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Modelling and operations of municipal membrane bioreactors: from conventional to novel applications

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Abstract

Mathematical modelling of activated sludge systems is used widely for plant design, optimisation, training, controller design and research. Activated Sludge Modelling or ASM-modelling represented an important milestone in modelling of biological treatment processes. ASMs were initially developed to describe Conventional Activated Sludge (CAS) processes under correspondingly typical operating conditions. Nevertheless, they have been used since the late nineties to simulate biomass kinetics in MBRs systems as well, provided that some necessary adaptations are made to allow for the specific behaviour of these systems.

The specificities of the MBR biological process compared to the CAS process have been extensively reported. These all influence and characterize the MBR process behaviour. The logical question one can pose now is whether all current knowledge about ASM based modelling for CAS is simply transferable to MBR systems, or in other words, how the current MBR process understanding can be merged into the ASM framework. In the years 2005-2010, very few studies were done on the applicability of activated sludge models (ASMs) on membrane bioreactors (MBRs). This PhD started with the idea of contributing to this subject, by providing an overview of the most recent literature on ASM-based MBR modelling, followed by a critical application of ASM models to a full-scale municipal MBR.

In chapter 2, a general description of the MBR concept and the most relevant operational issues are presented.

In chapter 3, a critical analysis of the ASM applications to MBRs environment proves that, when modelling purposes do not differ from effluent characterization, oxygen demand and sludge production, ASMs are very relevant to MBR applications. However, particular care needs to be taken since the specific conditions present in MBRs are reflected in some important discrepancies when compared to ASM default parameter values.

ASM fractions were increased in numbers as to provide a link between biological reactions and fouling indicators. In cases of ASMs developed for specific purposes related to MBR operations, and with particular care to fouling prediction modelling, the knowledge on soluble microbial products (SMPs) and extra-polymeric substances (EPS) modelling has been critically reviewed on the basis of the literature, including the most recent developments.

In chapter 4, an unmodified ASM protocol was applied to a full-scale MBR. The modelling exercise went through the determination of the kinetic parameters that were reviewed in the literature, confirming

the reduction of the half saturation coefficients for O_2 reported in literature. This reduction resulted in a higher total nitrogen removal rather than in significant aeration energy savings.

The study revealed how more than half of the total energy demand of the studied MBR is needed for the filtration compartment. The coarse bubbles provided for scouring purposes in the membrane chambers could potentially have a role in the biological process if a different process layout would be used. An energy optimization may not only be obtained by a better understanding of the fouling phenomena, as reported so far in the scientific literature, but also by giving proper attention to the MBR process layout.

In chapter 5, the most advanced literature on ASM-based models extended for SMP modelling was applied in a full-scale MBR. A new matrix has been created based on the ASM2d model. The study fractionated the soluble microbial product in two species. While the biomass associated products (BAPs) kinetics can be estimated, in tune with previous experiments, the utilization associated products (UAP) kinetics are instead hindered by storage phenomena (accountable only on ASM3) and by the non-uniformity between the polysaccharide fraction, easily biodegradable, and the protein fraction, which is refractory to biodegradation. The extension of an ASM model with SMPs and its experimental work impacts on the modelling exercise complexity. A number of drawback were defined, offering suggestion for an improved modelling calibration of the additional ASM fractions. In principle, nutrients removal, sludge production and energy fitting did not receive further benefit from the SMP modelling. Since SMPs did not correlate with fouling rates in this full-scale MBR, the main drive for these models was thus not accomplished.

The adaptation of ASM parameters for MBR sludge specificities was demonstrated in full-scale. In chapter 6, a hybrid MBR-CAS system was operated as to inoculate MBR sludge into a parallel CAS biology. The results highlighted benefits and drawbacks: while MBR augmentation was found to improve nutrient removal of the parallel CAS system, the benefit was found MBR sludge loading dependent. On the other side, the MBR flocs, grown without settling selection pressure, were not embedded in the CAS flocs, and the lower sludge quality, in terms of settling, reflected in deterioration of effluent CAS quality.

In chapter 8 and 9, an MBR was used as environment for bio-augmentation while targeting recalcitrant pharmaceuticals compounds in municipal waters. *Microbacterium sp strain BR1* was inoculated in order to degrade Sulfamethoxazole (SMX) in municipal wastewaters. But evidence of SMX removal facilitated by *Microbacterium sp strain BR1* was observed only at concentrations far higher than the municipal influent/effluent concentrations. By use of molecular tools a scarce capability to survive, both in post-treatment and in secondary treatment, was assessed. The inoculated strain had an observed

growth rate during operations 30 times lower than activated sludge. Its presence was reduced to a small % of the total viable biomass, and it would be outcompeted during long term operations.

The bio-augmentation was instead proven successful when seeding an aquatic fungi, *Phoma sp.,* capable to degrade carbamazepine (CBZ) and diclofenac (DF). *Phoma sp*. was able to survive in municipal wastewater and in competition with activated sludge. Despite the slow growth of the micro-organism, degradation was proven with both pharmaceuticals. The mechanisms of degradation were proven to differ. While the CBZ removal is not boosted by the extra-polymeric laccase, DF is affected by it. The work could also unambiguously prove the absence of sorption mechanisms of the target compounds into activated sludge or the bio-augmented biomass.

A financial comparison between MBR and CAS technology was attempted. In this study both operational and investments have been extracted from a full-scale case, and partially extracted by aid of an ASM model. For the definition of the investment costs, an analysis of the MBR life-time concept, and its determination methods was carried out.

With regards to operational costs, the MBR technology was found more energy intensive than a CAS system, even when the latter is equipped to deliver a comparable water quality (by post-treating the CAS effluent). Energy wise, the MBR technology is outcompeted.

When looking at both investments and operational costs, hybrid MBR systems were found less competitive than CAS system even when adjusting their sludge production, as the absolute barrier provided by their filter would allow. However these calculations forget that the MBR technology is primarily an application for water re-use. And therefore the water production should be accounted in the financial analysis. Moreover this work overall promotes the use of MBRs for alternative applications, as in chapter 6, 8 and chapter 9.

MBRs are an integrated resource recovery systems, and opposite to a CAS system, capable to deliver: water for agricultural purposes; a polishing step towards recalcitrant pharmaceuticals load; a support to CAS systems operations; an effective water re-use solution with a small footprint. And it is in this sense that a true financial analysis should be framed.
But a typical western misconception brought MBRs to be applied only for effluent concern, forgetting that water re-use was its main field of application. Only when MBRs are conceived for their multiple applications possibilities, this technology is to be considered pioneering and financially rewarding.

Samevatting

Wiskundige modellering van actief slibsystemen wordt vaak toegepast bij het ontwerpen van rioolwaterzuiveringsinstallaties, het optimaliseren van processen en sturingen, en in onderzoek. Actief Slib Modellering (ASM) is een belangrijke mijlpaal in het modelleren van biologische behandelingsprocessen. ASM werden in eerste instantie ontwikkeld om conventionele actief slib (CAS) processen onder normale werkomstandigheden te beschrijven. De specifieke kenmerken van het biologisch proces van Membraan Bioreactoren (MBR) in vergelijking met het CAS proces zijn uitgebreid beschreven. De vraag is nu of al de bestaande kennis van ASM gebaseerde modellen voor CAS rechtstreeks overdraagbaar is naar MBR-systemen of, met andere woorden, hoe het huidige MBR-proces kan kaderen binnen ASM. In hoofdstuk 3 bewijst een kritische analyse dat de doeleinden niet verschillen qua effluent karakterisering, zuurstofverbruik en slibproductie, ASMs zijn dus zeer relevant voor MBR-toepassingen.

In hoofdstuk 4 werd een niet-gemodificeerd ASM protocol toegepast op een *full-scale* MBR. In hoofdstuk 5 werd de meest geavanceerde literatuur over ASM-gebaseerde modellen uitgebreid met SMP modellering en op een *full-scale* MBR toegepast. Een nieuwe matrix op basis van het "ASM2d" model werd gecreëerd. De aanpassing van ASM parameters voor MBR slib werd op *full-scale* gedemonstreerd. In hoofdstuk 6 werd een hybride MBR-CAS-systeem bediend om MBR slib te enten in een parallelle CAS biologie. In hoofdstuk 8 en 9 werd een MBR als omgeving voor bio-augmentatie gebruikt om onafbreekbare farmaceutische componenten te verwijderen. Hoofdstuk 7 omvat een financiële analyse van het verschil tussen MBR en de CAS-technologie. In deze studie werden operationele kosten en investeringen opgenomen van een *full-scale* situatie en deels via een ASM model bepaald. Voor de definitie van de investeringskosten werd een MBR *life-time*-analyse uitgevoerd. Met betrekking tot de operationele kosten werd de MBR technologie energie-intensiever bevonden dan een CAS-systeem, zelfs wanneer deze een vergelijkbare waterkwaliteit levert (per post-behandeling van het CAS-effluent). Zuiver op energiebasis wordt de MBR-technologie weggeconcurreerd.

MBRs zijn geïntegreerde resource recovery-systemen en zijn, in tegenstelling tot het CAS-systeem, in staat volgende zaken te leveren: (i) water voor landbouwdoeleinden, (ii) een zuiveringstap voor farmaceutische vrachten en (iii) ondersteuning van CAS-systemen operaties, (iv) een effectief water hergebruik oplossing met een kleine footprint. Het is in die optiek dat een werkelijke financiële analyse moet uitgevoerd worden. Het is een typisch westerse misvatting om MBRs toe te passen voor afvalwaterkwaliteit en men vergeet hierbij dat hergebruik van water het belangrijkste toepassingsgebied

is. Enkel wanneer MBRs ontworpen worden met het oog op hun bredere toepasbaarheid, is deze technologie baanbrekend en financieel lonend.

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Abbreviations

AOB	Ammonia Oxidizing Bacteria
AS	Activated Sludge
ASP	Activated Sludge Process
ASM	Activated Sludge Model
BAP	Biomass Associated Products
b_A	Autotrophic decay rate
b_H	Heterotrophic decay rate
BNR	Biological Nutrient Removal
BOD	Biological Oxygen Demand
BW	Backwash
CAS	Conventional Activated Sludge
COD	Chemical Oxygen Demand
COD_{EPS}	Chemical Oxygen Demand Content of EPS
COD_{cell}	Cellular Chemical Oxygen Demand
$COD_{sol,in}$	Soluble Influent Chemical Oxygen Demand
COD_{sol}	Soluble Chemical Oxygen Demand
COD_b	Biodegradable Chemical Oxygen Demand
$COD_{tot,IN}$	Total influent Chemical Oxygen Demand
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DWF	Dry Weather Flow
EPS	Exo-cellular Polymeric Substances
f_B	Fraction of Biomass that ends up as Microbial Products
f_{BAP}	Fraction of BAP Produced during Cell Lysis
f_{UAP}	Fraction of UAP Produced during Substrate Production
fp	Fraction of inert COD generated in biomass lysis

F/M	Food to Micro-organisms ratio
HRT	Hydraulic Retention Time
J	Flux
K_{BAP}	Half saturation coefficient for BAP
$k_{h,BAP}$	Hydrolysis Rate of BAP
K_{eps}	EPS formation coefficient
K_{mp}	Half saturation Coefficient For Microbial Products
K_{NH}	Half saturation Coefficient For Ammonia
K_{NO}	Half saturation Coefficient For Nitrate
K_{OA}	Autotrophic Saturation Coefficient for Oxygen
K_{OH}	Heterotrophic Saturation Coefficient for Oxygen
$k_{h,UAP}$	Hydrolysis Rate of UAP
k_{UAP}	UAP formation rate coefficient of Heterotrophs
k_{UAPa}	UAP formation rate coefficient of Autotrophs
K_{SMP}	SMP Half saturation coefficient for Heterotrophs
i_{TS_X}	Ratio between the mg/l of Xtss and the COD of the different fractions
LC-OCD	Liquid Chromatography - Organic Carbon Detection
LMH	Liter per Meter Square per Hour
MBR	Membrane Bioreactor
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed liquor volatile suspended solids,
M_{NO3}	Nitrified Load
MP	Microbial products
MSS	MBR Sludge Seeding
MW	Molecular Weight
NOB	Nitrite Oxidizing Biomass
NPV	Net Present value
OM	Organic Matter
OHO	Ordinary Heterotrophic Organism

O_{sp}	Oxygen Set-Point
PAO	Phosphate Accumulating Organisms
P	Permeability
PE	People Equivalent
PN	Proteins
PHA	Polyhydroxyalkanoate
PS	Polysaccharide
PT	Protein
q_{fe}	Maximum Rate For Fermentation
q_{pp}	Rate Constant for Storage X_{PP}
RC	Recovery Cleaning
r_s	Specific substrate utilization rate
$r_{S,BAP}$	Production/Consumption Rate of BAP
RSF	Relative Sensitivity Function
S_{BAP}	BAP concentration
Si	Inert Soluble Fraction
sMBR	Submerged Membrane Bioreactor
SMP	Soluble Microbial Products
S_{NH}	Ammonia Concentration
S_{NO}	Nitrate Concentration
S_{PO4}	Ortho-phosphate Concentration
SRT	Sludge Retention Time
Ss	Biodegradable Soluble Fraction
SS	Suspended Solids
S_{UAP}	UAP concentration
SVI	Sludge Volume Index
T_{life}	Membrane Life Time
TKN	Total Kjeldahl Nitrogen
TMP	Transmembrane Pressure

TN	Total Nitrogen
TP	Total Phosphorous
UAP	Utilization Associated Products
VSS	Volatile Suspended Solids
WWTP	Waste Water Treatment Plant
X_{aut}	Autotrophic Biomass Concentration
X_{DNPAO}	Fraction of denitrifiers in the PAO biomass
X_i	Inert particulate fraction
X_{het}	Heterotrophic Biomass Concentration
X_{PAO}	PAO Biomass Concentration
X_{sto}	Organics stored by heterotrophs
Xs	Biodegradable Particulate Fraction
X_{TSS}	Total Sludge Suspended Solid Concentration
X_u	Non-biodegradable Organic Particulate Matter
Y_a	Yield Coefficient For Autotrophic Biomass
Y_H	Yield Coefficient For Heterotrophic Biomass
Y_{HD}	Yield Coefficient For Heterotrophic Biomass In Anoxic Conditions
Y_{PAO}	Yield Coefficient (Biomass/PHA)
Y_{SMP}	Yield coefficient for growth on SMP
Y_{MP}	Yield coefficient for growth on MP
Y_{obs}	Observed Yield
$\gamma_{UAP,H}$	Heterotrophic UAP Formation Constant
$\gamma_{MP,A}$	Autotrophic MP formation constant
$\gamma_{MP,H}$	Heterotrophic MP formation constant
$\gamma_{UAP,A}$	Autotrophic UAP formation constant
μ_H	Heterotrophic maximum growth rate
μ_A	Autotrophic maximum growth rate
μ_{SMP}	SMP maximum growth rate
η_{NO3}	Anoxic reduction factor

Chapter 1

Introduction, objectives, outline

1.1 ***Background***

Membrane filtration is a separation process in which a membrane acts as a physical and selective barrier between two phases. In the water treatment field, a membrane is a finely porous medium allowing water to pass through the pores while retaining water constituents. The effectiveness of the separation process strongly depends on the membrane characteristics e.g., pore size, porosity and material of the membrane.

Membrane based treatment technologies represent an attractive tool in wastewater management, and its most popular reactor configuration is a MBR. MBRs became very popular starting from the nineties, and an increasing number of installations have been built. A decade of continuous research has been dedicated to the different aspects that characterize it in order to assess its competitiveness towards conventional activated sludge (CAS) systems (Judd, 2006).

Some advantages were clearly recognized by the research community: the effluent is free of solids and pathogens and is suitable for water reuse applications; systems are more compact since they can be operated at elevated sludge concentrations; the hydraulic retention time and sludge retention time (SRT) can be selected independently; the biological process becomes independent from sludge settling quality.

Besides the advantages, there are also some aspects that have been clearly recognized as major bottlenecks of this technology: (i) fouling mitigation and control; (ii) the specific energy consumption in municipal systems.

It is recent news that the Dutch Water Boards have decided to close the full-scale municipal MBRs of Varsseveld and Heenvliet (H_2O, 2012). From their survey it resulted that the average cost of operations per m^3 water treated in MBRs is 20-25% more expensive than in conventional wastewater treatments. The additional costs are in the higher energy, cleaning chemicals, maintenance, because MBR more requires attention and more frequent maintenance components than CAS systems (H_2O, 2012). The Dutch Water Boards claim the additional costs were not a surprise. Yet the expectation that through future developments (energy optimization and cleaning procedures and lower membrane prices) operating costs of MBR would decline (H_2O, 2012) was not fulfilled.

MBR technology remains certainly competitive within clear boundary conditions: satellite wastewater treatment for small communities, housing developments, industrial wastewater treatment with severe space limitations, municipal treatment in places characterized by water scarcity or rising water demand such as Australia, Middle East, India and China (Judd and Judd, 2011; Lesjean *et al.,* 2009).

There are at the moment thousands municipal MBR installations operated. Research investigates further on those aspects that deserve improvement. The market remains very lively and much is left to be done.

1.2 Application of Activated Sludge Modelling platforms to MBRs

Activated Sludge Modelling or ASM-modelling represented an important milestone in modelling of biological treatment processes. However, ASMs were initially developed to CAS processes under typical corresponding operation conditions. Nevertheless, they have been used since the late nineties to simulate biomass kinetics in MBRs systems as well, providing some necessary adaptations. The specificities of the MBR biological process compared to the CAS process have been extensively reported (Aileen *et al.*, 2007). Higher SRTs, higher MLSS concentration and viscosity, accumulation of microbial products rejected by the membrane filtration step, high aeration rates for scouring purposes, good nitrification performances, they all influence and characterize the MBR process behaviour. The logical question one can pose oneself is whether the current knowledge about ASM based modelling is simply transferable to MBR systems, or in other words, how to merge the current MBR process understanding into the ASM framework. MBR literature has been very prolific lately but results on biological modelling are scattered, and a systematic overview of the state-of-the-art of all scientific work performed to date in this scientific area is missing. Both academics and end-users of biological modelling processes are in need of a concise summary to support their decision making process in terms of design and operations. A first part of this study is devoted in defining how activated sludge models have to be adapted when used towards MBR systems. How is the biology affected by an MBR process, and how parameters reflect these changes? Which model upgrade is necessary to comprehend all the characteristics of such reactors within an ASM framework?

1.3 Financial comparison between MBR and CAS systems

A financial comparison between MBR and CAS systems has already been subject of much attention. However many of the researchers that put effort in concluding on this issue have seldom extracted information from full-scale plants. Other times the results have been extrapolated from unhomogeneous cases: CAS and MBR plants have been compared while having different influent characteristics; forfaitar operational costs have been considered for both CAS and MBR systems; lifetime of the membrane, and therefore membrane replacement costs were unknown.

All these bottlenecks are in this study overcome. Full-scale MBR and CAS are operated in parallel by treating the same influent flow. Data have been partly provided by operational data, and partly extracted by an ASM model of the hybrid MBR-CAS plant.

The installations built a decade ago are now aging, offering new insights from an operational perspective. Several issues can in fact be disclosed only during the aging process: operations in sub-optimal conditions and membrane life-time (T_{life}) are typical examples. The latter aspect has recently come to the attention of the scientific community, since it strongly influences the competitiveness of the MBR technology. This study intends to provide more insight in defining the life-time of a full-scale MBR equipped with hollow fibers. Different methods to determine the T_{life} and possible end-of-life-triggers are discussed.

Investment cost of full-scale membrane according to a real database have to be complemented by the membrane replacement costs. Summing up investments and operational costs (determined in this study) will help in providing a comprehensive analysis of the MBR competitiveness in municipal full-scale applications.

*1.4 **Novel MBR applications***

Similarly to the micro-filtration (MF), the molecular weight cut-off of ultra-filtration (UF) membranes (10-100 kDa) does not allow sieving of most micro-pollutants. Experiments conducted (Jermann *et al.,* 2009, Majewska-nowak *et al.*, 2002) show that the removal of micro-pollutants by UF membranes is mostly limited to adsorption phenomena, which is not a reliable treatment on the long term. Besides the use of powdered activated carbon (PAC) that has attracted the attention of many researchers, another potential benefit of MBR is the possibility under specific conditions to remove micro-pollutants. However this enthusiasm was tempered over time by the many study which did not observe significant differences amongst CAS and MBR in terms of micro-pollutants removals (Clara *et al*., 2005). Most researcher describe instead high removals only when operating MBRs at high SRTs (*inter alia*, Reif *et al*. , 2007; Abegglen *et al*., 2009; Malpei *et al.*, 2009).

On the other side, the coupling of MBRs in bio-catalytic processes is gaining popularity. In MBR systems, there is no need for immobilization or settling since an absolute separation is provided by the membrane itself. This is an advantage that can be conjugated with novel processes for micro-pollutant degradation. Other advantages are: a higher product recovery along with heterogeneous reactions, and continuous operation of the reactor (Chakraborty *et al.*, 2014).

Different approaches may target the biological removal of micro-pollutants by use of MBR systems. Enzymatic membrane reactors represent an option, but they deal with gradual loss of enzymatic activity due to various physical, chemical and biological inhibitors in wastewater conditions (Nguyen *et al*., 2013). It would be necessary to periodically replenish the reactor with fresh enzyme. By contrast, a whole-cell reactor may bring about the added advantage of continuous enzyme production (Nguyen *et al*., 2013). Such approach is receiving much attention from many researchers, trying to target the

bio-degradation of recalcitrant compounds (inter alia, Zhang *et al.* (2012); Nguyen *et al* (2013); Liu *et al.*, 2007; Wen *et al.*, 2013); Cirja *et al.*, 2009).

This study intends to investigate the bio-augmentation of municipal MBRs in order to remove well known recalcitrant micro-pollutants: Sulphamethoxazole, Carbamazepine, and Diclofenac. In order to achieve this goal, micro-organisms selected in lab experiments have been bio-augmented in a municipal pilot MBR.

*1.5 **Aims and objectives***

The goal of this research is:

- Investigate on the applicability of ASM models to full-scale municipal submerged MBRs
- Analyze the competitiveness of MBR with regards to CAS systems. In order to do reach this goal, elaborate capital and investment costs based on full-scale experiences.
- Develop novel applications that can boost the value of municipal MBRs.

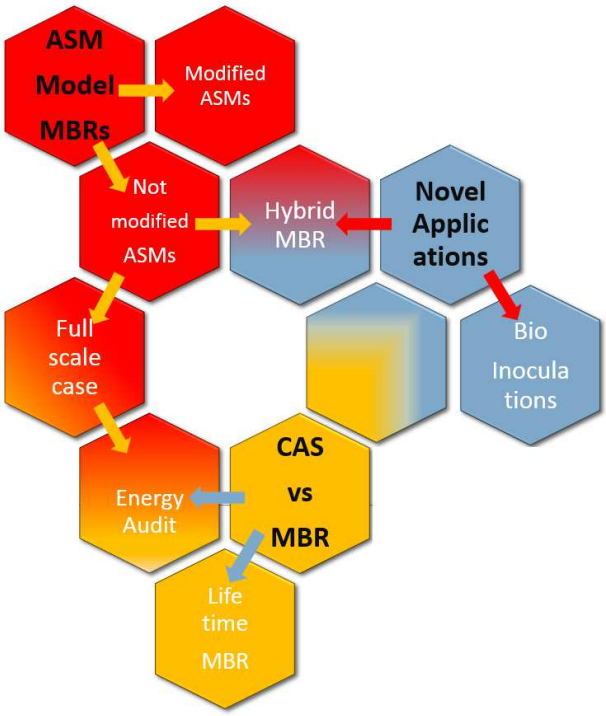

Figure 1.1. The three main research objectives are distinguished according to colours and they interact where the colours merge. The arrows indicate how the main research tasks (in bold) are elaborated further.

1.6 ***Outline***

The work is composed of 10 chapters:

Chapter 2: A general description of the MBR concept and the most relevant operational issues related to it.

Chapter 3: Activated sludge model (ASM) based modelling of MBR processes: A critical review with special regard to MBR specificities. Description: This is a critical study on the specificities of MBR modelling in comparison with CAS modelling. It serves as well as an introduction to let the reader enter the theme of MBRs and ASM modelling.

Chapter 4: Energy audit of a full-scale MBR system. Description: This work is a sort of base scenario where a full-scale is modelled and CAS/MBR differences are discussed with specific emphasis to modellling and energy consumption.

Chapter 5: Modelling soluble microbial products (SMPs) in a dynamic environment. Description: This work is an expansion of a normal activated sludge model where all fractions necessary to MBR modelling are included. The work analyses effectivity and usefulness of such modelling approach.

Chapter 6: MBR sludge inoculation in a hybrid process scheme concept to assist overloaded CAS process operations. Description: in this study the biological capacity of an MBR is used to support parallel operation in an overloaded CAS system. In this work plain ASM modelling is applied and tested in full-scale.

Chapter 7: Elaborating the membrane life concept in a full-scale hollow-fibers MBR. Description: A typical draw-back of an MBR system is the reduced life-time of the installation. Such aspect can strongly raise or reduce the investment cost of an MBR during its operational lifetime. This study analyze the concept of membrane life-time, offering methods to compute it and to predict it during operations. The study concludes with a financial analysis of MBR technology by use of the data collected in chapter 4 and 7.

Chapter 8 and 9: inoculation of biomass specialized to boost micro-pollutant removal in municipal MBRs. Description: MBRs are confined environments. This is an advantage to be exploited in several applications. MBR do not need biomass immobilization and their eventual properties in degrading micro-pollutants can be used. This work shows how fungi inoculated in the system are able to degrade recalcitrant micro-pollutants (Carbamazepine and diclofenac) in trace concentrations.

Chapter 10: research perspectives and conclusions.

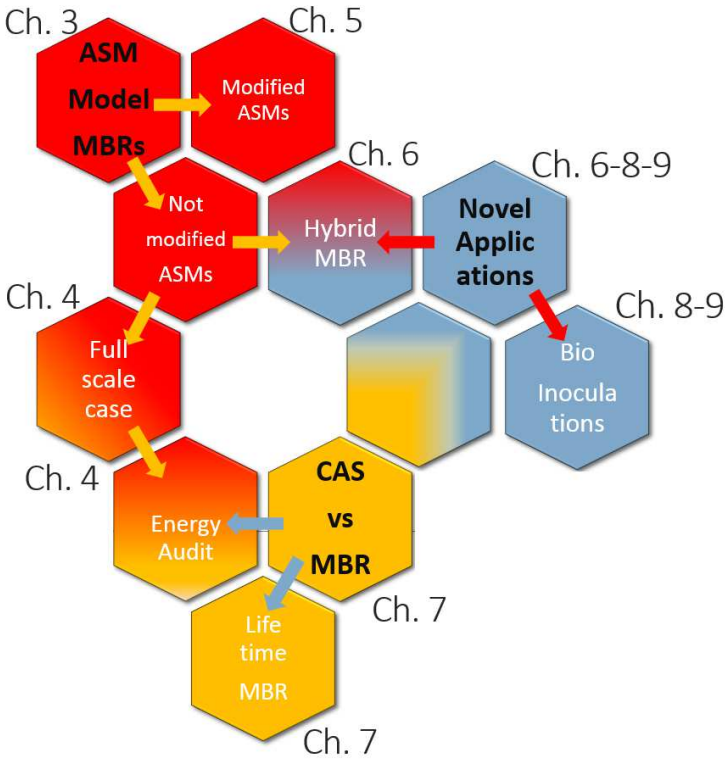

Figure 1.2. The three main research objectives are distinguished according to colours and they interact where the colours merge. The different topics are discussed in the chapters as indicated in the figure above.

1.7 ***References***

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Chapter 2

MBRs in general and the full-scale MBR in Schilde (Belgium)

2.1 *MBRs in general*

2.1.1 *A comparison between CAS and MBRs process*

A CAS process includes primary treatment (mesh, sand trap, primary sedimentation), secondary treatment (aeration and secondary clarification) and tertiary treatment. During the secondary treatment, micro-organisms use wastewater as a substrate for growth and remove dissolved organic matter. The principle is based on the microbiological degradation of organic compounds and removal of nitrogen: ammonium is converted to nitrate during the aeration phase (nitrification) and the formed nitrate is reduced to nitrogen gas (denitrification) during the anoxic phase (Henze *et al.* 2008). This is followed by sedimentation, in which the biological flocs are separated from the clarified secondary effluent. The treatment processes can be either suspended bacterial flocs (activated sludge) or attached growth (trickling filters). The most commonly used process for biological treatment of municipal and industrial wastewaters is the activated sludge process.

Table 2.1: Comparison of different MBR systems (adapted to Yang et al. 2006).

	Zenon	Kubota	Mitsubishi-Rayon
Membrane type	Hollow fibre	Flat sheet	Hollow fibre
Configuration	Vertical immersion	Vertical immersion	Horizontal immersion
Pore size (µm)	0.04	0.4	0.1/0.4
Material	Proprietary	Polyethylene	Polyethylene
Module size (m^2)	31.6	0.8	105
Cleaning	Backpulse and relax	Relax	Relax
Cleaning freq. (min/min)	0.5/15	1.0/60	2.0/12
Recovery method	Chemical soak	Chlorine Backwash	Chlorine Backwash
Recovery frequency	> 3 Months	> 6 Months	> 3 Months
Recovery location	Drained cell or in situ	In situ	In situ

An MBR is based on biological degradation and subsequent membrane separation of the biological sludge by microfiltration or ultrafiltration (Crittenden *et al.,* 2012b). This membrane separation replaces the clarifiers used in CAS systems that reach particle separation by gravity (Figure 2.1). Separation via membrane filtration provides a lower needed surface area, process control and disinfection of the influent without the need of chemicals. In MBR systems, filtration is used for biomass retention. It also enables operation at higher sludge concentrations (up to 20 g/l instead of 3-5 g/l with conventional systems). However MBR technology is usually related to a higher total cost due to the high energy cost. In addition, there are fouling problems. A lot of work still needs to be done on fouling control and membrane development (Henze *et al.,* 2008). Table 2.1 summarizes a comparison of the MBR systems manufacturers.

The membrane module can be either placed in an external side-stream circuit or submerged into the bioreactor as shown in Figure 2.2. The energy demand for a submerged system is twice as energy efficient as the side-stream system (Judd 2011). In all chapters or this study, only submerged modules are considered.

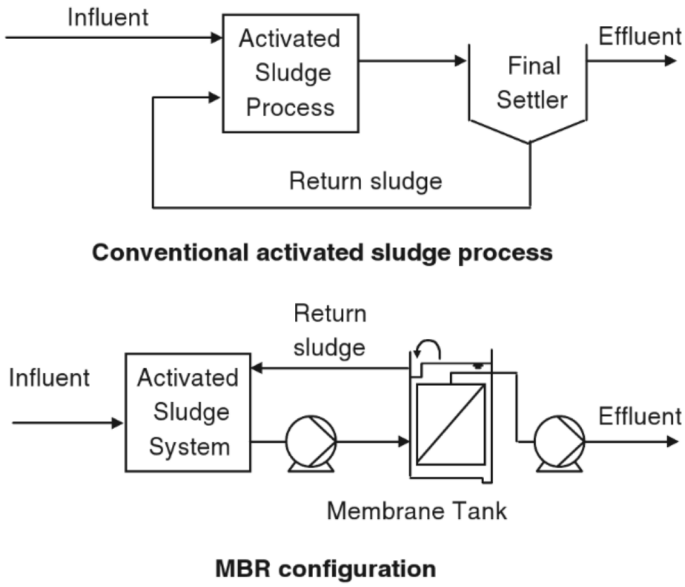

Figure 2.1: CAS process (above) versus MBR technology (below) (van Haandel and Van Der Lubbe 2007).

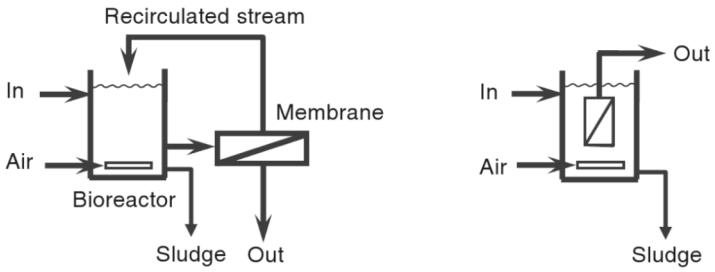

Figure 2.2: Side-stream (left) versus submerged (right) (Judd 2011).

*2.1.2 **Membrane configurations***

Two main flow configurations of membrane processes are frequently used in industry (Mota *et al.,* 2002): cross-flow and dead-end filtration (Figure 2.3). In a membrane cell with dead-end filtration, the feed is perpendicurarly filtered through the membrane. The cake thickness gradually increases to a certain level determined by the drop in pressure or flow velocity. In cross-flow filtration, the main

stream of the suspension is parallel to the filter medium. The turbulence generated during cross-flow filtration causes a thinner deposit layer. The cake layer resistance, which affects the filtration performance (Mendret *et al.,* 2009), differs when in cross-flow and in dead-end filtration cells (Chellam and Wiesner 1997, Mota *et al.,* 2002). Apart from the cake layers thickness, the difference in cake resistance is further influenced by the shape of the filtered particles, their size and cake compressibility (Mota *et al.,* 2002).

