolerated, in Australia up to 200mg/l and in Yemen up to 400mg/l. Intoxication by nitrates is not a real danger. The problem comes when nitrates are transformed to nitrites. However, nitrates are also important in alimentation, particularly in vegetables. The world health organization suggests that water with concentration under 100mgN/l could be well tolerated except for babies and pregnant women. Over 100mgN/l consumption should be forbidden. The recommendation is thus 50mg/l, value considered by most legislations but with specific considerations concerning nitrites.

Nitrites are very scarce in a natural environment. However, their presence is reported in rain waters and in water coming from snow, possibly explained by the atmospheric nitrogen oxides. For human consumption, the WHO suggests a nitrite tolerance value of 3mgN/L, but considering the nitrate concentration.
Summary of method employed: Chromatography is a physical-chemical process that allows the separation of the constituents of a mixed solution. The principle of separation being the distribution of solutes between two immiscible phases: one stationary phase contained in a column and a mobile phase that traverses the column and drags the sample that contains the mixed solution to analyse. The mobile phase drags the ion species that we seek to separate, while the stationary phase slows them out by diverse interactions. The stationary phase will retain higher charged ions which will take more time to traverse compared to ions with lower charges which will traverse rapidly. Finally, a detection step (frequently conductometry) allows identifying the different ions consistently with their different times (elution volumes) the column. The quantification is then performed with standard samples using the area of the Gaussian peak.

Scope and application: The method allows the determination of inorganic ions (bromide, nitrite, chloride, ortho-phosphate-P fluoride, sulphate and nitrate). It is applicable to drinking water, surface water, mixed domestic and industrial wastewater, groundwater, reagent waters, and leachates.

Interferences: Interferences can be caused by substances with retention times that are similar to, and overlaps those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Method interference may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artefacts or elevated baseline in ion chromatograms. Acetic acid influences the chromatographic runs through acetate ions so the method is not applicable when acetic acid is used for pH adjustment.

Apparatus: Ionic chromatography system (Metrohm 881 compact IC Pro), including eluant reservoir, high pressure pump, sample injection dispositive, a separation pre-column and column adapted to the ion we seek for, a detector with an ion suppressor in the case of a conductimetric detection, data acquisition system and sample preparations apparatus (filtration device, sample bottles, etc.).

Reagents: - Distilled or deionised water, free of the anions of interest
- Eluent solution: Sodium bicarbonate 1.7mM, sodium carbonate 1.8mM
- Regeneration solution: Sulphuric acid 0.025N
Stock standard solutions 1000mg/l. Stock standard solutions may be purchased as certified solutions or prepared from reagent grade materials. For more details refer to the EPA method 300.0 or the apparatus constructor guidelines.

Procedure: It depends on the system constructor but generally it involves the following steps:
- Preparation of eluants
- Adjustment and stabilisation of the chromatograph
- Audit of separation conditions for the element to separate simultaneously and identification of each element by his retention time thanks to the calibration standards
- Establish a calibration curve for the apparatus considering the range of concentrations to measure, using a mixed standard solution containing all the elements to measure
- Pretreatment of samples
- Injection of samples eventually after dilution in the case of being out of range compared to the calibration standards
- Test with blank samples
- Calculus of concentration in each sample

Precision and accuracy: It depends on the system used, but generally is very precise. Special concern must be taken for the preparation of samples, step where contamination risks are higher.

5.1.3 Chemical oxygen demand (COD)
[7, 8, 9]

Introduction: The chemical oxygen demand corresponds to the oxidable organic matter compounds present in the samples. Some inorganic compound could present interference. Concentrations of 30mgCOD/l are tolerated in superficial water destined to human consumption after treatment.

Summary of method: The chemical oxygen demand test uses a strong chemical oxidant in an acid solution and heat to oxidize organic carbon to CO₂ and H₂O. By definition, COD is “a
measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant”. Samples in sealed tubes are heated in an oven at 148°C in presence of potassium dichromate and silver sulphate as a catalyst. After two hours, oxidation is completed; the tubes are removed from the oven, cooled down and measured spectrophotometrically.

Scope and application: This method covers the determination of chemical oxygen demand (COD) in ground and surface waters, domestic and industrial wastes.

Interferences: Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercury sulphate is added to the digestion tubes to complex the chlorides and to eliminate interference.

Apparatus:  
- Glassware: Class A, volumetric flasks and pipettes as required  
- Drying oven capable of maintaining 148°C (Spectroquant® Thermoreactor TR620)  
- Photometric apparatus (Spectroquant® NOVA series)

Reagents:  
- Distilled or deionised water  
- Digestion solution (potassium dichromate + sulphuric acid + mercury sulphate)  
- Catalyst solution (silver sulphate + sulphuric acid)

Procedure: This method is implemented by the spectroquant kits in which digestion and catalyst solutions are already prepared in a sealed tube. The procedure thus is simpler and consists of introducing a pre determined volume of the sample in the tube, strongly mix and put in the heating module for 120 minutes. Then the sealed tubes are cooled down to ambient temperature. Finally, COD is measured with a photometric apparatus.

Precision and accuracy: The ranges measured during the research are 250mgCOD/l up to 3000mgCOD/l. According to ISO 8466-1 et DIN 38402 A51, the standard deviation is 15.7mg/l COD with accuracy as percent relative error (bias) of ±0.87%.
5.1.4 **Biochemical Oxygen Demand (BOD)**
[10,1]

*Introduction:* The degradation of organic matter compounds by micro-organism consumes oxygen. It starts rapidly and takes place for more than 20 days at 20°C. Nitrogen compounds degradation starts after carbon compounds, after more or less 10 days on domestic wastewaters. Most of the organic matter is consumed during the first 2 days. There is very low oxygen consumption associated to nitrogen compounds during this first period so it was decided to take the BOD₅ as a measurement of the biologically oxidable organic matter (blocking nitrification with an inhibitor).

Legislation about this parameter is primary refered to superficial waters for human consumption after treatment. 3mg/l of BOD₅ are tolerated when simple physical and disinfection treatment is applied. Up to 7mg/l of BOD₅ are toleroted when the process is improved.

BOD₅ parameter is used to determine the quality of the river water in terms of biodegradable organic pollution. Values under 3mg/l are considered as having very good quality, from 3 to 5 mg/l is considered good, from 5 to 8, medium and over 8mg/l is considered bad or very bad quality.

It must be noticed that this parameter is very dependent of the type of wastewater and could be influenced by a large number of situations like inhibiting substances, pH, etc. BOD₅ contains by definition several considerations that can be questioned [11]. However, it constitutes a valuable tool when it´s carefully interpreted.

*Summary of method:* The BOD is defined as the quantity of oxygen, consumed under controlled conditions, needed to degrade biologically the materials present in water. The method consists of filling with sample, an airtight bottle of specified size and incubating it at a specified temperature for 5 or more days at 20°C. Microorganisms and in some case chemical processes, will oxidize some material consuming oxygen. The depletion of the dissolved oxygen consumed during biodegradation induces a depletion of O₂ partial pressure in the sealed bottle which is measured with a manometer. This pressure drop can be
associated then to oxygen consumption in the liquid phase. The carbon dioxide produced is trapped by potassium hydroxide or sodium hydroxide tablet depending on the system used. In our case, the Oxitop® system was used.

Scope and application: The system was developed to evaluate the impact of biodegradable substances in water and wastewater. The range of measurement is from 0 to 4000mg/l.

Interferences: The interpretations of results as well as the reproducibility have application difficulties because of the biological character of the method. Organic matter oxidation is not the only phenomenon implicated; nitrite and ammonium oxidations are presents as well. In our case, a nitrification inhibitor (allylthiourea ATU) was used, considering the important amount of ammonium present in leachates. Furthermore, the initial concentration of microorganisms in the sample will influence the measurement. Finally, inhibitory substances to microorganism growth could be present in samples interfering with the BOD measurement.

Apparatus and reagents:
- OxiTop® measuring system
- Inductive stirring system
- Incubator thermostatic box (temperature 20°C)
- Brown sample bottles (nominal volume 510ml)
- Stirring rods
- Suitable overflow measuring beakers
- Rubber quivers
- Sodium hydroxide tablets

Procedure: Select the sample volume to introduce in the seal bottle according to the proposed volumes in operation manual and expected values in the samples. In general expected final BOD₅ values are approximated at 80% of COD. Once the liquid is inside, put the magnetic stirring rod into the bottle, insert the rubber quiver in the neck of the bottle and put two sodium hydroxide tablets into it. Finally screw the OxiTop® device directly on the sample bottle (tightly close). During the measurement days, the sample is continuously stirred. The system automatically stores one value every 24 hours for 5 days. Manual reading must be done to obtain BOD for longer or intermediate periods.
5.1.5 Total suspended solids (TSS) dried at 103-105°C [12]

Introduction: The suspended solids composition is very variable from one stream to another. Mineral and organic material concentrations will fluctuate depending on the soil composition, weather, human influence, etc. In natural streams, 25mg/l is a common amount of suspended solid found. For human consumption, no suspended solids are admitted.

Summary of the method: The wastewater sample well mixed is filtered through a previously weighed standard glass filter previously dried. The residue retained on the filter is dried to a constant weight at 103 to 105ºC. The increase in weight of the filter represents the total suspended solids. The diameter of the filter pore must allow retaining materials but if clogging occurs, pore diameter of the filter must be change or sample volume should be decreased.

Scope and application: This method is used to measure TSS in drinking water, surface waters, saline waters, industrial and municipal wastewater. The range of determination is between 2 and 20000 mg/l.

Interference: Filtration apparatus, filters, cleaning processes and oven temperature must be well controlled because it is known that these parameters could influence the results. Samples with high dissolved solids concentration like salt water or high mineral salt water as well as some residue could influence the result.

Apparatus: Filter (glass fiber type Whatmann GF/F 0.7μm)
-Oven recipient
-Oven (103-105ºC and 550ºC)
-Desiccator
-Precision balance
-Vacuum pump and glass material

Procedure: Put the previously weighed filters (numbered) into the oven at 103-105ºC at least for 1 hour. Cool in the desiccator to room temperature and weight. Note the weight of dry filters. Then, select the well mixed sample and measure the volume. Filter the sample with the
use of vacuum pumps if needed. Put the filter with the residue bended in four to avoid material lost into the oven. Wait two hours and then weight again the filters with residue that are already dry and cooled in the desiccator. To measure the volatile suspended solids (VSS), the same principle could be used, except that the oven must reach 550°C at least for 30 minutes.

*Precision and accuracy:* The standard deviation was 5.2mg/l (coefficient of variation 33%) at 15mg/l, 24mg/l (10%) at 242mg/l, and 13mg/l (0.76%) at 1707mg/l in studies by two analysts of four sets of 10 determinations each. Single-laboratory duplicated analyses of 50 samples of water, and wastewater were made with a standard deviation of differences of 2.8mg/l [12].

5.1.6 Kjeldahl nitrogen
[1, 13]

*Introduction:* Kjeldahl nitrogen does not represent the total amount of nitrogen contained in a sample. It only represents the reduced (organic) forms and ammoniac. Nitrogen could also exist in the form of nitrous nitrogen or nitric nitrogen and independently to dinitrogen gas.

*Summary of method:* The kjeldahl nitrogen (KN) measurement considers the sum of organic nitrogen and ammonia nitrogen into the sample. Organic material is first mineralised in acidic conditions and high temperature in presence of a catalyst. Then a sodium hydroxide solution is added in order to transform ammonium to ammonia. Finally, a distillation step is made to recover ammonia steam that will be determined by titration.

*Scope and application:* Samples of drinking, ground and surface waters and of domestic and industrial wastes.

*Interference:* Nitrate could be a negative interference as it could oxidize a portion of ammonia released from digested organic nitrogen. When organic matter at a low state of oxidation is present, nitrate can be reduced to ammonia resulting in a positive interference. Inorganic salts as well as the organic matter could also influence results by changing digestion temperature.

*Apparatus:* - Kjeldahl matrass (with Buchi K-424)
- Mineralization system with fume recuperation system (Buchi K-424)
- Distillation unit (Buchi K-360)
- 5ml microburette or 10ml precision burette

**Reagents:**
- Concentrated sulphuric acid (98%)
- Boric acid (10g/l solution)
- Sulphuric acid (0.05mol/l)
- Sodium hydroxide (400g/l solution)
- Mineralization catalyser
- Methyl red and bromocresol green solution

**Procedure:**
- Mineralization: Introduce 100ml of sample into the Kjeldahl matrass. Add some glass balls to regulate the boiling process. Also add 1g of catalyst and 10ml of concentrated sulphuric acid. Place the matrass into the mineralization unit. Boil slightly and evaporate until white smoke appears. Then continue to digest for two hours. Residual liquid must be clear, if this is not the case one should restart with less sample volume. Finally allow the sample to cool down.

- Distillation: Place the Kjeldahl matrass in the distillation system. Add 50ml of sodium hydroxide solution. Recover the distilled liquid in a 250ml Erlenmeyer with 10ml of boric acid.

- Measurement: Add 2 or 3 drops of methyl red and bromocresol green solution. Make the titration of ammonia with sulphuric acid (0.05mol/l).

**Precision and accuracy:** The precision of the method depends on the apparatus used and the sample characteristics. In this case, measurements were made with Büchi equipments.

5.1.7 Dissolved oxygen (DO) [1, 14]

**Introduction:** This element is very common in all sorts of waters. Its solubility is a function of temperature, atmospheric partial pressure and salinity. It is a common oxidant that acts
chemically over mineral compounds or biochemically. Electrochemical reactions are also a possibility.

Superficial water contains an elevated amount of dissolved oxygen sometimes close to saturation. In contrast, in ground waters the concentration is often very low or even absent. Dissolved oxygen can be expressed as a percentage of saturation at a determined temperature and pressure. Values lower than 80% of saturation in water for human consumption could present organoleptic problems. Saturated tap water at 20°C under normal pressure contains 9.1mg/l of dissolved oxygen. When the temperature increases, DO decreases. This effect is explained by the lower solubility but also by the enhanced activity of microorganisms in aquatic environments. When analysing samples, the amount of DO is important but the variation in this parameter could be even more interesting. Variations could be explained by photosynthetic activity, presence of biodegradable organic matter, a wide range of microorganism activities, and even because of perturbation in the exchange with the atmosphere caused by hydrocarbons or other pollutant at the interface. In a natural aquatic environment, diurnal and nocturnal fluctuations are typical because of light and temperature influence over the mentioned DO related activities.