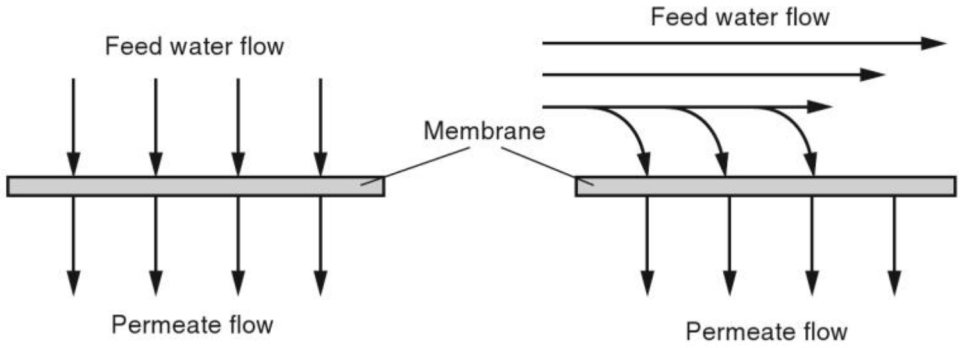

Figure 2.3: Dead-end filtration (left) and cross-flow filtration (right) (Crittenden et al., 2012b).

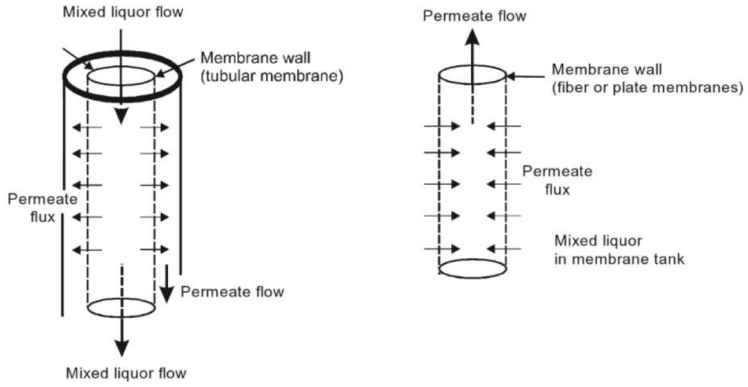

Figure 2.4: Membrane configurations: inside-out (left), outside-in (right) (van Haandel and Van Der Lubbe 2007).

In MBR configurations the mixed liquor can flow either inside-out (cross-flow configuration) or outside-in (dead-end submerged configuration). These two concepts are displayed schematically in Figure 2.4. The differential pressure over the membrane forces the permeate through the membrane (inside-out). In the outside-in configuration, a slight vacuum is applied by a permeate pump which induces a liquid flow through the membrane wall.

All chapters of this study are focused on a dead-end filtration, with fibers having the shape of hollow fibers, in outside-in and submerged configuration.

Commercially available membrane modules include spiral wound, hollow fiber, tubular and flat-sheet modules. Hollow fiber modules are used commonly due to their high membrane area to volume ratio (Schwinge *et al.,* 2004). Mitsubishi and GE-Zenon deliver MBR systems using hollow fiber modules, while Kubota uses flat sheet modules (Yang *et al.,* 2006).

A hollow fiber membrane module consists of numerous long porous filaments packed inside a cartridge. Each filament is very narrow in diameter and very flexible. Two such filaments are displayed in Figure 2.5. Broken hollow fibers however, cannot be replaced. Most commercially available hollow fiber membranes run at outside-in mode (Mulder 1996) and their design allows for backflushing (Seneviratne 2006). Because of its large active area combined with a small footprint (600-1200 m^2/m^3) (Seneviratne 2006), hollow fiber modules have great potential in commercial applications (Camacho *et al.,* 2013).

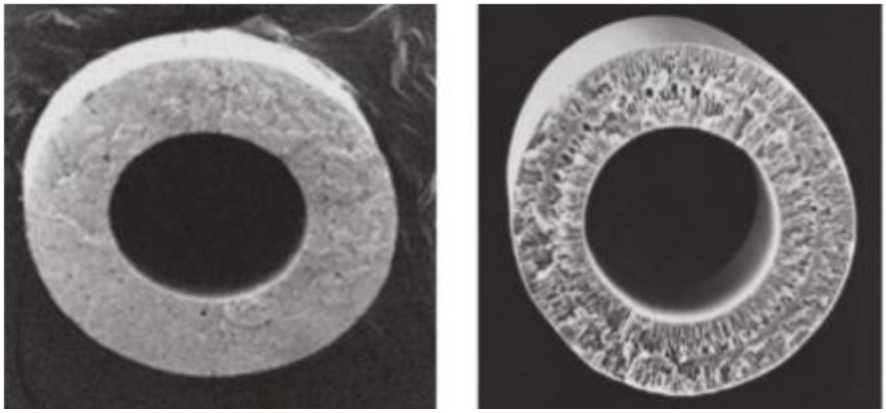

Figure 2.5: Hollow fiber membrane. On the left there is a symmetric membrane, on the right is an asymmetric membrane (Seneviratne 2006).

2.1.3 ***Membrane fouling and concentration polarization***

During membrane filtration two main problems occur: concentration polarization and membrane fouling, which both have a negative effect on the flux.

2.1.3.1 Concentration polarization

Concentration polarization originates from the accumulation of components that are rejected by the membrane. The convective flow of these components to the membrane surface is larger than the flow

to the bulk solution. This results in an accumulation of the rejected component at the membrane surface (Lee *et al.,* 1984, Matthiasson and Sivik 1980) which increases resistance to filtration flow and thus reduces the permeate flux (Figure 2.6). Concentration polarization however ends spontaneously after the operation. It is a reversible process by low forces between the macromolecules in the gel (Matthiasson and Sivik 1980).

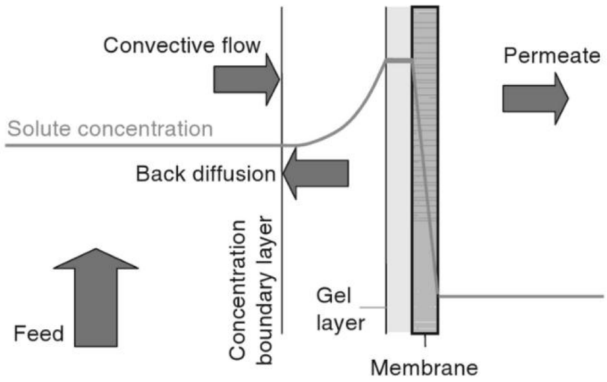

Figure 2.6: Concentration polarization (Judd 2011)

2.1.3.2 Membrane fouling

Fouling is defined as the result of interactions between particles in the influent and the membrane or previously adsorbed particles (Munir 1998) and is illustrated in Figure 2.7. Fouling changes the effective pore size distribution and thus flux. The result is a typical variation of flux with time. "External" fouling is formed by a cake layer that originates by the accumulation of solids on the membrane or a gel layer that can be formed due to the precipitation of colloids and inorganic salts (Le-Clech *et al.,* 2006b). "Internal" fouling is caused by the adsorption and deposition of solutes and fine particles by complete pore blocking of the pores or particle deposition within pores.

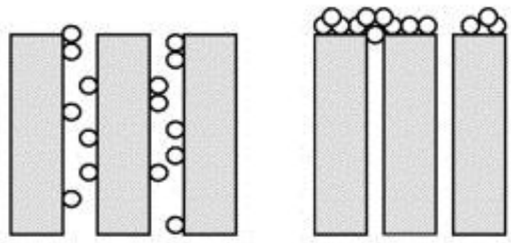

Figure 2.7: Schematic representation of internal (left) and external (right) fouling

There are different types of fouling that can occur in a membrane filtration system: fouling due to colloids, scaling, natural organic matter (NOM) and bio-fouling (Zhang *et al.,* 2012).

Scaling is mainly due to inorganic salts that are present in feed and process water. Fouling by salts and metal compounds generally occurs by precipitation within the porous structure of the membrane. Some examples are calcium sulphate ($CaSO_4$), calcium carbonate ($CaCO_3$) and calcium phosphate ($Ca_3(PO_4)_2$) and metal oxides.

There is a wide range of NOM that can cause significant fouling of membranes. Humic and fulvic substances are naturally occurring organic compounds originating from plant and animal materials in surface waters. They are highly surface active, a property which facilitates their fouling characteristics due to adsorption.

Fouling also involves living organisms (bio-fouling) causing biofilm formation and bacterial adhesion on the membrane surface. Once bound to the membrane surface, bacteria can grow and multiply using the nutrients present in the process stream. Part of the organic material are biopolymers originating from either attachment on micro-organisms (extracellular polymeric substances, EPS) or are present in the mixed liquor (soluble microbial products, SMP). These mechanisms are all self-accelerating (Le-Clech *et al.* 2006b) and it is probably that these mechanisms act simultaneously. For example due to limited oxygen transfer to the bacteria in the biofilm these bacteria die freeing extra EPS that makes the biofilm stronger and causes better adhesion to the membrane.

The intensity of fouling depends on pore distribution and the surface structure (hydrophobic/ hydrophilic character of the membrane).

2.1.3.3 Membrane fouling mitigation options

An increase in TMP is inevitable during filtration over a longer period of time (Meng *et al.,* 2009). In Figure 2.8, the TMP is displayed during a filtration process in function of time. The peaks in Figure 2.8 are in fact pressure increases as a result of membrane fouling. When TMP increases to a certain level, the fouled membrane is cleaned. Fouling is mostly removed by back-flushing (reversible fouling), resulting in a lower pressure when operating at fixed flux. A general rising trend of peaks can be observed. This is called irreversible fouling. Reversible membrane fouling could be cleaned physically for example with back-flush. Irreversible membrane fouling needs to be cleaned by use of chemicals (Lim and Bai, 2003).

Another common method to physical cleaning is relaxation of the membrane module. In this regard, filtration stops and the polarization of sludge concentration around the membrane surface may decrease due to mixing. Sometimes also air is used to enhance this removal by back-flushing with air instead of water.

A lot of research has already been done on methods to reduce fouling (Chen *et al.* 2007, Le-Clech et al., 2006a, Wu *et al.,* 2008a, b) suggesting adaptations in membrane material, feed or biomass modifications, operating conditions (hydrodynamic changes) and membrane cleaning (Howell *et al.,* 2004). Field *et al.,* (1995) suggested a constant flux at a constant transmembrane pressure (TMP). They defined this critical flux as the flux below which the decline of flux or the increase of TMP does not occur while above this critical flux, fouling is observed. Critical flux determination is interesting to assess fouling affinity for given operating condition, but that it cannot be used for long-term estimates (Le-Clech *et al.*, 2006b).

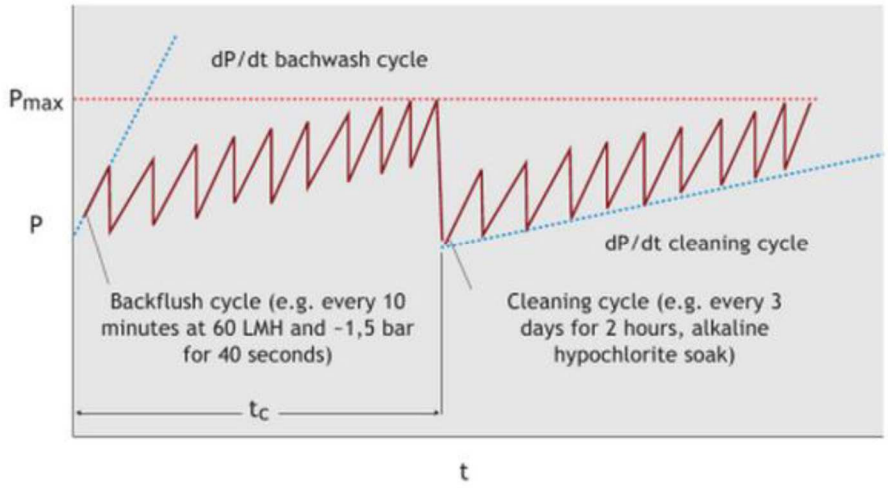

Figure 2.8: Trans-membrane pressure in function of time for constant flux operation (Henze et al., 2008).

Also in process-operation of MBR's the addition of coagulant material was suggested (Hwang *et al.,* 2007, Yoon *et al.,* 2005). Coagulation with so-called "membrane performance enhancers" (MPE) reduces membrane fouling significantly (Wozniak 2010) by adding modified biopolymers with a net cationic charge that react with the biomass. Polysaccharides and proteins secreted by bacteria (extracellular polymeric substance or EPS) are major causes of membrane fouling. By the addition of a coagulant, a significant decrease is observed in concentration of EPS because the EPS is caught in microbial clusters that are formed by coagulation due to the membrane performance enhancer. Larger flocs provide a more porous cake fouling (Hwang *et al.,* 2007). Nevertheless this solution needs dosage of a chemical and thus increases process complexity while addition of chemicals in water treatment should be avoided. Commonly used coagulants include ferric chloride and aluminum sulfate.

The surface of the membrane is known to determine the possibility of deposition and attachment of foulants. Surface modification could minimize membrane fouling (Le-Clech *et al.,* 2006b).

2.1.3.4 Membrane chemical cleaning

Physical cleaning methods will be less efficient when the membrane is in operation for a longer time. Certain intervals for a chemical cleaning of the membrane is necessary. Al-Amoudi *and* Lovitt (2007) mention that the success of a chemical cleaning is dependent on the type of pollution, chemicals, temperature, pH, concentration of the chemicals, contact time, and type of membrane. Chemical cleaning can be applied by a back-flush with chemicals (daily for external modules), maintaining the membrane by chemical cleaning with higher concentrations (weekly) and intensive cleaning (once or twice a year). Diverse membrane suppliers each have their own cleaning methods (see Table 2.2). Sodium hypochlorite (NaOCl), citric acid ($C_6H_8O_7$) or oxalic acid ($C_2H_2O_4$) are the most commonly used oxidants and acids for organic and inorganic fouling.

Table 2.2: Cleaning protocol used by different suppliers of MBR (Le-Clech et al. 2006b). BW = backwash

Supplier	*Chemicals*	*Concentration (%)*	*Protocol*
Mitsubishi	*NaOCl*	*0.3*	*BW (2h) + soaking (2h)*
	Ctric acid	*0.2*	
Zenon	*NaOCl*	*0.2*	*BW and recirculation*
	Ctric acid	*0.2-0.3*	
Tyco	*NaOCl*	*0.01*	*Recirculation and in-tank air*
	Ctric acid	*0.2*	
Kuboota	*NaOCl*	*0.5*	*BW (2h) + soaking (2h)*
	Oxalic acid	*1.0*	

2.2 The full-scale MBR of Schilde

The WWTP of Schilde is composed of two treatment lanes. The CAS lane was built in 1989 with a nominal capacity of 18,000 population equivalents (PE) and a hydraulic capacity of 150 l/s, i.e. 5 times the nominal dry weather flow (DWA), or 3 times the Q_{14}, defined as:

$$Q_{14} = \frac{150}{14} \cdot \frac{1iter}{PE \ . hour}$$

The facility was built to comply with the BOD, COD and suspended solids (SS) removal standards. After renovation (in 2003), the hydraulic capacity increased to 400 l/s, or 28,000 PE (i.e. 4.8 times the Q_{14}). The primary treatment consists of screens with a 6 mm mesh and a rectangular primary clarifier subdivided into 3 lanes (1200 m³). Secondary treatment is achieved by a conventional single-stage activated sludge system (2 x 600 m³). Secondary sludge is wasted from the aerated tanks. Primary and

secondary sludge are afterwards dewatered in a thickening table. Phosphorus is removed by simultaneous chemical precipitation. Sludge-effluent separation is achieved by three round clarifiers (total surface area of 1017 m²).

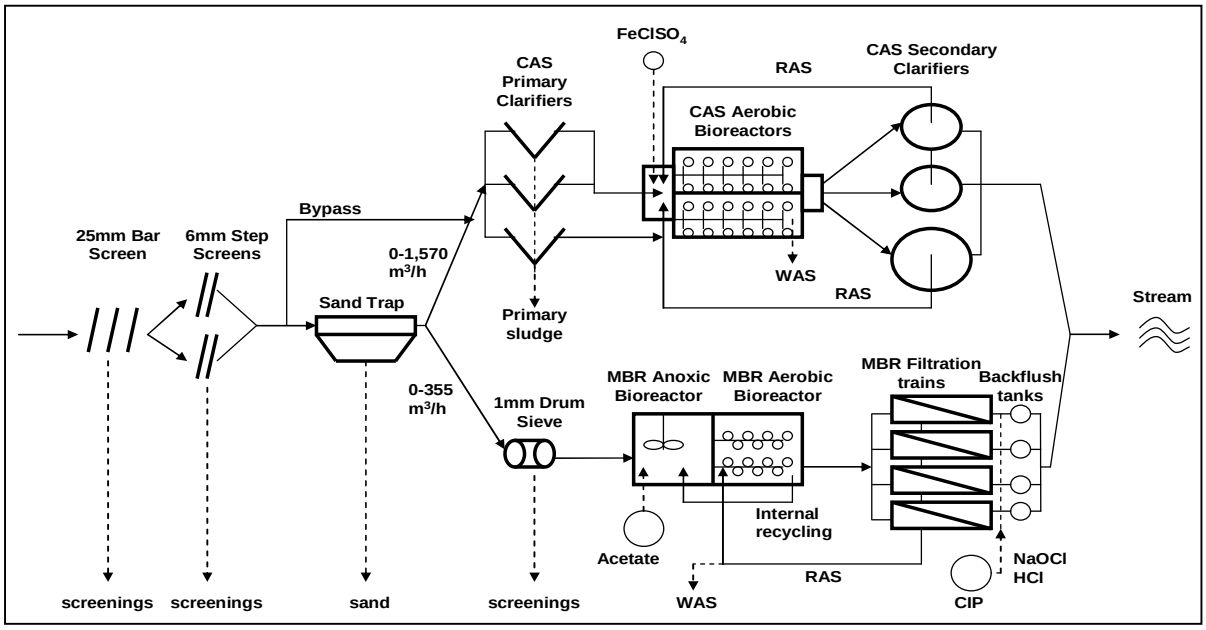

Figure 2.1. Layout of the Schilde WWTP (parallel CAS and the MBR lane).

The MBR lane was built with the aim of meeting more stringent water quality standards (including the requirement for nutrient removal), increasing the WWTP biological capacity to 28,000 PE and the hydraulic capacity to 6 times Q_{14}. The MBR lane is composed of a drum-sieve to protect the downstream system, a sand trap, a pre-denitrification tank (500 m³), an aeration basin (500 m³) and an aerated filtration unit (240 m³), (figure 2.1). Acetate is dosed into the MBR anoxic tank according to the nitrate permeate concentrations. The filtration unit is composed of 4 Zenon MBR filtration trains having a total surface area of 10,160 m².

The process lanes of the CAS and of the MBR run in parallel. The MBR lane treats an average flow of 230 m³/h, and a maximum peak flow of 355 m³/h. The CAS treats the remaining flows, resulting in a variable flow pattern with oscillating flows, and a maximum peak flow of 1450 m³/h.

The MBR lane aerates the biomass by means of fine and coarse bubble aeration. The fine bubble blowers are frequency controlled and operate in the bioreactor tank on a fixed O_2 set-point of 1-1.5 mg O_2/l (PID based). The aeration times are fixed and chosen during operations. The MBR coarse bubble aeration is instead constant (1000 Nm^3 /h per membrane tank). The CAS lane aerates the biomass through an on-off system (PID based) on a fixed O_2 set-point, tuned between 2 and 2.5 mg O_2/l. Simultaneous

phosphorous precipitation is used in the CAS lane by means of $FeClSO_4$, while no chemicals are dosed in the MBR lane.

Basic statistics of the Schilde WWTP influent loading and effluent quality (in Table 2.1 and 2.2) show that the WWTP is biologically overloaded. The observed operational conditions are reported in Table 2.3.

*Table 2.1. Influent loads of the Schilde WWTP in 2006***.**

		Design capacity	Influent loads 2006	
		Average	Average	Daily max
BOD	kg.d-1	513.0	929.0	3769.0
COD	kg.d-1	1.7	2974.0	8894.0
SS	kg.d-1	1.1	1708.0	5577.0
NTOT	kg.d-1	207.0	374.0	724.0
PTOT	kg.d-1	38.0	61.0	142.0

Table 2.2. Average effluent concentrations and removal efficiencies compared to the consent (Heyman and Smout, 2010). Removal efficiency of the combined MBR and CAS effluent in Schilde WWTP (2006).

		Effluent concentrations			Removal efficiencies	
		Effluent	Consent		Effluent	Consent
BOD	$mgBOD.l^{-1}$	4.0	25.0	%	93 .0	90.0
COD	$mgCOD.l^{-1}$	34.5	135.0	%	82.0	75.0
SS	$mgSS.l^{-1}$	11.5	35.0	%	89.0	84.0
NTOT	$mgN.l^{-1}$	12.2	15.0	%	48.0	50.0
PTOT	$mgP.l^{-1}$	0.8	1.0	%	78.0	80.0

Table 2.3. Observed operational conditions in Schilde WWTP (Bixio et al., 2006).

Parameter	CAS	MBR
biomass in biological reactor (g MLSS/L)	2.5 - 4.0	9.0 - 12.0
solids retention time (days)	4 .0- 9.0	14.0 - 21.0
Hydraulic retention time (hours)	3.0 - 75.0	3.5 - 5.0
Operating temperature (°C)	8.0 - 20.0	8.0 - 20.0
Operating pH	6.0- 7.0	7.0 - 8.0
net flux average-maximal (L/(m² h))	-	22.0 - 34.0
Trans-membrane pressure (bar)	-	0.2 - 0.6
filtration duration (s)	-	300.0
backwash duration (s)	-	25.0
relaxation duration (s)	-	5.0

The MBR is subdivided in 4 lanes. The 4 lanes were equipped in August 2003 (the start up of operations) with 4 modules in the second and fourth lane, and six modules in the first and third lane. Each module membrane area consists of 440 m^2. At the end of March 2004, in order to provide an equivalent membrane area in the 4 lanes, 4 modules of the same type were added in the third lane. The four used modules of the third lane were then placed in the second and fourth lane, as to have 6 modules per lane.

Since that date, the MBR operates at a gross flux of 25-45 LMH, with an average net flux of 20.8 LMH (220 m^3/h), and with maximum net flux of 24 LMH (250 m^3/h).

Filtration, backwash and relaxation time last respectively 300s, 25s and 5s respectively. The permeate is filtered through an absolute suction pressure of about 850-600 mbar, with a TMP limit at 500 mbar. Static pressure is at 1040-1070 mbar. Maintenance cleanings with chlorine and HCl are performed every week.

2.3 ***References***

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Chapter 3

ASM based modelling of MBR processes

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Abstract: MBRs have been increasingly employed for municipal and industrial wastewater treatment in the last decade. The efforts for modelling of such wastewater treatment systems have always targeted either the biological processes (treatment quality target) as well as the various aspects of engineering (cost effective design and operation). The development of Activated Sludge Models (ASM) was an important evolution in the modelling of CAS processes and their use is now very well established. However, although they were initially developed to describe CAS processes, they have simply been transferred and applied to MBR processes. Recent studies on MBR biological processes have reported several crucial specificities: medium to very high sludge retention times, high mixed liquor concentration, accumulation of soluble microbial products (SMP) rejected by the membrane filtration step, and high aeration rates for scouring purposes. These aspects raise the question as to what extent the ASM framework is applicable to MBR processes. Several studies highlighting some of the aforementioned issues are scattered through the literature. Hence, through a concise and structured overview of the past developments and current state-of-the-art in biological modelling of MBR, this review explores ASM–based modelling applied to MBR processes. The work aims to synthesize previous studies and differentiates between unmodified and modified applications of ASM to MBR. Particular emphasis is placed on influent fractionation, bio-kinetics, and soluble microbial products (SMPs) / exo-polymeric substances (EPS) modelling, and suggestions are put forward as to good modelling practice with regard to MBR modelling both for end-users and academia. A last section highlights shortcomings and future needs for improved biological modelling of MBR processes.

3.1 ***Introduction***

The membrane activated sludge process, commonly referred to as MBR, combines an activated sludge process and membrane micro or ultra-filtration to separate the treated water from the mixed liquor. The first MBRs were developed in the late 1960s, in “side-stream” configurations, but market penetration became significant only after the commercialization of submerged MBR configurations (Judd, 2006), which proved to be energetically superior. Since the advent of MBR technology, factors such as the need to comply with stringent environmental legislation and a reduced foot-print were seen as able to mitigate the higher capital and operational cost. Recently, technological advances (i.e., improved configurations) and scientific investigations have led to further significant cost reduction.

In early efforts on dynamic modelling of wastewater treatment processes, only two state variables were considered describing degradation of substrate and formation of biomass by first order kinetics (McKinney, 1962). However, the later models incorporated an increasing number of state variables and process descriptions based on widely accepted Monod-type kinetics. The increased understanding of various complex processes further enhanced the models and a steady-state aerobic model was developed (Marais and Ekama, 1976) which later evolved into a well established dynamic model (Dold *et al.,* 1980). The dynamic model included key hypotheses viz. bi-substrate and death regeneration. Such early dynamic models showed their very useful application to design, optimization and control of wastewater treatment systems with a variety of configurations for carbon, nitrogen and even phosphorous removal. Activated Sludge Modelling or ASM-modelling represented an important milestone

in modelling of biological treatment processes. ASMs were initially developed to describe CAS processes under correspondingly typical operating conditions. Nevertheless, they have been used since the late nineties to simulate biomass kinetics in MBRs systems as well, provided that some necessary adaptations are made to allow for the specific behaviour of these systems.

The specificities of the MBR biological process compared to the CAS process have been extensively reported (Ng and Kim, 2007): higher SRTs, higher MLSS concentration and viscosity, accumulation of microbial products rejected by the membrane filtration step, high aeration rates for scouring and good nitrification performance. These all influence and characterize the MBR process behaviour. The logical question one can pose now is whether all current knowledge about ASM based modelling for CAS is simply transferable to MBR systems, or in other words, how the current MBR process understanding can be merged into the ASM framework. MBR literature has been very prolific lately but studies and results on biological modelling are scattered, and a systematic overview of the state-of-the-art of all scientific work performed to date in this area is missing. More specifically, both academics and end-users of biological modelling processes are in need of a concise summary to support their decision making process in terms of MBR design and operations. This review paper aims to (i) provide a concise overview of the past developments and current state-of-the-art in biological modelling of MBR systems and (ii) highlight weaknesses in the current models and propose future needs.

For reasons of clarity, the review is broken down into two major sections: unmodified versus modified ASM models for MBR. The former contains the literature studies where the plain ASM models, as described in Henze *et al.* (2000), are used as such in MBR applications and where only parameter estimations have been performed to improve the model performance (i.e. matching model predictions with measured experimental data). Unmodified ASM models also contain efforts that expand the description of certain bio-kinetic processes, but without adding state variables to the model state vector. The decision to include those applications here was taken from the perspective that these models are more readily applicable in practice.

With modified ASM models, we target all applications where the plain ASM models are extended in terms of (1) bio-kinetic process models and (2) SMP/EPS models. Here, additional state variables are introduced in the model either for a better description of certain processes already present in ASMs or to allow for the description of processes formerly lacking in ASMs (e.g. EPS/SMP).

End-users will most probably be interested in the former section as the models described in that section are intended for use in practice, whereas the latter section focuses on academic work to improve process understanding and, hence, is still in a more basic research phase and further away from practical use.

Both sections deal with the typical aspects that are methodologically encountered during a modelling process such as (i) influent characterization and (ii) determination/calibration of kinetics and stoichiometry. A final section highlights shortcomings and the authors' conception of future needs for improved biological modelling of MBR processes. Finally, to limit the scope of the chapter, discussions have been kept to MBRs treating domestic wastewater. However, applications of models at different scales (lab, pilot and full-scale) are considered.

3.2 ***General overview***

Since MBRs encompass the Activated Sludge Process (ASP) as their fundamental process, ASMs have been applied for the biological modelling of MBRs as reported in various studies (*inter alia* Chaize and Huyard, 1991; Wagner and Rosenwinkel, 1999; Wintgens *et al.*, 2003; Delrue *et al.*, 2008). ASMs are robust dynamic models which are widely used for activated sludge based wastewater treatment process understanding, design, optimization and control. There are various versions of ASMs, and one or another is preferred on account of various factors e.g. modelling objective, desired accuracy, calibration effort, ease of use and relevance of process types, etc. Various versions of such dynamic models viz. ASM1, ASM2, ASM2d, ASM3 (Henze *et al.*, 2000) have been developed during the two decades since the introduction of the first version i.e. ASM1 (Henze *et al.*, 1987), by assimilating the developments in process understanding pertaining to wastewater treatment systems.

The advent of ASM1 introduced the Gujer matrix form of model presentation, which assimilates all the process descriptions in a condensed and elegant way. ASM1 does not incorporate biological phosphorous modelling although the process had already been established prior to the advent of ASM1. However, most of the plant at that time did not incorporate this process and only required predictions of C and N removal, aeration capacity requirements and sludge production. Later, biological P-removal gained importance and was therefore included in ASM2. The understanding of denitrification in the biological phosphorous removal processes evolved further, resulting in ASM2d, which incorporated the processes pertaining to denitrifying PAOs. ASM2d might not have been considered very important if only carbon and nitrogen removal had been targeted; however, the model played an important role in the understanding of the complexity of combined nitrogen and phosphorous removal processes (Henze *et al.*, 2000). Its practical application was hampered by the large number of parameters in the model. Hence, in the mean time, ASM1 continued to be the state-of-the-art model for dynamic modelling in wastewater engineering, despite certain defects that became apparent in its application, e.g. no nitrogen and alkalinity limitations for heterotrophic bacteria were included, no differentiated decay rates of nitrifiers under aerobic and anoxic conditions were considered and intracellular storage of PHAs was not addressed. The introduction of ASM3 (Gujer *et al.*, 1999) aimed to correct the defects of

ASM1 and presented a new standard for ASM based modelling. The original ASM3 did not incorporate biological P-removal (unlike ASM2 or ASM2d), chemical precipitation, growth of filamentous organisms or pH calculations. However, these processes can be connected as add on modules (Henze *et al.*, 2000). One example of this is the extended ASM3 for biological P-removal (Rieger *et al.*, 2001).

The process descriptions of anaerobic processes are not part of ASM1/ASM3. Their application is limited to (aerobic) ASP with possible extension to include the anoxic conditions and (partial) anaerobic reactor integration (for Bio-P processes only). For a complete description of anaerobic processes, other models such as the anaerobic digestion model (ADM) are used, which are not the part of current review.

The assumptions underlying the ASMs related with influent fractions might no longer be applicable when industrial wastewaters are mixed; various facets of influent fractionation are outlined in the section 3.2.

3.3 Application of unmodified ASMs to MBR processes

The objective of this section is to give a concise overview of the application of unmodified ASMs. The terminology "unmodified" should be interpreted in terms of modelling scope as well as model structure. Unmodified ASM models are to be used for modelling MBRs when objectives are similar to those originally stipulated for the use of ASM for CAS systems (Henze *et al*., 2000): process design, effluent characterization, oxygen demand and sludge production. In these cases, plain ASM models are used. The section includes efforts where plain ASMs were calibrated for MBR or where slight modifications to bio-kinetic processes were performed using solely the state variables defined in the original ASMs. This section includes the models that are closest to being applicable in practice and is, thus, very useful for end-users. It includes an introduction and treats two important aspects: (i) influent characterization and (ii) determination/calibration of kinetics and stoichiometry.

3.3.1 ASMs application to MBRs

The application of ASMs are presumably meant for ASP operation in the ranges of conventional ASP operating parameters, e.g. SRT range 3-15 d, HRT range of 3-5 hours and MLSS range 1.5 to 4 g/L for completely mixed systems (Metcalf and Eddy, 2003). A recent study on design and operating experience with municipal MBRs in Europe has reported the ranges of various parameters (Itokawa *et al.*, 2008). The HRT of 13 MBR plants have been reported to be in the range of 2.8 to 8.1 hours, with most of the plant operating at HRT between 4 to 6 hours. The MLSS of 11 MBR plants have been reported to be in the range of 7 to 13.5 g/L, with most of the plant operating at MLSS higher than 10 g/L. Further, the SRT values of 7 plants have been reported to range between 15 and 40 days. For municipal MBR

applications, it seems reasonable to define the SRT below 15 days as “low SRT range”, and SRT above 40 days as “high SRT range”.

Efforts have been made over the last 15 years towards appropriate application of ASMs for MBRs. While early trials (Chaize and Huyard, 1991) used the very basic form of ASM1, using default parameter values, performing no systematic calibration or influent characterization, recent efforts have presented various aspects of systematic calibration of key and sensitive parameters along with emphasis on the influence of influent wastewater characterization in terms of various ASM based fractions (Delrue *et al.*, 2008; Spèrandio and Espinosa, 2008). The early study of Chaize and Huyard (1991), based on a laboratory scale MBR fed with domestic wastewater, aimed to model effluent COD, TKN and sludge production at two HRT values (viz. 8h and 2h) and very high SRT (nearly 100 d). The MBR system was modelled with ASM1 using default values of parameters (Henze *et al.*, 1987). The predicted effluent COD was reported to be slightly lower than that observed, and the predicted TKN was found quite close to the observed value. However, the major disagreement was reported on solids concentration. The model predicted a lower solids concentration than observed, and the solids concentration prediction was relatively better at higher HRT. The probable reason was thought to be the very high SRT (i.e. 100 days). These outcomes illustrate that a non-calibrated ASM1 is able to give a reasonable estimate of effluent COD and TKN, but is insufficient for very low HRT and very high SRT systems. Hence, this imposes care in the application of those models and in the investigation of appropriate parameter sets valid for these systems under variable operational conditions. This sets the scene for investigating the whereabouts of the encountered limitations.