The WHO recommends that values of DO should be kept close to saturation for human consumption. For superficial water that is used for human consumption after treatment, 70% of saturation is allowed when simple physical and disinfection treatment is applied. Low values near 30% are tolerated when treatment in enhanced.

**Scope and application:** In our case, a Clark-type electrode will be used. Being completely submersible, their portability and easy operation makes them ideal for field applications, but they are generally used in laboratories as well. They provide an excellent method for DO analysis in polluted water, highly coloured waters and strong waste effluents.

**Summary of the method:** Amperometric oxygen sensitive membrane probes are composed of two solid metal electrodes in contact with supporting electrolyte separated from the test solution by a selective membrane. Membranes made of polyethylene and fluorocarbon are generally used. The “diffusion current” is linearly proportional to the concentration of molecular oxygen. This current has then to be converted in concentration units after
calibration. Temperature will affect the electrode sensitivity so a temperature compensation is needed. Salt content must be considered as well.

*Interference:* Few other gases beside oxygen could also permeate through the membrane and react at the electrodes (hydrogen sulphide for example). Rather frequent calibration and periodical replacement of the membrane is necessary.

**Apparatus:** Oxygen-sensitive membrane electrode with appropriate meter (WTW Oxi 197i).

**Procedure:** Calibration and sample measurement must be performed in accordance to manufacturer recommendations. In this case, calibration in water vapour saturated air is used thanks to the Oxical®-SL vessel accessory.

**Precision and bias:** Accuracy of ±0.1mgDO/l with precision of ±0.05mgDO/l can be obtained with most of the commercially membrane electrode systems.

5.1.8 **Conductivity**

[1, 15]

This measurement can be used to evaluate mineralisation of a stream but in a very approximate way. This is because conductivity tends to augment in a stream way to the sea. In water networks for human consumption, this parameter is continuously measured in order to detect possible variations that could have pollution origins. In natural streams and other surface waters, diurnal variations are possible. Values over 2000μS/cm are possible but atypical in human consumption with general measurement, between 200 and 1000μS/cm (in France). For reference, demineralised pure water conductivity value is 0.04μS/cm and for sea water it could be up to 30000μS/cm.

In general terms, the ability of a sample to carry an electric current is measured. Results will depend on solutions of most inorganic compounds and thus, on the presence of ions, their mobility and valence. Temperature is also important but the measurement can be compensated.
Measurements were made with a YSI-environmental multiparameters display systems and probes according to manufacturer recommendations. Precision is between 0.1 and 1%. Reproductibility of 1 to 2% is expected after an instrument has been correctly calibrated.

5.1.9  pH

[1]

The pH of water represents its acidity or alkalinity. Water at pH 7 (25°C) is considered neutral. It is one of the most important parameters so it is generally measured online checking for variations in wastewater treatment plants. In natural streams, the pH of the water is related to the soil characteristic. Typical values vary from 7.2 to 7.6, but special situations could increase this range. Natural waters with pH ≥ 8 and ≤ 6 are rare. Only in cases of stagnated waters, values can become more basic.

pH is an important value in order to define the aggressive and incrusting characteristics of the water. pH under 7 could corrode cement or canalisation metals leading to lead (Pb) problems for example. Because of high pH, deposits can incrust in the circuits. Furthermore, chlorine disinfection effects are decreased. It is closely related to many other parameters like temperature, alkalinity, etc. Microorganism behaviours are also closely related to pH. Flocculation and coagulation processes are influenced by pH as well.

WHO doesn’t fix a value, but consider values below 8 as acceptable. For aquatic life, the optimum range appears to be between 6 and 7.2 but fish range could be a little wider (5-9). It must be considered that these range values couldn’t be separated of the other parameters that are interconnected as temperature, DO, etc. when considering life adaptability. Measurements were made with a YSI-environmental multi-parameters display system and probes according to manufacturer recommendations after correct calibration.

5.1.10  Temperature

[1]

Temperature influences many parameters and reactions in water. European directives suggest a temperature of 12°C as a reference for human consumption. Above 25°C it is considered a
risk, because microorganism growth is enhanced. Ground water is less sensitive to temperature variations compared to surface runoffs. Typical ground water temperature is in the range 12 to 15°C. Surface runoff temperature is normally between 2 and 30°C. Warm water could also be considered as a pollutant because of its effects over natural environments. Furthermore, some dangerous types of microorganisms can be favoured at a temperature over 25°C. Dangerous amoeba *Naegleria fowleri* are amongst them in natural waters but also other pathogens like *legionella pneumophila* are likely to be developed in hot water circuits.

Temperature was measured with several kinds of thermometers. Most of the measurement equipments have incorporated temperature probes, data was taken directly, but occasionally digital thermometer and mercury thermometers were used as well.

### 5.2 Membrane bioreactor descriptions

#### 5.2.1 MBR pilot

A pilot plant is a useful tool to previously estimate full scale treatment. Operational troubles could be anticipated and removal performances checked [16]. When treating landfill leachates, the pilot configuration must be chosen in order to perform nitrogen removal. This objective in mind, a denitrification tank is placed first, followed by an aerated nitrification tank and finally by a small aerated tank in which the submerged membrane is placed. Nitrates and nitrites formed by ammonia oxidizing bacteria are recycled into the denitrification tank. The old leachate is introduced in this tank allowing heterotrophic bacteria to consume the organic matter still present (denitrification). Some external organic source may be added at this stage.

The flows (volumetric load) were chosen in order to emulate the MBR real facility of Muertendal. A treated flow of 80l/d was fixed. Recirculation flows were fixed to be 5 times the inlet flow. Considering the total volume of the MBR pilot, the HRT will be around 6-7 days, value comparable to the one found in Muertendal’s facility.

The MBR pilot is composed of three tanks elaborated in plastic material. The first tank (V=238 liters) is not aerated and thus will be considered as anoxic (nitrates will be present as
electron acceptor). An electric motor installed over the lid ensures the rotation of a propeller that induces mixing at lower rpm. The second volume (V=238 liters) is equipped with an aeration system. The pilot is fed with an electric centrifuge pump (COTTON pt216987) that takes leachates from three big plastic containers not drawn in the scheme of figure 5-1. These containers have a capacity for approximately 20 days. Leachates came from luxembourgish Muertendall’s landfill. The third tank (V=25.5 liters) is the one that contains the membrane. A Zenon membrane module of 0.93m² ensures the effluent filtration. A fourth plastic tank is also present after filtration in order to retain some clear water needed by the backwashing procedure. The instrumentation is composed of three flow-meters and two pressure sensors connected to a numerical recording device.

**Pumps**: Magnetic coupled pumps are used (IWAKI model MD-6-230GS). They provide flows in the range 5 to 150 liters per hour. They are connected to a variable-frequency drive (inverter drive) that includes a proportional-integral-derivative controller (PID controller) that is directly connected to flow-meters. These devices guaranty a perfect control of recirculation flows, considering of course that flow-meters give correct lectures.

**Valves**: Two motored three-way valves are used for the automation of back-washing. This system allows the filtrated flow to be inversed.

**Flow-meters**: Three Endress-Hauser electromagnetic Promag 50DN 04 flow-meters were used. The range of measurement goes from 10 to 200 liters per hour. They allow a precise measurement of recirculation flows and filtration flows. Originally, some problems occurred.
associated to these artifact measurements because they were initially misplaced at the higher part of the circuit. Direct measurement effectuated with a graduated cylinder showed that flow-meter measurements were under-evaluated. By being placed in the highest part of the circuit, it was probable that accumulated air bubbles disturbed the flow-meter performance. A simple solution was found by placing the tubes higher than flow-meters in order to accumulate bubbles at this place instead. Good correlation between graduated cylinder and flow-meter measurements were found with this simple adjustment (figure 5-2). Comparative tests were repeated constantly during all pilot operation with similar results, despite the increase of mixed liquor suspended solids concentrations.

![Figure 5-2 Flow meters adjustments and graduated cylinder used for measurement verification](image)

*Pressure meter:* Endress-Hauser (delta-bar) differential pressure meter was used for measurement of trans-membrane pressure.

*Central Data recorder:* Sensors and flow-meters are connected to a data recording unit (Endress-Hauser Ecograph T) that compiles information continually in order to facilitate operation control. The data recording unit allows to connect six channels at the frequency imposed by the operator. It can be programmed by local interface or by a computer with a RS232 connection cable. It shows data directly in a graphic form, plotted versus time in the screen, allowing the operator to detect easily eventual problems occurred without supervision. Furthermore, the unit is equipped with a memory drive, so data can be downloaded to a computer. Finally the data recorder is also equipped with relay outputs that can be connected to tank level alarms for example.
**Aeration:** Aeration in the second tank is performed with two Passavant-Intech BIOFLEX® membrane diffusers (diameter= 20cm). The air source varied according to availability and pilot location. The laboratory distribution network was used but also classical electrical piston compressors. Rota meters were installed to measure air flows.

**Membrane module:** The filtration membrane module is a hollow fibre named ZeeWeed®-10 (ZENON environmental). The module is cylindrical with 70cm length and a diameter of 11cm (figure 5-3). Hollow fibres are fixed to a plastic support device. In the superior part of it, an evacuation tube allows to extract by aspiration the filtrated effluent. In the lowest part, aeration is performed. The air arrives through a rigid tube placed at the centre of the cylinder. This tube plays also a structural role. The surface of membrane is neutral and hydrophilic, pore diameter is 0.1μm, maximal trans-membrane pressure of 0.62bar and a pH functioning optimal range between 5 and 9.

![Image of Membrane filtration module](image)

**Filtration pump:** A Shurflo 75420-17 diaphragm pump that needed a variation-frequency drive for power supply was used (figure 5-5). Originally the pilot was conceived with a volumetric pump that presented numerous problems during initial trials, that’s why this modification was introduced just before starting the operation. However, the novel configuration doesn’t allow to use a PID controller to force a constant flux so a calculation technique was developed in order to obtain filtration flows per cycle, for example. Another
important characteristic of this pump is that it is able to perform not only filtration flow but also backwashing flow. The pilot is equipped with a timer that switches from normal filtration to backwashing due to three-way valves using the same pump. From initial tests, it was evident that backwashing time-lapse needed to be very short compared to filtration time-lapse because in the first there is no forces against the driving force so the flow will be much stronger that in the filtration case, where fouling is present. In figure 5-4 it is shown the difference between three filtration-backwashing cycles with and without the PID controller that corrects and thus imposes a constant flow.

![Figure 5-4 Representation of filtration flow (blue) and trans-membrane pressure (red) with and without potentiometer during three filtration cycles](image)

A relaxation period is also a common technique used to control fouling in membrane filtration. It consists in a lapse of time with no filtration or backwash flow. During this pause time, mechanical cleaning is performed by aeration bubbles in the absence of a pressure gradient force. In order to incorporate this option to the filtration cycle, several important modifications were introduced in the cabling of the pilot. Furthermore the LOGO (SIEMENS 12/24RC) that controls most of the system was re-programmed.

![Figure 5-5 Filtration pump and variable-frequency drive used for pump power supply](image)
One of the problems encountered was the difference of the water levels in the tanks when using the recirculation pumps. The problem is that each couple of tanks is interconnected by two tubes. In one of the tubes, the recirculation pump is situated and the other is placed in order to equilibrate the water levels by pressure equalization. Having a strong flow in one direction (pump), and another very weak in the other (the pressure equalization) generates imbalances. Cycles of functioning/stops were a simple solution. A period of no functioning of the pump gives time to the pressure equalization, and thus water levels were kept equal in the three tanks.

5.2.2 Muertendall MBR

Muertendall’s landfill situated in east Luxembourg is operated by the inter-communal syndicate SIGRE (Syndicat Intercommunal pour la collecte, l’évacuation et l’élimination des ordures de Grevenmacher, Remich et Echternach). It started January 1979 but by the time it has the characteristics of a midden or a simple dump site for domestic wastes, proper operation started in 1984. In order to respect European directives, a renovation project was initiated during the year 1995. In a first step, the landfill was doted with and impermeable layer in order to prevent leachates leaking. An in situ treatment station for leachates was the second step to be implemented. The construction started in 1995 and ended 2001. During this period, the ancient material of the landfill was relocated during three years. The site was renovated with the installation in the bottom, a 2 meter geological layer, impermeable textile membranes and 6 collectors for the percolated leachates. From 2003 to 2004, the onsite membrane bioreactor station was constructed and put into operation. Actually the MBR station is in operation with an excellent ammonia removal. When treated, wastewater is incorporated to the municipal wastewater of Grevenmacher’s city. Further investments are planned; particularly the incorporation of activated carbon process for leachate post-treatment is in study as well as the biogas utilization.
The MBR facility has a similar configuration when compared to the MBR pilot (figure 5-7). An anoxic tank with a volume of 42m$^3$ is placed at first. Leachates are directly pumped in from the reservoir tanks. Then, two aerated tanks of 75m$^3$ each follows. A recirculation is placed between the aerated and the anoxic tank in order to ensure nitrates and nitrites circulation.