The application of ASM1 moved towards better understanding of model parameters and, hence, a more systematic calibration, taking into account the nature of the MBR biology and specific operating conditions. The ASM1 application on side stream MBR by Jiang *et al.* (2005) stressed the importance of various sensitive bio-kinetic parameters and influent wastewater characterization. More recently, Delrue *et al.* (2008) commented that despite some difficulties, ASM1 is suitable for modelling MBR plants if influent characterization and systematic calibration of aeration can be taken care of.

The incorporation of storage phenomena (Krishna and van Loosdrecht, 1999; Gujer *et al.*, 1999) is a unique feature of ASM3 and might play a role in the case of MBRs on account of possibilities of low organic load conditions (Wintgens *et al.*, 2003). Nevertheless, ASM1 has been shown to be sufficient where conditions are not favourable to storage phenomena (Delrue *et al.*, 2008). In the aim of modelling MBRs over a large range of SRTs, Spèrandio and Espinosa (2008) used ASM1 and ASM3 and commented that ASM models could provide satisfactory prediction of aerobic biological processes in submerged MBRs, although these could be improved for high SRT conditions.

Studies so far are not conclusive as to whether ASM1 or ASM3 is better for MBRs. It appears that the application of ASMs, in their original forms, often needs careful calibration of parameters, especially for sludge production and nitrification modelling. The issue of the significance of high SRT, which was a matter of further attention even in early MBR modelling studies (Chaize and Huyard, 1991), remains a relevant point. It has been reasoned in recent research (*inter alia* Masse *et al.*, 2006; Spèrandio and Espinosa, 2008) that high SRT operation of MBRs is linked with corresponding influence on MBR specific sludge production and autotrophic biology. Throughout, it can generally be observed that all the recent efforts aiming at an accurate biological modelling of MBRs focus on MBR specificities (e.g. high SRT operation, membrane retained microbial metabolites etc.) and the corresponding parameter adjustment and modifications required in ASMs.

3.3.2 ***Influent fractionation for unmodified ASMs***

The monitoring practice for municipal WWTPs typically relies on collecting influent and effluent wastewater samples to assess the inlet organic and nutrient loading and the impact on the receiving water body. However, when process modelling is carried out, a more detailed characterization of feedwater COD is needed, which supplies the modeller with information about the degree of biodegradability (readily, slowly and inert) and the physical aggregation state (soluble, particulate) of the influent substrate. Generally, two different approaches are reported in the MBR-modelling literature for COD characterization: (i) integration of chemical/physical/biological methods and (ii) application of *"trial-and-error"* procedures which aim to fit experimental observations (i.e. MLSS in the biotank) with model simulation by tuning the different COD fractions in a reasonable range of values. In the following subsections inferences from these two different approaches are presented and discussed.

Experimental measurement of influent COD fractions in MBR studies

Jiang *et al.* (2005) compared two methods for wastewater characterization to calibrate ASM1 in a side-stream MBR (sludge age ~20 days, HRT ~8 hours). The first method (also referred to as "chemical-biological") combined the respirometric technique proposed by Vanrolleghem *et al.* (1999) and physical separation (filtration on 0.45 µm fiberglass paper). First, the 0.45 µm filtration was carried out to quantify soluble versus particulate COD. Once assessed, the soluble and particulate biodegradable COD (S_S and X_S respectively) were determined with a respirometric test (S_0/X_0 = 1/200). By assuming the soluble inert fraction of influent COD (S_I) to correspond to 90% of effluent COD (according to Vanrolleghem *et al.*, 2003), the authors determined the inert particulate fraction (X_I) as the difference between $COD_{tot,IN}$ and ($S_S + S_I + X_S$). In order to evaluate the effectiveness of this method, a trial-and-error procedure was also used to determine X_I and X_S, by comparing a steady-state COD mass-balance with measured and simulated MLSS concentration in the biotank. The two methods provided very close

results (~ 2.7% on X_S value). The second approach applied by the authors ("physical-chemical method") used the STOWA protocol for wastewater characterization (STOWA, 1996; STOWA, 1999, Roeleveld and van Loosdrecht, 2002) and coupled physical separation (0.45 µm) with BOD analysis. The soluble inert COD (S_I) in the influent was calculated as 90% of soluble effluent COD and soluble biodegradable COD (S_S) was given by the difference ($COD_{sol,in} - S_I$). Then, biodegradable COD ($COD_b = S_S + X_S$) was calculated as a function of BOD_5 and X_S was calculated from COD_b and S_S; finally, X_I was determined as the difference between $COD_{tot,IN}$, S_I, S_S and X_S. The mean results of the wastewater fractionation on 16 influent samples are summarized in Table 3.1.

Table 3.1: Comparative evaluation of the two methods for wastewater characterization. Total COD: 579 g m^{-3} (adapted from Jiang et al., 2005)

Parameter	Chemical-biological	Physical-Chemical
	(g m-3)	(g m-3)
SI	33 (5.7%)	33
SS	214 (37.0%)	228
XI	58 (10.0%)	141
XS	274 (47.3%)	177

The most significant difference between the two approaches occurred in the X_I fraction, which was significantly higher when determined with the "physical-chemical" method compared to the "chemical-biological" one. This discrepancy reflected a relevant over-estimation of the MLSS concentration in the biotank for the "physical-chemical" method under steady-state conditions (13245 g m^{-3} for the physical-chemical method *versus* 10020 g m^{-3} experimentally measured).

A bench-scale MBR (0.016 m^3) was modelled by Spérandio and Espinosa (2008) with ASM1 and ASM3 over a wide range of sludge ages (10÷110 days), with special focus on wastewater characterization and excess sludge. During the four experimental periods, a combined physical-biological method was used for influent wastewater fractionation: the non-biodegradable soluble COD (S_I) was assumed to be equal to the effluent COD, the inert particulate COD (X_I) was measured at the end of long-term BOD measurement (30 days), the slowly biodegradable (X_S) and readily biodegradable COD (S_S) were obtained by combining respirometry (Spèrandio and Paul, 2000) and 0.45 µm filtration. The simulated MLVSS trend indicated that ASM1 was able to predict sludge production at SRTs shorter than 50 days, while an overestimation was observed at SRT = 110 days. In contrast, an underestimation is reported by the authors in the application of ASM3 at SRT values of 10 days and 30 days, and a slightly better

prediction of the MLVSS concentration at 110 days. According to the authors, most of the discrepancy between the ASM1 model and the experimental observations is due to the large quantity of non-biodegradable organic particulate matter (X_U) related to the death-regeneration concept, which is replaced by the endogenous decay concept in ASM3. In terms of surplus sludge production (expressed as Y_{obs}) the work points out that, the longer the SRT, the more relevant the impact of the inert fraction in the influent feedwater (X_I) on the sludge composition. Therefore, the authors recommend introducing a slow hydrolysis mechanism in the standard ASM1 and ASM3 to correctly predict sludge production at very long SRT. This also matches the conclusion of other groups (Rosenberger *et al*., 2000; Rosenberger, 2003), who demonstrated that, for SRTs above 80d, an hydrolysis factor could be used to better simulate the MBR sludge production. Witzig *et al*. (2002) later demonstrated that there was actually no hydrolysis at high sludge age, but that the bacteria went into maintenance mode and did not grow any more, mathematically impacting the sludge yield in a similar way to hydrolysis (Drews *et al.,* 2005). This fact, known for pure cultures, was shown to be also applicable for mixed cultures in activated sludge.

In a recent work, a small pilot-scale MBR (sludge age ~36 days) was modelled by Sarioglu *et al.* (2009) with a modified ASM1 to describe the simultaneous nitrification-denitrification process. All the growth and decay processes were coupled with switching functions defining the diffusion limits of oxygen and substrate. A combined physical-chemical-biological method was used for COD characterization; the biodegradable COD (COD_b) was determined according to Roeleveld and van Loosdrecht (2002), while the S_I and X_I fractions were measured according to Germirli *et al.* (1991) and Orhon *et al.* (1999) respectively. Once S_S was calculated as the difference between influent soluble COD and S_I, the X_S fraction was determined by mass balance. This calibration resulted in a fairly good fit of MLVSS and MLSS in the biotank.

A respirometry-based approach for wastewater fractionation has been reported by Guglielmi *et al.* (2009), who calibrate an extended version of ASM3 that includes the simultaneous growth of heterotrophs on both storage products (X_{STO}) and readily biodegradable substrate (S_S), originally proposed by Sin *et al.* (2005). The model has been successfully validated in terms of sludge production under dynamic conditions on a large pilot-scale MBR run under an SRT of 20÷25 days. In detail, the total biodegradable COD was determined according to Ekama and Marais (1986), whereas the soluble biodegradable COD was estimated according to the single-OUR method proposed by Ziglio *et al.* (2001), with sodium acetate as standard. Afterwards, S_I was calculated as the difference between filtered COD in the influent (0.45 μm) and the soluble biodegradable COD, being usually equal to 90-95% of COD concentration in the permeate. Finally, X_I was quantified with a mass balance.

"Assessment of influent COD fractions with trial-and-error methods in MBR studies"

When ASM-modelling tools are used for process optimization in a full-scale installation, there is typically a general tendency towards "*trial and-error*" procedures.

In the application of ASM1 to a full-scale MBR in Guéthary, France (10,000 PE, 1,600 m^3 d^{-1}; SRT = 30÷60 days; F/M = 0.02÷0.05 $kgBOD_5$ $kgMLVSS^{-1}$ d^{-1}), Delrue *et al.* (2008) compared three different methods for soluble/particulate fractionation, namely filtration on fiberglass filter, 0.1 µm membrane filtration and coagulation-flocculation followed by a 0.1 µm filtration. Then, in order to divide COD into biodegradable/non-biodegradable organic matter, the method proposed by Roeleveld and van Loosdrecht (2002) was compared with a trial-and-error procedure based on MLVSS steady-state mass balance (fitting method). In their conclusion, the combination of fiberglass filtration and MLVSS fitting was chosen as the most reliable protocol for influent COD characterization.

A model-based optimization of a full-scale MBR was carried out at Rödingen, Germany (Erftverband, 2001), in which the influence of the weather conditions on the COD fractionation was described. The plant (3,000 PE, SRT ~ 25 days; combined sewer) was modelled in ASM1 and calibrated by means of a trial-and-error procedure on the observed sludge production over two different periods (57 and 28 days). A comparative evaluation of inert fractions (S_I and X_I) is shown in Table 3.2, with an increase of both non-biodegradable components during rainy events. The catchment area of the MBR was small but widely ramified and the sewer had only a mild slope so that effects of run-off, the flushing out of deposits and dilution by the rain water were very pronounced and produced a visible effect on the plant. Unlike what is observed in CAS modelling, the need for a more frequent calibration of influent COD fractions was reported by the authors, due to the shorter HRT and reduced buffering volume.

Table 3.2: Results of the COD fractionation of a large scale MBR working on combined sewer influent (Erftverband, 2001)

	Dry weather	Rain weather
XI, % of COD	20	40
SI, % of COD	8	15

Outlines

Summing up the inferences for ASM applications to MBRs, the available literature highlights the crucial role that design/operational SRT plays in influent COD characterization. Particularly, the actual operational sludge age can influence the choice of a proper method for the determination of X_S and X_I fractions since at very long SRT a slow but significant hydrolysis of the "inert" fraction takes place. From the modelling point of view, this results in a general overestimation of the sludge production. This issue is strictly related to the biodegradability concept itself, which depends not only on the substrate characteristics and the substrate/biomass affinity but also on the time available for biological degradation. In terms of practical process design and operation, this aspect has great relevance for MBR installations with noticeable seasonal fluctuations of the influent organic loading (e.g. tourist areas), where SRT can increase up to 50-60 days or more. In this case, a trial-and-error method tuning X_S and X_I seems more appropriate. On the other hand, when operating at more conventional sludge ages (<30÷40 days), respirometry-based fractionation seems to be able to provide satisfactory characterization.

3.3.3 ***Process kinetics and stoichiometry***

Next to influent characterization (previous section) and module structure (unaltered in this case), kinetic and stoichiometric parameters provide degrees of freedom for matching ASM model predictions with experimentally collected data.

The standard ASM models come with default parameter values, obtained from wide experience at both lab-scale and full-scale. However, the inclusion of membranes in activated sludge systems may cause associated changes in these default kinetic parameters compared to CAS systems. The main effects on process kinetics are possibly due to (i) specific biomass selection (high SRTs, free bacteria retention), (ii) high biomass concentration, and (iii) high hydrodynamic constraints imposed by continuous or cyclic air scouring of the membrane element instead of quiescent conditions in the settler. The crucial parameters for design and control of MBRs are: the sludge suspended solids (X_{TSS}) impacting the excess sludge production and the oxygen transfer rate (α-factor), the removed and residual nitrogen species (S_{NH}, S_{NO}), the residual phosphorus concentration (S_{PO4}) and the oxygen consumption rate (OUR, and S_O).

In the next subsection, the parameter sensitivity will be primarily discussed. The following subsections will look more deeply at the impact of MBR on the kinetics of the different processes.

Parameter sensitivity in MBR vs CAS

Given the similar nature of the process, it would be reasonable to think that the influence of most kinetic constants is comparable in CAS and MBR processes. The reasons pointed out above might, however, lead to different system behaviours. During the calibration exercise, sensitivity analysis can help by assessing the most influential parameters for a given process and biological reaction (sludge production, uptake of COD, denitrification and nitrification). The results of such a sensitivity analysis for ASM1 applied to an MBR are given in Table 3.3. Relative sensitivity functions (RSF) were calculated by Jiang *et al.* (2005) for several model variables (Y) towards all model parameters (θ), as described by the equation (i).

$$RSF = \frac{\theta}{Y}\frac{dY}{d\theta} \qquad \text{(i)}$$

RSFs rescale the sensitivity function in order to allow easy comparison and fair ranking accounting for different orders of magnitude in parameters and variables. Ranking is done according to the absolute values of RSF as shown in Table 3.3. A finite difference approach is typically used to compute the derivative.

The influent wastewater characterization, with particular regard to X_I, X_S, S_S and S_{NH} fractions, appears to be extremely influential on MLSS concentration and effluent quality, which confirms the importance of the previous discussion (Section 3.2). The stoechiometric parameter (Y_H) and kinetic parameters (b_H, b_A, μ_{maxH} and μ_{maxA}) are very to moderately influential on the MLSS concentration and effluent quality, whereas the remaining parameters do not seem to be candidates for change when performing a calibration.

Petersen *et al*. (2002) used the same sensitivity function applied to CAS (with an SRT of 8.6 days). The most influential parameters were the same as for MBR but with different degrees of importance. Kinetics parameters (K_{OA}, K_{NH} and kh) which had no influence in Jiang *et al.*'s (2005) model became moderately to very influential, depending on process operational conditions. In fact, Jiang *et al.* (2005) studied the local parameter sensitivity in a model calibrated for a specific case, with specific operating conditions (SRT=20 days, DO range=3-8mg/l). At different operating conditions, the sensitivity of the parameters might change. That is why sensitivity analysis is systematic and necessary in every calibration exercise. An alternative to this approach is the use of global sensitivity analysis which explores the entire parameter space and yields average sensitivities (and not just locally around a single point in this space), as performed by Benedetti *et al. (2008),* with an ASM2 model for BSM2 (Benchmark Simulation Model no.2). Global methods are, however, always more computationally expensive and interpretation of their results also needs scrupulous care.

Nitrification kinetics

As autotrophic bacteria are very sensitive to the environmental conditions, the impact of including membranes for the solid-liquid separation on the kinetics of nitrogen removal has received considerable attention. Ammonium consumption and residual concentration is sensitive to nitrification parameters, in decreasing order of influence: μ_A, b_A, K_{NH}, K_{OA} and Y_A (Jiang *et al.*, 2005). In ASMs, the nitrification rate is controlled by the concentration of active autotrophic bacteria (X_{aut}) stabilized in the process, which is imposed by the conversion yield Y_A, the influent nitrifiable nitrogen, and the decay rate b_A. The nitrification rate is basically linked to the product $\mu_A X_{aut}$. For this reason, the parameters b_A and μ_A are highly correlated and it is impossible to identify them simultaneously if the active biomass is not stabilized at different levels, i.e. data should be collected at different SRTs in a continuous process (Spèrandio and Espinoza 2008).

Munz *et al.* (2008) highlighted the difference between the ammonium-nitrogen concentration in CAS and MBR effluents (both with 50 days SRT): for MBRs the nitrification was more stable and complete. In the same way Parco *et al.* (2006) found a specific autotrophic uptake rate for MBR 1.8 times higher than for conventional Biological Nutrient removal (BNR). By operating CAS and MBR in the same conditions (SRT), Manser *et al.* (2005) did not observe any significant difference in the maximum specific ammonium uptake rate but authors showed that the ammonium uptake rate became higher in MBR compared to the CAS during transient shock loads, especially at low temperature and relatively low DO (dissolved oxygen).

The difference between nitrifiers in MBRs and CAS may depend on cumulative factors such as: (i) the different micro-organism selection (not demonstrated); (ii) the higher bio-availability of substrates which can be due to the smaller size of flocs (Manser *et al.*, 2005); and (iii) the tendency of nitrifiers clusters to grow at different places in the flocs or with lower density (presence of Ammonia Oxidizing Bacteria aggregates on the surfaces of MBR flocs was observed only by Munz *et al*. 2008). These findings might however also depend on a different mass balance, i.e. higher autotrophic biomass concentration can be maintained by a better retention of solids (for example, it is clear that solids loss in the activated sludge can contribute to a more or less significant decrease of nitrifiers depending on the SRT). In this sense, to better understand this section, the reader must consider that lower affinity constants or higher growth rates do not necessary mean higher removal rates, since the nitrification mass balance must be taken into account entirely.

Several authors have found discrepancies when modelling MBR processes with ASM1 using the initial default values of Henze *et al.* (1987) for nitrification (Jiang, 2007; Spèrandio and Espinoza, 2008). Spèrandio and Espinoza (2008) used ASM1 and ASM3 to calibrate an MBR working at a large range of

SRT, through the parameters μ_A and b_A. The authors reported that ASM1 default values (0.8; 0.04d^{-1}) overestimated ammonia removal for all the SRTs studied, whereas ASM3 (1, 0.15d^{-1}) gave better results but minimized the SRT influence. The data obtained from this study led to a μ_A = 0.45 d^{-1} and b_A=0.04 d^{-1}. Autotrophic growth rate is known to be variable from one process to another even for activated sludge processes. This means that more data will be necessary to conclude on the best set of parameters for MBR, i.e. μ_A should be measured properly in future works on MBR. Since this parameter is bacteria-specific, an analysis of microbial species (AOB, NOB) by molecular techniques in MBRs would probably help in interpreting the observed changes in μ_A.

		Units	Experimental Methods references	Default ASM1	Jiang 2005	Spèrandio 2005	Manser 2005	Jiang 2007	Sarioglu 2008	Delrue 2008	Jimenez 2008	Erftverband 2001, 2004	RWTH 2008	Range of values
	Model				ASM1	ASM1-ASM3	ASM1	ASM2d	ASM1 endogenous decay model	ASM1	ASM1 modified	ASM1	ASM1	
	SRT	d			20	10-110	20		38	30-60	15			
Nitrification	μ_{maxA}	d-1	[2], [5]; [7], [8], [6],[10]	0.8		0.45			1		0.8			0.45-1.00
	ba	d-1	[1], [5], [7], [8], [10]	0.05-0.15	0.08	0.04		0.055	0.06		0.15			0.04-0.15
	K_{NH}	mgN-NH_4/l	[8], [10]	1		0.25-0.6		0.2	2	1	1	0.1		0.10-2.00
	K_{OA}	mgO_2/l	[4], [8], [9], [10]	0.4			0.18	0.2	1.25	1	0.25			0.18-1.25
	Y_A	gCOD/gN	[3], [8]	0.24	0.25									0.24
Denitrification / COD oxydation/ Sludge prod.	$\%X_I$	% COD		15						17.5	15			-
	Y_H	gCOD/gCOD	[3], [8]	0.67	0.72				0.66			0.67	0.52-0.92	0.63-0.67
	b_H	d-1	[2], [4], [8]	0.62	0.25			0.4	0.24				0.03-0.47	0.24-0.4
	$K_{O,NOB}$	mgN/l	[9]	0.5			0.13		2	1				0.13-2
	K_{OH}	mgO_2/l	[4], [8]	0.2			0.05		1	0.22	0.1			0.05-1
Comment	Jiang, 2005: Y_H with acetate addition overestimated, inducing an underestimation of fp. Spèrandio, 2005: Assessment of (μ_a, b_a) valuable in a large range of SRT. Manser, 2005: Accurate estimation of K_{OA}: Correlation with floc size distribution. Jiang, 2007: Biological P removal calibration (cf. paragraph P removal). Sarioglu, 2008: Specifically adapted for modelling simultaneous nitrification-denitrification. Jimenez, 2008: Correlation with floc size distribution. Erftverband, 2001, 2004: Assessment for simulation of timeline over several weeks.													

Table 3.4 Parameter set from the different studies on MBR in urban wastewater treatment: [1] Henze et al. *(1987), [2] Ekama et Marais (1986), [3] Solfrank et Gujer (1991), [4] Kappeler et Gujer (1992), [5] Lesouef et al. (1992), [6] Nowak (1994), [7] Spanjers et al. (1995), [8] Vanrolleghem et al. (1999), [9] Ficara et al. (2000) [10] Van Haandel (2007).*

Concerning the better behaviour of MBRs reported by Munz *et al.* (2008), Parco *et al.* (2006), and Manser *et al.* (2005), an explanation may be offered by the reduction of the half saturation constants K_{NH} and K_{OA}, which directly influence the residual ammonia concentration model predictions.

Regarding the $K_{NH,}$ experiments on MBRs in the literature report values from 0.15 to 1 mgN/l and tend, in some cases, to be lower than the ASM1 default value (ASM default values is 1 mgN/l), leading to an improvement of ammonia transfer (Delrue *et al,* 2008; Spérandio *et al.*, 2005; Jiang*, et al.* 2009; Jimenez *et al.* 2008; Erftverband 2001, 2004). A parameter set from the different studies on MBRs in urban wastewater treatment is reported in Table 3.4. On the other hand, Manser *et al.* (2005) reported observed K_{NH} values lower than ASM1 default values but similar for CAS (0.14 mg N/l) and MBR (0.13 mg N/l), concluding that the limitations induced by larger floc density were not that significant for ammonia transfer. It should also be noted that K_{NH} also varied significantly from one activated sludge to another (Spérandio and Espinoza, 2008).

The K_{NH} value seemed to be linked to internal transfer resistance but also to external mass transfer resistance. K_{NH} was reported to change from 0.3 to 0.6 when MLSS increases from 3 to 8 g/l, pointing to an increase of viscosity (Spèrandio *et al.*, 2005, Sarioglu *et al.,* 2009) and an increase of external transfer resistance. When MLSS increased, ammonia uptake rate (AUR) and μ_A decrease indicating a concentration effect (Pollice *et al.*, 2008; Ramphao *et al.,* 2006). Parco *et al.* (2006) explained that the MLSS effect is related to ammonia diffusion limitations and not to DO transfer limitation

Regarding K_{OA}, ASM1 models fitted to respirometric data resulted in a K_{OA} range of 0.18 to 0.4 mgO_2/L in MBR (Spérandio *et al.*, 2005, Jiang, 2007, Jimenez *et al.* 2008) and tended to be lower than the ASM1 default value of 0.4 mgO_2/l. A parameter set from the different studies on MBRs in urban wastewater treatment is reported in Table 3.4. Manser *et al.* (2005) showed that values differed significantly from MBR to CAS. In detail, he observed lower K_{OA} values for MBR (0.18 mg O_2/L) in comparison with the CAS (0.79 mg O_2/l) and explained this variation with the lower transfer resistance induced by MBR smaller floc size (which became negligible for floc sizes under 100 μm). Similar conclusions have been drawn in other studies (Jiang *,* 2007; Jimenez *et al.*, 2008) as shown in Table 3.4 and 3.5. Jimenez *et al.*, (2008) observed that K_{OA} had a very high sensitivity to nitrification (based on RSF results) when DO concentration was lower than 2 mg/l and average floc size was lower than 35 μm.

However, it is not always obvious that floc sizes are lower in MBRs than in CAS, since they depend on the hydrodynamic conditions and on the type of aeration (intermittent or continuous). An inverse tendency was obtained by Spèrandio *et al.* (2005), who reported results indicating that an sMBR can have larger flocs and larger values for $K_{NH,}$ if aeration and shear stress are limited. Similar results were recently found by Sarioglu *et al.* (2008, 2009). On the other hand, floc size is also influenced by SRT

(Masse, 2004). This author showed that an SRT increase from 9 to 106 days led to a diminution of the average floc size in the MBR from 240 to 70 μm. Deflocculation of biomass could be due to the increase in aeration when MLSS increases, or to the reduction of F/M ratio, leading to the decrease in the active fraction of the sludge (Spèrandio *et al.*, 2005).

Therefore, although there is a tendency in MBRs to find a value for the half saturation constants, K_{OA} and K_{NH}, lower than the ASM1 default values, these parameters depend on the operating conditions (SRT, MLSS concentration, viscosity, oxygen concentration, floc size distribution).

Concerning the autotrophic decay rate (b_a), Manser *et al.* (2006) did not find significant differences between CAS and MBR concerning the ammonia oxidizing biomass (AOB), but a slight difference concerning the nitrite oxidizing biomass (NOB): AOB b_a was found to be $0.13d^{-1}$, both in CAS and MBR, while the NOB b_a was $0.28d^{-1}$ and $0.17d^{-1}$ for CAS and MBR respectively.

The conversion yield Y_A does not seem to be influential (see Table 3.3) but can become relevant when dissolved oxygen sensitivity is studied under dynamic conditions (Jiang *et al.*, 2005). Moreover, this parameter was measured by Jiang *et al.*, (2005), yielding the value (0.25 gN/gCOD), close to the ASM default value (0.24gN/gCOD).

In order to obtain a clear independent estimation of nitrification parameters, tailored batch tests are suggested. Substrate excess or substrate absence conditions would be necessary to respectively determine μ_A and $b_{A,}$ (Henze, 1992; Vanrolleghem *et al.*, 1999, Lesouef *et al.*, 1992) while batch tests with substrate addition at various oxygen concentrations would be necessary to estimate the oxygen half-saturation constant (Kappeler and Gujer, 1992, Ficara *et al.*, 2000). Y_A and K_{NH} could be estimated with ammonia addition in batch tests, as in methods described by Vanrolleghem *et al.* (1999), Van Haandel *et al.,* (2007).

Table 3.5: Bio-kinetic parameters and size distribution found in MBR modelling literature. N.d. : not determined. SNdN : simultaneous nitrification and denitrification

	Mean floc size	K_OA	K_OH	K_O,NOB
	(µm)	gO_2/m^3	gO_2/m^3	gO_2/m^3
ASM1		0.40	0.20	0.50
Manser et al. (2005)	35	0.18	0.05	0.13
CAS (Manser at al., 2005)	307	0.79	0.16	0.47
Jimenez et al. (2008)	35	0.25	0.10	-
Jiang et al. (2009)	30-50	0.20	0.20	0.17
Sarioglu et al. (2008) SNdN	N.d.	1.25	1.00	-
Sarioglu et al. (2009) SNdN	N.d High viscosity (SVI=800-1000ml/g)	2.00	1.75	

Denitrification kinetics

Nitrate concentration in the bioreactors and in the effluent depends on both nitrification and denitrification. It is dependent on the nitrified nitrogen, which is linked to the amount of nitrogen entering the system and indirectly to the amount of nitrogen assimilated into the sludge. But more significantly, removal of nitrate depends on the amount of easily and slowly biodegradable substrate used for denitrification (Xs, Ss), and also the heterotrophic yield Y_H (Jiang *et al.*, 2005).

Obviously the residual nitrate also depends on denitrification kinetic parameters. However, the higher the SRT, the more sensitive the denitrification rate will be to total biodegradable COD (Xs+Ss) and to the endogenous respiration. Specific denitrification rates are extremely dependent on SRT via mass organic load (denitrification rates measured in MBRs are often very low at high SRT) and consequentially design guidelines (Pinnekamp, 2006) recommend a ratio volume aerated / volume anoxic of 50/50%, whereas it could be at least 75/25% in CAS.

Denitrification rates were measured by Parco *et al.* (2007) for an MBR in UCT configuration (20 days SRT and a mass load of 0.14 gCOD/gMLSS.d). Conventional denitrification rates of 0.25 $mgNO_3/mgSS.d$ (similar to CAS) were obtained. The authors concluded that kinetic parameters for denitrification could

be applied directly to MBR BNR systems. From these results, the conclusion is that the reduction factor for anoxic growth (ηg), and the anoxic heterotrophic yield (Y_{HD}) are probably not different in MBR compared to CAS. In contrast to the nitrification process, denitrification is apparently less modified by the membrane configuration. However, half-saturation constants (K_{NO}, K_{OH}) which control the effect of low concentrations of nitrate or oxygen on the kinetics have not been specifically determined yet for MBR. As for the nitrification, Manser *et al.* (2005) showed that floc size distribution had an influence on oxygen transfer and consequently on oxygen transfer in the denitrification zone. In fact, some MBR configurations present sludge recirculation from the aerated membrane tank to the denitrification zone and, hence, the level of dissolved oxygen has an important effect on denitrification potential (Sarioglu, 2008). The dissolved oxygen level can inhibit denitrification in anoxic growth reaction modelling, through the parameter K_{OH}. Manser *et al.* (2005) found in MBRs, a K_{OH} value of 0.05 mgO_2/l, lower than the 0.16 mgO_2/l for a CAS process working at the same conditions. However, this parameter also depends on system hydrodynamics and configuration.

Phosphorus removal kinetics

From an extensive study on an MBR UCT process, Parco *et al.* (2007) concluded that kinetic parameters for biological P-removal are comparable in MBR and CAS. The anaerobic P-release and acetate consumption rates, and the anoxic and aerobic P uptake rates were very close to the range of values in the literature for conventional BNR systems with mixed cultures. Moreover, the rates obtained for different concentrations of volatile suspended solids (VSS) indicated no effect of the sludge concentration on these rates. Acetate consumption rates were zero order with respect to acetate concentration in agreement with the studies in the literature. Aerobic and anoxic P-uptake rates indicate a relatively low fraction of denitrifiers in the PAO biomass (X_{DNPAO}/X_{PAO} was around 15 to 36 %).

Jiang *et al.* (2008) used ASM2d to predict phosphorous removal. With default parameters, the model overestimated nitrate concentration while underestimating phosphorous concentration. The authors calibrated the model simultaneously reducing S_A production in the anaerobic compartment and the aerobic/anoxic phosphorous uptake rate (q_{fe} =1d^{-1}, q_{pp} =1.1 d^{-1} and $\eta_{NO3,PAO}$ =0.4), by trial and error. However, it should be noted that, after including the SMP concept, these parameters could be restored to default ASM2d values.

Recently, MBR research at full-scale (Silva *et al.,* 2009) showed that unexpected high biological phosphorous removal was obtained in MBRs not designed for enhanced biological phosphorous removal (EBPR). In the full-scale MBR located in Schilde (Belgium), significant biological P removal was reported though the process scheme did not contain anaerobic compartments, effluent nitrate concentration was generally higher than 3 mg/l, and no dead zones were identified during a CFD study (Bixio *et al.*,

2006; Fenu *et al.*, 2010). Silva *et al.,* (2009) explained this phenomenon by the high floc compactness and density of EPS inducing anaerobic micro-niches. The higher sludge viscosities in MBR systems (when compared to CAS systems), might also impede mixing and hydrodynamic homogeneity, creating artificial local anaerobic zones. These assumptions have not been fully demonstrated and need further investigation.

Oxygen uptake rate (OUR)

The dynamics of the oxygen uptake rate (OUR) are generally considered sensitive to kinetic parameters. For example, a highly loaded period can result in Xs accumulation, whereas during low loaded periods hydrolysis of these slowly biodegradable compounds controls the OUR dynamics (Ekama and Marais, 1986). However, in MBR processes this conclusion is no longer valid during very low-loaded operation (high SRT). In that condition, the actual oxygen uptake rate (instantaneous oxygen demand) varies mainly with the flux of biodegradable substrate (Ss, Xs and S_{NH}) entering the system. The stoichiometric parameters (Y_H, Y_A) are then more important than the kinetics, as no Xs, Ss or S_{NH} accumulation is normally observed in that condition.