Total suspended solids were kept close to 15g/l in this station. Leachates flows depends on rainwater falls and other properties of the landfill so flows are variable going from less than 20m$^3$ per day up to 100m$^3$ per day. The primary difference with the MBR pilot is the membrane unit. The MBR pilot has a submerged configuration contrasting with the real facility that has an external type membrane configuration.
5.3 References

[5] U. S. Environmental protection agency (EPA), method EPA 300.0A.
[8] Standard methods for the examination of water ans wastewater (SMEWW), method 5220 D.
[10] Standard methods for the examination of water and wastewater (SMEWW), method 5210 A.
[12] Standard methods for the examination of water and wastewater (SMEWW), method 2540 D.
Abstract: Landfill leachates can be characterized correctly in terms of ASM1 and ASM3 variables. The wastewater characterisation was based on a physical chemical method combined with a BOD analysis for the COD fractions and on standard analysis for nitrogen forms. Results show important differences compared to municipal wastewater. High amounts of organic matter with low biodegradability were found beside a high concentration of ammonia nitrogen. Based on average values, a generic ASM characterisation is proposed for landfill leachates. It can be directly employed in early stages of simulation of landfill leachates treatment with activated sludge models.
6.1 Introduction

Landfill leachates contain a complex mixture of organic and inorganic compounds. In most cases, high concentrations of ammonia nitrogen and organic matter represent the primary environmental risk. However, the organic matter has a low biodegradability because it is composed principally of fulvic and humic acids, particularly in case of old landfills [1, 2]. The objectives of the treatment to be implemented are thus: in the first place, the reduction of the toxic ammonium ion concentration and in second place, the reduction of the organic matter. Biological treatments with activated sludge are capable of obtain high performances, thanks to bacterial colonies, particularly autotrophic bacteria for the ammonia consumption and heterotrophic ones for the carbon fraction [3, 4, 5, 6]. The behaviour of these micro organisms can be mathematically described and models like the Activated Sludge Model’s (ASM) family had proven to simulate it correctly, at least for municipal wastewater treatment conditions [7]. ASM models consider the compounds of wastewater as a number of variables. These variables represent thus the organic matter present, measured as chemical oxygen demand (COD) and nitrogen forms. Biomass is also represented and is as well measured as COD. Alkalinity and dissolved oxygen completes the picture. Good model calibration requires knowledge of model parameters and also influent wastewater characteristics, which can significantly influence plant performance, especially in biological nutrient removal systems [8].

Characterization of landfill leachates into ASM’s variables is thus necessary to obtain a realistic simulation of a real or a pilot treatment plant. Since most of the ASM characterisation data available in literature corresponds to municipal wastewater, this work constitutes a valuable tool for simulation of landfill leachates treatment plants. It must be noticed that this work focuses on a characterization method and not on the definition of the variables or processes in the models. For more details about the models see [9].
6.2 Material and methods

6.2.1 Wastewater characteristics: ASM’s partitioning of material

Carbonaceous material partition:

Inert soluble COD ($S_i$): This fraction of wastewater COD is considered inert for the system and will not be consumed. This means that this fraction of material doesn’t react in the system or reacts too slow (compared to his residence time). Being soluble, and as it is not produced in the process, inert soluble COD will pass directly through the process, and the outlet concentration will be the same as the inlet one.

Inert particulate COD ($X_i$): This particulate inert fraction will not react in the process either. However, there is a production caused by the biomass endogenous respiration concept in ASM3 and by biomass decay in ASM1 (considered as $X_p$). Normally, this fraction will more or less accumulate in the system depending on the sludge purge.

Biodegradable soluble COD ($S_s$): The biodegradable fraction is considered as a substrate for the heterotrophic biomass. Being soluble, it will be consumed rapidly because it is directly available for micro-organisms. It is produced in the system by hydrolysis of the biodegradable particulate fraction.

Biodegradable particulate COD ($X_s$): The biodegradable particulate fraction is also considered as a heterotrophic biomass substrate but as mentioned, it needs previous hydrolysis so it can be available for direct bacteria consumption. Concerning $X_s$ production, there are remarkable differences between ASM1 and ASM3. In the first case, $X_s$ is produced in the biomass decay and in the second, $X_s$ only comes from the wastewater influent with no production in the system.

Heterotrophic and autotrophic biomass ($X_h$ and $X_a$): $X_h$ and $X_a$ takes into account the heterotrophic and autotrophic biomass fraction, respectively, measured as COD. In the case of ASM3, the organic matter stored by heterotrophs ($X_{sto}$) is also considered to represent the storage concept of heterotrophic biomass.
Nitrogen material partition:

Free and saline ammonia (Snh): Ionized (ammonium) and non-ionized (ammonia) are considered in this variable. Because at a pH value near neutrality the non-ionized form is almost absent and because this is generally the case for wastewater treatment, it is satisfactory to consider ammonia oxidation in terms of the total ammonium nitrogen concentration.

Nitrate/nitrite concentration (Sno): Nitrate nitrogen is produced during aerobic growth of autotrophic bacteria and is consumed by anoxic growth of heterotrophic bacteria. Even if it is known that nitrite nitrogen is an intermediary compound of nitrification, it is not considered in order to simplify the models. The amount of nitrite nitrogen measured must be considered as nitrate nitrogen, which is the second electron acceptor considered in addition to the dissolved oxygen.

Organically bound nitrogen (Snd, Xnd): These fractions are only considered in the ASM1 case. Snd is formed by hydrolisis of particulate organic nitrogen and converted to ammonia nitrogen by ammonification. Xnd is the result of decay of biomass. However, these fractions can’t be easily measured and complicate unnecessarily the model, reason why ASM3 doesn’t include them.

Dinitrogen (Sn2): Sn2 is the only product of denitrification, and has a negative theoretical oxygen demand. Its inclusion allows checking continuity on nitrogen mass balances. It is not considered in the ASM1 version.

Others

Alkalinity: The incorporation of this variable is not essential. However, it inclusion is recommended because it provides valuable information about changes in the chemical equilibrium of carbonate system, potentially allowing pH falls to be predicted. This is important because low pH decreases the nitrification rate and is associated with other process problems (corrosive effluents, bulking). Even if the proper input is not known, this variable permits a user to evaluate whether the process configuration under consideration allows
sufficient recovery of alkalinity during denitrification to maintain a proper pH range considering the proton release during nitrification.

**Dissolved oxygen concentration (So):** It is the primary electron acceptor considered by the ASM family models. An important difference between ASM1 and ASM3 is that in the first, oxygen utilization is associated only with aerobic growth of biomass and not with microbial decay or endogenous respiration as it is the case for ASM3. Anyway, the biological processes considered only takes into account oxygen removal from solution. To simulate correctly the variation of So, specially for aerated systems, oxygen transfer must be considered.

**Suspended solids:** This fraction is introduced to the biokinetic model in ASM3 to compute their concentration via stoichiometry.

<table>
<thead>
<tr>
<th>Table 6-1 Variables of ASM1 and ASM3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inert</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>ASM1</td>
</tr>
<tr>
<td>ASM3</td>
</tr>
</tbody>
</table>

6.2.2 **Leachates under study**

The leachate used in this study comes from the Muertendall sanitary landfill located in East Luxembourg, which operates since 1984. The facility is operated by the SIGRE syndicate (Syndicat Intercommunal pour la gestion des déchets ménagers, encombrants et assimilés en provenance des communes de la région de Grevenmacher, Remich et Echternach) and receives the residential waste from 25 municipalities (50000 inhabitants) which corresponds to 11.5% of Luxembourg’s population. The bottom geomembrane which collects the leachates was installed between 1995 and 1998 and a membrane bioreactor for the on-site treatment is in operation since 2005.
The leachate characteristics based on the analysis performed by the landfill’s management are resumed in table 6-2. The values are validated four times per year by external laboratories and correspond to the period from March 2008 to March 2009. The high amounts of ammonium nitrogen and non-biodegradable COD suggest that the leachate is coming from an old landfill [10]. However, biodegradable oxygen demand (BOD$_5$) was measured without addition of a nitrification inhibitor, so the real biological oxygen demand associated with the carbonaceous material should be even lower considering the high ammonium concentration.

### Table 6-2 Average characteristics of the Muertendall leachates

<table>
<thead>
<tr>
<th>Variable</th>
<th>Unit</th>
<th>Value</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>7,8</td>
<td>(7,5 - 8,1)</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>18,7</td>
<td>(10,9 - 23,4)</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/cm</td>
<td>7,63</td>
<td>(5,12 -13,18)</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>1631</td>
<td>(813 - 3602)</td>
</tr>
<tr>
<td>BOD$_5$</td>
<td>mg/L</td>
<td>526</td>
<td>(93 - 950)</td>
</tr>
<tr>
<td>NH$_4$-N</td>
<td>mg/L</td>
<td>271</td>
<td>(116 - 586)</td>
</tr>
<tr>
<td>NO$_2$-N</td>
<td>mg/L</td>
<td>23</td>
<td>(7 - 89)</td>
</tr>
<tr>
<td>NO$_3$-N</td>
<td>mg/L</td>
<td>0,9</td>
<td>(0,1 - 1,8)</td>
</tr>
</tbody>
</table>

6.2.3 Membrane bioreactor pilot

The landfill leachates were fed to a micro-organism colony present in a membrane bioreactor composed of three volumes. One anoxic in which the inlet carbon was consumed with the recirculated nitrate as electron acceptor, one aerated in which the nitrification occurs and a final one, also aerated in which a filtration membrane is located. The filtration process by a hollow fibber membrane (Zenon, ZeeWeed®-10, 0.93m$^2$ with a mean pore diameter of 0.1µm) allows to retain most of the particulate matter. The total volume of the pilot is near 500 litres, and the theoretical hydraulic retention time close to 150 Hours.

6.2.4 Measuring campaign

Two measuring campaigns were performed, the first during January, February and March 2009, and the second during August, September, October and November 2009. Samples were collected one time per week including influent, and effluent. The influent and effluent samples were analysed for ammonium nitrogen (NH$_4^+$-N), nitrites (NO$_2^-$-N), nitrates (NO$_3^-$N),
filtered and non-filtered chemical oxygen demand (COD), 7 day biological oxygen demand (BOD₇), total nitrogen, temperature, pH and alkalinity. BOD tests were performed with and without addition of a nitrification inhibitor (allylthiourea, ATU). All analyses were made using standard methods. In general, samples were analysed just after they were taken to eliminate time related interference. Average values and range obtained are presented in figure 6-1 and in table 6-3.

Table 6-3 Resume of the data resulting of the measuring campaign

<table>
<thead>
<tr>
<th>Variable</th>
<th>Unit</th>
<th>Value</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>7,9</td>
<td>(7,7-8,6)</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>19,8</td>
<td>(16,8-24,8)</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/cm</td>
<td>7,74</td>
<td>(5,25-10,64)</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>mmol HCO₃/L</td>
<td>47,52</td>
<td>(45,34-50,49)</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>1549</td>
<td>(620-2820)</td>
</tr>
<tr>
<td>filtered COD</td>
<td>mg/L</td>
<td>1107</td>
<td>(448-1700)</td>
</tr>
<tr>
<td>BOD7</td>
<td>mg/L</td>
<td>234</td>
<td>(155-361)</td>
</tr>
<tr>
<td>BOD7 with ATU</td>
<td>mg/L</td>
<td>134</td>
<td>(100-207)</td>
</tr>
<tr>
<td>NH₄⁺-N</td>
<td>mg/L</td>
<td>261,26</td>
<td>(144-454)</td>
</tr>
<tr>
<td>NO₃⁻-N</td>
<td>mg/L</td>
<td>10,85</td>
<td>(0-59,63)</td>
</tr>
<tr>
<td>NO₂⁻-N</td>
<td>mg/L</td>
<td>0,05</td>
<td>(0-0,89)</td>
</tr>
<tr>
<td>Total nitrogen</td>
<td>mg/L</td>
<td>303,73</td>
<td>(178,42-506,3)</td>
</tr>
</tbody>
</table>

6.2.5 Characterization method employed

As mentioned before, characterization of the carbonaceous material presents in the wastewater is done in terms of chemical oxygen demand (COD). Thus:

\[
\text{Inlet COD} = S_s + S_i + X_s + X_i + X_a + X_h
\]

For ASM1, the inlet Xₚ fraction is zero as it is a product of a biological process in the system considered. For ASM3, initial Xₚ will not be considered as it represents a very low fraction, and it is almost impossible to measure.
The leachate characterisation employed in this study is based on a physico-chemical method combined with a BOD analysis. The guidelines were proposed by the Dutch Foundation for Applied Water Research (STOWA) [11]. For the nitrogenous material, it will be fractionated based on direct ammonia, nitrite and nitrate measurement, complemented with total nitrogen analysis.

6.3 Results

6.3.1 Organic material

Figure 6-1 COD fractions according to ASM during the two measuring campaigns (one characterisation per week)

*Inert soluble COD*: This fraction is calculated based on the assumption that there is no generation of it in the system and that the biodegradable fraction of COD in the effluent is very low. Si is generally considered to be equal to the filtered effluent COD. However, it must be considered that residual biodegradable organics, most of the time could be found in systems effluent, even in cases like this where a filtration membrane is used, and a long wastewater residence time is applied. To include this fact, the STOWA guidelines suggest the use of a correction factor of 0.9 in the case of low loaded systems.
As a result of the study, filtered effluent COD is 61.35% (39.05-73.49%) of the influent COD. The BOD$_5$ of the effluent found is 11.77mgO$_2$/l (0-26mgO$_2$/l) which represents 0.77% (0-2.86%) of the influent oxygen demand. Considering that the BOD$_5$ does not represent the total biodegradable fraction, but only between 50 to 95% and that the differences found between effluent filtered and non filtered COD are very low (sometimes even negative), a factor of 0.99 is proposed. Thus:

$$Si = 0.99 \times \text{Filtered effluent COD}$$

Considering this correction factor, $Si$ is 60.74% (38.66-72.76%) of the total inlet COD.

**Biodegradable COD:** This fraction is the sum of the soluble (Ss) and particulate (Xs) biodegradable COD, also differentiated as readily and slowly biodegradable COD. It is determined by data obtained from a BOD analysis. The BOD analysis, where the consumption of oxygen is measured as a function of time is widely used and easy to implement, reason why it was chosen. Generally, the test is performed in 5 days, but it is known that not all the biodegradable matter is oxidized during this time.