Oxygen transfer rate (α-factor)

The α-factor is defined as the ratio of the volumetric transfer coefficient under process conditions (i.e. with mixed liquor) to the clean water transfer coefficient. This is therefore a normalized parameter depending primarily on the mixed liquor characteristics. Together with the hydrodynamic conditions (such as aeration types and powers), it determines the standard aeration efficiency (SAE) of aeration systems (Krause and Cornel, 2007) (figure 3.1). In these respects, the energy efficiency of activated systems can be described as inversely proportional to the α-factor, and the modelling of the biological aeration demand in MBRs should account for the effect of specific process conditions on the α-factor.

The α-factor is mainly influenced by the viscosity of the activated sludge which is associated with the MLSS concentration (Krause *et al.*, 2003 ; Germain *et al.*, 2007). As the viscosity is unknown in many cases, Krause (2005) gives an approximate function of the α-factor versus the MLSS concentration of $\alpha = e^{-0.056MLSS}$ for the design of municipal MBRs. As a result, α then equals 0.5 for an MLSS concentration of 12 g/L.

Actually, a bandwidth of values can be found. However, the lower α-factor in MBR applications constitutes a significant difference compared with the CAS processes: while for an MLSS concentration lower than 5 g/L the α-factor may be in the range 0.7-1, it drops to a value of about 0.5 for 10 gMLSS/L

and may go down as low as 0.2 for 20 gMLSS/L. Despite this, other factors also contribute to this behaviour. Results from Germain *et al.* (2007) suggested that bound carbohydrates and soluble COD also had a secondary impact on the α-factor : α -factor increased with increasing bound carbohydrates (facilitating the formation of large flocs), and decreased with increasing soluble COD (probably due to the presence of surfactants), although with specific impact about half of that generated by the MLSS concentration. Note that the parameters of bound proteins, bound COD, soluble carbohydrate, soluble protein, and mass median diameter of the floc were monitored but not identified as variables having a significant influence on α-factor within the range of parameters studied.

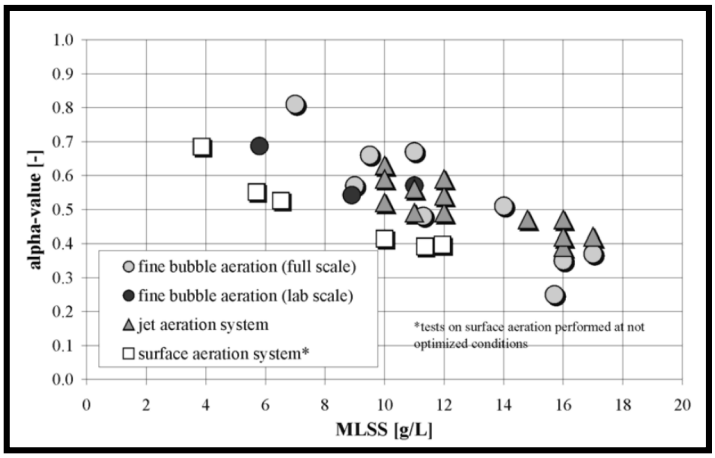

Figure 3.1: alpha-value in dependence of MLSS concentration in activated sludge of MBR systems (Krause and Cornel, 2007).

Sludge production

Total sludge suspended solid concentration and excess sludge production are clearly of great importance in WWTPs. A realistic prediction of the concentration of active components (X_{HET}, X_{AUT}, X_{PAO}) is in fact crucial for dynamic simulations.

MBRs systems are run at average to very high SRTs. In these operating conditions, suspended solids are mainly composed of inert particulate matter, originating from both influent and biomass decay. High SRTs increase the amount of energy spent on maintenance rather than on growth, and average biomass concentration notoriously increases, due to the reduced quantity of biomass wasted. In aerobic zones, specific OUR will decrease as a result of inert compounds accumulation and reduction in the active fraction of biomass (Tan *et al.*, 2008).

Moreover, in MBR systems operated at very high SRTs, biodegradation of COD fractions, considered inert in ASMs as described in the previous sections, induces an overestimation of sludge production. This is definitely a major drawback of ASM models for modelling MBR in a large range of SRTs (Spèrandio and Espinosa, 2008). Changes in the parameters Y_H, b_H and fp can severely modify the predicted X_{TSS} (Jiang *et al.*, 2005; Spèrandio *and* Espinosa, 2008). The experimental estimation of these parameters has been attempted by several research groups and the main outcomes are reported below. Jiang *et al.* (2005) measured the conversion yield of heterotrophs (Y_H) in MBR processes, through respirometric measurement with acetate. The obtained Y_H (0.72 gCOD/gCOD at 23°C) was higher than the default value in ASM1 (0.67 gCOD/gCOD at 20°C), but this higher value is not specific to MBRs and it is probably due to the storage phenomenon with acetate which is easily converted to PHA (Majone *et al.*, 1999; van Loosdrecht and Heijnen, 2002). Y_H values obtained with a single carbon source should be considered with precaution as they are substrate-specific. A similar value can be obtained with acetate as a pure substrate in the activated sludge process. The mean value of 0.63 to 0.67 gCOD/gCOD is then more valuable for domestic wastewater considering the large variety of carbon source (carbohydrates, proteins, alcohols, carboxylic acids…).

Heterotrophic decay rate (b_h) seems to be close to the ASM default value. In a first study, Jiang *et al.* (2005) measured b_H with respirometric tests (Vanrolleghem *et al.*, 1999) and found a value of 0.25 d^{-1}, lower than the default value (0.4 d^{-1}). The authors explained this lower value by the decrease of predation in the MBR. However, in a subsequent study using ASM2, Jiang (2007) used the default value for b_H in ASM2 (0.4 d^{-1}) with a good fit of the mixed liquor COD. Sarioglu *et al.* (2008) estimated b_H = 0.24 d^{-1} (endogenous respiration concept), similar to the value in ASM3.

Modifications of Y_H, b_H, and fp parameters need to be carefully examined as they play a major role in other processes. For example an increase of Y_H would reduce the electron consumption, i.e. oxygen consumption or nitrate removal. For this reason, it is considered preferable to fit X_I, which is logically wastewater specific, rather than other parameters.

Table 3.4 summarizes the parameter set found by the authors who have calibrated MBR systems in urban wastewater treatment. It includes some comments and references to methods.

Outlines

Nitrification parameters seem to be the most affected by the differences between CAS and MBR. However, they depend on both hydrodynamic and operational conditions. It is relatively risky to choose μ_A, b_A, Y_A, and K_{NH} and K_{OA} by combining values obtained from different studies, as the coherence of each

set of parameters is necessary. It is thus recommended to give special attention to these parameters, measuring them with proper methods if necessary.

Denitrification rates seem to be similar to CAS ones, and consequently parameters are not different. An exception is the oxygen half-saturation constant K_{OH} (used as inhibition parameter of oxygen for denitrifiers). This parameter could be affected, depending on the oxygen level in the denitrification zone and the small floc size which could ease the oxygen mass transfer. Moreover, a detailed characterization of the anoxic hydrolysis rate and the endogenous respiration rate is still needed, controlling both the slow and endogenous denitrification rate.

Concerning kinetic parameters for biological phosphorus removal, data and literature are still insufficient on this topic. Phosphorus removal performance in MBRs seems to be slightly better than in CAS in some cases, but data are still needed to demonstrate whether these differences are explained by kinetic parameters of PAO species or different operating conditions (local anaerobic zone in biological tank, absence of anaerobic zone of settlers,…).

3.4 ***Application of modified ASMs to MBR processes***

The objective of this section is to give a concise overview of the application of modified ASMs. The terminology “modified” should be interpreted in terms of modelling scope as well as model structure. This section discusses the following aspect: (i) the impact of the phase separation mechanism on the ASMs (ii) the influent fractionation for modified ASMs (iii) an overview of the EPS and SMP models (iv) an overview of ASM extensions with EPS/SMP concepts (v) the over-parametrization of modified AS

3.4.1 ***Integrating membrane rejection studies in ASM models***

The phase separation mechanism is the main technological distinction between CAS and MBR systems. The mechanism is essentially a sieving effect performed by membranes with a nominal pore size of typically 0.02 up to 0.2 µm: all particles whose size is larger than the membrane pore size are retained, whereas the smaller dissolved fractions are not. Hence, flocs, bacteria, biopolymers such as polysaccharides and proteins, and organic colloids are to a great extent retained. Humic and low molecular weight substances can instead pass the membrane (Drews *et al.,* 2006). The retention of the biopolymers is in fact a specificity of MBR systems compared with conventional ASP.

The above mentioned fractions accumulate in the mixed liquor (*inter alia*, Drews *et al.,* 2007; Malamis and Andreadakis, 2009), and are susceptible of biodegradation. Shin and Kang (2003) report an initiation of the reduction of microbial products at SRTs longer than 10-20 days. This reduction is commonly agreed to be more significant for polysaccharides than for proteins (*inter alia*, Al-Halbouni *et al.,* 2008). With increasing SRTs, a reduction in the molecular weight distribution of the mixed liquor supernatant particles has also been reported (Shin and Kang, 2003; Ng *et al.,* 2006). In contrast, the accumulation of microbial products did not appear to trigger any deviation from the expected biomass metabolic activity (Shin and Kang, 2003).

Current ASM models fail to account for many of these specific MBR features. They neither distinguish between protein and polysaccharide fractions, nor account for shifts in the molecular weight distribution. But it is important to realize that, in systems with low organic loads (such as MBRs), the retained molecules may have a significant impact on the metabolic path, allowing further use of carbon based metabolites (Furumai and Rittmann, 1992). These shortcomings in the current ASM models could be overcome by expanding the models with EPS/SMP concepts.

EPS and SMP definition

EPS are a complex mixture of Proteins (PN), acid, polysaccharides (PS), lipids, DNA and humic acids. They surround cells, create a matrix for microbial flocs and films (Liao *et al.,* 2001) and allow microorganisms to live continuously at high cell densities in stable mixed population communities (Wisniewski, 1996; Laspidou and Rittmann, 2002). They are further differentiated into bound EPS, the fraction bound to the sludge flocs, and soluble EPS, the fraction able to move freely between sludge flocs and the surrounding liquor (Rosenberger and Kraume, 2002). As it is difficult to differentiate between SMP

and soluble EPS, the latter are commonly denominated as SMP. It must also be inferred that EPS analysis relies on its extraction from the sludge flocs. So far, the scientific community has not agreed on a standard procedure, and a comparison of data sets generated from different extraction methods becomes complex (Judd, 2006; Liu and Fang, 2002).

SMPs are defined as soluble cellular components or debris that are released during cell lysis, diffuse through the cell membrane, are lost during synthesis, or are excreted for some purpose. Substrate utilization, biomass decay, and EPS hydrolysis are believed to be the major processes contributing to SMP formation. With respect to "SMP formation through substrate utilization", if intermediate products of metabolic processes are included in the SMP definition, substances that do not have a microbial origin but come directly from the substrate tend to be wrongly included (Noguera *et al.*, 1994). The problem has been taken into serious consideration by a number of researchers, but within the scopes of this chapter, it is sufficient to refer to SMPs as "any soluble material that leaves the effluent from a biological system that was not present in the influent", (Barker and Stuckey, 1999).

Modelling objectives of modified ASMs to MBR processes

From a end-user point of view, expanding the models with EPS/SMP concepts is suggested only if the following modelling objectives are pursued:

- Linking biology with fouling

The extension of ASM models with SMP and EPS concepts is undoubtedly crucial when predicting membrane fouling. SMP/EPS have been proved to accumulate in MBR systems as a consequence of a high membrane rejection and low biodegradability (Shin and Kang, 2003; Drews *et al.*, 2007; Liang *et al.,* 2007). Their influence on fouling, or their use as indirect indicators of fouling propensity through biomass deflocculation (de la Torre *et al.*, 2009), has been evaluated and acknowledged by numerous researchers (*inter alia* Rosenberger *et al.,* 2005, 2006; Jarusutthirak and Amy, 2007; Le-Clech *et al.,* 2006; Zhang *et al.,* 2006; Wu *et al.*, 2007). Based on these considerations, the SMP/EPS would be a necessary input for a filtration model and, hence, needs to be incorporated in the biological model in order to explain or predict the filtration performance of the system.

- Soluble COD prediction

The supernatant of settled mixed liquor is mainly composed of living cells and microbial products. So far it is certain that, in municipal applications, effluent soluble organic matter of activated sludge water from CAS systems is mainly SMP (Namkung and Rittman, 1986; Jarusutthirak and Amy, 2007) and the same can be said for MBR processes (Lu *et al.,* 2002; Le-Clech *et al.,* 2006; Rosenberger *et al.,* 2006; Aquino and Stuckey, 2008). SMP and EPS are microbial products, not active cells, and represent energy

that is not invested in cell growth (Laspidou and Rittmann, 2002). Ignoring SMP and EPS formation could lead to a general overestimation of true cellular growth rates and this would severely under predict the COD effluent (Jiang *et al.,* 2008). This is commonly artificially corrected by an over estimation of Si in the conventional ASM1 model. Finally, it should be pointed out that the COD effluent predictions are not a real concern in municipal MBR systems since values are generally low and stable.

- Model high SRT processes

Furumai and Rittmann (1992), investigated the interactions between nitrifiers and heterotrophs. They reported that, in a CAS at high SRT, SMP formed by nitrifiers promoted heterotrophic growth and reduced the minimum substrate concentration necessary for heterotrophs, allowing heterotrophic growth at very low influent organic concentration. MBR processes generally run with average to high SRTs and the above considerations could be relevant at low F/M ratio (in MBRs, easily as low as 0.01 g COD/g MLSS.d).

Bound EPS has been experimentally shown to accumulate with decreasing SRTs (Ng and Hermanowicz, 2005; Masse *et al.*, 2006), with a corresponding trend on SMP (Rosenberger *et al.*, 2006, Al-Halbouni *et al.*, 2008). Beyond the prediction on membrane filtration, a proper modelling of this fraction is beneficial for sludge production prediction.

In this work, efforts at ASM model extensions with SMP and EPS concepts in the literature are reviewed along with their relevance for MBRs.

*3.4.2 **Influent fractionation for modified ASMs***

When introducing the SMP concentration as a state variable in the model, one of the key issues for COD fractionation is the determination of inert components (Si, Xi) with proper methods, considering the fact that new "inert" substances can be produced in the process as by-products of the microbial metabolism.

In this sense, an early modification of ASM1 was proposed by Lu *et al.* (2001) by modelling a bench-scale MBR fed with synthetic sewage. Wastewater was characterized by means of batch tests aimed at quantifying the inert soluble fraction according to the method proposed by Henze *et al.* (1987). Activated sludge from the bioreactor (MLSS ~ 13,000 g m^{-3}) was washed by ultrafiltered effluent and, after washing, it was diluted to about 2,000 ÷ 3,000 g m^{-3}. The filtered feedwater was afterwards fed to the sludge with an initial COD concentration of 200 g m^{-3}. The steady value of soluble COD concentration reached after approximately 4 to 5 hours was assumed to represent the inert soluble COD in the influent (S_I). This concentration was slightly reduced in order to take the presence of SMP into account. Similarly, the X_I fraction was determined by the same method using substrate pre-treated by

sonication and by subtracting the S_I contribution. Finally, S_S and X_S were given by the difference between soluble COD and S_I and particulate COD and X_I respectively.

More recently, an extension of ASM1 to the SMP concept has been proposed by Di Bella *et al.* (2008) in an integrated model for physical-biological wastewater organic removal in MBRs. The model couples the SMP-extended ASM1 firstly proposed by Lee *et al.* (2002) with a physical model accounting for organics removal in both the membrane and the cake-layer. Here, the COD fractionation comes from a multi-step process including the trial-and-error on MLSS and effluent COD concentrations and an automatic calibration with 10,000 Monte Carlo simulations intended to define the values for the most sensitive parameters of the whole model (including the physical sub-model). Interestingly, in this work, a relevant fraction of influent COD is attributed to the heterotrophic active biomass in the wastewater (X_{het}), which is usually assumed to be negligible in the above mentioned research.

In the successful application of a modified ASM3 including SMP to a pilot-scale MBR treating pre-settled municipal wastewater working at almost 50 days, Oliveira-Esquerre *et al.* (2005) used OUR profiles to quantify the S_S and X_S fractions in the influent feed. In detail, they measured the inert soluble fraction as COD concentration in the permeate after 12 hours' aeration, thus degrading the SMP contribution.

To sum up, the implementation of additional processes for specific MBR modelling purposes in the ASM framework is not reflected in a different COD fractionation. As for unmodified activated sludge models, a general trend towards the trial-and-error fractionation is observed when longer sludge ages are operated, whereas the respirometry-based approach is generally preferred at more conventional values of SRT.

3.4.3 ***Overview of stand-alone EPS and SMP models***

Some models have been developed as standalone descriptions of the concepts of production and degradation of EPS and SMP. Others have focused on integrating the latter concepts into the ASM type of models. This distinction is used in the overview given below.

Table 3.6: EPS model rates in literature.

Leudeking and Piret., 1959 (Eq. 1)	*Laspidou and Rittmann et al., 2002 (Eq. 2)*	*Aquino et al., 2008 (Eq. 3)*
$r_{eps} = K_1 \mu X + K_2 X$	$r_{EPS} = K_{eps} r_s X_a - K_{hyd} EPS$	$r_{EPS} = K_{eps} X_a - K_{hyd} EPS$

Stand-alone EPS models

An early model to characterize microbial products formation was proposed by Luedeking and Piret (1959) for the fermentation of lactic acid (Eq. 1 in Table 3.6). In this equation, the first term accounts for EPS formation associated with a first order growth (with K_1 as the fraction of substrate electron shunted to EPS formation) and the second term represents EPS formation associated with a non-growth term. The main objections to this simple model were (i) the inconsistent production rate values proved by Luong and Muchaldani (1988); (ii) the fact that a mechanism of EPS dissolution was not included although theoretical evidence supported this hypothesis (Laspidou and Rittman, 2002).

Laspidou and Rittman (2002) studied the EPS mass balance in a continuous flow reactor (Eq. 2 in Table 3.6). In this equation, the first term is the product of the substrate utilization rate r_s, the active biomass X_a and the part of substrate electrons shunted to EPS formation, K_{eps}. The second term quantifies the rate of EPS loss due to hydrolysis, using a first-order relationship with respect to EPS. The hydrolyzed EPS would then become soluble EPS or SMPs.

The Laspidou and Rittman model was criticized on 2 major points:

(i) the formation of bound EPS is said to be growth-associated, and produced in direct proportion to substrate utilization. During transient conditions of organic shock loads this would theoretically lead to very high EPS concentrations. Aquino and Stuckey (2008) did not observe this, and proposed to model the formation of EPS as a non-growth-associated product (Eq. 3 in Table 3.6). This entails that the EPS formation rate can only be high at high concentrations of biomass. (ii) the EPS hydrolysis/dissolution rate was 0.17 d^{-1} in Laspidou and Rittmann's works, but was recently reduced to 0.02-0.03 d^{-1} by Jang *et al.,* 2006, and Aquino and Stuckey, 2008. In this respect, a valuable hypothesis is that the high concentration of "hydrolysis end products" would reduce the hydrolysis rate (Jang *et al.,* 2006).

It is interesting to note that, regarding EPS formation kinetics, Aquino and Stuckey (2008) proposed to calculate the EPS formation rate K_{eps}, so that the steady state model would yield a ratio of bound EPS to VSS (bEPS/VSS) close to the experimental value of PN-like-EPS to biomass. K_{eps} resulted in 0.03 $mgCOD_{EPS}/mgCOD_{cell}/d$, which is in accordance with Robinson *et al.* (1984).

Stand-alone SMP models

SMP models have been developed since the late eighties. Namkung and Rittmann (1986) put forward the following SMP subdividision: 1. UAP, i.e. SMP that are associated with substrate metabolism and biomass growth and are produced at a rate proportional to the rate of substrate utilization. 2. BAP,

i.e. SMP that are associated with biomass decay and are produced at a rate proportional to the concentration of biomass. This method of subdivision has been widely accepted.

Table 3.7: Summary of main formation and degradation rates for UAP and BAP (*) Switching functions are not reported since their introduction depends on the process where UAP is formed or degraded.

UAP formation rate	
Laspidou and Rittmann, 2002 *(Eq. 4)*	*Lu et al., 2001* *(Eq. 5)*
$r_{UAP} = K_1 \overset{\therefore}{q}_{uap} \frac{S}{K_s + S} X_{bm}$	$r_{UAP} = \mu_{het} X_{het}$ or $r_{UAP} = \mu_{aut} X_{aut}$ *
UAP degradation rate	
Laspidou and Rittmann, 2002 *(Eq. 6)*	*Lu et al., 2001* *(Eq. 7)*
$r_{UAP} = -\overset{\therefore}{q}_{uap} \frac{UAP}{K_{uap} + UAP} X_{bm}$	$r_{UAP} = -\mu_{SMP} \frac{S_{SMP}}{K_{SMP} + S_{SMP}} X_{het}$ *
BAP formation rate	
Laspidou and Rittmann, 2002 *(Eq. 8)*	*Aquino et al., 2008* *(Eq. 9)*
$r_{BAP} = K_{hyd} EPS$	$r_{BAP} = K_2 X + K_{hyd} EPS$
BAP degradation rate	
Laspidou and Rittmann, 2002 *(Eq. 10)*	*Jiang et al., 2008* *(Eq. 11)*
$r_{bap} = -q_{bap} \frac{BAP}{K_{bap} + BAP} X_{bm}$	$r_{bap} = -K_{h,bap} S_{bap} X_H$

There seems to be a general consensus on UAP formation and degradation mechanisms. UAP formation results from substrate utilization and is proportional to the rate of substrate utilization and biomass concentration (Luedeking and Piret, 1959; Namkung and Rittmann, 1986; Lu *et al.,* 2001; Laspidou and Rittman, 2002). Contrary to Laspidou and Rittmann's approach, Lu *et al.* (2001) differentiated the active biomass into X_{het} and X_{aut} (Eq. 4, 5, 6 and 7 in Table 3.7) and UAP cannot be consumed but only produced by X_{aut}. Recently, a modelling study conducted with aid of LC-OCD and batch tests characterization (Jiang *et al*., 2008) further hypothesized two types of UAPs: the UAPs produced during storage formation of readily biodegradable COD would have a lower MW and would be biodegradable;

the UAPs produced during the utilization of storage products would instead have a higher MW and would be more refractory. However the study was limited to the modelling of the first proposed UAP type.

Unlike for the UAP case, there is no consensus on BAP production and degradation mechanisms. With regard to the BAP production, Laspidou and Rittmann (2002) suggested that BAP were produced solely by EPS hydrolysis (Eq. 8 in Table 3.7). This hypothesis was shown to be weak. (i) hydrolyzed (soluble) EPS and BAP revealed different physicochemical properties (Ramesh *et al*., 2006). Aquino and Stuckey (2008) demonstrated that both soluble EPS and cell lysis products were the sources of BAP (Eq. 9 in Table 3.7). (ii) regarding the kinetics, Jang *et al*. (2006) found that the BAP/UAP kinetics of the Laspidou and Rittmann model could not be applied in their specific tests. When employing a maximum utilization rate for UAP/BAP, they found that the UAP/BAP utilization exceeded the formation. It was therefore assumed that UAP/BAP accumulation inhibited the degradation rate.

In the ASM models experiences, EPS are generally not considered and BAP are not produced from EPS hydrolysis but from cell lysis processes (Jiang *et al*., 2008) or additionally from hydrolysis of particulate biodegradable organic matter (Lu *et al*., 2001).

The BAP degradation has been considered by many researchers (Lu *et al.,* 2001; Laspidou and Rittman, 2002; Aquino and Stuckey, 2008; Oliveira-Esquerre *et al.,* 2006) as a direct degradation and only Jiang *et al*. (2008*)* assumed hydrolysis (Eq. 11 at Table 3.7). Jiang reported that 63% of the BAP had a molecular weight larger than 20 kDa, which makes it unlikely that such large molecules pass the cell membranes directly. They therefore concluded that BAP were hydrolyzed yielding fermentable COD. Overall, Jiang *et al.* (2008) proposed 3 steps for each biomass type to determine the complete BAP dynamics (formation, hydrolysis, degradation).

The SMP equilibrium concentration results from production/degradation mechanisms but also depends on SMP retention by the membrane. The latter aspect is given little consideration in MBR modelling. Authors have mainly measured or fitted it as a steady value, independently of the process specificities. The *percentage of SMP permeating through the membrane* ranges from 0 to 100% (Jang *et al.*, 2006; Jiang *et al.,* 2008; Zarragoitia *et al.*, 2008; Silva *et al., 1998*; Lu *et al., 2001, 2002*). Drews *et al.* (2007) studied the impact of ambient conditions on the rejection of MBRs. According to the latter authors, the rejection of SMP components appears to decrease at higher temperatures and higher nitrification activity. The modelled rejection factors should thus take experimental observations in considerations.

The predominance of UAP over BAP or *vice versa* needs to be discussed for two main reasons (i) one of the two fractions could have more impact in terms of soluble COD, and an SMP fraction could be neglected leading to a simplification of the model. The exclusion of a fraction would be of great benefit in terms of modelling since it would reduce the number of variables. In fact ASM models in the early nineties used to consider only BAP fractions. However, the process conditions may determine the predominant fraction case by case. A rule of thumb is that the BAP fraction tends to dominate at high SRTs (Furumai and Rittmann, 1992) or in steady state conditions (Aquino and Stuckey, 2008), while UAP predominate in the SMP production when the rate of substrate degradation is high (Aquino and Stuckey, 2008; Laspidou and Rittmann, 2002) ; (ii) one of the two fractions could have more impact in terms of fouling predictions. Zhang *et al.,* (2007) operating an MBR fed with external carbon source proved that the concentration of large molecule OM was greater in BAP than that in UAP, (over 18 % of molecules with more than 100 K), being the main cause of the increasing resistance. Conversely, Rosenberger *et al.* (2006) observed that the SMP fraction produced at different SRTs in MBR units operated with municipal wastewater led to a specific long-term fouling rate (per SMP mass unit) higher with 15d SRT than with 8d SRT, even though much more SMP was produced at 8d SRT than at 15d SRT. This demonstrates that the SMP fraction produced by the biological system differs not only in quantity but also in quality depending on the environmental conditions, with crossed impact of both criteria on the fouling propensity of the mixed liquor.

3.4.4 ***Overview of ASM-extensions incorporating EPS/SMP concepts***

The SMP concept was incorporated into activated sludge model No. 1 (ASM1) in the early 90s (Orhon *et al.,* 1989; Artan *et al.,* 1990). First, a very simple SMP model including only BAP was developed (Orhon *et al.,* 1989). So-called SP (equivalent to BAP) is produced proportional to the hydrolysis of particulate COD (Xs) and they are assumed non-biodegradable. The model was further developed to include UAP (Artan *et al.,* 1990). However, this model combines the concepts and degradation kinetics of UAP and BAP resulting in strong parameter correlations. Moreover, the model lacks experimental support.

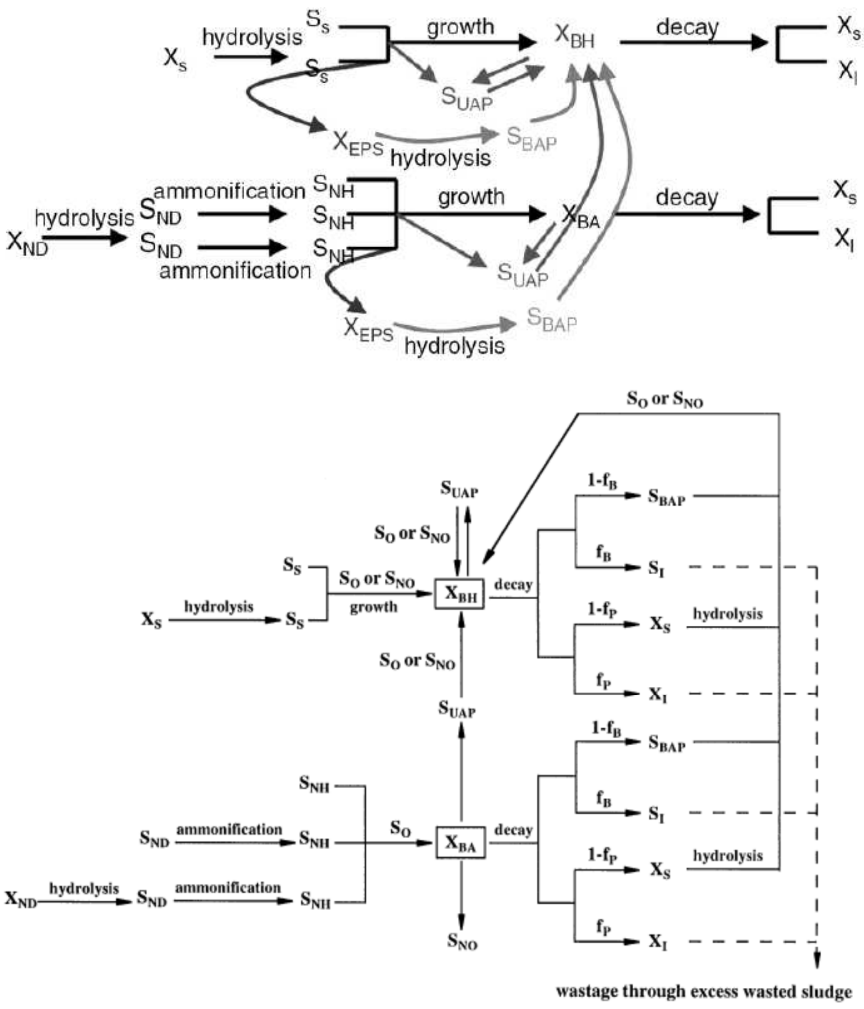

Figure 3. 2: Concepts of the Lu et al. model (2001) (bottom) and the Ahn et al. model (2006) (top)

Lu and coworkers have incorporated a very complex SMP model into ASM1 (Lu *et al.,* 2001) and ASM3 (Lu *et al.,* 2002) in MBR studies (Figure 3.2). However, the COD of their SMP model is not balanced, i.e. the loss of substrate COD is not equal to the sum of formed UAP COD, formed biomass COD and consumed oxygen. In addition, 8 SMP-related parameters are introduced, but the experimental results available for model calibration are limited to steady state soluble COD measurements (Jiang *et al.*, 2008). The kinetic parameters are estimated by calibration but strong parameter correlation may hamper correct determination. Thus, the fitting does not convincingly demonstrate the validity of the model structure and parameter values.

Other authors have also adopted the Lu model. Zarragoitia *et al*. (2008), adopted the Lu ASM1 model (with the exception of nitrification processes) and linked it with a membrane fouling model where SMPs were used to estimate the bound EPS concentration in the sludge supernatant according to the

equation $S_{UAP}+S_{BAP}/0.8X_{TSS}$. Kinetic parameters of Lu's model were partly adopted. This work did not include SMP modelling results.

Di Bella's (2008) work was also based on Lu's model. The work was important since it focused on describing the fate of COD through the pilot MBR by distinguishing the COD removal contribution of (i) the physical membrane and (ii) the cake layer according to its depth. COD effluent was fairly well predicted. However, the model parameters were not in line with other experiments (Table 3.8). SMP kinetic parameters were calibrated by fitting but the SMP concentrations were not shown. Sensitivity tests report that Y_{SMP}, and $\gamma_{UAP,A}$ have a strong influence on the majority of output variables while $b_{BAP,h}$ and μ_{SMP} mainly affect NH_4 and NO_3. The sensitivity tests confirm that, once SMP are embedded in the ASM model, their intermediate role in decay and substrate metabolism is very relevant. Identification of the kinetic parameters introduced is thus crucial for the prediction of the effluent quality.

Ahn *et al.* (2006) tried to include EPS in the ASM-SMP models, though their use in ASM works has generally been avoided. EPS were modelled in Eq. 1 in Table 3.6, thus excluding an explicit EPS loss term, and BAP were produced uniquely by EPS hydrolysis. For the modelling process, 5 processes were added: hydrolysis of EPS, EPS formation by heterotrophs, EPS formation by autotrophs, UAP formation by heterotrophs, and UAP formation by autotrophs (Figure 3.2). In order to describe the newly added processes, 8 new parameters were introduced (μ_{SMP}, k_{UAP}, k_{UAPa}, k_{BAP}, K_{SMP}, k_{EPS}, k_{EPSa}, and K_{XEPS}), yielding an over parameterized model. In this model, the effect of SRT was not observed in SMP production but rather in EPS production, and the experimental results showed good agreement with the simulation results. EPS concentration was sensitive to K_{eps}, K_{bap} and SRT, while K_{uap} sensitivity was low. However, kinetic parameters are not reported, SMP behaviour not described, and the model lacks an appropriate calibration (Jiang *et al*., 2008).

Oliveira-Esquerre *et al.,* (2006) introduced SMPs in ASM3. UAP and BAP were lumped into a general term MP. Overall, the model comprised 5 new SMP kinetic parameters ($\gamma_{MP,H}$, $\gamma_{MP,A}$, k_{MP}, f_b, Y_{mp}) whose values were adopted from Lu *et al*., 2001, and 2 new processes. The work focused on understanding the peculiarities of an SMP model in ASM3 when compared to the ASM1. In the ASM1 model it is assumed that slowly biodegradable substrates are hydrolyzed before their use for growth. In the ASM3 model it is assumed that all organic substrates are directly converted into stored material and that stored compounds are subsequently used as a carbon and energy source for growth purposes. Consequently, as the specific rate of hydrolysis of MPs in ASM1 is considerably lower than the specific rate of storage in ASM3, it becomes a rate-limiting factor in the uptake of MPs. This explains why ASM3 gave a markedly low MP concentration (0.75 gCOD m^{-3}), while a value of 80 gCOD m^{-3} was obtained

with ASM1. Both models would, however, give similar values of MP concentration if no storage was considered in ASM3 and MPs were directly used for bacterial growth, as assumed in ASM1.

Table 3.8: SMP/EPS Kinetic parameters in recent literature works. (*) in [mgCODproduct / mgCODcell / d]; (**) in [mgCODuap / mgCODsub]; (***) in [mgCODcell/ mgCODsmp];(****) in [mgCODeps/ mgCODsub];

EPS/SMP modelling										
	Affinity constants		*Formation*			*Degradation*			EPS	
	K_{UAP}	K_{BAP}	$_{SMP}$	$_{UAP}$	$_{BAP}$	K_{BAP}	K_{UAP}	f_{SMP}	K_{EPS}	K_{HYD}
	[$gCOD_{SMP}$/l]		***	**	[d^{-1}]	[$mgCOD_{product}$ / $mgCOD_{cell}$ / d]				[d^{-1}]
Furumai *et al.*, 1992			0.5	0.2	0.1*			1		
Laspidou *et al.*, 2002	100	85		0.05	0.17	0.07	1.27		0.18****	0.17
Jang *et al.*, 2006	100	85		0.05	0.02	0.07	0.4		0.18****	0.02
Aquino *et al*, 2008	500	500		0.2	0.0034	0.03	1.2		0.03	0.03
ASM related works										
	Affinity constants		*Formation*					Degradation rates		
	K_{SMP}		μ_{SMP}	K_{BAP}	f_{SMP}	f_{UAP}	f_{BAP}	K_{SMP}	$K_{h,BAP}$	$K_{h,UAP}$
	[$gCOD_{SMP}$/l]		[d^{-1}]	[d^{-1}]	[-]	[-]	[-]	[d^{-1}]	[d^{-1}]	[d^{-1}]
Lu *et al.*, 2001	30		0.7	0.4		0.38				
Lu *et al.*, 2002	60		2.5	0.01		0.3				
Lee *et al.,* 2002	30		0.7		0.4			0.1		
Oliveira *et al.,* 2006	30				0.4					
Zarragoitia *et al.,* 2008	30		0.7	0.22		0.38				
Di Bella *et al.2008*	133		8.3	0.33		0.82				
Jiang *et al.*, 2008						0.0963	0.0215		7.4E-7	0.0102

Jiang *et al.* (2008) introduced the SMP concept in an ASM2d model. This work differed considerably from the previous ASM SMP models. BAP and UAP were degraded by hydrolysis steps, creating 3 new processes and imposing variations in 13 other processes. SMP kinetic parameters, production and hydrolysis rate of SMPs (subdivided by UAPs and BAPs) were investigated through specially designed experiments. The experiments were associated with a LC-OCD characterization, offering interesting

outcomes. Jiang *et al.*'s (2008) UAP and BAP model peculiarities are in this review discussed in the stand-alone models section.

3.4.5 ***Model identification – UAP/BAP kinetics***

Two problems have been identified with SMP/EPS models. The kinetic parameters are not easily determinable experimentally and the models are usually over parameterized. Saroj *et al.* (2008) infer that incorporation of EPS/SMP in ASM would tend to worsen the model identification process, which is crucial in any ASM calibration exercise.

As can be seen in Table 3.8, in order to overcome these problems several recent models made use of the Lu *et al.* model identification values, but this is not a good practise if SMP dynamics are related to specific processes or influent composition. The lack of validation campaigns confirming the theoretical models is striking. Few researchers have made efforts in the experimental determination of the new kinetic parameters. Jiang *et al.* (2008) calibrated their model once BAP and UAP kinetic parameters had been experimentally derived. BAP parameters were calculated by COD_{sol} monitoring of a batch system in famine conditions. UAP parameters were calculated by PN and PS concentration monitoring of a batch system in external substrate excess conditions. The degradation rate equations were chosen in order to minimize the number of unknown parameters. The determination of the unknown parameters was reported by the authors as complex, especially in the case of UAP, because BAP and acetate could interfere in the UAP measurements. The main criticism with regard to this batch approach could reside in: (i) the BAP batch test is run up to COD_{sol} values of 200 mg COD/l. This value is very high when compared to WWTP supernatant COD; (ii) UAP tests are substrate specific; (iii) both BAP and UAP tests are dilution dependent as shown by Laspidou and Rittmann; (iv) the washing of biomass prior experiments is arguable because the initial soluble COD of the supernatant would consequently be very low. But it is questionable whether the rate of SMP production/degradation are concentration dependent. This issue deserves further attention.

Outlines

The use of an ASM expansion with the EPS/SMP concept is encouraged only if the following modelling objectives are to be pursued: (i) linking biology with fouling, (ii) soluble COD predictions (iii) model high SRT processes.

The ASM extension with EPS/SMPs concept creates difficulty in identifying the newly proposed parameters. Modellers have to implement strategies to reduce these parameters according to experiences reported in the literature and the process specificities. Parameter reduction strategies have been adopted by (i) coupling UAP/BAP into SMPs (Oliveira-Esquerre *et al.,* 2006); (ii) excluding EPS modelling

(Lu *et al.*, Oliveira-Esquerre *et al.*, Lee *et al.*, Jiang *et al.*); (iii) modelling the EPS (as sole AS foulants) with equations external to the ASM model (Saroj *et al.,* 2008); (iv) excluding a water fraction UAP/BAP when negligible (Orhon *et al.*, 1989).

It would always be preferable to determine the kinetics parameters by specific batch tests, as suggested by Jiang *et al.*, (2008), despite the limitation of this approach as discussed above.

3.5 ***Outlook and future perspectives***

In this final section, the authors would like to point out what they feel as the main shortcomings of the current state-of-the-art of and future challenges in biological modelling of MBRs. The section is structured similarly to the previous sections.

- Influent characterization for the unmodified ASMs:

Notwithstanding the fact that a large number of ASM applications have been reported in MBRs, some key factors still have to be further investigated and considered in wastewater characterization. One of these relates to the assessment of the active heterotrophic biomass X_{het} in the influent wastewater that, although usually neglected in CAS modelling, needs to be better addressed when modelling MBRs. In fact, from a theoretical point of view, longer sludge ages lead to decreases in the percentage of active biomass in the MLVSS. Therefore, the higher the SRT, the less negligible the new biomass entering the plant via the influent becomes. This contribution is influenced by the characteristics of the sewage system (separate/combined), the presence and typology of pre-treatment units, the residence time in the sewage pipelines and the possible presence of toxic compounds due to industrial discharges. Possibly, a combination of well-known respirometric methods for X_{het} determination (Kappeler and Gujer, 1992) and advanced biomass characterization tools such as flow-cytometry (Ziglio *et al.*, 2002; Foladori *et al.*, 2007) can be adopted at experimental level to actually understand the need for further calibration efforts.

Another open issue in the application of ASMs to long-SRT MBRs is the fate of inorganic compounds in the influent (mineral suspended solids), whose concentration clearly depends on the upstream operation units (presence/absence of sand removal and/or primary settling tank, fine screening meshes, run off, infiltration into the sewers). Some experimental evidence reports solubilization of inorganic solids entering the system: Laera et al. (2005) showed the loss of a significant amount of inorganic particulate matter in a bench-scale MBR operated with no sludge wasting, and they suggested that hydrolysis and solubilization produce molecules with a smaller size than the membrane pores, which leave the reactor with the effluent permeate. In the above mentioned work, Spérandio and Espinosa (2008) found that up to 50% of influent mineral solids were converted into soluble inorganics at a sludge age of 110 days. Therefore, in the specific case of ASM3 application to MBRs, this would mean

at very long SRT an adjustment of the absolute values of composition parameters for MLSS (i_{TS_XI}, i_{TS_XS}, i_{TS_XBM}, i_{TS_XSTO}). An alternative option could be given by the introduction of the model proposed by Ekama and Wentzel (2004) for Inorganic Suspended Solids (ISS) in the ASM framework. This model assumes ISS in the sludge to be due to the accumulation of influent mineral solids and the uptake of inorganic dissolved solids (IDS) by ordinary heterotrophic organism (OHO) and phosphate accumulation organisms (PAO). In this case, a suitable calibration of parameters "f_{OHO}" and "f_{PAO}" (inorganic solids content for OHO and PAO respectively) could "mask" the gradual solubilization of influent inorganics at long sludge ages. In addition, a solubilization mechanism should be mathematically introduced in the ASM matrix.

- Process kinetics for the unmodified ASMs

Concerning the bio-kinetic parameters of unmodified ASM1, most of the biological processes have been widely investigated. Little, on the other hand, is known about the possible specificities of bio-kinetics for phosphorus removal in MBR. The available literature does not show significant differences between MBR and CAS calibration parameters. However, recent microbial studies have shown the presence of PAOs in several full-scale MBR not specifically designed for biological phosphorous removal. Considering that a volume percentage of the anoxic reactor is anaerobic is not an applicable solution in all cases (since nitrate supernatant concentration may not allow it) and predicting phosphate effluent concentrations in these conditions remains rather problematic. This aspect needs further investigation.

- Process kinetics for the Modified ASMs

EPS and SMP concentrations are sensitive to biomass production, hydrolysis and degradation rate. Few detailed experimental data are available for calibrating the rates of each process independently. Models including the EPS/SMP concept show that EPS constitute a large amount of the organic reserve in a bioreactor and their hydrolysis can impact the SMP release in the sludge water very significantly. Slow hydrolysis of microbial products (in aerobic, anoxic or anaerobic conditions) is a poorly understood process which definitely needs more attention.

The SMP equilibrium concentration results from production/degradation mechanisms but also depends on SMP retention by the membrane. The latter aspect is not sufficiently considered in the works reviewed and authors have mainly measured or fitted it as a steady value, independent of the process variations. The percentage of SMP permeating through the membrane ranges from 0 to 100% (Jang *et al.*, 2006; Jiang *et al.,* 2008; Zarragoitia *et al.*, 2008; Lu *et al., 2001, 2002*). Quantification of this transport depending on membrane type, process conditions and fouling characteristics needs further investigation.

The subdivision among UAP and BAPs has been widely acknowledged and modelling efforts for their production and consumption are under way. However, recent observations tend to show how the SMP / bound EPS ratio (i.e. the state of flocculation of the biomass) also depends on process disturbances such as shock loads, shear stress, temperature, pH and oxygen shocks (*inter alia* Drews *et al.* 2007). An important question is whether the current models are valid for inclusion of these process disturbance effects. Most probably they are not and model extensions are required in order to predict SMP dynamics with regard to process operation and process disturbances.

Finally, as sufficiently noted in the text, the determination of kinetic parameters of the SMP/EPS models is a major concern. Over-parametrization or lack of identifiability appears as a typical problem of ASM model extensions. Is it possible to mathematically overcome the problem or do we need to systematically characterize each process experimentally?

- Application of ASM models at full-scale, hydraulics and aeration.

Most modelling exercises and conclusions are based on lab-scale or pilot-scale experiments. However, in order to take the step to usage and full exploitation of the benefits of bio-kinetic models for plant design and operation, more full-scale studies are required. More attention should be paid to full-scale model applications in order to confirm the applicability of the current findings. This problem is not new, however, as it is a known issue in CAS modelling as well. In principle, the models described in chapter 3 (unmodified ASM) should be suitable for full-scale use, bearing in mind some points requiring attention as stipulated.

Full-scale plant aeration as well as hydraulic characterization are key issues in modelling MBR. However, they have not received much attention to date (especially hydraulics). The contribution of coarse bubble aeration (membrane scouring) to the overall oxygen supply for oxic processes needs to be better characterized. In the case of sMBR systems, there is a need to couple valid kinetic ASM models with more accurate hydraulic models (e.g. CFD). Intensive hydraulic characterization of aerobic/anoxic basins is still insufficient. When membranes are directly submerged in the bioreactor, it becomes difficult to correctly predict the influence of membrane aeration on the overall performance. Fine bubble aeration (for biological needs) is generally regulated by on/off control, for minimising energy consumption and promoting denitrification through increased anoxic reactor volume. But membrane coarse bubbles aeration rate is more or less constant and contributes to the oxygen supply, influencing nitrification in a complex hydraulic system with heterogeneous oxygen concentration. A better balance between the different sub-models (bio-kinetic model, aeration model, hydraulic model) should, therefore, be investigated.

3.6 Conclusions

A concise overview of the most recent literature on ASM-based MBR modelling is given in this review work. Clarity was sought by categorizing models as unmodified or modified ASMs, underlining the strong relationship with the modeller's target: modelling to improve process performance or modelling for further understanding of the process.

The chapter has aimed to extract relevant information that seems commonly agreed on within the scientific community in this particular area, and also to highlight contradictory observations and conclusions present in scientific papers. The summarizing paragraphs at the end of each section are intended to guide end-users in the current availability and applicability of specific models and techniques, their limitations and possible pitfalls. This should assist in modelling municipal laboratory, pilot and full-scale MBRs, either for performance optimization or for decision support.

The experience reported in this review proves that, when modelling purposes do not differ from effluent characterization, oxygen demand and sludge production, ASMs are very relevant to MBR applications. However, particular care needs to be taken since the specific conditions present in MBRs are reflected in some important discrepancies when compared to ASM default parameter values. In terms of bio-kinetic studies of the different processes, the authors have preferred not to propose a general set of values, since, as research results show, the values are very dependent on the operating conditions. Instead, researchers' work has been brought together in concise tables that can, indicate common directions for each process.

In cases of ASMs developed for specific purposes related to MBR operations, and with particular care to fouling prediction modelling, the knowledge on SMP and EPS modelling has been critically reviewed on the basis of the literature, including the most recent developments. Progress in tackling the over-parametrization of the extended models has been highlighted, as this book intends to serve as an incentive to bring scientific efforts into practice.

Finally, the outlook and future perspectives have been systematically highlighted and proposed for each section.

The chapter provides a guide for different end-users of mathematical models for MBR, be they people active in process design and operation, or academics who want to learn about the current state-of-the-art or detect current shortcomings in MBR modelling.

3.7 ***References***

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Chapter 4

Energy Audit of a full-scale MBR

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Abstract: A calibrated dynamic biological ASM model of a full-scale MBR was used to analyze the energy costs of different compartments and devices. The overall energy consumption (0.64 kWh/m³ of permeate) of the studied MBR in Schilde (Belgium) was good compared to other full-scale municipal MBR plants. It is however still much higher than CAS treatment (0.3 kWh/m³). Energy demands of the full-scale MBR system were compared with a treatment train believed to deliver a comparable effluent quality: CAS followed by Ultrafiltration and UV. It was concluded that from an energy perspective the MBR technology is not yet sufficiently competitive.

The MBR technology leads to process specificities which all impact on the energy consumption. While the higher MLSS concentrations implied significant mixing energy costs and reduced oxygen transfer, the smaller floc size did not reflect in a significant aeration energy saving. The impact of the filtration process on the overall energy consumption could be reduced if the coarse aeration flow would be better integrated in the biological process scheme of submerged MBRs. However this work indicates a minimal contribution of the coarse aeration flow to the biological oxygen requirements.

4.1 ***Introduction***

Footprint limitation, strict effluent consent and local environmental or socio-economic considerations act as a driving force for applying MBR technology. The MBR market has in fact recently strongly risen (Judd, 2006), either promoting independent process lanes or in parallel with CAS systems. However the competitiveness of this technology is threatened by the lower operational cost of CAS systems and reports of full-scale experiences that act as an update of the technological and operational advances which have been put into practise are necessary.

Information on energy requirements of full-scale MBR plants in scientific literature is scarce. Cornel and Krause (2004) reported the energy requirements of two municipal full-scale MBRs, equipped with Zenon membranes, in the range of 1-2 kWh per m^3 of permeate produced. Mulder (2009) observed for the full-scale MBR in Heenvliet equipped with Toray flat sheet membranes, a range between 0.8-1.2 kWh per m^3 of permeate produced. Pilot scale MBR experiences do not seem to offer a reliable view on MBR energy costs probably since the small scale negatively influences the energy performances: Gil *et al.* (2010) and Gnirss *et al.* (2009) reported respectively 5-6 and 1.8-6 kWh per m^3 of permeate produced.

Dynamic models of full-scale MBRs are rare (Ng *and* Kim, 2007) because complex. The dynamic loads, the necessity to account for the efficiency of the pre-treatment steps, the influence of the strong hydrodynamics in the membrane chamber and the aeration efficiency evaluation are complications that arise when modelling full-scale plants. Several ASM modelling studies (*inter alia* Jiang *et al*., 2009; Manser *et al*., 2005) converged in identifying a number of process specificities when comparing MBRs to CAS systems, e.g. the lower affinity constants for oxygen and the lower oxygen transfer rates (OTRs).

Energy consumption and biological processes are reciprocally influenced. On one side, as we know, the energy consumption permits the exploitation of the biological processes, e.g. providing the necessary O_2 for the completion of the various biological processes, keeping the biomass in suspension, pumping the sludge according to the scheme, managing the filtration process. But on the other side, the impact of MBR process specificities on the energy consumption is also to be discussed.

While the scientific literature has mainly focused on fouling optimization to reduce energy demand, the aim of this study was to look at the global energy picture of a full-scale MBR. An energy and ASM model of a full-scale MBR was built to provide a numerical analysis of the problems. Relevant data of the energy monitoring are reported and compared with other full-scale systems data. Additionally the impact of the MBR process specificities on the energy consumption are investigated, as to: (i) provide an insight in the energy balance of MBR systems; (ii) highlight potential sources of optimization.

4.2 ***Materials and Methods***

4.2.1 ***The full-scale WWTP of Schilde.***

The WWTP of Schilde is described in chapter 2.

4.2.2 ***Calibration Methodology***

The model was calibrated and validated using a data set of several hundred days. This assures the correctness of the model in different conditions. The Schilde WWTP model was calibrated with January-October 2006 data, and validated with January-May 2009 data.

Real MLSS concentrations and measured fine bubble aeration energy (CAS and MBR aeration tanks) were used as inputs for the model. The Schilde WWTP model was implemented in MATLAB-SIMULINK within a model library developed by Aquafin. ASM2d was used to include the inorganic fraction. The flow division between MBR and CAS (splitter), permeate extraction, MBR acetate dosing, pre-treatment, aeration systems, PID settings, and recycle flows were implemented in the model identical to the real life situation. The CAS clarifiers were modelled by use of the Takacs model (Takacs *et al*., 1991). The membrane itself was modelled by a “point clarifier” with 100% solids separation. Modelling of the fouling phenomena was not carried out.

The investigation methodology is composed of 7 main steps: (i) the waste water fractionation; (ii) the pre-treatment efficiency estimation; (iii) the aeration efficiency estimation; (iv) the measurement of the energy demand of all devices; (v) additional biomass characterization; (vi) the fine tuning of the

ASM parameters and the half saturation coefficients (during the calibration phase); (vii) the validation phase.

With regards to the energy loads of the different devices, the energy loads may differ from the nominal given values for the following reasons: (i) the devices may be frequency driven, i.e. the control can let the motor turn at different speeds; (ii) the power factor of the device needs to be assessed, i.e. the power factor is the ratio of the real power flowing to the load to the apparent power and is a dimensionless number between 0 and 1. An energy sampling campaign is held.

4.2.3 ***Samples and analysis***

Every 2 weeks, daily composite samples were collected of the WWTP influent, the MBR effluent and the combined effluent (CAS+MBR). Samples were analyzed for BOD_5, COD, suspended solids (SS), Kjeldahl nitrogen (KJN), ammonia (NH_4-N), oxidized nitrogen (NO_3-N and NO_2-N), ortho-phosphate (PO_4-P) and total phosphorus (TP). All samples were analyzed according to the Standard Methods (APHA, 1999).

The STOWA protocol was used to fractionate the influent. The micro-filtered COD was determined by use of a 0.45 µm filtration step. The BOD of two influent samples have been recorded during 20 days incubation. The K_{bod} was then determined.

Methylene-blue and Sudan staining techniques have been applied on fresh sludge samples to investigate the presence of PAOs in the MBR activated sludge.

Particle size distribution of MBR sludge samples was measured with a Mastersizer S (Malvern, UK). The sludge water was sampled in the MBR tanks with a sample shipping time of about 1 hour. The samples were shortly vortexed prior analysis.

Two samples of the sand trap and the rotary drums (1 mm) waste material have been analyzed in the lab in order to assess the organic content, and the kgCOD/kg dry solids. The COD of 50 grams of material in 1 L water was measured as mgO_2 per kg of disposed material. The inlet and the outlet of the primary settling tanks (PSTs) efficiency have been sampled to determine the BOD_5 removal efficiencies.

The standard aeration energy (SAE) of the MBR fine bubble (aeration tank) and coarse bubble aeration systems (membrane units) was determined through a non steady state approach in full-scale. The following procedure was followed: (i) influent pumps were stopped during 8 hours and aeration was switched on until BOD and NH_4-N were depleted; (ii) all the recycle pumps were switched off in order to isolate the biomass in the aeration basin (mixers were active to favour O_2 distribution); (iii) when the endogenous respiration was reached, the biomass was aerated up to 3-4 mg O_2/l, and then allowed

to reach again zero O_2 concentration. This procedure was repeated several times; (iv) During the non aerated phase, the endogenous respiration rate was calculated from the slope of the dropping O_2 concentration; (v) During the aerated phase, the O_2 input (kg O_2/h) was determined by the slope of the rising O_2 concentration, corrected by adding the endogenous respiration rate; (vi) the power used by the blowers was measured and the SAE was determined by dividing the O_2 input by the power input. The K_La was calculated with the following equation:

$$K_La = \text{Aeration Energy} * SAE / (V * So_{2\ sat})$$

A power meter "FLUKE 1735" was used to log the power consumption of different devices. The power logger accounts for the instantaneous energy load on the three phases. The energy measurements have a resolution of 1 W to 10 W with an operating error of ± 1.5 %. The power logger was logged for 10 minutes on each device, while the control frequencies were manually adjusted and the energy loads recorded.

4.3 ***Results and Discussion***

4.3.1 ***Energy Audit Results***

The results of the energy measurements are shown in Table 4.1, whereas the controlled devices were measured at different frequencies. The energy consumption of the non-sampled devices (mainly small energy consumers) was assumed identical to the suppliers indications. These energy consumption data were incorporated in the ASM2d model.

Table 4.1: Results of the energy sampling campaign. Sampled kWh, in function of the frequency (%), are compared to the nominal power in kW (last column).

	Controlled Frequencies							Power
	%	%	%	%	%	%	%	kW
	20	25	40	50	60	80	100	
Anaerobic mixer (kWh)							5	7
Aerobic mixer (kWh)							9	10
Influent pumps (kWh)							10	18
CAS surpressors (kWh)	15		15		16	17	18	18
MBR fine bubble blower (kWh)	17		23		26	29	30	30
MBR coarse bubble blower (kWh)		14			28			40
MBR Permeate pumps (kWh)					4		6	6
MBR sludge recycle pumps (kWh)				5			6	6

The modelled energy consumption was compared with the WWTP energy bill (the sum of the MBR and the CAS). The modelled monthly energy consumption diverged slightly from the real. In 2006, the total

modelled energy consumption was 3.3% higher than the real value, and with the exception of July, the monthly relative error was always below 5% (Figure 4.2).

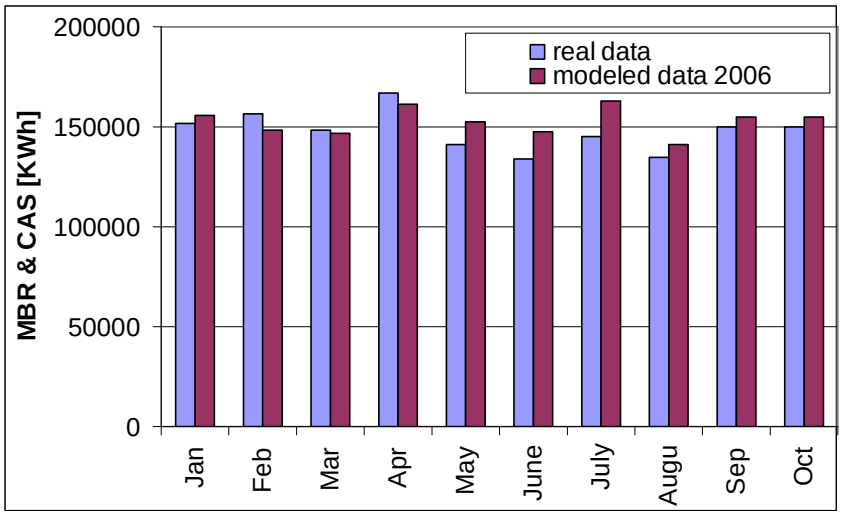


Figure 4.2: Measured versus modelled monthly energy consumption in Schilde WWTP (2006).

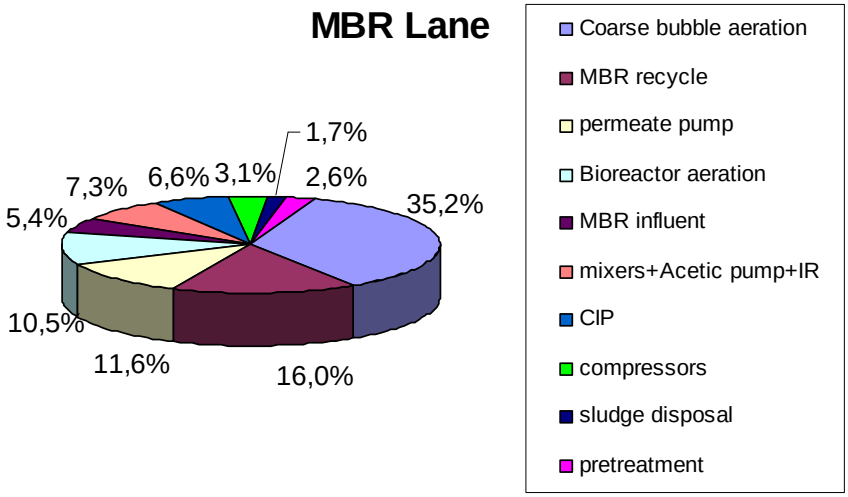


Figure 4.3: MBR energy contributions of the different devices: Coarse bubble aeration / Recycle pumps / permeate pumps / Bioreactor Aeration / MBR influent pumps / mixers + carbon dosing pumps + internal recirculation pump / electrical heating of backwash water / compressors for valve switching / sludge disposal pumps / drum sieve + sand Trap

In a recent study, Roels *et al.* (2010) reported on energy optimisation studies of full-scale CAS systems in the same geographic region. Based on the latter study the main energy consumers of CAS systems can be identified: the aeration energy accounts for 35-50% of the total energy, the influent flow for the 15-20%, the sludge recycle for 10-15%, mixers and propellers for 5-15%. The studied MBR system displayed a totally different energy distribution (Figure 4.3):

(i) The coarse bubble aeration is the largest consumer (35%) (Figure 4.3). The overall filtration process, including the permeate extraction, the electrical heating of the *cleaning in place* (CIP) tank, the compressors for activation of the valves, accounted for more than 56%. This number underlines the usefulness of the numerous fouling reduction studies in literature.

(ii) The energy needed for recycling the sludge in the MBR was higher than for the influent pumps. In CAS the opposite is true. The higher energy consumption for recycling in the MBR is caused by much higher recycling flows. In fact in MBRs the sludge concentration in front of the scheme (an anoxic CSTR) is typically lower than in the rear of the bioreactor, where the membrane modules are submerged. The different sludge concentration is controlled by adjusting the internal recirculation flow rate (Ramphao *et al*., 2005). Typically the sludge recycle ratio in CAS systems is 0.4. In the studied MBR it was 6.

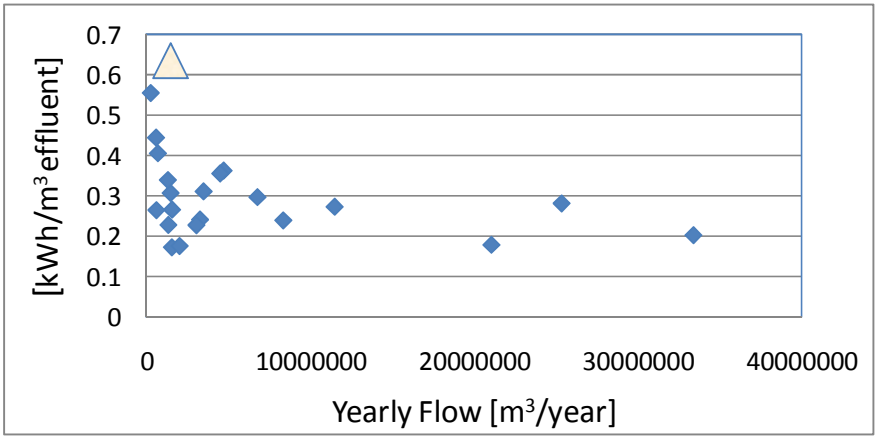


Figure 4.4: Comparison of the specific energy consumption in different Aquafin WWTPs. The Schilde MBR (triangle in the chart) is compared with other CAS systems of several sizes.

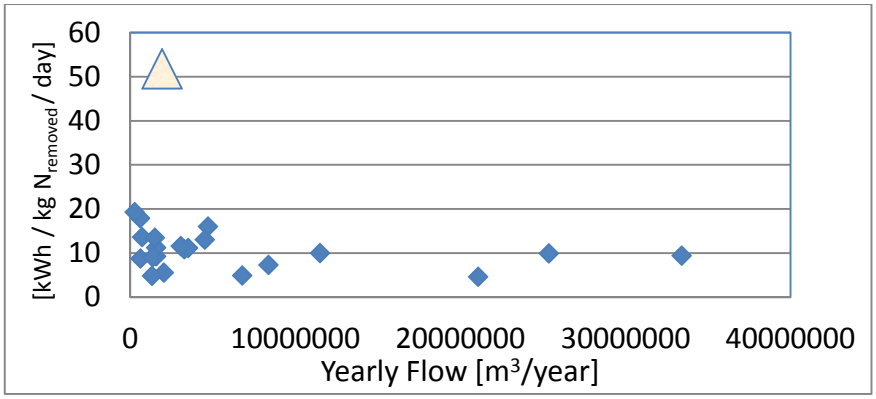


Figure 4.5: Comparison of the daily energy consumption per kg of Nitrogen removed in different Aquafin WWTPs. The Schilde MBR (triangle in the chart) is compared with other CAS systems of several sizes (same WWTPs as in Figure 4.4).

Based on the results, the CAS in Schilde consumes 0.19 kWh per m^3, whereas the MBR consumes 0.64 kWh per m^3. Due to the lower TN removal performance of the CAS system (below the 50% TN removal), no direct comparison between the two lanes is possible.

As stated in the introduction, the average energy cost of other municipal full-scale MBRs ranges between 0.8-1.2 kWh per m^3 (Mulder, 2009). At the full-scale MBR of Varsseveld, equipped with Zenon membranes, an optimization study allowed to lower the energy consumption from 1 to 0.88 kWh per m^3 (Van Bentem *et al.*, 2007). The lower energy consumption in Schilde might be explained by an intensive cost reduction program started in 2006 (Garcés *et al*., 2007).

The energy consumption of CAS installations in Flanders, treating municipal sewage, is on average 0.30 kWh/m^3. As expected, the energy demand of the MBR is higher than CAS systems both when expressed as kWh/m^3 and as kWh/$kgN_{removed}$/day (Figure 4.4-4.5).

With regards to the energy consumption, Brepols *et al*. (2008) stated that CAS systems appear as costly as MBR systems when a slightly comparable effluent water quality is to be obtained. This statement was checked by comparing the energy demand of the MBR with a CAS supplemented with ultrafiltration (UF) and ultraviolet disinfection (UV).

A CAS system, operated in the same geographic region (Flanders, Belgium), is equipped with UF and reverse osmosis for water reuse purposes. The UF is performed by a Zenon system with a nominal pore size (0.04 µm) comparable to Schilde MBR. The average energy consumption in 2005-2006 was 0.163 kWh/m^3 of UF filtrate produced (Van Houtte and Verbauwhede, 2007). The few UV disinfection full-scale data available in literature suggest an average specific energy consumption in the range of 0.04–0.13 kWh/m^3 (SBW Consulting, 2002). A recent study (Nyserda, 2008) reports full-scale UV performances in the water sector at a maximum specific consumption of 15 kWh/MGD, equivalent to 0.004 kWh/m^3 .

The latter figures would set the energy costs of CAS systems equipped with UF and UV between 0.467-0.593 kWh/m^3, averagely below the MBR technology.

4.3.2 ***Impact of the MBR specificities on the energy consumption.***

In the following section, the biological and process technological specificities of the full-scale MBR that have been identified during the ASM modelling exercise are reported. Options for energy optimization are discussed.

4.3.2.1 Effect of the floc morphology on the MBR energy consumption

The ASM model was successfully capable of modelling the TN removal of the CAS and the MBR lane (Figures 4.6-4.7). While considering the different operational conditions of both full-scale lanes (Table 4.3), the nitrification rates appeared not to be properly modelled by the ASM2d default values.