![Figure 6-2 Fitted ultimate BOD curve for determination of biodegradable COD](image)

To get an estimation of the total biodegradable matter, the Thomas method is applied. This estimation is based on a function similarity to the integrated first order kinetics’ equation that describes the BOD curve. This method was chosen by its simplicity over a non-linear method which is more complex but could give more accurate results [12].
In order to get accuracy, the BOD analysis was kept for 7 days. As shown in figure 6-2, measured data allows fitting a curve with the mentioned Thomas method, and the ultimate BOD can be obtained. For long term BOD measurement, a correction factor has to be used to consider the part of biodegradable COD that is converted into an inert fraction caused by the interaction of growth and decay of biomass. The correction factor applied is 0.15, which is in accordance with the fraction in the models for inert COD generated by biomass lysis. The values obtained for the biodegradable COD in this study are thus 17.42% (6.53-39.08%) of inlet COD.

![Figure 6-3 BOD with and without ATU](image)

**Biomass fractions**: The assumption of not considering this fraction of COD in the influent is generally proposed due to the difficulties of a direct measurement. The high grow rate of heterotrophic bacteria and the assumption of an initial concentration of these organisms in the activated sludge units allows the possibility to neglect the inlet part. For the case of autotrophic bacteria, the low growth rate forces its consideration but the influent fraction is generally very low compared to the total influent COD. Another theory that sustains the non inclusion of these fractions is the one that relates the bacterial population and diversity of a colony to the niche concept (environment) instead of relating it to wastewater inoculum [13]. On the other hand, the BOD-analysis performed to the raw leachates, with and without addition of a nitrification inhibitor clearly reveals the presence of autotrophic biomass in the influent as the oxygen consumed without ATU is enhanced (figure 6-3). The BOD test reveals itself the presence of heterotrophic biomass, which could be up to 20% of the influent COD for municipal wastewater [14]. Considering everything previous, this study will consider a 2%
of inlet COD as heterotrophic biomass and a 1% for the autotrophic fraction. Even if these assumptions appear somehow arbitrary, it seems to be a more coherent approach (taking into account the data available) than simply not to consider any biomass at all.

**Inert particulate COD:** 18.84% (3.14-40.80%) This fraction is obtained based on the difference between total inlet COD and fractions already presented, so all measurement errors will propagate into it. Considering this, the inert particulate COD in the influent can be used as a main calibration factor, in particular, for sludge production [15].

**Soluble biodegradable matter:** The estimation of this fraction is based on the difference between filtered inlet COD (Ss+Si) and the inert soluble fraction. Accordingly, Ss is 11.59% (4.03-33.66%) of inlet COD.

### 6.3.2 Nitrogenous material

**Nitrites/nitrates:** As mentioned before, the models do not consider the nitrite fraction so it must be added to the nitrate part. In this study, average inlet nitrate reported is 10.85mgN/l (0–59.63mgN/l). The average nitrite measured is 0.05mgN/l (0-0.89mgN/l) so practically none. Therefore, the inlet nitrate/nitrite proposed for modelling of leachate treatment is 10.85mgN/l (0-59.63mgN/l). This amount corresponds to 4.1% of total nitrogen.

**Free and saline ammonia:** Measured values obtained are in average 261.26mgN/l which corresponds to 85.57% of total nitrogen with a range going from 144mgN/l to 454mgN/l.

**Organically bound nitrogen:** This fraction is computed as the difference between total nitrogen and the nitrates/nitrites plus the ammonia part. As a result, an average of 31.62mgN/l (0.87-52.3mgN/l) was found. It is clear that not all forms of organic matter contain the same proportions of nitrogen but in order to simplify calculus and because differences are small, this assumption is usually made [16]. Considering this, the measured organically bounded nitrogen can be divided proportionally as the fractioning of the organic matter. Thus, the part bounded with the inert fraction which represents 79.58% (60.74%+18.84%), corresponding to 25.16mgN/l in average, can be neglected of the inlet characterisation as it doesn’t interact within the system so it cannot be unbounded. The rest of the nitrogen, assuming proportional to particulate and soluble organic matter will give Snd=3.47mgN/l and Xnd=2.7mgN/l.
Clearly these values and procedures are raw estimations but the lowest quantity of bounded nitrogenous material compared to ammonia concentration allows this degree of freedom. For the ASM3 case in which these fractions are not considered, the amounts of bounded nitrogen must be considered in the ammonia fraction. The bounded part corresponding to the biomass was not considered because the amount is very low.

_Dinitrogen_: This fraction can be used to predict problems of supersaturation in secondary clarifiers. In this study, membrane separation replaces clarifiers so $\text{Sn}_2$ may only be used to calculate the amount on nitrogen lost due to denitrification. Consequently, $\text{N}_2$ contained in the influent, and gas exchange can be neglected [17].

6.3.3 _Others_

_Alkalinity_: This variable is used to approximate the conservation of ionic charge in biological reactions and is assumed to be bicarbonate ($\text{HCO}_3^-$) only as it is the case for stoichiometric computations. The average value obtained for the raw leachates is $47.52\text{mmol HCO}_3^-/\text{l}$ ($45.34–50.49\text{mmol HCO}_3^-/\text{l}$).

_Suspended solids_: $\text{Xss}$ can be used to model volatile suspended solids beside suspended solids [17]. This leachate characterization considers the VSS approach as it is simpler to choose the relevant numbers for the composition parameters. This choice will also be relevant for the second part of this research work where a comparison between ASM1 and ASM3 simulation performances will be achieved, and similar considerations are needed for both models. Considering a VSS to COD ratio of 0.75gVSS/gCOD [17] for particulate organics, the value proposed for inlet Xss is $331.39\text{mgVSS/}\text{l}$.

_Dissolved oxygen concentration_: The dissolved oxygen concentrations measured in the raw leachates are very low (<0.2mgO$_2$/l). This can be explained because heterotrophic and autotrophic bacteria used it all to consume organic matter and ammonia, and because the landfill itself is anaerobic, at least in the lower parts. Considering this and as proposed for ASM1 and ASM3 modelling of municipal wastewater, the value for inlet soluble oxygen considered will be zero.
### Table 6-4 Values proposed for landfill leachates characterization according to ASM1 and ASM3 variables

<table>
<thead>
<tr>
<th>Value proposed</th>
<th>Si</th>
<th>Xi</th>
<th>Xp</th>
<th>Ss</th>
<th>Xs</th>
<th>Xa</th>
<th>Xh</th>
<th>Snh</th>
<th>Sno</th>
<th>Xnd</th>
<th>Sn2</th>
<th>So</th>
<th>Salk</th>
</tr>
</thead>
<tbody>
<tr>
<td>948.36</td>
<td>315.91</td>
<td>0</td>
<td>158.6</td>
<td>79.48</td>
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<td>10.85</td>
<td>2.71</td>
<td>3.47</td>
<td>-</td>
<td>0</td>
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</table>

<table>
<thead>
<tr>
<th>Value proposed</th>
<th>Si</th>
<th>Xi</th>
<th>-</th>
<th>Ss</th>
<th>Xs</th>
<th>Xa</th>
<th>Xh</th>
<th>Xsto</th>
<th>Snh</th>
<th>Sno</th>
<th>-</th>
<th>-</th>
<th>Sn2</th>
<th>So</th>
<th>Xss</th>
<th>Salk</th>
</tr>
</thead>
<tbody>
<tr>
<td>948.36</td>
<td>315.91</td>
<td>-</td>
<td>158.6</td>
<td>79.48</td>
<td>15.49</td>
<td>30.98</td>
<td>0</td>
<td>267.43</td>
<td>10.85</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>331.39</td>
<td>47.52</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Unité</th>
<th>mg COD/l</th>
<th>mg N/l</th>
<th>mgO2/l</th>
<th>mgVSS/l</th>
<th>mmol/l</th>
</tr>
</thead>
</table>

### 6.4 Discussion

The physical-chemical method employed for the characterization, in particular, to differentiate between particulate and soluble fractions is based on a filtration with a 0.45μm filter (the filtration with a 0.1μm filter was not considered because of the clogging problems, and the difficulty associated to obtain reasonable volumes of filtered samples). Thus, the colloidal fraction (or at least a part of it) will pass through the filter, and will be considered as soluble instead of particulate. But although, the differentiation of slowly biodegradable COD (particulates) and colloids is important when modelling primary settling tanks, this is not the case here. The division is less significant for the activated sludge system where colloidal material is adsorbed rapidly onto the sludge matrix [8]. Practical experience also suggests that full-scale simulation models are not that sensitive about the division between slowly and readily degradable COD [14]. Anyway the activated sludge model structures themselves are based on this division soluble/particulate that is very difficult to differentiate accurately and thus there is a degree of interpretation [18].

The biodegradable characterization employed is based on BOD analysis, performed without inoculum of the bioreactor sludge so results depends on the capability of raw wastewater micro-organisms to consume biodegradable organic matter. Furthermore, the BOD flask environment is different than the one found in the membrane bioreactor so there could be differences between what is biodegradable in the BOD flask and what is biodegradable in the complete system. It is important to understand that modelling activated sludge systems, particularly modelling the behaviour of micro-organisms, is just an approximation of what really occurs and there is always a degree of interpretation.
These conjectures which are true for municipal wastewater treatment, for which the ASM family models were originally conceived, must be considered even more for landfill leachate treatment.

The composition of leachates is very variable [19]. It depends primarily on the location of the landfill, which will determine the temperature, the amount of precipitation, and most of all the waste characteristics influenced by the surrounding population behaviour. In addition, government’s politics will influence through legislation the techniques used for disposal and the mix with industrial waste that will directly influence the quality of the leachates. Another factor to consider is the age of the landfill because being a real complex biological reactor, it will pass through several stages of decomposition and stabilization [20].

For all these reasons and maybe plenty of others, the composition of this wastewater can vary widely, specially compared with the municipal wastewater which presents a more regular composition. The organic matter involved can present different degrees of complexity and thus, more than the two speeds of biodegradation proposed by the ASM models. Moreover, the leachates can contain a lot of substances that, for example, could influence the COD measuring methods or could inhibit micro-organisms growth and then BOD test will be corrupted as well.

It is important for future modellers of landfill leachates treatment to consider these facts and thus to take account of it in the result interpretations. The landfill leachate characterization presented in this work can be used to start simulation efforts with ASM1 and ASM3, but it must be noticed that it can vary a lot from one landfill to another. Comparative results can be very interesting. Preliminary simulations with this characterization show good results, in particular, for organic matter and nitrogen removal.

The primary difference found when comparing COD characterization applied on landfill leachate with results obtained on municipal wastewater is the content of biodegradable matter. As seen in figure 6-4, more than 67% of municipal wastewater COD is biodegradable compared to only 17.42% for leachates. In contrast, inert fraction is more important in leachates. These variations are also enhanced by the fact that the leachates used in this work came in provenance of an old landfill. Highest heterotrophic biomass concentration in municipal wastewater could be explained by the presence of more substrate (biodegradable matter).
COD). The same argument could be used for autotrophic biomass concentration that is higher in leachates (more ammonia nitrogen content that constitutes the substrate in this case).

![COD characterization](image)

**Figure 6-4 COD characterization on landfill leachates (this study) and the one proposed for municipal wastewater [14]**

### 6.5 Conclusion

The characterization protocol proposed by the Dutch foundation to characterize wastewater in terms of the ASM1 and ASM3 differentiation was successfully applied to landfill leachates with few modifications. The results show that the total inlet COD as a measure of the organic matter present is 79.54% inert for the processes considered in the models. More specifically, the soluble inert part is the principal component of the inlet COD as it represents 60.74% followed by the particulate part which is 18.84%. The biodegradable fraction found makes up 17.42% with 11.59% soluble and 5.84% particulate. The bacterial charge proposed is up to 3% of total inlet COD which in average is 1548.82mgCOD/l. Nitrogenous material found was in average 261.26mgN/l for the ammonia, 10.85mgN/l of nitrates plus nitrites, and 6.17mgN/l of organically bound nitrogen. The dissolved oxygen found was very low and alkalinity corresponds to 47.52mmol HCO₃⁻/l.

Landfill leachates can thus be characterized correctly to simulate the biological process with activated sludge models ASM1 and ASM3. The differences with municipal wastewater (for which ASM models were initially conceived) are substantial so this work constitutes a
valuable tool for landfill leachates treatment modellers, in particular, for early stages of simulation.

6.6 References


Chapter 7: Simulation of a membrane bioreactor pilot treating old landfill leachates with activated sludge model No.1 and No.3.

(Galleguillos M., Keffala C., Vasel J.L.)

Article accepted for publication in Environmental Technology on February 2011. (DOI number: 10.1080/09593330.2011.561878)

Activated sludge model No.1 (ASM1) and activated sludge model No.3 (ASM3) can simulate correctly the behaviour of a pilot membrane bioreactor treating old landfill leachates. Both models show similar results that are consistent with measured data. In this work, a simplified calibration procedure is applied including hydrodynamic and oxygen transfer characterization. The wastewater characterisation was based on a physical-chemical method combined with a BOD analysis for the COD fractions and on standard analysis for nitrogen forms. Default parameters were used for both models and despite this, good simulations were obtained showing the flexibility and accuracy of the well achieved ASM family models. The sensibility analysis performed allows identifying the most important kinetic, stoichiometric or operational parameters that should be measured in order to confirm or replace default values. In this specific case, the simulation is most sensitive to heterotrophic yield particularly under anoxic conditions.

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7.1 Introduction

Residual wastes can be treated in several ways but nowadays the deposit in sanitary landfill constitutes the most popular technique. The process has economic advantages but produces highly polluted leachates that must be treated. The pollution is principally composed of high amounts of ammonia nitrogen and organic matter considered un-biodegradable (or inert), measured as chemical oxygen demand (COD). COD is mostly composed of fulvic and humic acids in the case of old landfills [1,2]. There are different ways to treat this industrial wastewater, physically-chemically or biologically [3]. The membrane bioreactor (MBR) which couples these two paths, shows excellent removal performances [4,5] and is emerging as the technology for the future in many kinds of wastewater applications [6]. In general terms, a MBR is a common bioreactor that has been equipped with a membrane which constitutes a very performing separation unit replacing the old settling technique. This improvement allows the MBR to retain most of the bacteria and particulate matter into the system. Furthermore, it allows the MBR to maintain an important sludge age. Thus the need of space is reduced in favor of a more concentrated sludge. Several other advantages are found depending of the use. The implications for the activated sludge microorganism’s colony are numerous and for the moment, not always well described [7].

The general process to treat nitrogen pollution by biological means involves bacterial nitrification coupled with denitrification. During the first process, autotrophic bacteria transform the ammonia nitrogen (NH₄⁺) into nitrate (NO₃⁻). This process takes place in the presence of oxygen. Afterwards the nitrate is transformed to atmospheric nitrogen gas by heterotroph bacteria in anoxic conditions. Inlet, decay or externally added COD is used as a carbon source [8]. This simplified description can be complemented with intermediates or other processes that are also present in the nitrogen cycle, depending on the conditions applied to the biomass. Carbon consumption must be included as well.

Biological degradation processes can be represented by dynamic mathematical models that allow simulating the behavior of a treatment facility. ASM1 [9] and ASM3 [10] are the more commonly used ones. Adaptations of both models have been used in simulation of nitrogen removal oriented systems [11,12]. However, they were originally conceived to simulate domestic wastewater treatment so results, with landfill leachates before the introduction of adaptations, are interesting to evaluate.
In this paper, a model calibration procedure based on literature protocols was followed for a pilot MBR treating old leachates of a Luxembourgish landfill. The purpose of the model calibration was to evaluate the capability of ASM1 and ASM3 models to predict the behavior of the pilot, in particular, for COD and nitrogen removal. A sensitive analysis will allow to check which parameters are the most relevant and must be measured in order to obtain a more accurate simulation.

7.2 Material and methods

7.2.1 Leachates under study

The leachates used in this study come from the Muertendall sanitary landfill located in East Luxembourg, which operates since 1984. The facility is operated by a syndicate of local authorities (SIGRE, Syndicat Intercommunal pour la gestion des déchets ménagers, encombrants et assimilés en provenance des communes de la région de Grevenmacher, Remich et Echternach), which is responsible for waste management and related fields, and receives household waste from 25 municipalities (50000 inhabitants, corresponding to 11.5% of Luxembourg’s population). The bottom geomembrane which collects the leachates was installed between 1995 and 1998 and a membrane bioreactor for the on-site treatment is in operation since 2005. The leachates contain an important amount of COD (1549mgCOD/l) with low biodegradability (COD/BOD5 ratio of 13.7) and high ammonia concentrations (261mgN-NH4+/l).

7.2.2 Pilot MBR

The pilot MBR wastewater treatment plant (WWTP) is composed of three PVC tanks as showed in figure 1. The first tank has a volume of 238 liters (radius = 29cm, depth = 90cm). It operates under anoxic conditions. A mechanical artefact is installed to help the mixing of the sludge with the incoming leachates and the occasional external carbon source addition. The second 238 liters tank, similar to the first, is aerated by two diffusers disc (Passavant Intech, Roeflex®) and alimented with an electric air pump. The third tank of 25.5 liters (radius = 9.5cm, depth = 90cm) is where the membrane filtration (Zenon, ZeeWeed®-10, 0.93m² with a mean pore diameter of 0.1µm) occurs. Air is also pumped below the membranes to decrease
the clogging effect. The pilot configuration is thus an anoxic/aerated/membrane. A fourth tank is necessary to assure a reserve of treated water for the membrane backwashing (B-S tank). No significant bacterial activity is supposed to be present in this tank where the treated leachates samples are taken for laboratory analysis. The recirculations are guaranteed by two magnetic pumps (Iwaki, MD-6-230GS). They were used with an “on/off” system to avoid mixed liquor accumulation in one reactor and thus have the same depth in all of them. The filtration and backwash are performed by the same diaphragm pump (Shurflo®, 75420-17). Trans-membrane pressure and sludge flows are continually recorded by Endress-Hauser equipment (Promag 50, Delta bar).

![Figure 7-1 Pilot MBR plant layout](image)

7.2.3 Tracer test

Three independent tracer tests were carried out to characterize the hydraulics of the process under study. During each one, 2kg of table salt were introduced diluted in 5 liters of water to simulate a pulse at the entry of the system. The conductivity of the treated leachate was measured for 420 hours at intervals of 5 minutes. The increase of conductivity generated by the salt addition is clearly detected. After a preliminary calibration, it is possible to transform this conductivity into salt concentration at the outlet.

7.2.4 Measuring campaign

The measuring campaign was carried out during January, February and March 2009. The following measures were taken for the inlet and treated leachates: ammonium nitrogen (NH$_4^+$-
N); nitrites (NO$_2$-N); nitrates (NO$_3$-N); total nitrogen (TN); filtered and non filtered chemical oxygen demand (COD); biochemical oxygen demand (BOD) up to seven days; pH; and temperature. Suspended solids (MLSS); volatiles suspended solids (MLVSS); pH; and temperature were measured in the sludge (also called mixed liquor). BOD measurements were performed with and without addition of 5mg of allylthiourea (ATU) per litre of sample to inhibit nitrification. All the analyses were made via standard methods [13]. In general, the samples were analysed just after they were taken in order to eliminate time related interference; otherwise, a biological activity inhibitor (mercuric chloride) was applied combined with conservation at a low temperature.

7.2.5 Calibration procedure

The calibration procedure used in this study is an adaptation based on the work of [14] and complemented with [15]. It can be summarized as a first step of data collection, followed by several calibration levels, including steady state and dynamic simulations. Steady state simulations were performed with average characterization values contrasting with dynamic simulation that uses weekly characterization. The information needed includes design data, operational data, characterization of the hydraulics, characterization of the separation unit and characterization of the biological model, including influent and effluent wastewater analysis, sludge composition, reactions kinetics and stoichiometry. The quality and quantity depend on the purpose of the simulations. In this case, our aim is to check if models are capable of good prediction although the fact that landfill leachates are being treated instead of municipal wastewater. Furthermore, default stoichiometric and kinetic parameters will be used in order to check if biomass has a similar behavior. A complete list of default parameters could be found in [16].

7.2.6 Oxygen transfer characterization

ASM1 and ASM3 do not include the aeration or oxygen transfer process of an aerated tank associated to air injection modelled as the first term in equation 7-1, but simulation software does usually include it. $K_{La}$ is the overall oxygen transfer coefficient, $Cs*$ is the saturation oxygen concentration in liquid phase and $C_{O2}$ is the actual oxygen concentration in this liquid phase [17]. The * is to indicate that both values correspond to the mixed liquor in order to differentiate from clear water values. They are both inputs of the model to be simulated. The models do not consider, for example, the changes in these parameters caused by sludge
concentration or temperature. However, in this experiment and simulations, the temperature is almost constant (20ºC) and the sludge concentration is kept below 10g/l so as not to limit the oxygen transfer efficiency too much [18].

$$\frac{dC_{O2}}{dt} = K_L a \cdot (C_s - C_{O2}) - \text{OUR} + \text{inlet} - \text{outlet} \quad \text{(Equation 7-1)}$$

To consider the total variation of the dissolved oxygen present in the aeration tank, the consumption, inlet and outlet are considered as well (equation 7-1). In ASM1, the processes involved in the biological Oxygen uptake rate (OUR) are the aerobic growth of heterotroph and autotroph microorganisms. ASM3 also involves the aerobic storage of the readily biodegradable organic substrates and the aerobic endogenous respiration of heterotroph and autotroph biomass.

The inlet and outlet terms of equation 7-1 correspond to the amount of oxygen added and extracted by the recirculation pumps. They were kept functioning during oxygen transfer characterization in order to assure a minimum mixing in the tank and to avoid sludge decantation. Their influence will be appreciable as a regular sinusoidal disturbance, which is not going to be considered for the dynamic analysis as the magnitude of these variations is low and constant compared to the oxygen transfer or consumption.

### 7.2.7 Influent characterization

An ASM characterization of the untreated leachates was obtained based on the analyses taken during the measuring campaign. The ASM components were estimated based on a physical chemical method combined with a BOD analysis and others direct measurements presented elsewhere [19]. The procedure was repeated weekly to obtain a characterization of the untreated leachates in time, and thus the inlet file for the simulations. This approach has the important advantage that it uses common analysis that most of the WWTP generally measures. The aim of the influent characterization is to have a standard ASM description of the wastewater to introduce as the inlet in the simulations. The ASM characterization includes several components separated in particulates (X) and soluble (S) ones and presents small differences between ASM1 and ASM3. The particulate components considered are a non biodegradable COD (inert) part (Xi), a slowly biodegradable COD part (Xs), and the autotroph and heterotroph bacterial charge (Xbh, Xba). ASM1 also includes the nitrogen
trapped in biomass part (Xnd) and an inert part resulting from the decay of biomass named Xp. ASM3 includes a particulate part corresponding to the biological storage (Xsto). The soluble fractions are: a non biodegradable COD (inert) part (Si), a readily biodegradable (Ss) one, ammonia and nitrate (Snh and Sno), the dissolved oxygen part (So), the nitrogen trapped in Ss (Snd) and the nitrogen gas part for the ASM3 case (Sn2). More details for both models can be found in [16].

Several characterization methods exist, going from complex respirometric techniques [20, 21] to simpler and economic approaches like the one used in this study who is based on the sequence proposed by [22].

7.2.8 Carbon source addition

An external carbon source is eventually needed to obtain a complete denitrification, in case of low biodegradable COD wastewater. The theoretical optimum COD/N ratio needed is close to 4 but very dependent on the COD and N considered and on conditions of the studied system [23]. Addition of high COD load substances is a common procedure in real facilities like the MBR of Muertendall’s landfill. In this case, acetic acid is used as an external carbon source; 75ml were added daily from day 47 to increase the COD/N ratio to values closer to 5. It must be noticed that this carbon addition is made to create an important perturbation in the system and thus to evaluate the capability of both models to simulate it. Anyway if considering the total energy consumption it could be better, perhaps, to have an aerated/anoxic/membrane configuration with external carbon injection in the anoxic tank and as a result eliminate a recirculation pump. In that last case, the effect of membrane aeration on the anoxic zones should be evaluated.

7.2.9 Simulation

Simulations were performed using the WEST® simulation package (Wastewater treatment plant Engine for Simulation and Training also renamed Worldwide Engine for Simulation, Training and Automation) which provides a user friendly platform with existing models and the possibility to implement and test new ones. The software is implemented in the MSL-USER modelling language and consists of two environments: the modelling environment, in which the user can graphically implement the system under study by placing and connecting several icons that represent the different parts of the WWTP; and the experimental
environment where the user can perform simulations, scenario analysis, sensitivity analysis and optimal experimental design calculations. In the first envoirnement, the graphical information is combined with the information of the model base to produce MSL-EXEC code, which can be compiled in the second with a C++ compiler. A more detailed description can be found in [24].

7.3 Results

7.3.1 Design, operational and measured data compilation

Design data are mentioned in description of the pilot. The influent flow rate was fixed at 80 liters per day (3.58 liters per hour per square metre of membrane (l∙h⁻¹∙m⁻²) in order to have a hydraulic residence time comparable with the one of Muertendall’s MBR plant. The recycled sludge flow rates are three times the inlet flow, thus 240 liters per day. This recycled flow assures the recirculation of nitrates and the homogenisation of the mixed liquor microorganism concentration in the system. An external carbon source was added from day 47, and no sludge extraction was performed, except for sample analysis. Measured data are summarized in table 7-1 (acetic acid addition is not considered).

<table>
<thead>
<tr>
<th>Variable</th>
<th>Unit</th>
<th>Mean value and range (untreated leachates)</th>
<th>Mean value and range (treated leachates)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>8 (7.8-8.3)</td>
<td>8.4 (8.1-8.6)</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>20 (16.8-24.8)</td>
<td>18.8 (16.6-20.4)</td>
</tr>
<tr>
<td>COD</td>
<td>mg/l</td>
<td>1127 (620-1760)</td>
<td>686 (290-1200)</td>
</tr>
<tr>
<td>BOD₅</td>
<td>mg/l</td>
<td>129 (105-185)</td>
<td>7 (0-23)</td>
</tr>
<tr>
<td>NH₄⁺-N</td>
<td>mg/l</td>
<td>217 (144-321)</td>
<td>12 (0-61)</td>
</tr>
<tr>
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<td>mg/l</td>
<td>16 (0-31)</td>
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<td>NO₂-N</td>
<td>mg/l</td>
<td>0.1 (0-0.9)</td>
<td>0.4 (0-3.4)</td>
</tr>
<tr>
<td>TN</td>
<td>mg/l</td>
<td>260 (178-385)</td>
<td>131 (25-223)</td>
</tr>
</tbody>
</table>

For the period before the external carbon source addition, the pilot shows good performance in ammonia and BOD₅ removal. An important COD removal is also present considering the low biodegradability of the leachates as shown in table 7-2. The total nitrogen removal is low; denitrification is limited by carbon source and thus important nitrate concentration leaves the system. This could be explained by the lack of biodegradable matter (carbon) in the leachates.
A confirmation for this is found with the augmentation of total nitrogen removal up to 81.65\% after acetic acid injection.