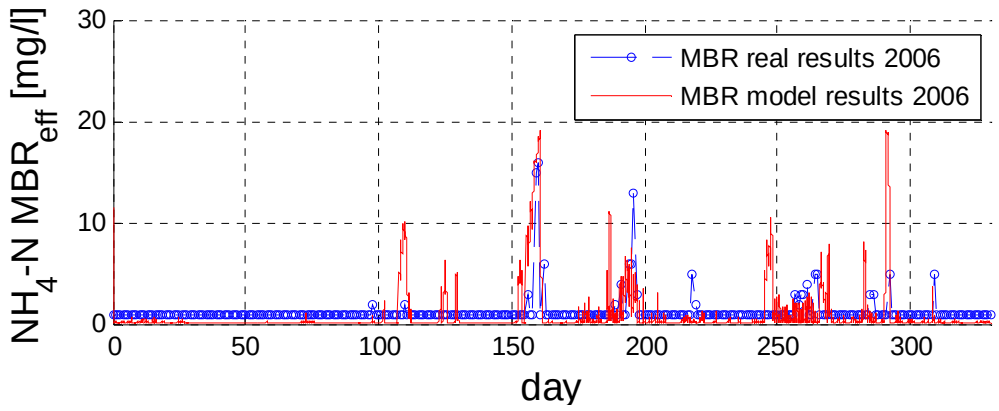


Figure 4.6: NH_4-N MBR effluent concentration (2006 data set).

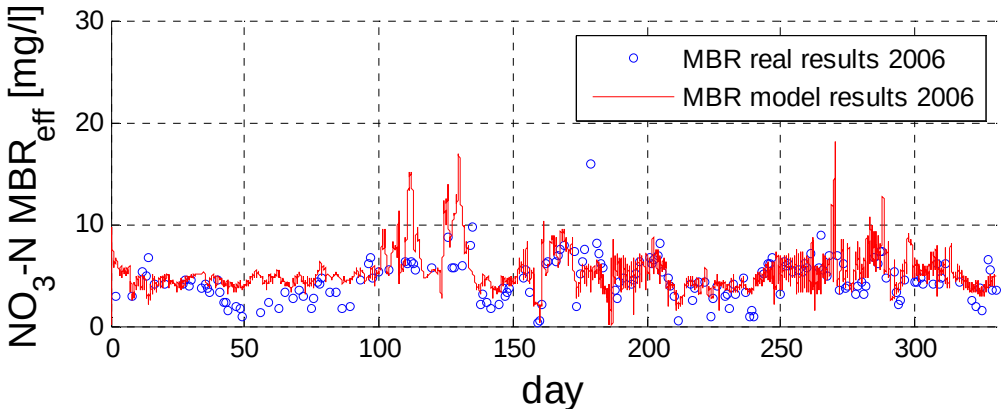


Figure 4.7: NO_3-N MBR effluent concentration (2006 data set)

The half saturation coefficient were therefore fine tuned. The K_{OA_AUT} was lowered in the MBR system from 0.5 to 0.2 mgO_2/L, while ASM2d default value were used in the CAS. The half saturation coefficient K_{NH_AUT} was lowered from 1 to a 0.2 mgN/L for both lanes. The latter parameter is generally lowered in all the modelling exercises carried out by the Aquafin R&D department. The identified parameters highlight how the MBR lane has a higher specific nitrification rate than the CAS lane and these findings find confirmation in what literature have so far reported in pilot studies. Manser *et al.* (2005) have studied the substrate and oxygen affinity of nitrifiers. They found that the half saturation coefficients for the substrate did not differ significantly between MBR and CAS processes. However, the half saturation coefficients for oxygen exhibited a significant difference. The lower values obtained in the

MBR are attributed to the smaller size of activated sludge flocs that developed under conditions without selection pressure of settling but under increased shear-rate conditions (Jiang *et al.,* 2009). Hence, floc size characteristics imply a lower substrate diffusion limitation for MBR sludge (Shanahan *and* Semmens, 2006).

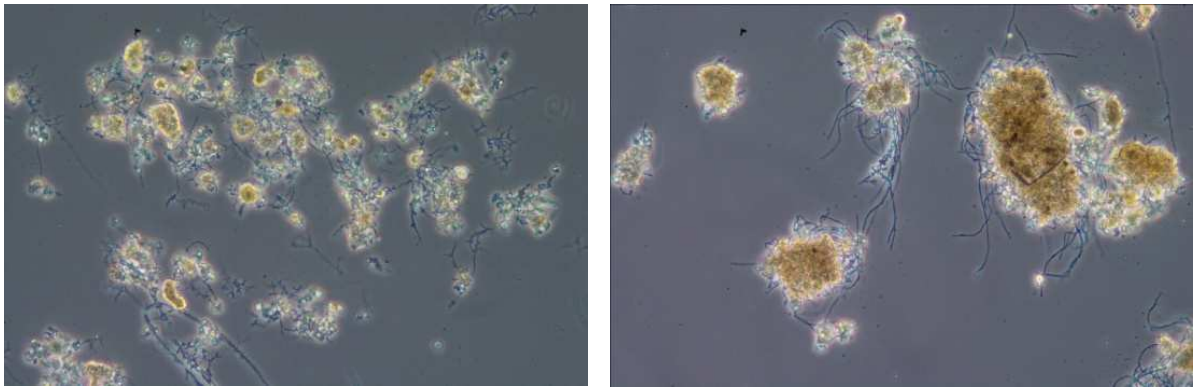


Figure 4.8 (left side): Microscopic observation (100x) of sludge from the full-scale sMBR system of Schilde. Figure 4.9 (right side). Microscopic observation (100x) of sludge from the full-scale CAS system of Schilde

A microscopic evaluation of the sludge from CAS and MBR was carried out. The MBR flocs were characterized by a very open form and were composed of many sub-compartments (Figure 4.8), including compact cores, cell clusters, and filamentous bacteria. The particle size distribution of both sludges was measured, yielding an average floc size of 40-50 µm for the MBR and 200 µm for the CAS, as in Masse *et al.* (2006). The CAS flocs were characterized by a non-dispersed form (Figure 4.9). Although they received the same influent, dimensions and overall floc morphology of CAS and MBR sludge were very different.

A lower K_{OA_AUT} would theoretically improve the aeration energy performance by increasing the O_2 mass transfer. Some ASM simulations were run to assess the sensitivity of this parameter on the overall MBR performances. It was found that a variation of the parameter from 0.5 to 0.2 mgO_2/l (the former is the default ASM2d value) yielded a very modest decrease in the aeration power consumption. At the same time the TN removal increased significantly with 2.5%. The low impact on the energy consumption can be explained by the fact that only the fine bubble aerators (bioreactor) are controlled by the O_2 set-point, while the coarse bubble aerators (membrane tanks) operate constantly. Hence, despite the O_2 mass transfer rate through the floc improves with decreasing K_{OA_AUT}, only a small portion of the MBR aeration can profit. Despite the irrelevant energy saving, the TN performance increase is significant since the O_2 mass transfer rate improvement is applicable both in fine and coarse bubble aeration.

It can be concluded that with the present aeration controllers (with constant coarse aeration flow), a lower floc size leads to a higher TN removal and a negligible aeration energy saving.

Table 4.2: Comparison between the mixing energy consumption of different full-scale CAS systems and this MBR system. (= related to intermittent aeration). (** = Roels et al., 2010).*

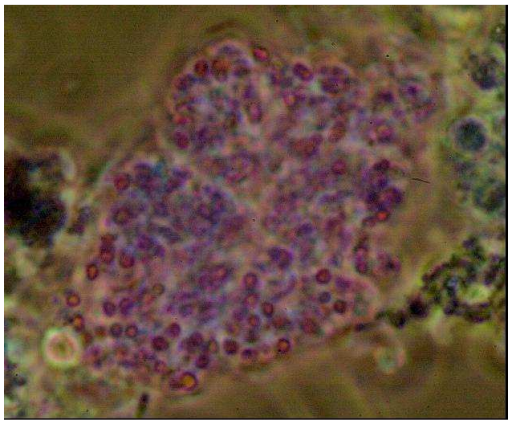
WWTP	Anoxic Volume	Consumption	Consumption	References
	m^3	*kWh*	*kWh / m^3 Volume / year*	
MBR Schilde	500+500*	123500	123	*This work*
Bree	1537	45000	29	**
Aalst	4500	300000	66	**
Brugge	10000	963600	96	**

4.3.2.2 Effect of the MLSS concentration on the MBR energy consumption

MBR systems are known to operate at high MLSS concentrations. In the Schilde MBR process the MLSS ranges from 9-11.5 g/l, while the MLSS in the CAS system fluctuates between 2.5-4 g/l. In Table 4.2, the energy consumption for mixing of the MBR is compared with other Aquafin CAS installations. It is clear that a high MLSS concentration is accompanied by high mixing costs. The only installation that comes close to the MBR is the WWTP of Brugge. This can be explained by a high sand content in the tanks due to an inefficient sand trap. To avoid excessive sedimentation extra mixers were installed.

Despite the high energy input for mixing, Prieske *and* Buts (2009) studied the hydrodynamic conditions in the Schilde MBR lane, reporting low velocities in the centre of the anoxic tank (below 0.2 m/s) and a consequent possibility of sedimentation.

The phosphate removal could not be modelled successfully with ASM2d. The modelled PO_4 concentration in the effluent was higher than the observed values. In the model, the phosphate accumulating organisms (PAOs) were outcompeted since polyhydroxyalkanoate could not be sufficiently stored, despite the fact that the rate of storage was arbitrarily increased. Tests on the MBR sludge proved the presence of PAOs biomass in reality. Both Methylene blue and Sudan staining of the MBR mixed liquor indicate the presence of a reasonable amount of poly-P and polyhydroxyalkanoate storage (Figure 4.10-4.11). The experimental results thus show that PAOs were able to survive without an anaerobic reactor and with a sensible NO_3 concentration all over the MBR lane.



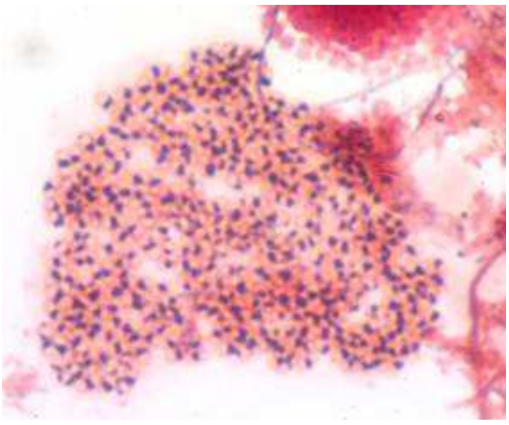


Figure 4.10 (left side): Poly-P in the MBR mixed liquor highlighted with the Methylene blue staining technique. Figure 4.11 (right side): The Polyhydroxybutyrate storage (in blue) in the MBR mixed liquor highlighted with the Sudan staining technique.

Silva *et al.* (2009) sampled several full-scale MBRs and they also found the presence of PAOs in MBRs not designed for EBPR. According to the authors, this phenomenon could be related to high floc compactness and density of EPS. The authors infer that MBRs tend to contain anaerobic micro niches in higher proportion than CAS systems, giving PAOs the competitive conditions to thrive. In the Schilde MBR, as stated before, the flocs were also very compact (Figure 4.8). But using this argument to explain anaerobic zones sounds contradicting with the high O_2 diffusion through the floc. We believe that anaerobic zones may exist in MBRs as a consequence of insufficient mixing conditions.

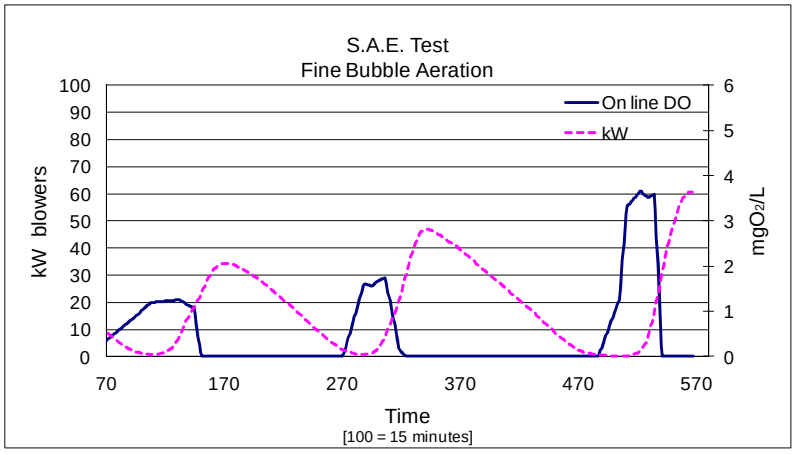


Figure 4.12: Aeration test performed to determine the standard aeration efficiency (SAE) of the aeration tank, as described in the methodology. On-line DO and kWh trends are plotted.

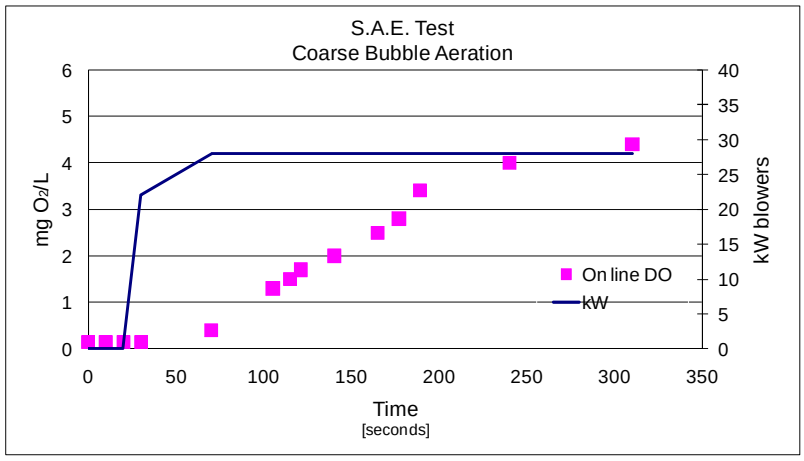


Figure 4.13: Aeration test performed to determine the standard aeration efficiency (SAE) of the filtration tank, as described in the methodology. On-line DO and kWh trends are plotted.

As already investigated (*inter alia* Germain *et al.,* 2007), the high MLSS concentration influences also the aeration efficiency. The standard aeration efficiency (SAE) of the fine and coarse bubble aeration systems was determined using the methodology defined in section 4.2.3. During the tests, the power uptake and the O_2 content in the mixed liquor behaved as depicted in Figure 4.12 (fine bubble aeration) and Figure 4.13 (coarse bubble aeration). In the fine bubble aeration system large variations in SAE (1 to 1.7 kgO_2/kWh) were recorded depending on the air flow rate that was varied by changing the number of active blowers (Table 4.3). These variations are to be attributed to the efficiency of the membrane diffusers. It is known that the efficiency decreases with increasing air flows. For the coarse bubble aeration, an SAE of 0.85 kgO_2/kWh was found at a constant operational flow rate. This small difference in SAE between the coarse and fine bubble system is remarkable.

Table 4.3. SAE of the MBR fine bubble aeration is determined in kgO_2/kWh *with blowers working in different configurations.*

Blower 1	Blower 2	Blower 3	Total Power	End. rate	SAE
%	%	%	kWh	kgO_2/h	kgO_2/Kwh
100			30	7.21	1.70
100	100		60	8.30	1.04
100	100	100	90	8.70	1.10

In aeration systems the a factor is defined as the ratio of the O_2 transfer coefficient (KLa) obtained in the activated sludge mixed liquor and the one obtained in clean water. The a factor has been widely

investigated as function of the MLSS. While some studies tend to depict a strong inverse relation between MLSS and a (*inter alia* Krampe *and* Krauth, 2003), others would seem to show a milder inverse relation (inter alia Muller et al., 1995; Rosenberger, 2003). In this work, the ratio between SAE in the mixed liquor and the SAE in clean water, leads to an a factor of 0.39 at an MLSS concentration of 10.5 g/l. The value obtained in Schilde MBR seems to confirm the results of Krampe and Krauth.

*4.4 **Suggestion for energy friendly MBR process layout***

The Schilde MBR process scheme has a very distinctive feature when compared to CAS systems. The aeration is provided either in the middle (fine bubble) and in the rear (coarse bubble) of the process scheme (Figure 4.1).

In Schilde, the coarse bubble flow is constant (since designed for fouling control). The fine bubble aeration instead varies along with operations, i.e. it can be tuned on longer or shorter aeration times and on higher or lower O_2 set-points. During operations it fluctuates seasonally, between 30% (summer) and 50-60% (in winter) of the aeration cycles. In fact, considering the coarse aeration flow as a mere tool for scouring purposes does not correspond with reality, and its contribution to the overall O_2 transfer to the activated sludge would need to be quantified.

The fine bubble system is responsible for 10.5 % of the total energy demand and the coarse bubble system accounts for 35.2% (Figure 4.3). Considering the amount of kWh provided in the two aeration systems, the different SAE and the high O_2 concentrations in the permeate, the ASM2d model shows that 70% of the O_2 is averagely supplied by the coarse aeration flow. However, when subtracting the dissolved O_2 that leaves the system with the permeate flow, the O_2 transferred through the coarse aeration flow becomes 28% of what is used by the biological process.

Thus the coarse aeration flow consumes 3 times more KWh than the fine bubble aeration, while contributing less than one third to the total biological oxygen requirements. The high amount of air provided for scouring purposes in the membrane chambers could potentially have a role in the biological process if better integrated in the biological process scheme. This observation seems to indicate that an energy optimization may not only be obtained by a better understanding of the fouling phenomena, as the scientific literature has so far done, but also by giving proper attention to the MBR process layout.

*4.5 **Conclusions***

A dynamic biological model was calibrated for the full-scale hybrid installation of Schilde with specific focus on a correct prediction of energy consumption. The following conclusions were drawn:

- More than half of the total energy demand of the studied MBR is needed for filtration.
- The full-scale Schilde MBR consumes 0.64 kWh/m^3 permeate production. This is low when compared to other full-scale municipal MBRs. It is however much higher than CAS systems treating municipal sewage Flanders.
- The MBR technology is more energy intensive than a CAS system with UF and UV disinfection, a system believe to deliver a comparable effluent water quality.
- The modelling exercise confirmed the reduction of the half saturation coefficients for O_2 reported in literature. This reduction resulted in a higher TN removal rather than in significant aeration energy savings.
- The high MLSS concentrations in the studied MBR system have an impact on the mixing energy requirements. The power consumed per m^3 stirred volume is substantially higher than in the CAS systems.
- The coarse bubbles provided for scouring purposes in the membrane chambers could potentially have a role in the biological process if a different process layout would be used. An energy optimization may not only be obtained by a better understanding of the fouling phenomena, as reported so far in the scientific literature, but also by giving proper attention to the MBR process layout.

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Chapter 5

Modelling Soluble Microbial Products in a full-scale MBR

Re-drafted from: A. Fenu, T. Wambecq, C.Thoeye, G. De Gueldre, B. Van de Steene, 2011, Modelling Soluble Microbial Products In A Dynamic Environment. Desalination and Water Treatment, 29.

Abstract: A calibrated ASM2d model of a full-scale MBR is modified as to include the soluble microbial products (SMPs) fractions and study their dynamics in full-scale. Batch tests were conducted to estimate the SMP kinetics. The biomass associated products (BAPs) kinetics were estimated with results in tune with previous experiments. The utilization associated products (UAP) kinetics estimation was instead complicated by two aspects which regularly occur when spiking readily biodegradable COD: storage phenomena (not accountable in ASM2d); the non-uniformity between the polysaccharide fraction, easily biodegradable, and the protein fraction, which proved to be refractory to biodegradation. The procedure for UAP kinetics estimation would thus require further analysis. UAPs were found in full-scale markedly predominant compared to the BAPs.The data analysis revealed that the membrane rejection mechanism was identified as SMP loading rate dependent, emphasizing the need of a more careful consideration towards this parameter when working in a dynamic environment. The work discusses the feasibility of the SMP extension studies in dynamic conditions. Fine tuning of the membrane rejection factor, the necessity of more frequent sampling, and experimental determination of the additional kinetics SMP parameters become necessary and burdensome adaptations of the ASM calibrations. However both nutrients removal, sludge production and energy consumption modelling were not improved by including the SMP fraction in the modelling. SMPs did not correlate with fouling rates in this full-scale MBR, indicating a strong drawback, since the main drive for these models is thus not accomplished.

5.1 ***Introduction***

In the last decade, several studies have been carried out to include the SMPs concept in the activated sludge model (ASM) framework. The main drive for this extension was that SMPs were considered up to now a crucial fouling indicator (Meng *et al.,* 2009). The correlation between SMP fraction and fouling events was highlighted *inter alia* by Le-Clech *et al.* (2006), and Rosenberger *et al.* (2006). A model extension from the general ASM models with the SMPs always implies the introduction of several extra kinetics parameters, i.e., Lu *et al*. (2001) introduces 8 SMP related parameters in the ASM1 platform. Saroj *et al.* (2008) infers that incorporation of SMPs in ASM would enhance the practical identifiability problem which is considered a crucial issue of the ASM calibration process. Jiang *et al.* (2008) tackles this problem by setting up specific batch tests in order to evaluate separately the SMP related parameters.

The general aim of this work is to analyze the advantages and feasibility of the ASM-SMP approach in full-scale modelling according to the most updated research proposals. Several questions will have to be answered: is it possible to determine experimentally reliable SMP kinetic parameters? Does this procedure impact on the modelling exercise complexity? And last but not least, are the SMPs a relevant indicator for fouling prediction?

5.2 ***Materials and methods***

The MBR of Schilde (Belgium) was built in 2003. The MBR is composed of a sand trap and a drum-sieve to protect the downstream system, a pre-denitrification tank (500 m^3), an aeration basin (500 m^3), and

a filtration unit (240 m³). The filtration unit is composed of 4 Zenon (Zeeweed 500c) MBR filtration tanks having a total membrane surface area of 10,160 m² treating in total an average flow of 230 m³/h, and maximum peak flow of 355 m³/h. The sludge recycle flow from the filtration to the aerobic compartment is 6 times the influent MBR flow.

The Schilde MBR model was calibrated in year 2006, and validated in year 2009, with routine daily composite samples of influent and effluent flows. Sample frequency was every 2 weeks in 2006 and every 1 to 2 weeks in 2009. During both phases, influent and effluent samples were analyzed for BOD, COD, SS, TN, KJN, ammonia, nitrate, ortho-phosphate and TP. All samples were analyzed according to Standard Methods (APHA, 1999). Samples filtration step was performed with a 0.45 µm polyester filter. MLSS concentration was calculated by the Standard Methods (APHA, 1999). Nitrate, kWh of coarse and fine bubble aeration, flows, and dissolved oxygen were monitored with on-line probes.

With regards to the influent soluble inerts (Si) measurements, the procedure of Lu et al. (2001) was employed: MBR sludge biomass was centrifuged at 3000 rounds per minute (RPM) for 5 minutes, washed with permeate water and centrifuged again. The biomass was then added to the soluble influent in a concentration of 3 g/l and aerated in a Erlenmeyer flask for about 4 hours. Afterwards the sample has been filtrated and the soluble COD (COD_{sol}) measured.

Protein (PT) content in the SMPs were measured on filtrated samples (0.45 ùµm polyester filter), according to Lowry *et al.* (1951). For the calibration Albumin bovine, BSA, (Acros) fraction V, in a concentration range between 0-25 mg/l was used. Polysaccharides (PS) content in the SMPs were measured on filtrated samples (0.45 µm polyester filter), by the Anthrone method based on Dreywood (1949). For the calibration D(+)- anhydrous Glucose (Acros) in a concentration range between 0-100 mg/l was used. Factors are applied for conversion of PT and PS from mg/l in mg COD/l, (respectively 1.5 and 1.0 gCOD/gsubstance), by assuming that Bovine Serum Albumin (BSA) represents PT and glucose represents PS. Conversion factors have been cross-checked in the lab.

Fresh sludge was sampled from the connection between the MBR biology and the filtration tanks. This was immediately poured in the batches ready for experiments. All batch experiments were conducted at room temperature (20 °C), and pH was adjusted by NaOH (0.1 M) and HCl (0.1 M) solution.

To determine the biomass associated products (BAP) kinetics, batch experiments were conducted under starvation conditions without substrate addition. The produced SMP, dominated by BAP according to Jiang *et al.*, (2008), were measured along 15 days. The experiment was repeated twice. COD_{sol}, MLSS, MLVSS, O_2 and SMPs concentration were measured.

To determine the utilization associated products (UAPs), batch experiments were spiked with acetate (HAc) in different concentrations under continuous aeration. The HAc solution is neutralized before being added to the batch. The experiment had 12 hours duration. Meanwhile, a reference batch experiment was conducted without HAc addition to obtain the background COD_{SOI} and SMP concentration. The net UAP concentration was determined with respect to the reference batch concentration. This method eliminates the BAPs in the UAP batch, as proposed by Jiang *et al.*, (2008). Experimental errors are expressed as mean average deviations.

A model library in MATLAB environment, developed by Aquafin, was used to perform model simulations and parameter estimations. The experimental batch test was reproduced on the ASM2d_SMP model and the kinetics values of the UAP/BAP derived. The model was tested on the validation campaign (20.01.09 – 31.05.09) of the full-scale MBR plant.

5.3 ***Results and Discussion***

5.3.1 ***Matrix modifications***

SMP models have been developed since the late eighties. The SMP subdivision among UAPs and BAPs species has been widely accepted (Namkung *et al.*, 1986): (i) UAPs, i.e. SMPs that are associated with substrate metabolism and biomass growth and are produced at a rate proportional to the rate of substrate utilization. (ii) BAPs, i.e. SMPs that are associated with biomass decay and are produced at a rate proportional to the concentration of biomass. Jiang *et al.* (2008), review the ASM2d matrix with some interesting upgrades: amongst others, substrate degradation is accompanied by UAP formation (from 0 to 100 %), and fuap represents this percentage (* in Table 5.1). According to the authors, UAPs need to be hydrolyzed before being available for metabolic processes. Therefore 3 new hydrolysis steps (aerobic, anoxic, anaerobic) are added in the ASM2d matrix (not shown in this book). Cell lysis is accompanied by BAP formation (from 0 to 100 %), and fbap represents this fraction. Also BAPs would need to be hydrolyzed before being available for metabolic processes. Therefore 3 new hydrolysis steps will be added in the ASM2d matrix.

Table 5.1 – In line (*), an example of the original Jiang's et al., (2008) mode with regards to the "aerobic growth of Xh of Sf". In line(**), the modifications in this work for the very same process.

	So	*Sf*	S_{UAP}	X_H	*Rate*
Aerobic growth of X_h on S_f (*)	$-\frac{1-Y_H-f_{UAP}}{Y_H}$	$-\frac{1}{Y_H}$	$\frac{f_{UAP}}{Y_H}$	1	$\mu_H X_H \cdot switches$
Aerobic growth of X_h on S_f (**)	$-\frac{1-Y_H\cdot(1-f_{UAP})-f_{UAP}}{Y_H\cdot(1-f_{UAP})}$	$-\frac{1}{Y_H\cdot(1-f_{UAP})}$	$\frac{f_{UAP}}{Y_H\cdot(1-f_{UAP})}$	1	$\mu_H X_H \cdot switches$

When the ASM2d version matrix was updated as above, a difficulty immediately emerged in the UAP process. In fact, it appeared that the sludge production would have to increase accordingly to increasing f_{uap} percentage. For instance, in the heterotrophic growth on fermentable substrate (S_f) , a unit of S_f would produce Y_H biomass, notwithstanding the amount of substrate diverted into UAPs (* of Table 5.1). In this way, biomass would be produced immediately from S_f degradation, but also afterwards from UAP degradation, overcoming the maximum Y_H conversion (mg biomass / mg substrate). For example, if 50% substrate would be converted into UAP (f_{uap}=0.5), the system would produce immediately Y_H biomass plus other $0.5 \cdot Y_H$. The COD mass balance is thus not valid anymore. In truth, if the UAP concept is correctly implemented, a unit of S_f would at first yield "$Y_H \cdot (1-f_{uap})$" biomass, and the remaining UAP would produce a maximum of "$f_{uap} \cdot Y_H$" biomass only once converted, i.e., after hydrolysis. Matrix modifications were implemented as such to consider the heterotrophic sludge yield as $Y_H \cdot (1-f_{uap})$, instead of $Y_H/(1+f_{uap})$, i.e., the correction factor applied in Jiang *et al.* (2008). The updated process is shown in Table 5.1, for the "Aerobic growth of heterotrophs (X_H) on fermentable substrate (S_f)" process. The BAP process was not modified.

Another modification was made as to assume that the degradation of UAP and BAP produces intermediate products and biomass but does not lead to the production of new UAP or BAP. This assumption was employed by several research groups (Aquino *et al.,* 2008; Laspidou *et al*., 2002). Any carbonaceous substrate is partly converted to UAPs according to the f_{uap} percentage. The latter are now converted into a newly made fraction, S_f^*, modelled as the original S_f in ASM2d (a unit of substrate yields Y_H biomass and no UAPs). Differently from S_f, S_f^* can only be produced by UAP hydrolysis.

The last modification regards the role of the autotrophic biomass (X_{aut}) in the UAPs formation. The UAPs production mechanism from the X_{aut} would imply a reduction of the autotrophic sludge yield of $Y_A \cdot (1-f_{uap})$ in favour of the UAP formation. Consequentially, the autotrophic population would be reduced in favour of the heterotrophic population. This step requires attention when fitting the nitrogen removal. Lu *et al*. (2001) fitted a specific parameter for the UAP formation during autotrophic conditions. However this practice increases the amount of unknown kinetics variables when calibrating the model. The option of running batch tests for the determination of the SMP kinetics of the X_{AUT} has been excluded. We observed instead that the extension of SMPs on the X_{AUT} would not produce a significant UAPs, given their low concentration (250 mg COD/L) compared to the X_{HET} concentration (1800 mg COD/L). The UAPs mechanism was not modelled on the X_{AUT}.

*5.3.2 **Batch experiments for the SMP kinetics determination***

With regards to the UAP batch test: batch experiments with different HAc concentrations were run. A reference batch was conducted without HAc addition, to obtain the background soluble COD and SMP

concentration. The highest concentration, 500 mg COD/l, is representative of a high load in full-scale. SMPs concentration in the reference batch is constant, and mainly assimilated with BAPs, as justified by the low degradation (red dots in Figure 5.1 and 5.2) . PT content in the SMPs exhibit an immediate degradation followed by a very low degradation rate. A concentration of 5 mg/l remains in the system at the end of the test. PS content in the SMP exhibit a peak at 1 hour and are then completely degraded within 4 hours (Figure 5.2). PS an PT content in the SMP peaks do not occur at the same moment but within the same first hour. Net production of PS and PT would then be summed up to yield the net produced UAPs. COD_{sol} is high at t_0 and then steadily drops. After 10 hours the COD_{sol} of the 3 batches almost coincide again.

According to the procedure defined in the methodology, the batch test results must be modelled on the ASM2d $_{SMP}$ model. The model will have to fit first the COD_{sol} when degrading the HAc, and secondarily the SMPs concentration. The kinetic values of the UAP would be consequentially derived. MLSS concentration was measured in the plant (9 g/l) and biomass fractions were predicted in the ASM2d model.

Due to the high heterotrophic concentration, the μ_H (growth rate of heterotrophs) governs the speed of the carbon source degradation (default value of μ_H in ASM2d is 3-6 for temperature 10-20 °C). The μ_H has been adjusted to fit the COD_{sol} concentration. But as in Figure 5.3, the COD_{sol} could not drop sufficiently, and the modelled COD_{sol} remains far higher than the experimental COD_{sol}. Guidasola *et al*., (2006), pointed out that ASM1 is not capable to model properly the feast conditions when influent is characterized by readily biodegradable COD. The data analysis showed that the COD_{sol} fate in the batch could not be properly modelled, and that the ASM2d is not able to reproduce this batch condition. The problem could be overcome by considering that a part of the HAc is immediately used for growth, and a part is simultaneously stored. The net experimental SMPs production backs up this assumption. If HAc would have been entirely degraded, the SMPs concentration would have been much higher than the 25 mg/L measured (the fraction of produced UAPs according to literature is generally about 0.3 mg UAPs / mg substrate, meaning that 180 mg COD/l of UAPs should be produced from a HAc spike of 500 mg COD/l).