<table>
<thead>
<tr>
<th>COD removal efficiency</th>
<th>BOD\textsubscript{5} removal efficiency</th>
<th>NH\textsubscript{4}\textsuperscript{+}-N removal efficiency</th>
<th>N removal efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.14%</td>
<td>94.34%</td>
<td>98.96%</td>
<td>32.61%</td>
</tr>
</tbody>
</table>

7.3.2 Hydraulic characterization

The tracer tests were performed with a constant inlet flow and feeding the bioreactor with leachates of similar characteristics that during the normal operation. The results of the three tracer tests were similar so only the first test will be presented as an example. Reproducibility is, however, important to consider. Measures were taken by a conductivity probe (YSI , 600R) placed in the B&S tank. Results are shown in figure 7-3. The outlet concentration of salt shows a sharp peak of 4207mg/l at t = 33h. Considering a constant flow of 3.33 liters per hour, 99\% of the tracer was collected. In order to get a rapid estimation, a first approach considering the N tanks-in-series model (Equation 7-2) was applied, thus the outlet concentrations were normalized by the mass of salt added divided by the total volume, and the time was normalized by the average hydraulic residence time (\(\theta\text{H} = 150.5\) hours) during the test [25].

\[
C_{Nt} = \frac{N}{(N-1)!}(N \theta_t)^{N-1}e^{-N\theta_t} \quad \text{(Equation 7-2)}
\]

With this simple model, it was found out that the best fit was obtained by considering N=1.8 reactors (figure 7-3). This result, considering the fractional tank extension is not far from reality. However, important system parts like recycled flows and different tank volumes can be considered to improve precision of the hydraulic model. Considering this, the WEST® modelling and simulation environment was used to obtain a better fit. Different schemes were simulated to find finally the plant configuration that describes the best the pilot used as can be seen in figure 7-2.
The simulated tracer test with WEST® is shown in figure 7-3. Both curves are well fitted so it can be concluded that the chosen configuration gives a good description of the hydrodynamics of the real system. The little differences in the curves can be explained by the B&S tank that is present in the reality but is not considered for the simulation. Not considering this tank was based on the assumption that low microbial activity is present, and on the difficulty to simulate cleaning processes. Anyway this tank has a role related to the backwash cleaning procedure that is also not simulated. Another possible explanation for differences is that mixing could not be complete leading to zones into the reactor of non circulation called dead zones.
7.3.3 Oxygen transfer characterization

Figure 7-4 shows the dissolved oxygen concentration in the aerated tank during a stable phase and during an air injection stop and restarts. As the response time of the rapid pulse dissolved oxygen sensor (YSI 6562) is under 4s, which is very low compared to $1/\text{KLa}^*$, there is no need to include the probe dynamics in the model [26, 27]. During the stop of aeration (period II), the dissolved oxygen decrease caused by the microorganism oxygen uptake rate is usually linear, and the slope of the plot as a function of time provides a direct estimate of the OUR. The underlying hypothesis consists in that the rate of oxygen utilization is unaffected by the absence of air bubbling and by lower dissolved oxygen concentration [28]. The test was performed in a short lapse of time. Therefore, no lack of heterotroph or autotroph substrate that could influence the kinetics are considered. The average OUR measured after several tests like the one presented in figure 7-4 is $15.478\text{mgO}_2/(\text{l-h})$. All tests were performed with MLVSS in the ranges of 4 to 6g/l.
During period III, the aeration pump is reestablished, and the oxygen transfer process is considered as well as the OUR (equation 7-3). This equation can be solved by separation of variables. After integration and consideration of initial conditions, equation 7-4 is obtained. This expression was plotted for several $K_{L}a^*$ in order to obtain the best fit with measured data (figure 7-4). The overall value obtained for $K_{L}a^*$ was 2.25h$^{-1}$. Another approach is drawing the slope of this increase curve versus the corresponding oxygen concentration in each measured point. This allows to obtain a straight line with $K_{L}a^*$ as the slope. The overall $K_{L}a^*$ value obtained by this method is 2.26h$^{-1}$. Considering average MLVSS for the period, the specific oxygen uptake rate (sOUR) is 3.29mgO$_2$/(gMLVSS·h). $Cs^*$ was also evaluated with consideration of the period I, where no oxygen variation is considered. The saturation oxygen concentration obtained is 12.36mgO$_2$/l. This number is higher than the one generally proposed for tap water at 20ºC [29] but the presence of particulates, salt, and surface active substances can increase or decrease $Cs^*$ in wastewater [30]. $KLa^*$ and $Cs^*$ estimations were obtained and included in the models for simulation. The simpler procedure, the little amount of material needed, and the poor influence over the biomass were considered in the choice of this dynamic method.

$$\frac{dC_{O_2}}{dt} = K_{L}a^* \cdot (C_s - C_{O_2}) - OUR$$  \hspace{1cm} (Equation 7-3)

$$C_{O_2} = C_s - \frac{OUR}{K_{L}a^*} + \left( C_{min} - C_s + \frac{OUR}{K_{L}a^*} \right) \cdot \exp(-K_{L}a^* \cdot t)$$  \hspace{1cm} (Equation 7-4)
7.3.4 Separation unit characterization

The membrane separation unit is simulated as a perfect particle separator coupled with a perfect mixed activated sludge tank unit as it can be seen in figure 7-2. The filtration process, being a very complex phenomenon is a modelling research topic itself [31] so, as it is not a primary objective of this work, it will be considered as simpler as possible. For simulation purposes, the filtration periods (backwash and relaxation) are not considered. The underlying assumption is that filtration periods will not have a remarkable influence over the suspended biomass behavior. For the simulation, a constant flow of 80 liters per day will traverse the membrane. Actually, the daily filtration of the period under study was very close to that value (figure 7-5). The clogging effect is not considered in the simulation. The membrane is not ideal so a factor of non retainable SS of 0.1% is fixed to consider particulate lost.

![Figure 7-5 MBR pilot daily filtration](image)

7.3.5 Biological characterization

ASM influent wastewater characterization: The characterization protocol proposed by the Dutch foundation to characterize wastewater in terms of the ASM1 and ASM3 differentiation was successfully applied to landfill leachates with few modifications. Details are presented elsewhere [18]. The results show that the total inlet COD as a measure of the organic matter present is 79.54% inert for the processes considered in the models. More specifically, the soluble inert part is the principal component of the inlet COD as it represents 60.74%
followed by the particulate part which is 18.84%. The biodegradable fraction found is 17.42% with 11.59% soluble and 5.84% particulate. The bacterial charge proposed is up to 3% of total inlet COD which in average is 1548.82mgCOD/l. Nitrogenous material found was in average 261.26mgN/l for the ammonia, 10.85mgN/l of nitrates plus nitrites, and 6.17mgN/l of organically bound nitrogen. The dissolved oxygen found was very low and alkalinity corresponds to 47.52 mmol HCO$_3^-$/l. Results are resumed in table 7-3.

<table>
<thead>
<tr>
<th>Table 7-3 Average results of characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Value proposed</strong></td>
</tr>
<tr>
<td>** ASM1**</td>
</tr>
<tr>
<td>948.36</td>
</tr>
<tr>
<td>** ASM3**</td>
</tr>
<tr>
<td>948.36</td>
</tr>
</tbody>
</table>

**Sludge characterization:** The sludge samples for MLSS and MLVSS analyses were taken in the upper and lower part of each tank. The average presented in table 7-4 was calculated considering the different volumes. The results of the measurement campaign show that the concentration of MLSS is higher in the membrane tank followed by the aerated tank and finally the anoxic tank. The micro-organisms are thus concentrated in the aerated areas downstream the system even with the high recirculation rates. It is possible that the overall hydraulic behavior lead to this situation, but high microorganisms ‘activity in aerated zones could explain the effect as well. The filtration capabilities can be affected by this situation. The debate on the positive or negative influence of MLSS on the clogging effect is still discussed in the literature [32].

<table>
<thead>
<tr>
<th>Table 7-4 Average measured characteristics of the mixed liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Variable</strong></td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>MLSS</td>
</tr>
<tr>
<td>MLVSS</td>
</tr>
</tbody>
</table>

**Kinetic and stoichiometric parameters:** No respirometric tests were performed, default values (for 20°C) presented in [16] were chosen for each model to start the calibration efforts as recommended by several authors, even if important differences can be found by the fact that the wastewater used is considered as an industrial wastewater.
7.3.6 Steady state model calibration

The inlet file with the characterization of the leachate corresponds to the average of the dynamic influent data. At first, 50 days of simulation were performed to obtain the initial conditions from where measurements begin. The real previous period of non-measured functioning was longer and with lower temperature and technical problems so it was not a surprise that both models underestimate measured MLSS. In order to reach initially measured MLSS the initial simulation time was adjusted to 60 days for ASM1 and 63 days for ASM3. Afterwards sludge production consistency was tested. With ASM1 steady state simulation, an average of 0.044 grams of MLSS is produced per liter of mixed liquor per day, for ASM3 the value is 0.043. The value obtained experimentally is 0.066 grams of MLSS per liter of mixed liquor per day. These values are comparable. However, inlet Xi was adjusted in order to get a better fit. Other parameters of long term behavior like biomass decay were not adjusted because of the very little variations found in preliminary trials compared to Xi influence. The best values were obtained considering all system inlet Xs fractions as Xi. Sludge production obtained was 0.052g of MLSS per liter of mixed liquor per day with ASM1 and 0.051g of MLSS per liter of mixed liquor per day with ASM3, which allows a better description of MLSS concentration in the system.

7.3.7 Dynamic model calibration

The dynamic calibration procedure was performed including all the information presented before. The results show that both models with default kinetics and stoichiometric parameters can predict in a satisfactory way the outlet nitrate and ammonia concentrations (figures 7-6b and 7-6c). It must be noticed that influence of external carbon source addition is well simulated with a marked reduction of effluent nitrate concentration after day 47. The outlet carbon matters were also satisfactorily simulated (figure 7-6c) as well as the MLVSS present in the system (figure 7-6a). Decrease of outlet COD after day 20 of operation could be explain by a decrease in COD concentration of the untreated leachates. Nitrate forecast shows more important differences compared to measured values, but tendencies are clearly well related.
In order to get a better understanding of the forecast behavior, a sensitive analysis proposed by the WEST® software was executed to check the parameter (P) influence on followed variables (V). Procedure could be resumed is like this: first a reference simulation is run, next the parameter is altered by a certain perturbation factor (p) and a new simulation is run ($P_{altered} = (1+p)\times P_{reference}$). Then the absolute sensitivity is calculated for each time point as the difference between the variable value of the reference simulation and the variable value of the perturbation simulation ($\Delta Y$) divided by the difference between the parameter value of the reference simulation and parameter value of the perturbation simulation ($\Delta P$). Then the relative function is calculated as follows:

$$RSF = \frac{\Delta Y}{\Delta P} \times \frac{P}{Y}$$

In this case, the relative sensitive function (RSF) was calculated for each day of operation. Then the sums of absolutes of RSF during the measuring campaign were considered for comparison. It must be noticed that parameters with bigger ranges can be important to the forecast of variables independently of the sensitivity, as the RSF compares all parameters considering a perturbation factor and not the range of variation.

ASM1 processes involved in outlet nitrate variation are anoxic growth of heterotroph bacteria and aerobic growth of autotroph biomass. In ASM3 processes, this remains the same with the addition of anoxic storage and anoxic endogenous respiration for heterotrophic ones and
anoxic endogenous respiration for autotrophic ones. Considering sensibility, heterotrophic yield appear to be the more relevant parameter for both nitrate model forecasts. In the ASM3 case, that includes the storage concept; the use of two heterotrophic yields is imposed leading to more details but also to an additional parameter to measure. Heterotrophic decay coefficient is also important in both cases. Operational parameters also appear in the significance list, particularly recirculation between anoxic and aerated tank, with more relevance to the ASM1 forecast.

Outlet ammonia variations are principally related to aerobic growth of autotroph biomass and to heterotrophic growth. Important differences are found between both model forecast sensitivity. ASM1 forecast appears to be more sensitive to heterotrophic yield than ASM3 (table7-6). Autotrophic yield and the maximum specific growth rate of autotrophs are parameters of importance for both models. Ammonium substrate saturation for autotrophs is also a relevant parameter to consider.

MLVSS variation is very sensitive to initial conditions in the systems particularly to inert particulate matter (table7-7). Operational parameters like recirculation are also important to measure and control in both cases. Heterotrophic yield also appears in the relevance list in particular in anoxic conditions.

Considering all these calculated relative sensitive functions, it can be concluded that ASM1 and ASM3 behave in a similar way. ASM1 appears to be more dependent of heterotrophic

<table>
<thead>
<tr>
<th>The most sensitive parameters for outlet nitrate (using ASM1)</th>
<th>Z [RSF]</th>
<th>The most sensitive parameters for outlet nitrate (using ASM3)</th>
<th>Z [RSF]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heterotrophic yield</td>
<td>30.87</td>
<td>Heterotrophic anoxic yield of stored product</td>
<td>43.75</td>
</tr>
<tr>
<td>Recirculation (anoxic/aerated tanks)</td>
<td>16.72</td>
<td>Anoxic reduction factor</td>
<td>11.15</td>
</tr>
<tr>
<td>Mass of nitrogen per mass of COD in biomass</td>
<td>7.99</td>
<td>Maximum specific growth rate of Heterotrophs</td>
<td>10.53</td>
</tr>
<tr>
<td>Decay of Heterotrophs</td>
<td>5.73</td>
<td>Nitrogen content of readily biodegradable substrates</td>
<td>8.96</td>
</tr>
<tr>
<td>Initial nitrate concentration</td>
<td>5.06</td>
<td>Aerobic endogenous respiratory rate of Heterotrophs</td>
<td>7.34</td>
</tr>
<tr>
<td>Autotrophic yield</td>
<td>2.10</td>
<td>Heterotrophic aerobic yield</td>
<td>6.58</td>
</tr>
<tr>
<td>Mass of nitrogen per mass of COD in products formed</td>
<td>1.85</td>
<td>Anoxic endogenous lepotation rate of Heterotrophs</td>
<td>5.71</td>
</tr>
<tr>
<td>Correction factor for anoxic growth of Heterotrophs</td>
<td>1.86</td>
<td>Nitrogen content of biomass</td>
<td>5.44</td>
</tr>
<tr>
<td>Dissolution saturation concentration</td>
<td>1.75</td>
<td>Initial nitrate concentration</td>
<td>5.02</td>
</tr>
<tr>
<td>Fraction of biomass converted to inert matter</td>
<td>1.48</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>The most sensitive parameters for outlet ammonia (using ASM1)</th>
<th>Z [RSF]</th>
<th>The most sensitive parameters for outlet ammonia (using ASM3)</th>
<th>Z [RSF]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heterotrophic yield</td>
<td>164.49</td>
<td>Maximum specific growth rate of Autotrophs</td>
<td>110.29</td>
</tr>
<tr>
<td>Autotrophic yield</td>
<td>109.55</td>
<td>Ammonium substrate saturation for Autotrophs</td>
<td>101.66</td>
</tr>
<tr>
<td>Maximum specific growth rate of Autotrophs</td>
<td>108.57</td>
<td>Autotrophic yield</td>
<td>107.27</td>
</tr>
<tr>
<td>Ammonia half saturation coefficient</td>
<td>100.41</td>
<td>Aerobic endogenous respiratory rate of Autotrophs</td>
<td>87.50</td>
</tr>
<tr>
<td>Decay of Autotrophs</td>
<td>100.20</td>
<td>Aerobic endogenous respiration rate of Heterotrophs</td>
<td>52.28</td>
</tr>
<tr>
<td>Maximum specific ammonification rate</td>
<td>98.81</td>
<td>Nitrogen content of biomass</td>
<td>43.09</td>
</tr>
<tr>
<td>Mass of nitrogen per mass of COD in biomass</td>
<td>78.67</td>
<td>Recirculation 2 (aerated/membrane tanks)</td>
<td>26.76</td>
</tr>
<tr>
<td>Recirculation 2 (aerated/membrane tanks)</td>
<td>26.31</td>
<td>Maximum specific growth rate of Heterotrophs</td>
<td>25.04</td>
</tr>
<tr>
<td>Decay of Heterotrophs</td>
<td>26.31</td>
<td>Heterotrophic anoxic yield of stored product</td>
<td>21.52</td>
</tr>
<tr>
<td>Maximum specific growth rate of Heterotrophs</td>
<td>21.50</td>
<td>Anoxic endogenous respiratory rate of Autotrophs</td>
<td>15.99</td>
</tr>
</tbody>
</table>
yield than ASM3. This can be explained by the dead regeneration concept used in ASM1 contrasting with the endogenous decay concept used in ASM3.