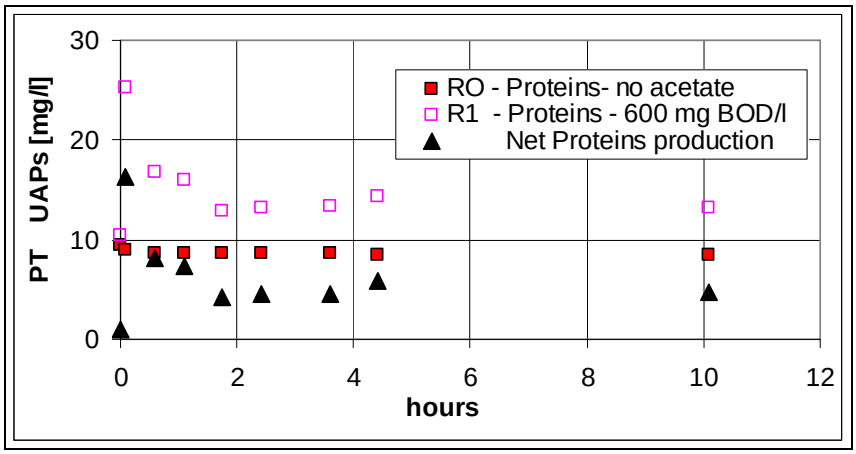

Figure 5.1: PT content in the *SMPs in the lab batch test spiked with 600 mgCOD/L HAc. PT* content in the *SMPs in the reference lab batch test.*

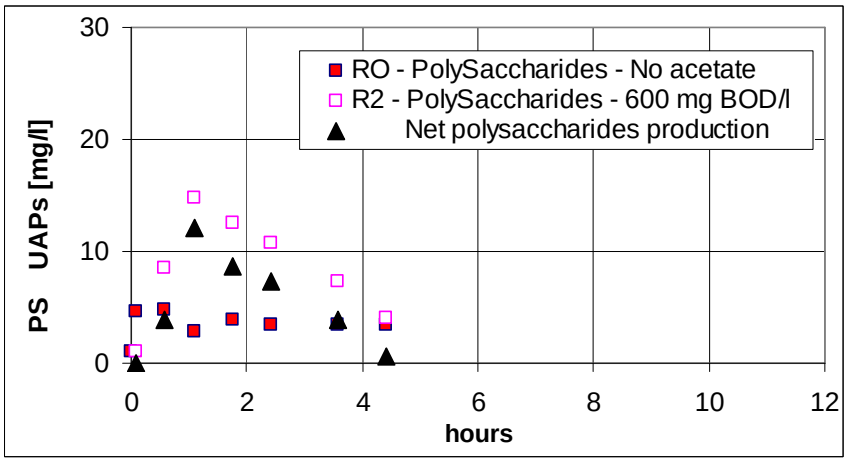

Figure 5.2: PS content in the *SMPs in the lab batch test spiked with 600 mgCOD/L HAc. PS* content in the *SMPs in the reference lab batch test.*

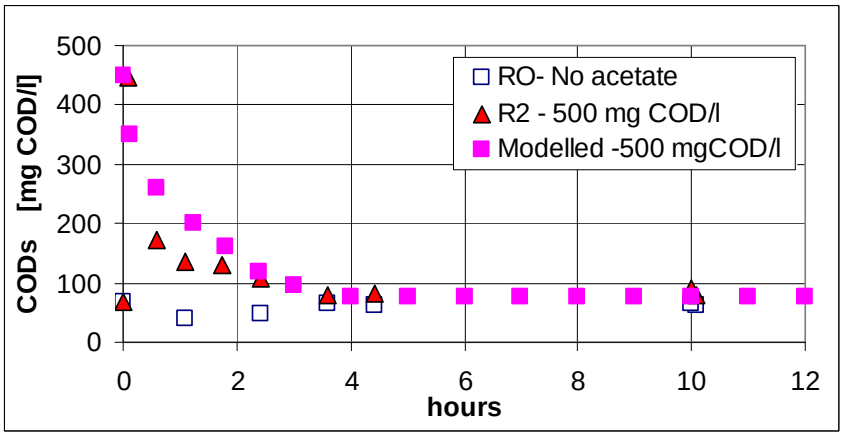

Figure 5.3: Experimental and modelled soluble COD fate in the lab batch reactor.

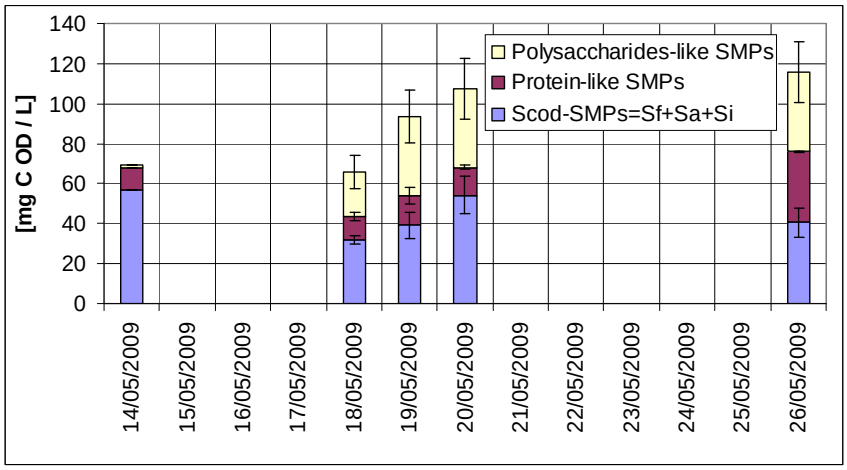

Figure 5.4: Average SMPs and mean deviation error in lab batch 1 and 2

The UAP kinetics appear different during the experiment. In the second part of the experiment (after the second hour in Figure 5.1), the PT fraction is more recalcitrant to degradation. As already highlighted by several authors two phases are distinguishable: growth on substrate and growth on storage products (Van Loosdrecht *et al.*, 1997). The problem of the uncertain kinetics determination that rises when comparing first and second phase was avoided by Jiang *et al.* by ignoring the second phase. However, this is risky since it may lead to an overestimation of the net UAPs formation. Due to (i) storage phenomena occurring with readily biodegradable COD spiked, and (ii) different degradation rates between the UAP fractions, the protocol described in the methodology cannot yield valuable data and UAP kinetics data will be simply fitted. The batch protocol should be updated as to overcome these problems.

With regards to the BAP batch test: two parallel experiments were conducted in order to verify the results reproducibility. The operational conditions were controlled as described in the material and methods section. O_2 increased during the experiment (3-6 mg/l), as a result of the active biomass reduction. This was confirmed by a decrease of the MLVSS fraction, from 70 up to 40 %, meaning that the lysed cells were transformed in inert and inorganic material. Both reactors behaved similarly. SMP concentration increases over time in both reactors and eventually saturating, since biomass lysis impedes further degradation. Both fractions (COD_{sol} and SMP) tend to increase in concentration. Overall results are displayed in Figure 5.4, where an average value and standard errors of the two parallel reactors are computed. COD_{sol} of the settled sludge supernatant is subtracted from the SMP concentration of the settled sludge supernatant, in order to give inert and readily biodegradable COD fractions.

ASM2d was extended according to the processes described above, implemented in Matlab and used to model the experiment, within the same experimental conditions. BAP test was fitted with an f_{BAP} of 0.05 and an hydrolysis rate $K_{h,BAP}$ of $1*10^{-6}$ d^{-1} (Figure 5.5-5.6). These values are comparable with Jiang *et al*. (2008) figures, where an f_{BAP} of 0.0215 and an hydrolysis rate $K_{h,BAP}$ of $7.41*10^{-7}$ d^{-1} was found.

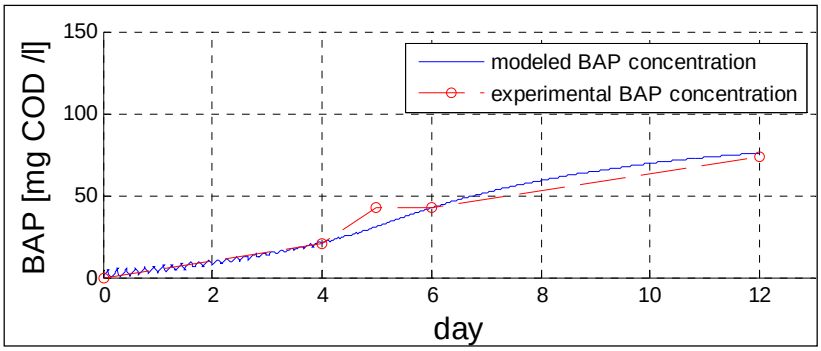

Figure 5.5: Experimental and modelled BAP concentration in the lab batch reactor.

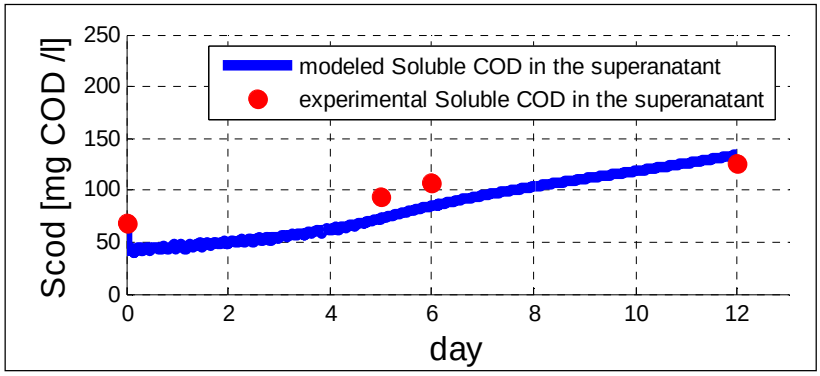

Figure 5.6: Experimental and modelled soluble COD concentration fate in the lab batch reactor.

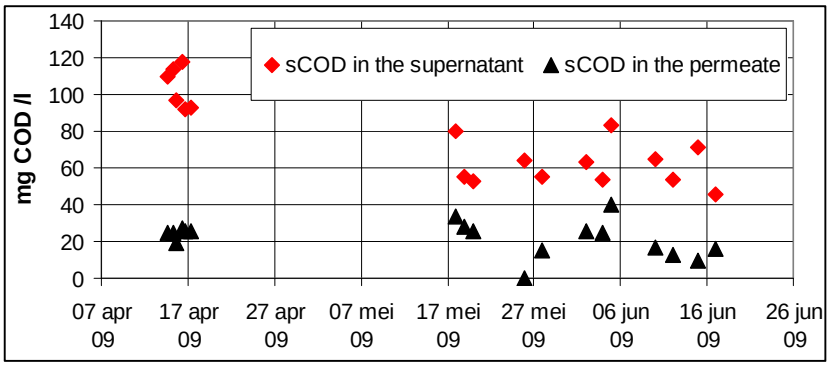

Figure 5.7: Soluble COD concentration measured in supernatant and permeate waters of Schilde MBR.

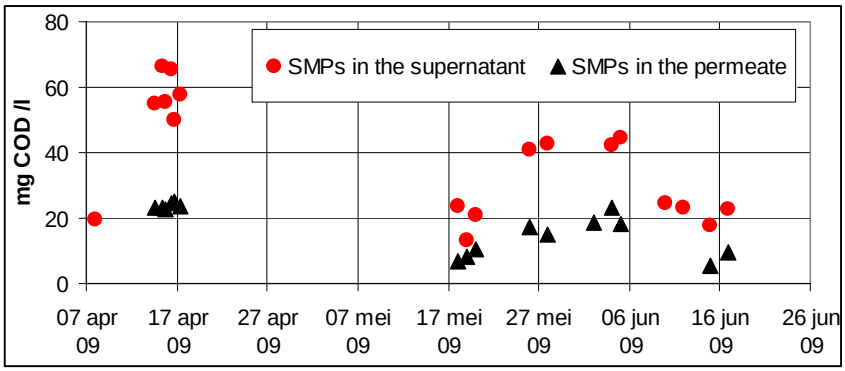

Figure 5.8: SMP concentration measured in supernatant and permeate wates of Schilde MBR.

5.3.3 ***SMP sampling campaign in dynamic conditions***

The ASM models extended with the SMPs concept are typically differentiated by the need of characterizing two fractions: influent Si and SMP fractions. In an ASM-SMP model, the influent Si cannot be anymore estimated by the effluent COD since effluent MPs have to be excluded and properly modelled. The procedure of Lu *et al*. (2001) was employed to determine the influent Si.

With regards to the SMP measurements, a sampling campaign has been performed during the period 10.04.09-15.06.09. COD_{sol} and SMPs have been quantified in supernatant and permeate. In both cases SMPs were always found as expected smaller than the COD concentration. It is important to stress that, while the permeate sample is a flow proportional sample, the supernatant is a grab sample (the sludge water filtration impedes the collection of flow proportional samples). This implies that the supernatant will be much more dependent on the peak loads than the permeate samples.

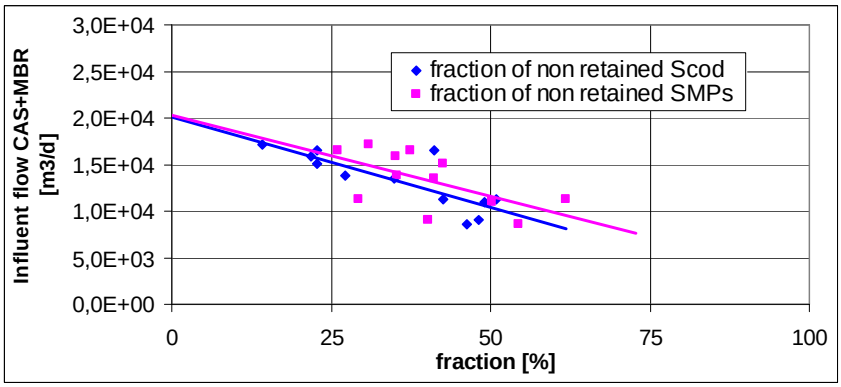

Figure 5.9: Influent flow versus "fraction of non retained CODsol" and "fraction of non retained SMPs".

If the SMP in the permeate is divided by the SMP in the supernatant, and plotted against the relative total daily influent flow, a correlation (R^2=0.67) appears between the fraction of non retainable SMPs

and the total influent flow (Figure 5.9). A similar correlation can be seen for the COD_{sol} of the permeate and the supernatant (Figure 5.9). In full-scale, the higher the total flow, the higher the dilution, exception provided for the first flushes events. But a daily constant flow is diverted to the MBR process, since the limited membrane area restrains the MBR hydraulic dynamics. Thus higher influent flows generally imply lower loads to the MBR lane. The experimental results in Figure 5.9 show a dependency among the influent load (Y axes) and the SMP removal (X axes). This finding will be discussed in the next section.

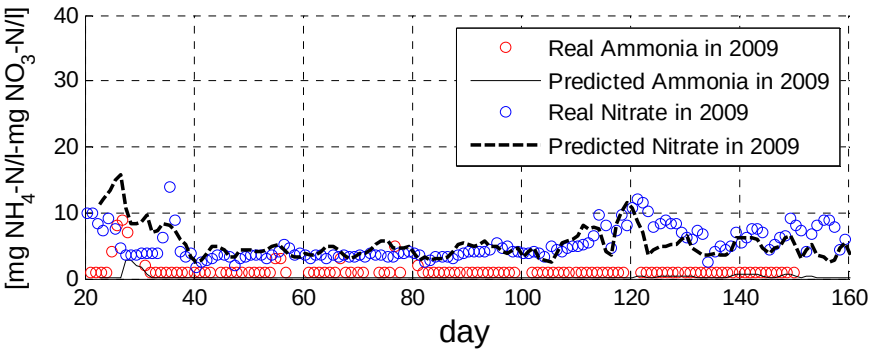

Figure 5.10: Predicted vs measured Ammonia and Nitrate in the permeate waters of Schilde MBR.

5.3.4 ***Model comparison***

The ASM-SMP model has been implemented with the following procedure: (i) the ASM2d model (in Fenu *et al.*, 2010a, 2010b) has been updated with the extended matrix; (ii) influent file, influent converter parameters, removal rates of particulate matter in the pre-treatment, ASM2d kinetics parameters, dosed HAc and controls have not been modified. (iii) the effluent file has been modified in order to yield a Si concentration according to the experimental work. As a result of the lower Si concentration, the sludge production has to be fitted again; (iv) BAP specific kinetics parameters derived in the batch tests are inserted in the model; (v) UAP specific kinetics parameter will be inserted (as a trial and error procedure) in order to fit the SMPs in the permeate; (vi) SMP dynamic is completed by fine-tuning the retention factors at high-low flows; (vii) in case of deviation, the real total aeration energy would be matched by fitting the specific aeration energy (in kgO_2 per kWh blown).

Since the matrix has been set in order not to include UAP mechanisms in the nitrification processes, ammonia effluent does not report significantly different results (Figure 5.10). Moreover the slowly biodegradable content added in this procedure is not sufficient to yield significantly different denitrification rates. Fitting of the nitrate effluent is overall very good. Cumulative dose of HAc was also fitted since crucial when modelling the denitrification rates.

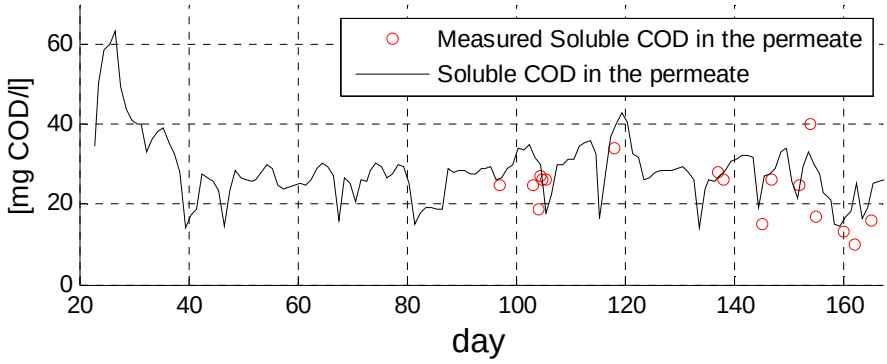

Figure 5.11: Predicted vs measured soluble COD concentration in the permeate waters of Schilde MBR.

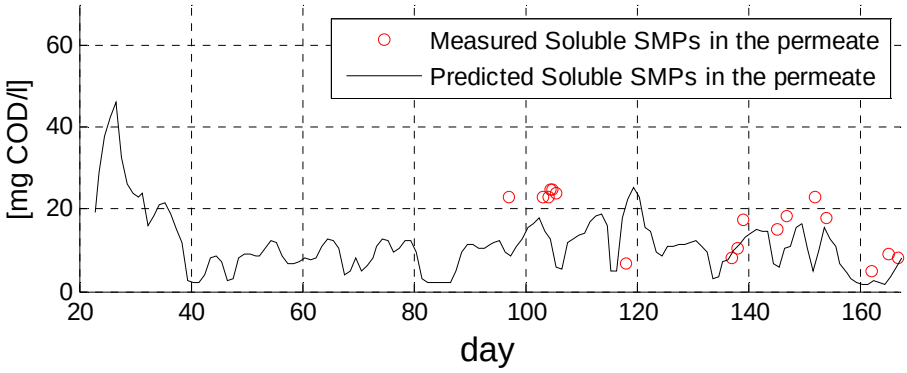

Figure 5.12: Predicted vs measured SMP concentration in the permeate waters of Schilde MBR.

The average reduction of Si (from 25 mg COD/l to 17 mg COD/l) will correspond to a slightly higher particulate inert content Xi (since the total inert content does not change). In reality the Xi variation did not have a marked influence on the sludge production. Hence, the K_{bod} (0.27) was not modified. The introduction of SMPs did not reflect in a significantly different energy consumption. Thus nutrients removal, sludge production and energy fitting did not receive further benefit from the SMP modelling.

The fractions of non retainable SMP and COD have been modelled as linear function of the incoming flow, according to experimental results and fine-tuned by a *trial and error* procedure. In terms of COD effluent, fluctuations are fitted, due to the modelled fraction of non retainable COD, and the model predictions are excellent (Figure 5.11).

In terms of SMPs, several points must be commented: (i) BAP have been determined by inserting the specific parameters obtained during the experimental part, (f_{bap} of 0.05 and $K_{h,bap}$ of $1*10^{-6}$ d^{-1}). The impact of the BAP fraction is minimal, and higher values of f_{bap} do not lead to increased significant SMPs

concentrations. It appears that most of the SMPs will have to be produced through the UAP metabolic path, being thus very sensitive to the influent loads; (ii) UAP have been fitted with a trial and error procedure. Results yield a f_{uap} of 0.6 and $K_{h,bap}$ of $1*10^{-6}$ d^{-1}. SMPs in the permeate have been reasonably fitted along the days 110-150, but a poor fitting has occurred during the days 95-105, where the SMP effluent values were as high as the COD effluent (Figure 5.12).

If the BAP concentrations are not so significant, the higher influent loads will necessarily generate higher SMPs, according to the UAPs definition. The Figure *5.9* would then imply that SMPs are less retainable with increasing loads, i.e. increasing SMP loading rates. This result was already observed by Drews *et al.,* (2007). Recent literature on SMP modelling has instead simplistically considered the COD retained fraction as a constant parameter (Fenu *et al.,* 2010c), ranging from 0 to 100%. The difference between this experimental finding and the recent literature (*inter alia* Jang *et al*., 2006) can be explained by the non-dynamic conditions of pilot scale academic works: low variability in flows and concentrations will yield quasi constant retention factors.

It must be reported that SMPs were slightly underestimated in the supernatant. These values are very difficult to be matched because the supernatant samples are grab samples (fetched always at 15.00 PM). Grab samples are certainly sensitive to the peak loads which might result in higher SMPs measured concentration. However, a model calibration based on shorter frequencies than a daily base would require a burdensome sampling work for long calibration campaigns in full-scale.

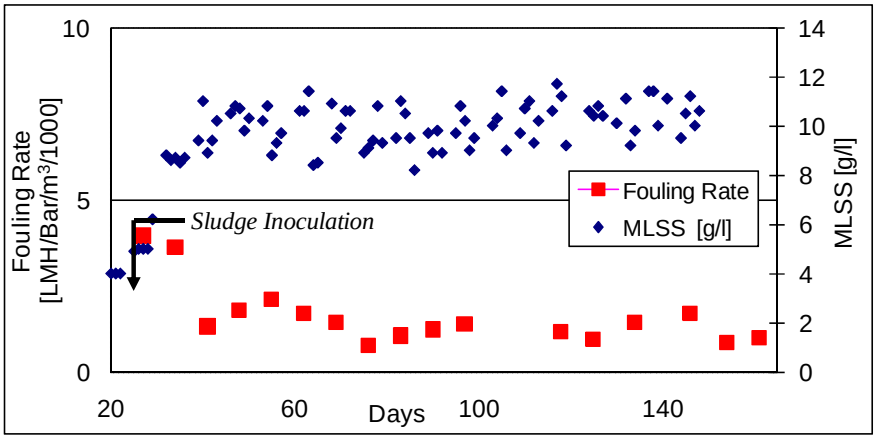

Figure 5.13: Fouling rates during the period of 20.01.09 to 20.06.09 at Schilde MBR.

With regards to the fouling rates, they have been computed in Figure 5.13 (in LMH/bar/$m^3_{permeate}$) through the dataset of Figure 5.14. Fouling rates are characterized by relatively constant values with the exception of high fouling rates for low MLSS concentrations (4-8 g/l after sludge inoculation). Fouling propensity of low MLSS concentrations (from day 20 to 40 in Figures 12, 13 and 14) has already

been reported by Bin *et al*., (2004). When fouling rates are plotted against the supernatant SMP concentration, the results are very scattered and tend to show no correlation, meaning that SMPs do not trigger higher filtration resistances. This fact indicates a strong drawback in the use of these models since, at least in case of this full-scale MBR, the main drive is not accomplished. It is thus strongly recommended to assure such correlation before starting this modelling procedure.

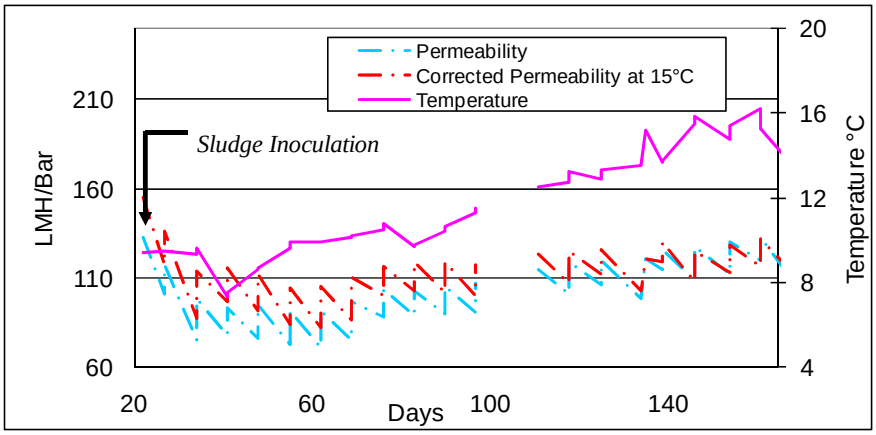

Figure 5.14: Fouling history during the period of 20.01.09 to 20.06.09 at Schilde MBR.

5.4 ***Conclusions***

The work represents a rare application of the most advanced literature on ASM-based models extended for SMP modelling, in a full-scale waste water treatment plant. A new matrix has been created based on the ASM2d model. Main conclusions are:

- While the biomass associated products (BAPs) kinetics can be estimated, in tune with previous experiments, the utilization associated products (UAP) kinetics are instead hindered by storage phenomena (accountable only on ASM3) and by the non-uniformity between the polysaccharide fraction, easily biodegradable, and the protein fraction, which is refractory to biodegradation.
- The BAP modelling results in a f_{bap} of 0.05 and $K_{h,bap}$ of $1*10^{-6}$ d^{-1}. UAP kinetics were fitted by trial and error procedures yielding a f_{uap} of 0.6 and $K_{h,uap}$ of $1*10^{-6}$ d^{-1}. UAPs were found markedly predominant compared to the BAPs.
- The membrane rejection mechanism was identified as SMP loading rate dependent, showing the need of a more careful consideration towards this parameter when modelling in full-scale or in a dynamic environment.

- The extension of an ASM model with SMPs and its experimental work impacts on the modelling exercise complexity. Some of the problems originated by the experimental work cannot be easily solved: (i) UAP kinetics estimation in batches is not accurate. (ii) the SMP batch experiments protocol is a burdensome procedure; (iii) flow average samples cannot be collected for the sludge water samples, being the results thus very dependent on the daily peak loads. A more frequent sampling campaign would thus be required; (iv) the fine tuning of the membrane rejection factor appears a necessary adaptation. Both nutrients removal, sludge production and energy fitting did not receive further benefit from the SMP modelling.
- SMPs did not correlate with fouling rates in this full-scale MBR, indicating a strong drawback, since the main drive for these models is thus not accomplished.

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Chapter 6

MBR sludge inoculation in a hybrid process scheme concept to assist overloaded CAS process winter operations.

Re-drafted from: Fenu, J. Roels, S. Van Damme, T. Wambecq, M. Weemaes, C. Thoeye, G. De Gueldre, B. Van De Steene, 2012, Membrane bioreactor (MBR) sludge inoculation in a hybrid process scheme concept to assist overloaded conventional activated sludge (CAS) process winter operations. Water Science & Technology, 66, 2, 457-63.

Abstract: this study analyzes the effect of spiking MBR sludge in an overloaded CAS system, while operated in a parallel hybrid scheme. Through model studies and full-scale tests, this study illustrates that the CAS bio augmentation is possible, it is MBR load dependant and energy neutral. A full-scale test confirmed by a higher seasonal TN removal and higher nitrate formation rates during seeding that an advantage was achieved.

The bio augmentation was followed up also in terms of sludge quality mixing. The MBR flocs, grown without settling selection pressure, were not transformed in regular flocs. MBR sludge inoculation in the CAS sludge waters coincided instead with an increase in supernatant turbidity, filamentous presence, and dispersed material. No difference was reported in terms of sludge volume index. More importantly, the system appeared less able to retain the suspended solids in the clarifier during rain events. Lab tests permitted to determine the threshold volume of MBR sludge to be seeded to the CAS reactor. Above a 16-30% of MBR sludge in the CAS sludge, the CAS supernatant turbidity and the scum formation markedly raised posing a serious problem to the sludge settling performances.

6.1 ***Introduction***

Since full-scale MBR technology has been established in municipal installations, several problems related to this applications have been faced. An important point of discussion is the design of hybrid systems, i.e. how to integrate MBR and CAS processes in a wastewater treatment plant (WWTP). A single sludge may be continuously re-circulated between CAS and MBR lane, as in Heenvliet WWTP (Mulder, 2009). Alternatively CAS and MBR processes can be completely independent as in Ootmarsum WWTP (Futselaar *et al*,. 2007), configured thus as parallel lanes.

The scientific community has not yet decided which of the scenarios is optimal. However the design aspects of hybrid installations should be critically analyzed. The MBR lane is generally designed on the dry weather flow (DWF). This is meant to provide the MBR a constant flow, and to avoid that the MBR would be designed to handle the peak flows, overestimating the membrane surface in dry weather flow. On the other hand, if the average influent flow is as low as the DWF, the MBR will handle all the influent, and the load to the CAS lane may be critically low to support biomass maintenance.

Several studies have investigated the effect of MBR processes on the biomass kinetics. The nitrification process was found the most affected by the process scheme differences when MBRs are compared to CAS systems (Fenu *et al.,* 2010a, Parco *et al*., 2006), resulting in higher specific nitrification rates (Manser *et al*., 2005; Jiang *et al*., 2009; Fenu *et al*., 2010b).

This study analyzes the option of using the MBR sludge to assist an overloaded CAS system in daily operations, and counter balance eventual load misbalances. Could this contribute to a significant nutrient removal advantage? And what would be the fate of the MBR sludge flows in the CAS system? Would the mixing of the two sludges be successful in term of sludge settling quality?

6.2 Materials and method

6.2.1 The Full-scale hybrid WWTP

The Schilde WWTP is described in chapter 2. The installation has undergone the necessary adaptations to realize this study in full-scale: (i) the excess MBR sludge, previously wasted from the recycle channel directly in the buffer, is now pumped at a rate of 0 to 15m^3/h into the CAS basin. In average, 60 m^3/day of MBR sludge can be evacuated while maintaining an average MLSS concentration of 10 g/l in the bioreactor; (ii) the sludge waste operations from the CAS to the thickening table have been potentiated with a second pump, as to avoid an accumulation of sludge in the CAS system during MBR sludge seeding (MSS).

6.2.2 Samples and Analysis

The effect of the MSS is evaluated by: (i) an ASM full-scale model analysis. The Schilde WWTP model was implemented in MATLAB SIMULINK within a model library developed by Aquafin. The ASM2d model platform was used with incorporation of the inorganic fraction; (ii) a sampling campaign data analysis. Composite samples were collected at the WWTP influent and effluent (in both cases summing up CAS ad MBR) with 2 weeks frequency in 2006-2011. The samples were analyzed according to the Standard Methods (APHA, 1999) for BOD_5, COD, suspended solids (SS), ammonia, nitrate ad nitrite, organic nitrogen, ortho-phosphate and TP; (iii) maximum nitrification rates of MBR and CAS sludges were occasionally assessed in controlled batches (pH 7.2-7.5 at 20°C, stirring at 500 round per minute, Oxygen set-point of 3 mg/l); (iv) calculations to evaluate the autotrophic biomass in static conditions by use of the Eq. 1 below:

$$X_{AutBM} = \frac{M_{NO3}}{(1+b_{aut} \cdot SRT)} . Y_a \cdot SRT$$

The MBR and CAS sludges mixing was analyzed both in lab and full-scale conditions. The following methods were employed: (i) activated sludge floc size monitoring by microscopy; (ii) activated sludge filamentous bacteria monitoring. Phase contrast (wet preparation) and bright field (stained preparation) microscopy were used at different magnifications (100X, 200X, 400X and 1000X). The qualitative and quantitative assessment of the issues were based on a defined reference. This reference consists of detailed descriptions (for a qualitative assessment) of the determinants or by a scoring system (for a quantitative assessment). The amount of the filamentous bacteria is also based on reference photographs. The filaments were identified by using the Eikelboom scheme (Eikelboom, 1999) and staining methods, referring to morphological and color characteristics of the filaments; (iii) monitoring of the

CAS supernatant turbidity by use of a turbidity analyzer (Nephla - Dr. Lange); (iv) daily monitoring of the full-scale diluted sludge volume index (DSVI) (according to Jenkins *et al.,* 2003); (v) daily measurement of MLSS and MLVSS in both lanes.

6.3 ***Results and discussion***

6.3.1 ***Feasibility study***

The MBR process accomplishes complete nitrification as well as solids retention all over the year. The CAS winter performances are instead generally very poor. The system is overloaded, and the SRT, estimated in 5-9 days, cannot be increased due to a restricted clarifiers design. Severe flows peaks and rigid winter water temperatures challenge regularly the nitrifiers retention and consequently the biological reactor is often continuously aerated. The average on line ammonia in winter was 13.5 mg/l in 2009, 8.43 mg/l in 2010, and 9.49 mg/l in 2011. This value is to be summed up to the KJN resulting from the effluent SS.

Nitrification batch tests, repeated in winter and summer 2010, confirmed in fact how the specific nitrification rate is 5-10% higher in the MBR sludge. It is important to understand whether, in conditions of overloaded CAS operations, the MBR sludge can be inoculated in the CAS system to support nitrifying biomass (X_{aut}), instead of being wasted in the buffer.