<table>
<thead>
<tr>
<th>Table 7-7 Sensibility of MLVSS in the aerated tank (ASM1 left, ASM3 right)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>Initial particulate inert concentration</td>
</tr>
<tr>
<td>Recirculation 1 (anaerobic/aerated tanks)</td>
</tr>
<tr>
<td>Initial product formed concentration</td>
</tr>
<tr>
<td>Decay of Heterotrophs</td>
</tr>
<tr>
<td>Autotrophic Yield</td>
</tr>
<tr>
<td>Initial Autotrophic concentration</td>
</tr>
<tr>
<td>Recirculation 2 (aerated/membrane tanks)</td>
</tr>
<tr>
<td>Production of $Y_c$ in aerobic endogenous respiration</td>
</tr>
<tr>
<td>Heterotrophic anoxic yield</td>
</tr>
<tr>
<td>Autotrophic yield</td>
</tr>
</tbody>
</table>

When comparing sludge composition (figure 7-7b), ASM1 simulates more biomass than ASM3 and, consequently, fewer inert particulates. More details are shown in figure 7-7a, where it is clear that heterotrophic micro-organisms are simulated very similarly with both models, but that autotrophic ones are more important in ASM1. This is not only due to the differences in model configuration but also to different default values for the parameters in each model. When considering equivalent default values, the same biomass concentration could be obtained.

Figure 7-7 a) biomass simulation with ASM1 and ASM3 b) Biomass and inert particulate simulation with ASM1 and ASM3

7.4 Conclusions

A calibration protocol was successfully applied in order to obtain a simulation with ASM1 and ASM3 of a pilot membrane bioreactor treating landfill leachates. The calibration procedure included a tracer test performed to check if the hydraulic behavior is respected. Oxygen transfer tests were also performed; measured parameters were incorporated in the model.
Simulations show good correlations with measured data, particularly in the case of MLVSS present in the system and in the case of outlet nitrate, ammonia and COD. ASM default parameters, which are normally used to simulate municipal wastewater treatment, permit the simulation of landfill leachate treatment in a satisfactory way.

A sensitive analysis was performed to check which parameters are more important to measure in order to get a more accurate simulation of landfill leachate treatment. The results show that heterotrophic yield appears to be the main parameter to measure, particularly under anoxic conditions. The simulation is also sensitive to other parameters such as heterotrophic decay coefficient, autotrophic yield, and heterotrophic and autotrophic maximum specific growth rate. The ammonium half saturation coefficient is also important. Accurate measurement of operational parameters like the recirculation between tanks must be also considered.

7.5 References


Chapter 8: Optimization of N removal in landfill leachates treatment with membrane bioreactor: pilot plant and full scale studies

Galleguillos M. Vasel J.L.

The abstract of this article was accepted on March 2011 for oral presentation at the thirteenth international waste management and landfill symposium to be held in Sardinia, Italy.

Biological treatment of landfill leachates was followed during a year in a membrane bioreactor (MBR) facility located in east Luxembourg. Good removal performances were observed but at high aerated volumes ratio. A pilot scale MBR was put into operation, treating the same leachates to demonstrate that similar performances could be reached with lower aeration volumes (lower cost). Results show that a removal of 99.4% of ammonia could be maintained with an aeration volume decrease from more than 75% to near 5% of the total volume. TN removal was also enhanced with no external carbon addition. Simulations with activated sludge model nº1 were performed with good predictions when aeration was high. When aeration was lowered, ASM1 predictions failed, so an adapted model for the particular case of nitrogen removal was tested. The adapted model that includes two-step nitrification and anammox activity shows better results, demonstrating the potential of these processes in landfill leachates biological treatment.

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8.1 Introduction

Landfill constitutes the most common technique used worldwide for waste disposal [1]. Upon its economic advantages, it minimizes the negative impacts on the environment and allows waste to decompose under controlled conditions. The landfill is in simple terms a big reactor, impermeable (watertight) at the bottom and semi-impermeable at the top, where crouched and compacted wastes are disposed for biochemical transformation until stabilization. The main effluents of this kind of bioreactors are leachates and biogas. The leachates, which treatment is the focus of this research work, are defined as the aqueous effluent generated as a consequence of rainwater percolation through wastes, biochemical processes in waste cells and the inherent water content of waste itself [2]. It’s a highly polluted liquid with variable composition that threatens surface and groundwater if directly discharged [3]. It can contain an important amount of organic matter; biodegradable but also refractory compounds (humic and fulvic acids)[4]; high ammonia nitrogen concentrations; some heavy metals; and numerous other substances that can be considered as pollutants. Another associated difficulty are the enormous variations in composition and flows, that depends on many parameters such as time of disposal (age of the landfill); quantity of precipitation; temperatures; waste type and composition; disposal technique; etc. To reduce pollution content in this wastewaters, divers treatments exist going from physical/chemical techniques to biological treatments and several combinations of them [5,6]. Nowadays, the membrane separation techniques associated with an activated sludge in a membrane bioreactor (MBR) allows excellent removal performances, and it’s a common technique used in real facilities [7]. The sludge is composed of autotrophic bacteria that consume ammonia nitrogen and use it for growth (nitrification), producing nitrite and nitrate. Heterotrophic bacteria are also present consuming organic matter with nitrite, nitrate (denitrification) or oxygen as electron acceptor depending on the applied conditions. Aeration, that supplies the oxygen needed for nitrification is generally applied in excess in order to completely eliminate ammonia, despite the high cost associated. Furthermore, with high aeration, denitrification is inhibited and high amounts of nitrates are not consumed. This may lead to an effluent with high nitrate concentration that is now focused by European disposal restrictions. Indeed, nitrates may contribute to the eutrophication of aquatic environment [8].

The objective of this research work is to show that it is possible to maintain good removal performances with lower aerated volumes in a membrane bioreactor treating landfill
leachates. Energy used in excessive aeration can be saved. Denitrification, particularly endogenic is enhanced as well as other strain activities as anamox bacteria. Hence, outlet nitrate concentration is reduced. To this purpose, a pilot MBR was built and put into operation. The results obtained were contrasted with the luxembourgish full scale facility data. Furthermore, simulations with ASM1 model and a nitrogen removal adapted model, including two-step nitrification and anamox bacteria were performed to clarify the processes involved and their role in leachate treatment by membrane bioreactors.

8.2 Materials and methods

8.2.1 Muertendall MBR

The leachates used in this study come from Muertendall´s MSW sanitary landfill located in East Luxembourg, which operates since 1984. The facility is operated by the SIGRE syndicate (Syndicat Intercommunal pour la gestion des déchets ménagers, encombrants et assimilés en provenance des communes de la région de Grevenmacher, Remich et Echternach) and receives the household waste from 25 municipalities (50000 inhabitants) corresponding to 11.5% of Luxembourg´s population. The bottom geomembrane which collects the leachates was installed between 1995 and 1998 and a membrane bioreactor for the on-site treatment is in operation since 2005. MBR configuration comprises an anoxic volume of 42m$^3$, followed by two aerated tanks equivalent to 130m$^3$. The aerated zone corresponds to a 75.6% of the total volume. Membranes are used in a sidestream configuration. The flows of leachates treated are variable. Often, values close to 25m$^3$ per day are reported but they can rise up to 100m$^3$. The leacheates feed an (MBR) activated sludge with an average VSS concentration of 14.2g/l. The hydraulic residence time varies also from less than 8,6 days to values near to 2 days. In average, 1.8mg/l of dissolved oxygen is measured in the aerated tanks. The MBR is located in an insulated structure that allows rather constant temperature conditions. Eventually, an external carbon source is added in order to boost denitrification, pH can be controlled that way through alkalinity [9]. However, this pH control is not used frequently because raw leachates have a rather high alkalinity (average 47.5meq/l).
8.2.2 Pilot MBR

The pilot MBR is composed of three PVC tanks. The first tank has a volume of 238 liters and operates under anoxic conditions. A mechanical artefact is installed to provide mixing of the sludge with the incoming leachates and the occasional external carbon source addition. The second (238 liters) tank is aerated by means of two disc diffusers (Passavant Intech, Roeflex®) and alimented by an electric air pump. The third tank of 25.5 liters is where the membrane filtration occurs (Zenon, ZeeWeed®-10, 0.93m² with a mean pore diameter of 0.1µm). Air is also pumped below the membranes to decrease the clogging effect. The pilot configuration is therefore an anoxic/aerated/membrane. A fourth tank is necessary to store treated water for the membrane backwashing (B-S tank). No significant bacterial activity is supposed to be present in this tank where the treated leachates samples are taken for laboratory analysis. The recycle is guarantied by two magnetic pumps (Iwaki, MD-6-230GS). The filtration and backwash are performed by the same diaphragm pump (Shurflo®, 75420-17) by means of an electronic valve system. Trans-membrane pressure and sludge flows are continually recorded by Endress-Hauser equipment (Promag 50, Delta bar).

8.2.3 Measuring campaign

Two measuring campaigns were performed, the first during January, February and March 2009, and the second between August and November 2009. Samples were collected once per week including influent, and effluent. The influent and effluent samples were analysed for ammonium nitrogen (NH₄⁺-N); nitrites (NO₂⁻-N); nitrates (NO₃⁻-N); filtered and non-filtered chemical oxygen demand (COD); 7 day biochemical oxygen demand (BOD₇); total nitrogen; temperature; pH; and alkalinity. BOD tests were performed with and without addition of a nitrification inhibitor (allylthiourea, ATU). The suspended solids; volatiles suspended solids; electrical conductivity; pH; and temperature were also measured in the sludge. All analyses were made via standard methods. In general, samples were analysed just after they were taken in the interest of eliminating time related interferences.

8.2.4 Simulations with ASM1

Simulations were performed using the wastewater treatment simulator WEST®. ASM1 model was chosen to perform initial simulations, even if some trials were also executed with ASM3.
Similar results were found with both models so it was decided to continue with the simplest one (ASM1). The calibration procedure applied included oxygen transfer characterization and a tracing test for hydrodynamics validation. Further details of the simulation work could be found in [10]. The characterization used to define the leachate composition in terms of ASM partitioning of material was also presented formerly [11]. It was based on a physical-chemical method combined with BOD analysis for the COD fractions and on standard analysis for nitrogen forms.

8.2.5 Simulations with autotrophic removal model (ASM1e)

A special adaptation of the ASM1 model for autotrophic removal [12] that incorporates nitritation by ammonia oxidizing bacteria and nitrification by nitrite oxidizing bacteria and Anammox bacteria was used, particularly for the second part of the experiment in which aeration is reduced. Heterotrophic activity is also included in the model as it is often the case in nitrogen removal bioreactors. Bacterial growth was modelled according to ASM1 as well as decay. Endogenous respiration was not considered because there are not clearly documented models for ammonium and nitrite oxidizers and Anammox. The model is composed of eleven processes: Hydrolysis of entrapped organics, growth and decay of ammonia oxidizers, growth and decay of nitrite oxidizers, growth and decay of anammox bacteria, and growth and decay of heterotrophic biomass, including anoxic growth on nitrates and on nitrites. Default parameters were used and temperature dependency was eliminated because in our case, constant temperature was kept close to 20ºC during all the experiment. For further details about the model, the components, the representation matrix and default parameters refer to [12].

8.3 Results

8.3.1 Muertendall MBR

Raw leachates contain 281mgN-NH$_4^+$/l in average with a slightly increase during summer months (figure 8-2). Even with values up to 700mgN/l, a 99.98% removal of N-NH$_4^+$ is maintained. Ammonia nitrogen is well transformed to nitrate; however, considering the total nitrogen removal in figure 8-2, clearly denitrification is not achieved. An average removal of 43.6% of total nitrogen reveals that nitrogen is leaving the system as nitrates, instead of being
transformed into nitrogen gas through denitrification. This could be partly explained by the lack of biodegradable carbon source in leachates [13] necessary for the heterotrophic bacteria to grow or the lack of anoxic conditions in which bacteria consume nitrates instead of oxygen as electron acceptor.

Figure 8-1 Inlet and outlet ammonia of Muertendall’s MBR with percentage of removal

Figure 8-2 Inlet and outlet TN of Muertendall’s MBR with percentage of removal (TN calculated as ammonia+nitrites+nitrates)

Periods of high total nitrogen removal are present, contrasting with general low nitrogen removal. A possible explanation could be the external carbon source addition; however, there is no consistent data about this because carbon addition was only performed to control pH through alkalinity and not properly followed with flows and concentration data.

Inlet COD presents concentrations in a range from 1000mg/l to more than 3500mg/l also with a slightly increase during summer months. Figure 8-4 shows leachates rapidly biodegradable COD approximated with BOD₅ analysis. Clearly, the COD present in raw leachates is mainly
non biodegradable or at least slowly biodegradable (ratio BOD₅/COD = 0.3 in average). Nevertheless, a 58.5% COD removal is achieved, meaning that part of the “recalcitrant” fraction is consumed [4], the outlet COD (645.44mgCOD/l in average) contains thus, low biodegradability (BOD₅ = 4.7mgBOD/l in average) respecting disposal restrictions. Occasional formation of foam was observed in aerated tanks representing extra operational costs to control it.

Based on mass balances, specific ammonia uptake rate (sAUR) and specific nitrate uptake rate (sNUR) were computed. Average sAUR found was 9.5mgNH₄⁺-N(d)⁻¹(gVSS)⁻¹ and sNUR was 13.9mgNO₃⁻-N(d)⁻¹(gVSS)⁻¹.
8.3.2  Pilot MBR

During the first measurement campaign, the pilot was operated with an aerated volume corresponding to 52.5% of the total volume. The influent flow rate was fixed to 80 liters per day (3.58 liters per hour per square meter of membrane (l·h⁻¹·m⁻²)). The sludge recycles ratio=3, thus 240 liters per day. This recycles flow ensures the recirculation of nitrates and the homogenisation of the mixed liquor micro-organism concentration in the system. No sludge extraction was performed, except for sample analysis. Volatile suspended solids increased from 2.3g/l at beginning to more than 10g/l during the second campaign. Ammonium nitrogen (figure 8-6) was consumed almost completely (99%), contrasting with the case of total nitrogen. A 32.6% total nitrogen removal was measured. An external carbon source was added in order to boost denitrification. The theoretical optimum COD/N ratio needed is close to 4 but very dependent on the COD and N considered and on the conditions applied to the studied system [14]. In this case, acetic acid is used; 75ml were added daily starting on day 47 conducting to increase the COD/N ratio to values closer to 5. Total nitrogen removal increased rapidly to 81.7%. In the case of COD removal, a 35.4% was achieved, slightly increased until 48.4% during acetic acid injection (COD of external source not included).

![Figure 8-5 COD, NH₄⁺ and TN in the raw and treated leachates with removal percentage during the first measuring campaign](image)

Considering aerated VSS, average sAUR found was 16.9mgNH₄⁺-N(d⁻¹)(gVSS)⁻¹. Specific nitrate uptake rate considering VSS in anoxic conditions was 9.4mgNO₃⁻-N(d⁻¹)(gVSS)⁻¹. Both values are rather similar to those measured on the real facility. After acetic acid injection, sAUR decreased to 10.6mgNH₄⁻-N(d⁻¹)(gVSS)⁻¹ and sNUR rises to 10.9mgNO₃⁻-N(d⁻¹)(gVSS)⁻¹ showing even more similarities.
During the second measuring campaign, all operational parameters were maintained except the aerated volume which was decreased even more, reaching a 5.1% of total volume and the external carbon source was stopped. In these conditions, ammonia nitrogen continues to be consumed almost completely with 99.4% removal. TN removal increases, reaching a 49.3%, meaning that fewer nitrates are leaving the system. COD removal measured is 32.1% in average, slightly lower than during the first campaign. Average sAUR found was 94.7mgNH$_4^+$-N(d)$^{-1}$(gVSS)$^{-1}$, and sNUR equal to 3mgNO$_3^-$-N(d)$^{-1}$(gVSS)$^{-1}$.

8.3.3 Simulations

The results of simulation with ASM1 and ASM1e of outlet ammonia are shown in figure 8-7. For the period before day 100, that is to say with large aeration volume, both models show similar results. During the second part of the experiment in which aeration volume is reduced, the ASM1e model represents better the outlet ammonia concentration.
According to the ASM1 model in which nitrification is modelled as one step and anammox bacteria is absent, dissolved oxygen concentration is not high enough to ensure that ammonia will be consumed by the considered autotrophic bacteria. This is why ASM1 simulation shows concentrations close to 100mgN/l in treated leachates. The ASM1e simulation shows important amounts of ammonia leaving the system from day 210 to 250, but values obtained are anyway lower than those calculated with ASM1. From day 250, outlet ammonia is almost absent consequently, to the analytically measured data. The incorporation of nitrification in two steps, and the ammonia consumption by anammox bacteria are important processes to consider because they may have an important role in low aerated bioreactors.

The results of simulations and the analytical measurement of the outlet total nitrogen (calculated as the sum of nitrates, nitrites and ammonia nitrogen) are presented in figure 8-8. Both models follow in a satisfactory way the tendency of the measured values but the ASM1e is more accurate, particularly for the second part in which aeration is reduced. Again, the effect of ammonia consumption by anammox bacteria could be responsible for the differences. Furthermore, it is possible that the incorporation of ammonia oxidizers separated from nitrites oxidizers (two-step nitrification) can lead to a nitrate shunt. In this situation, oxygen needs can be reduced by 25% and the reduction of nitrite to nitrogen gas requires 40% less carbon sources [15].

Additionally, the nitrification based process has the advantage of producing less sludge (approximately 40% less) [15]. This can be appreciated in figure 8.9 in which simulated and measured suspended solids (SS) are plotted. ASM1e produces less SS than ASM1. However,
it must be noticed that both models overestimate the values obtained by analytical measurement. Clearly, some important processes must be missing in the simulation of SS and so in the overall model. According to both models, SS is mostly composed of particulate inert organics which concentration in the bioreactor increases, particularly by biomass decay but also by inlet leachates content. This model assumption appears to be false and some consumption must be taking place. It is possible that due to very high sludge age obtained in MBRs, the microorganisms able to degrade refractory COD compounds are able to grow in the reactor [4].

![Figure 8-9 Simulation of suspended solids with ASM1 and ASM1e](image)

**8.4 Discussion**

Activated sludges are adaptable micro-organism communities that can consume several substances present in wastewater, depending on conditions applied. Consumption performances will change accordingly to micro-organism behaviour which depends on many different operational parameters. In our case, bacterial communities are primary responsible for pollutant consumption, particularly, autotrophic bacteria that consume the ammonia nitrogen using oxygen. As mentioned before, ammonia nitrogen is transformed into nitrite, and then to nitrate through nitrification. Taking a look into Muertendall’s facility performances, a 99.9% of NH$_4$+ removal reveals that the aeration is applied in excess. Indeed, the primary treatment objective is to reduce ammonia concentration, so excess aeration is well applied. Nevertheless, the problem related, is that ammonia reduction by nitrification leads to nitrate formation. The outlet nitrates concentration of the Muertendall facility reaches 161.5mgN/l in average, a high value that could be avoided.
Heterotrophic bacteria are the second important bacterial group present in the sludge. It consumes organic matter (measured as COD), and oxygen or nitrates as electron acceptor depending on conditions applied. When excess oxygen is used, nitrates will practically not be consumed, a situation that may explain low TN removal (43.6%). A low biodegradable carbon in leachates must be considered also, taking into consideration the occasional external carbon addition.

With the MBR pilot, excellent ammonia removal was maintained with an aeration volume kept near 52.5% of the total volume. However, TN removal was lower. Lack of biodegradability of leachate’s COD was a plausible explanation, which was tested and demonstrated by external carbon addition in the anoxic tank that boosted TN and COD removal. Afterwards, it was decided to eliminate external carbon source addition.

During the final campaign, a 99.4% of NH$_4^+$ removal was obtained, even with a much lower aerated volume of 5.1%. At the same time, the anoxic volume was larger and nitrate consumption was enhanced. COD removal, however, returns to lower values. sAUR computed values suggest that ammonia oxidizing bacteria consume more nitrogen under these conditions but the presence of other bacterial groups as anaerobic ammonium oxidising bacteria (anammox) could be responsible for ammonia consumption as well [16]. Furthermore, partial nitrification may give some answers concerning lower needs of aeration, and lower carbon consumption [17]. Another advantage of small aerated ratio is the elimination of foam, problem also detected in the Muertendall station.

| Aerated volume: 75.6% With external carbon source | NH$_4^+$-N removal: 99.9% | COD removal: 58.5% | Total nitrogen removal: 43.6% |
| Aerated volume: 52.5% Without external carbon source | 99% | 35.4% | 32.6% |
| Aerated volume: 52.5% With external carbon source | 99.9% | 48.4% | 81.7% |
| Aerated volume: 5.1% Without external carbon source | 99.4% | 32.1% | 49.3% |

It must be underlined that low aeration may have some influence over membrane filtration (clogging effect)[18], but this issue was not considered within this study, so further research is needed to clarify this aspect. At least we did not observe any difference during the tests.
8.5 Conclusion

Muertendall’s MBR which is operated with a large aerated volume (75.6%), presents an excellent removal of ammonia nitrogen. Nevertheless, total nitrogen removals are low, indicating high nitrate concentrations contained in treated wastewater. In the case of organic matter, good removal performances are observed, considering the low biodegradability of leachates.

With the MBR pilot, the aeration volume was first reduced to 52.5%. Under these conditions, excellent ammonia nitrogen removal was maintained, but total nitrogen and COD removal decreases. To increase denitrification, an external carbon source was added. Total nitrogen removal rapidly increases to values up to 81.7%, as well as COD removal that rises up to 48.5%.

During the final part of the study, no external carbon source was added and the aeration volume was decreased to reach a 5.1% of total volume. Under these conditions, Ammonia nitrogen is still consumed over 99%, and TN removal increases to values higher than the ones found in the full scale facility. The aeration, with its associated costs can be lowered, with similar nitrogen removal performances. In the case of COD removal, a slightly decrease was observed and must be considered. External carbon source addition under these low aerated conditions can be tested.

Simulations performed with ASM1 and the nitrogen removal adapted model ASM1e enhances the active role of different autotrophic strains. Particularly, the inclusion of ammonia oxidizers (separated from nitrites oxidizers) and anammox bacteria which appear to be necessary in low aeration conditions. Also, the high sludge age encountered in MBR allows the growth of micro-organisms capable of consuming refractory compounds so they could be considered when modeling these processes.

8.6 References


General conclusions

The goal of this research project was to optimise the treatment of landfill leachates by membrane bioreactors, particularly acting on the aeration process. A full scale MBR is in operation at Muertendall’s landfill in east Luxembourg with excellent removal of ammonia nitrogen but operated at a large aerated ratio. The initial hypothesis was that aeration could be reduced maintaining good removal performances but at lower costs. The underlying hypothesis was that when increasing the anoxic volume (i.e. reducing the aerated volume) the bacterial community would change in favor of the nitrate shunt and other bacterial groups as anammox bacteria.

A pilot MBR was put into operation with similar conditions than the real scale one. Similar removal performances were obtained. Then, the aeration was decreased obtaining still satisfactory removal performances.

In parallel, pilot MBR simulations were achieved using activated sludge models, in order to gain information and to clarify the possible involved processes. ASM models were initially conceived for the simulation of municipal wastewater treatment, so differences were expected when other wastewaters are used.

The first problematic encountered was that landfill leachates have to be characterized in terms of the ASM components. A characterization protocol was applied with success yielding important differences when compared with municipal wastewaters. The characterization obtained allows future modellers to have a starting point when simulating biomass treating landfill leachates. Furthermore, the approach used is somehow simple because data are based on a physical chemical method combined with a BOD analysis for the COD fractions and on standard analysis for nitrogen forms.

Simulations were thus performed with ASM1 and ASM3 yielding good simulations when compared with analytical measurements. ASM1 model shows better results when using default parameter values, but it was concluded that similar results could be obtained with both
models if parameters were adjusted. These simulations were performed under the initial conditions of the pilot MBR, ie with high aerated volumes. However, when aerated volume ratio was decreased, simulations failed and results were not consistent with analytical measurements.

During the second part of the experiment, the aerated volume was reduced. A specially adapted model for nitrogen removal was tested. The model is an adaptation of the ASM1 model including two steps nitrification and anammox bacteria, allowing to simulate correctly the behaviour of the MBR pilot. These results suggest that in the case of nitrogen removal with MBR, working under low aerated volumes and high sludge retention times, nitritation and anaerobic ammonia oxidation could have important roles.

Therefore, this work has proven by tests with a pilot and by simulations with adapted models, that it is convenient to the nitrogen removal treatment, to work with low aerated volumes, augmenting anoxic zones. MBR operators should keep in mind that similar removal performances could be obtained using less resources.

**Perspective**

There are some limitations and perspectives of this study that are important to signal. The impact of operating under lower aerated volumes over the membrane fouling was not studied. It will be interesting to check if the amount of soluble microbial products into the sludge matrix varies. Trans-membrane pressure variations could also be compared under different aerated volumes.

Notice that another aspect is that the pilot was operated with rather constant inlet flows of leachates, which is obviously not the case in the real scale bioreactor. Variations in flowrates and concentrations have to be considered as they will influence the F/M ratio and thus the general behaviour of the biomass. However, variations depend on many environmental factors related to the landfill so it is very difficult to replicate them under the controled conditions of a pilot experiment.

The results of this work suggests that when aeration is reduced in MBR treating landfill leachates, other bacterial groups emerge resulting in similar removal performances; however it was impossible to find the optimal amount of aeration, because the aeration was reduced at
the maximum capabilities of the pilot bioreactor. Furthermore, the fact that the pilot MBR uses a submerged membrane constrains the operation because aeration is also used for fouling control.

The amount of the external carbon source addition could also be optimized in order to obtain better denitrification results. However, it was reported that in the real scale bioreactor, external carbon source was only applied for pH control and not to increase denitrification performances. The type of external carbon source added could also be studied as the biomass will act different, depending on the degradation characteristics. Denitrification should also be studied in detail under the conditions of this study, particularly because it is possible that intermediate compounds like nitrous oxides and nitric oxide may be released.

Finally, simulation results must be considered with precaution because they were obtained using default parameters for the corresponding models. Parameter estimations through respirometry or other techniques would be very interesting to check under the conditions applied in this work. Unfortunately, it was not possible to perform them during this study because they are highly time consuming and the analytical measurement resources were completely used during the long measurements campaigns.

Other references used