The opportunity of MBR sludge seeding (MSS) was studied by means of static and dynamic assessments. Static calculations were performed, based on seasonal averages, aiming at evaluating the gradient between the MBR and CAS autotrophic concentration. In winter, according to equation (1), a higher SRT_{MBR} (21 in spite of 6 days of the CAS), a complete MBR nitrification in spite of a partial CAS nitrification, the lower MBR b_a due to the bigger MBR anoxic volume (the b_a is halved in anoxic conditions, as in Nowak *et al.*, 1994; Siegrist *et al.*, 1999; Salem *et al.,* 2006), yield a superior MBR autotrophic biomass concentration which becomes strongly superior in case of washout. In summer instead, the total influent flow decreases from average 700 to 350 m^3/h. Being the control as such to prioritize the MBR process, the influent flow to the CAS is below the average 100 m^3/h. This yields a markedly higher amount of nitrifiers in the MBR system (21 mg X_{Aut}/g against 17 mg X_{Aut}/g).

The impact of the MSS was also evaluated by means of a dynamic ASM model, i.e. the model, calibrated on 2006 and validated on 2009 data, has been described in Fenu *et al*., (2010b, 2010c). In the data set of 2009, the MBR operations were interrupted from day 6 to 20 (Figure 6.1), and, in that time-window, the CAS treated the complete influent flow with consequent nitrification washout (ammonia reaches 25 mg/l in day 12). The biological reactors were controlled on the same MLSS concentrations, and the

sludge production produced by both lanes was not modified. Between days 25-90 (X axis in Figure 6.1), the modelled MSS scenario quicker recovers from washout events when compared to the modelled and real operations without bio-augmentation.

After day 300, persistent peak flow events in correspondence to lower temperatures, typical of the Flanders region, caused a reduction of nitrification activity. In that time window, the modelled results in the bio augmented scenario show markedly lower effluent ammonia.

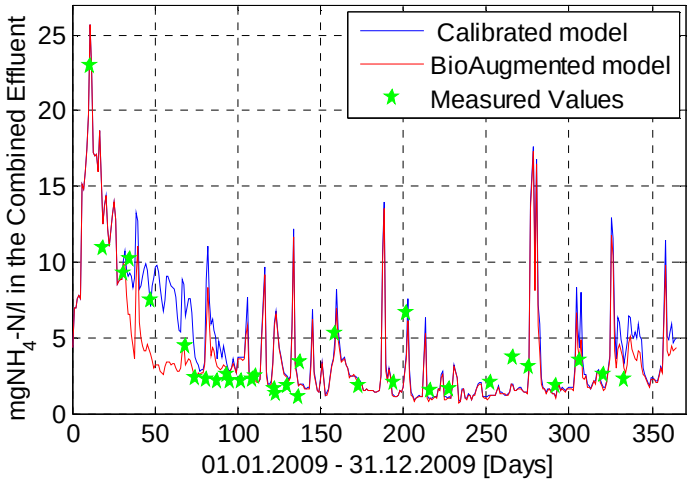

Figure 6.1: Modelled versus measured soluble ammonia in the combined effluent. The effluent ammonia was measured in a year (2009) whereby no MSS operations were applied. Read "0" as 01.01.2009 and "365" as 31.12.2009.

6.3.2 ***Performances***

The performances were studied by applying the seeding in full-scale while monitoring operations in January-April 2010. The MSS flow was 1.25-7.5 m^3/h, as resulting from the MBR sludge in excess, with daily flow between 30-90 m^3/day. A sampling campaign was performed in 2010 and the results compared with the past winter performances (whereby MSS operations were never applied). An ammonia and TN removal of respectively 72% and 47% was recorded in the effluent at an average water temperature of 8.9°C. Until 2009, the highest ammonia and TN removal ever recorded in Schilde were in 2007 respectively with 67% and 45% at an average water temperature of 10.4 °C.

In winter 2011 instead, the MBR installation had discontinuous operations because the sludge was in two different occasions completely wasted, bringing the MLSS concentration from 10 to 2 g/l. The membrane permeability was low, due to the membranes aging, generating a scarce feed flow to the MBR, i.e. the system was in winter 2011 operated at 160 m^3/h, but the MBR design flow is 270 m^3/h.

The MSS was in 2011 only occasionally performed, and the results are mainly used to evaluate the effect of occasional MSS on CAS sludge quality.

The nitrate on-line sensor data help explaining the effect of MSS on the CAS process. In presence of MSS operations, first flush events cause a higher MBR sludge production. But at the same time, since the MBR achieves always complete nitrification, the first flush represents a net higher growth for the autotrophic biomass. If the excess sludge is then afterwards seeded in the CAS, it results in a higher nitrification capacity during first flush events. In Figure 6.2, it is shown how the sludge poured at high MSS rate to the CAS basin in 2010, increased the measured specific nitrate formation rate in correspondence with high MSS flows (Figure 6.2).

There is an aspect which could be important in determining the MBR sludge superiority in Schilde WWTP. The MBR sludge has a higher SRT than the CAS. This produces a higher X_{aut} content as resulting from Eq. 1. But a higher SRT is generally counter balanced by a sludge mineralization which increases the inorganic content of the sludge. However, the two lanes yield a comparable % of organic matter (OM) of the sludge waters, generally ranging at an average 70%. This data was confirmed in winter 2011.

A comparable % OM at so different SRTs can be related to the severe MBR pre-treatment which would filter out part of the inert particulate in the MBR lane , i.e. the MBR system is sieved down to 1 mm. A lower inorganic content than expected in the MBR sludge, could well allow for a higher concentration of active biomass.

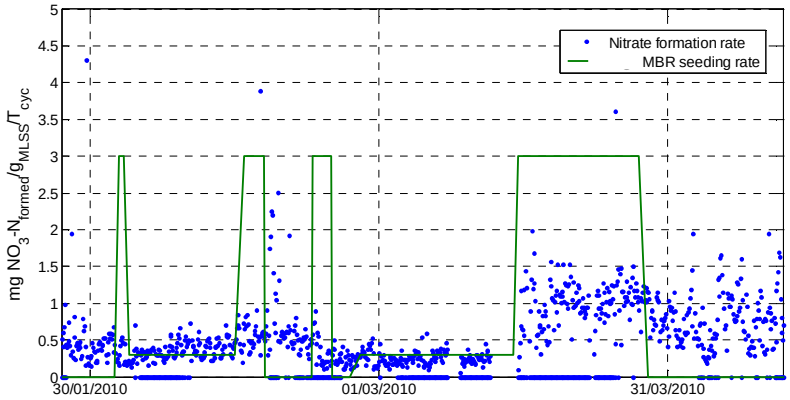

Figure 6.2: Measured specific nitrate formation rate in the CAS aeration tank during MSS operations. The sludge dosing (in green) is reported for low or high flow rate.

The MBR seeding was performed whenever excess sludge was present. The MBR lane produces an average 60 m^3/day sludge to maintain 10 g/l MLSS in the bioreactor. It is thus a question of how to

produce enough MBR sludge. The lowering of the SRT_{MBR} would increase the sludge production but at cost of the X_{aut} concentration reduction (as in equation 1) and thus this solution is not optimal.

The only possibility to boost efficiently the MBR sludge production is by having a higher influent loading in the MBR reactors, i.e. this possibility is dependent on membrane area and permeate extraction flow. Despite not directly applicable in reality, the effect of a higher MBR sludge loading was analyzed throughout the model. TN removal and overall costs are displayed with increasing the flow % to the MBR lane in Figure 6.3. Certainly, since the more the flow to the MBR lane, the less flow goes into the CAS lane, the total TN removals increase because the MBR lane has high nutrient removal performances. But it is important to note how the TN results progressively improve in the MSS scenarios when compared to the respective case without MSS operations.

Finally it is relevant to note how the MSS scenarios corresponded to about a 1% increase in yearly aeration demand of the CAS lane, being thus energy neutral.

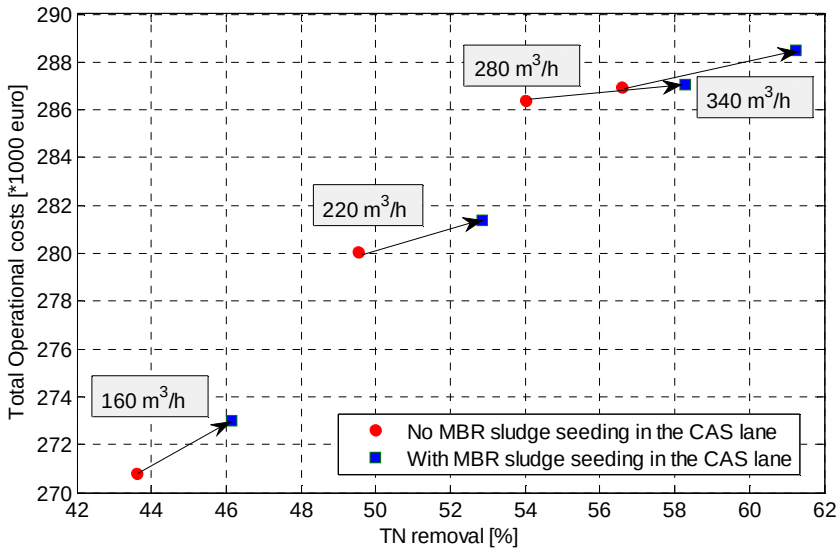

Figure 6.3: Costs and TN removal while varying the influent flow to the MBR system. Scenarios with MSS and without MSS operations have been compared.

6.3.3 ***Sludge settleability and flocs morphology***

A microscopic evaluation of the sludge from CAS and MBR was carried out to assess the basic morphological differences between the two sludges. While the CAS sludge (before any seeding) appears more compact, the MBR flocs were characterized by a very open form and were composed of many subcompartments, including compact cores, cell clusters, and filamentous bacteria. In the latter sludge

the filamentous bacteria presence is very high, with a co-domination of *Nocardia* and *Microthrix parvicella*, and high presence of *Type 0041/ Type 0675*. The particle size distribution of both sludges was measured (Fenu *et al*. 2010b), yielding an average floc size of 40–50 µm for the MBR and 200 µm for the CAS, as in Masse *et al*. (2006).

The fate of the MBR sludge in the CAS sludge matrix during full-scale seeding was followed up through microscopy analysis. It was observed that the CAS flocs evolved into a more open and irregular form, including often small compact clusters (Figure 6.4). As in the MBR sludge, frequent *Nocardia* are found loose in the CAS sludge water. The MBR flocs, grown without settling selection pressure, are incorporated in the CAS flocs structure, but the CAS settling process appears however not able to transforming them in regular settleable CAS flocs. It is possible that the marked presence of *Nocardia*, by growing loose out of the flocs, does not allow floc compactness.

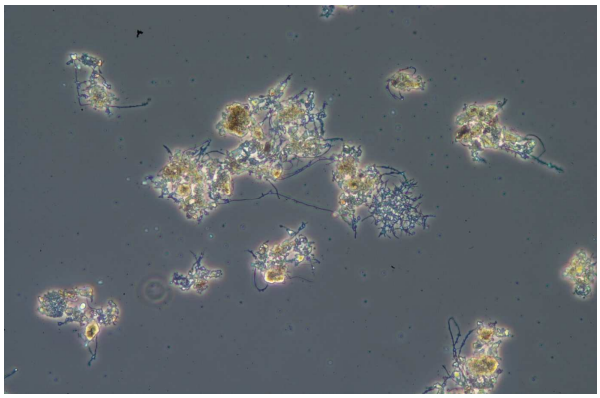

Figure 6.*4: CAS sludge during MBR sludge seeding operations (2010).*

Consistently with the microscopic results, the continuous seeding, in 2010, caused a persistent increase of *Nocardia* and dispersed material. The acute effect instead was evaluated in one of the occasional MSS of 2011, i.e. between 28.02.2011 and 07.03.2011, the sludge seeding corresponded to an increase of dispersed material as well as of the *Nocardia* filaments in the CAS supernatant.

The full-scale operations analysis offers the possibility of further considerations. With regards to the reliability of operations, the SVI and the effluent SS were followed up over time. The DSVI did not show significant variations that could be related to MSS, even after massive seeding. The influence of the seeding was instead noticeable over the effluent SS, which is in fact a very crucial operational parameter. The effluent SS on line were plotted with the influent flow, between January-march of 2009-2011 (Figure 6.5), i.e. only in 2010 there was continuous MSS. The effluent SS baseline didn't report variations amongst the analyzed years. However, given the clarifiers design, high flows are always challenging due to the sludge table rising, representing an overall test for the sludge settleability. At maximum

flows, it is evident how the winter 2010 is by far less reliable in containing the biomass inside the clarifiers, i.e. see circle in Figure 6.5.

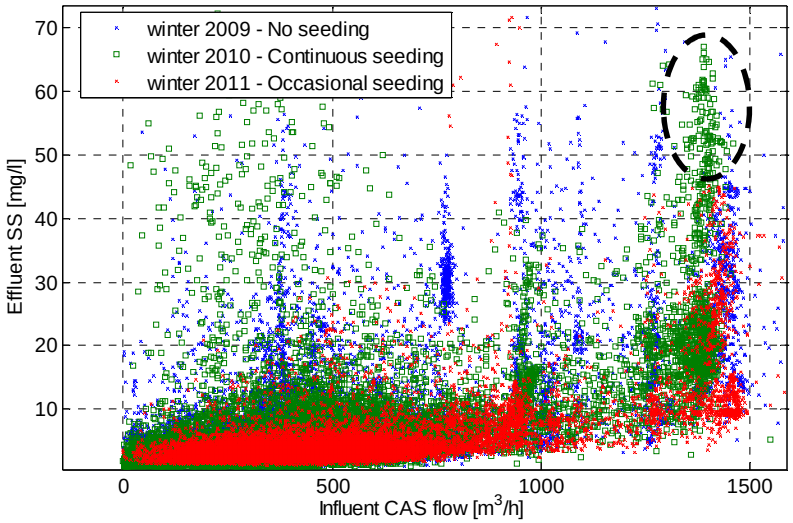

Figure 6.*5: Effluent SS on-line data plotted with the relative CAS influent flow. Dataset belongs to years 2009-2010-2011. The black circle in figure shows that: (i) whenever maximum flow is reached (at heavy raining events) this corresponds to an effluent flushing of suspended solids during all 3 investigated years of operations; (ii) the experiment with continuous seeding of MBR sludge provokes effluent concentrations up to 50-70 mgSS/L.*

The mixing of CAS and MBR sludges was studied also both through lab batches. Different % of fresh MBR sludge were mixed in batches with CAS sludge. The different dilutions yielded different sludge concentrations in the different batches. With no surprise the settling rate was found proportional to the MLSS concentration.

Following the DSVI protocol, the batches were re-diluted with permeate water up to a proper dilution (Jenkins *et al*., 2003). A similar DSVI was found at different % MBR sludge percentages, confirming how the SVI is not sufficiently modified during MBR sludge seeding. However above a 16% MBR mixing (V/V), the sludge collapsed and a thick layer scum of 28 ml formed at the top of the batch (Figure 6.6). The turbidity of the sludge supernatant raised as well. The MBR sludge, when undiluted, performed better in terms of scum formation, SVI, and supernatant turbidity than with others dilutions. This study showed that the MSS volume should not overcome a certain % CAS biology volume. In detail, it should be avoided to come over the 16-30 % V_{MBR}/V_{CAS} (water volumes), i.e. in full-scale a maximum of 15% was reached.

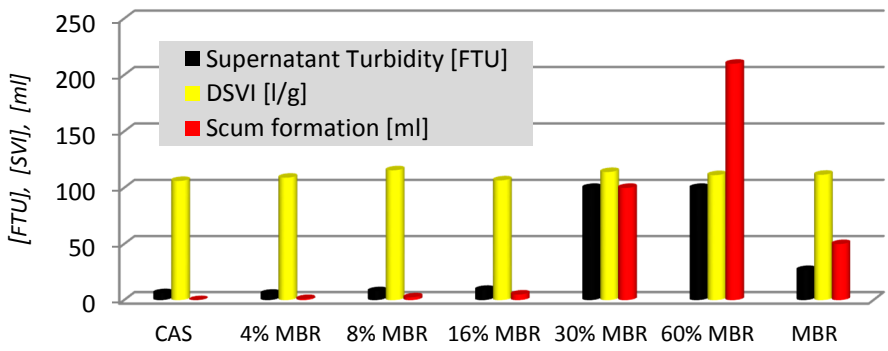

Figure 6.6: CAS supernatant turbidity, DSVI and scum formation in function of the ratio between the Volume of MBR sludge water and the Volume of CAS sludge water.

6.4 ***Conclusions***

This study analyzes the option of using the MBR sludge to assist a CAS system while operating MBR and CAS in parallel. The potential advantages in terms of nutrients removal have been tested in full-scale. But the seeding of MBR sludge poses several feasibility question that this study tries to answer throughout operational data. The major results are below listed:

- The study illustrates, through static and dynamic calculations that MBR augmentation in a hybrid installation is possible. A full-scale experience in 2010 confirmed by higher seasonal TN removals and higher nitrate formation rates that an advantage was achieved.
- The advantage in terms of nutrient removal is MBR sludge loading dependant;
- The MBR flocs, grown without settling selection pressure, are not embedded in the CAS flocs. MSS coincided with increase in supernatant turbidity, filamentous presence, and dispersed material in the CAS sludge. No difference was reported in terms of SVI. More practically, the system bioaugmented with MBR sludge appeared less able to retain the sludge in the clarifiers during severe rain events;
- The study suggests to seed MBR sludge until the 16-30% Volume MBR water / Volume CAS water are reached. Above this ratio, the supernatant turbidity and the scum formation raise problematically, giving a serious problem in containing the settling solids in the clarifiers.

6.5 ***References***

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Chapter 7

The MBR life-time concept in a full-scale hollow fiber MBR

Re-drafted from: Fenu A., Weemaes M., De Gueldre G., Van De Steene B., 2012, Elaborating the membrane life-time of a full-scale MBR. Journal of Membrane Science, 421–422, 349–354.

Abstract: The membrane life-time has a strong impact on competitiveness and viability of MBRs. This study critically analyzes the membrane life-time concept, approaching it through different assessment methods. A full-scale MBR's membrane life-time was assessed on: (i) maintaining the permeate flow throughput to the MBR; (ii) the permeability decline; (iii) oxidative aging; (iv) the increase in energy costs; (v) mechanical aging. The method based on permeability decline provides a membrane life-time estimate up to a theoretical end. It was further elaborated inherently to operations with no long-term flux decline. The increase in operating pressure remains the main end-of-life trigger for deciding when to replace membrane modules. On the contrary, mechanical and permeate flow throughput analysis of the data are not able to provide a clear estimate of the membrane life-time. As for the membrane life-time estimation based on chlorine contact, it was found to be too optimistic. Complete irreversible fouling occurs before maximum contact time with chlorine is reached. At end-of-life operating conditions, the energy consumption raised of 170% due to the reduced flow rate. The cost raise appears high but still affordable. Earlier membrane replacement thus cannot be counterbalanced by energy costs saving.

7.1 ***Introduction***

Footprint limitation, strict effluent standards and local environmental or socio-economic considerations act as a driving force for applying MBR technology. In the last decade, the implementation of MBR technology in full-scale faced a serious growth (Judd *et al*., 2006). Wastewater treatment with MBRs has been expanded to municipal installations and many MBRs have been built all over the world in the last decade. The Schilde full-scale MBR, scenery of this study, was started up in August 2003 as the first municipal MBR in the Benelux.

The installations built a decade ago are now aging, offering new insights from an operational perspective. Several issues can in fact be disclosed only during the aging process: operations in sub-optimal conditions and membrane life-time (T_{life}) are typical examples. The latter aspect has recently come to the attention of the scientific community, since it strongly influences the competitiveness of the MBR technology. The cost of large-scale hollow fibers MBR has been investigated. It was concluded that the membrane replacement is critical in determining the net present value (Verrecht *et al*., 2010). In a 'worst case' scenario of 5 years, this would result in a 23% net present value compared to the base cost, assuming membrane replacement every 10 years. Other operational experiences report that with membranes being replaced every 8 years, the cost of an MBR system is equivalent to CAS installations of comparable load and effluent quality (Brepols *et al*., 2010).

The "T_{life} concept" remains debated. For instance, suppliers define this concept as the time when the design flux cannot no more be guaranteed. Other authors (Brehant *et al.*, 2011; *Hajiababania et al., 2011)* analyze the T_{life} from a chemical and mechanical stand-point by accelerating the aging on a lab scale.

T_{life} can on the other hand be considered as the moment at which chemical cleaning cannot recover anymore permeabilities (De Wilde *et al.,* 2007). The authors worked on Schilde full-scale MBR data, predicting a 13.5 year replacement interval by means of the first 3 years data. Zenon (recently acquired by GE Water & Process Technology) installations are successfully operated from 2000 (Verrecht *et al*., 2010; Brepols *et al*., 2010), but there is no insight in the decay of performances that would truly define the life-time. A recent analysis of full-scale Zenon MBRs operated in North America, concluded that a 10 years T_{life} can be expected (Cote *et al*., 2012). A slow increase in operating pressure and the need for more frequent chemical cleaning was considered as the dominant end-of-life trigger for current Zenon products.

This study intends to provide more insight in defining the life-time of a full-scale MBR equipped with hollow fibers. Different methods to determine the T_{life} and possible end-of-life-triggers are discussed.

7.2 Methods And Methodology

7.2.1 The full-scale Mbr of Schilde.

WWTP Schilde (Figure 2.1) was retrofitted in 2003 with the construction of a low-loaded MBR (nutrient removal) in parallel with the existing high-loaded conventional infrastructure. The MBR and CAS processes are operated in parallel. In case of a lower permeate flow production, the CAS process treats the remaining influent flow. The full-scale MBR is described in chapter 2.

7.2.2 Samples and data analysis

Influent and effluent samples were analyzed every 2 weeks for BOD_5, COD, suspended solids, total nitrogen, organic nitrogen, ammonia, nitrate, ortho-phosphate and TP. All samples were analyzed according to Standard Methods (APHA, 1999). The samples filtration step was performed with a 0.45 µm polyester filter. The MLSS concentration was calculated with the Standard Methods (APHA, 1999).

With regards to the monitoring of the MBR performances, each of the four filtration lanes has on-line measurements of flux, suction pressure, coarse air flow, influent and recycle flows. The temperature is monitored online in the aerated bioreactor. Energy consumption of coarse bubble aeration, fine bubble aeration, mixers and pumps, were monitored on-line.

An ASM2d model of the MBR lane was calibrated based on January-October 2006 data on sludge production, effluent water quality and energy consumption. A validation phase followed based on January-May 2009 data. The Schilde WWTP model was implemented in MATLAB-SIMULINK with a model library developed by Aquafin, with addition of the inorganic fraction. The investigation methodology

is based on 7 main steps: (i) the waste water fractionation; (ii) the pre-treatment efficiency estimation; (iii) the aeration efficiency estimation; (iv) the measurement of the energy demand of all devices; (v) additional biomass characterization; (vi) the fine tuning of the ASM parameters and the half saturation coefficients (during the calibration phase); and (vii) the validation phase. The details of the methodology are described in Fenu *et al*., (2010).

The MBR data were fully available from April 2004, despite filtration operations started since August 2003. Suction pressure was recorded with a 1 second frequency by an on-line meter: measurement accuracy is estimated in ±0.1%. Flux was recorded with a 1 second frequency by an on-line electromagnetic meter: measurement accuracy is estimated in ±0.01%. Permeability is estimated by equation (1). Backwashes, relaxations, cleaning events, and system failures values have been filtered out from permeabilities and flux data. The filtered data have been then normalized with regards to temperature (15°C) according to equation (2) (De Wilde *et al*., 2007).

$$P = J / (TMP) \quad (1)$$

$$P_{15°C} = P_t * (42.5 + 15)^{1.5} / (42.5 + t)^{1.5} \quad (2)$$

It is important to remark that the gradual loss of flux and permeabilities can be explained by several factors, other than fouling. However being all effects lumped, a differentiation amongst different factors is not analyzed.

*7.3 **Results and Discussions***

Five different T_{life} concepts are elaborated, leading to further implications. The concepts are based on: (i) maintaining the permeate flow throughput to the MBR; (ii) analysis of the permeability decline; (iii) aging due to chlorine contact; (iv) operational energy costs; (v) mechanical stress aging. Possible end-of-life triggers are like-wise discussed.

7.3.1 T_{life} concept based on permeate flow throughput

Membrane suppliers consider the T_{life} as the time when the filtration process can no longer extract the design flux. The reduction of the permeate extraction is for a long period visible in 2008 (circle in Figure 7.1 or days 1500-1700 in relative scale). Within this concept, the Schilde T_{life} would amount to only 4.5 years, as in the winter of 2008, less than 200 m^3/h were extracted, instead of the normal average of 220 m^3/h.

This approach, generally used on-site by operators, leaves no possibility to distinguish amongst temporary detrimental conditions (high fouling propensity or low temperatures) and a stable loss of performances. The presence of several factors hinders a proper reading of the time-series permeate flow data. It is clear that, if the filtration flow would be considered as an end-of-life trigger, operators would risk a premature membrane replacement.

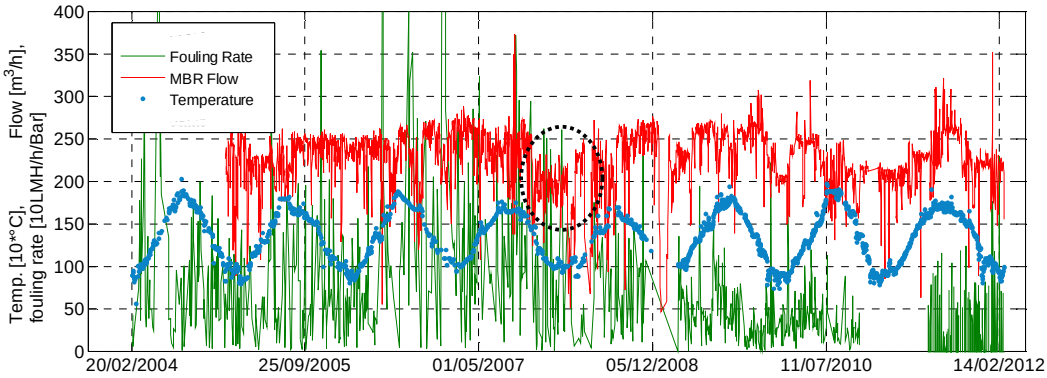

Figure 7.1: MBR flow, fouling rate and temperatures during operations. The "0" corresponds to 01/08/2003.

7.3.2 T_{life} *concept based on permeability decline*

The MBR data are only fully available from April 2004, though filtration operations started in August 2003. Lanes 1, 2 and 4 show similar permeability trends (Figure 7.2). The permeability of lane 1 dramatically dropped in winter 2011 (days 2600-2800 in relative scale). A good permeability recovery was achieved after a thorough recovery cleaning (RC), while pushing chemicals on the fibers' inside. Sludge deposit inside the fiber due to fibers' ruptures was removed by this procedure. Lane 3 on the contrary shows higher performances (crosses in Figure 7.2) since the beginning with an offset of 40 LMH/bar. This can probably be attributed to the replacement membrane modules in March 2004.

The increased irreversible fouling deposition is accompanied by lower fouling rates (not shown in figures) in the last years of operations. This should not be interpreted as a result of improved fouling strategies. The operators instead, being aware of the lower safety margins, have operated the MBR with less risks and lower TMPs. With regards to effluent water quality, no performances deterioration was noted in these years.

Permeability data is characterized by top and bottom points (Figure 7.2 and 7.3):

(i) The top points (maxima's in the curve): these are the points with the highest permeability as a result of successful cleaning or low fouling events. Through these points, the trend of mere irreversible fouling can be followed up. The irreversible fouling formation rate accelerates only at mid-life, increasing from the initial 0.015 LMH/Bar/day to 0.1 LMH/Bar/day in the year 2012. This fact can explain the optimistic T_{life} foreseen by De Wilde *et al.* (2007) for the same full-scale MBR: the authors considered a permeability trend based on the first 3 years of filtration.

(ii) The bottom data points (minima's in the curve): they are characterized by the lowest permeabilities in a given period, resulting from heavy fouling events whereby the MBR had to be operated at very high trans-membrane pressures (TMP) to achieve the necessary flux. Starting from the fourth year in operation, the bottom points are characterized by suction pressures amongst 500-600 mbar (alarm range). These latter points allow to draw a line. Below this line, no further permeate flow can be extracted, i.e., the net permeate flow reduces at limit TMPs because it is not possible to increase the suction pressure.

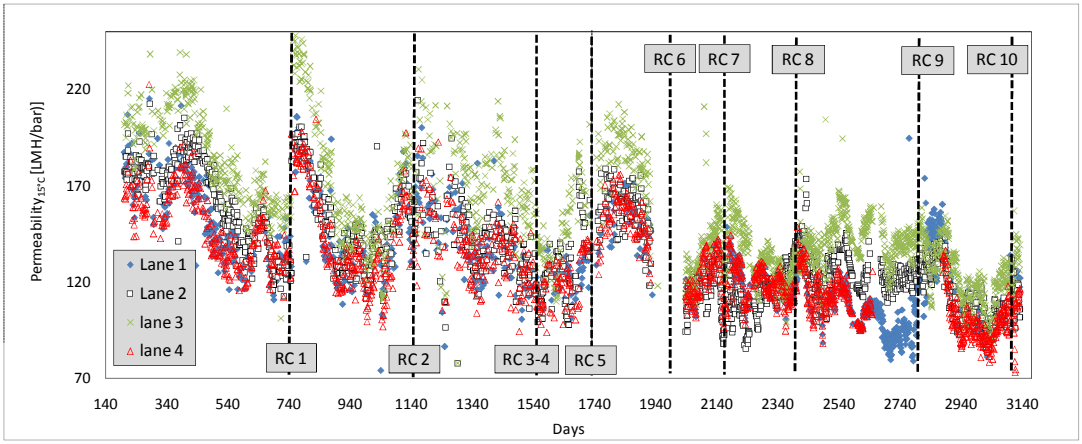

Figure 7.2*: Corrected permeability trends of 1-2-3-4 lanes. RC stands for "recovery cleaning event". On the X axis, the days in operation. The day "0" corresponds to 01/08/2003. The day "140" corresponds to the first data logged.*

As both trends (maxima's and minima's) are declining, the two trends will converge into an end-point of operations (Figure 7.3). In this point, filtration is still theoretically possible since membranes' permeability can be determined, but the initial TMP reaches maximum as filtration begins.

This implies:

(i) A T_{life} concept is applicable to a full-scale MBR installation. On this premise, the T_{life} in the Schilde membranes is calculated as to be 11.7, 12.1, 11.9 and 10.8 years respectively for lanes 1, 2, 3, 4;

(ii) The cleaning efficiency will reduce over time, i.e. the distance between low and high TMP operations gradually reduces over time.

Nowadays, the Schilde MBR is already operated as such that, depending on low temperature, the nominal permeate flow per lane (220/4 m^3/h) cannot be guaranteed. But, since the MBR is coupled to a CAS process, the latter lane treats the remaining influent water. In case of a standalone MBR process, instead, the hydraulic capacity must be always fulfilled.

The end-point of operations is, as defined above, impractical. The concept is elaborated to define a domain within which hydraulic capacity is still guaranteed. The bottom line in Figure 7.3 is determined by low permeability in combination with limiting TMP for lane 4. A projection of this line allows to forecast the future decline of the filtration fluxes in the most detrimental conditions. When considering the influence of temperature in the bottom line of Figure 7.3 (by use of equation 2), 3 separate lines can be derived for 8, 13 and 18 °C. A seasonal effect can now be taken into account (red, orange and blue line in Figure 7.4). All curves are interrupted when the membrane reaches the end-point of operations, established in 10.8 years for lane 4.

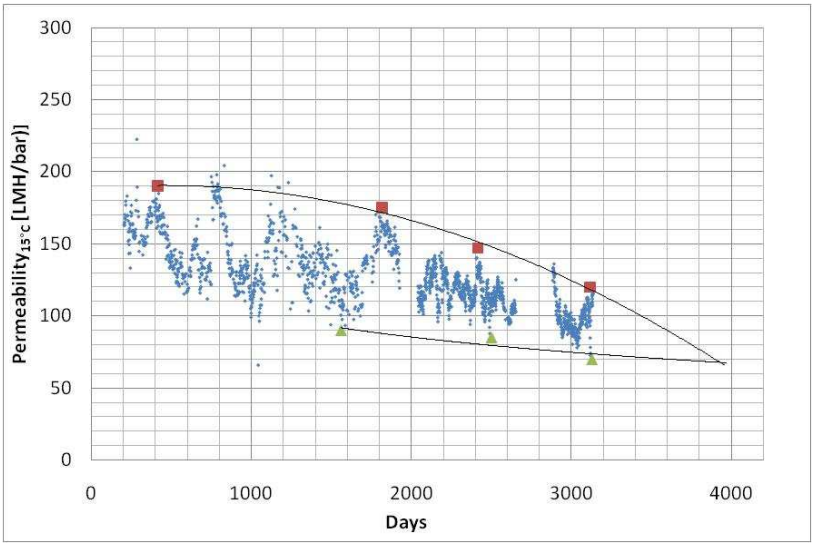

Figure 7.3: Determination of the end-point of operations in MBR 4. On the X axis, the amount of days of operations. On the Y axis, the average permeability on that day. The day "0" corresponds to 01/08/2003. Red squares are the days with the highest permeability as a result of successful cleanings or low fouling events. The green triangles are characterized by suction pressures amongst 500-600 mbar (alarm range).

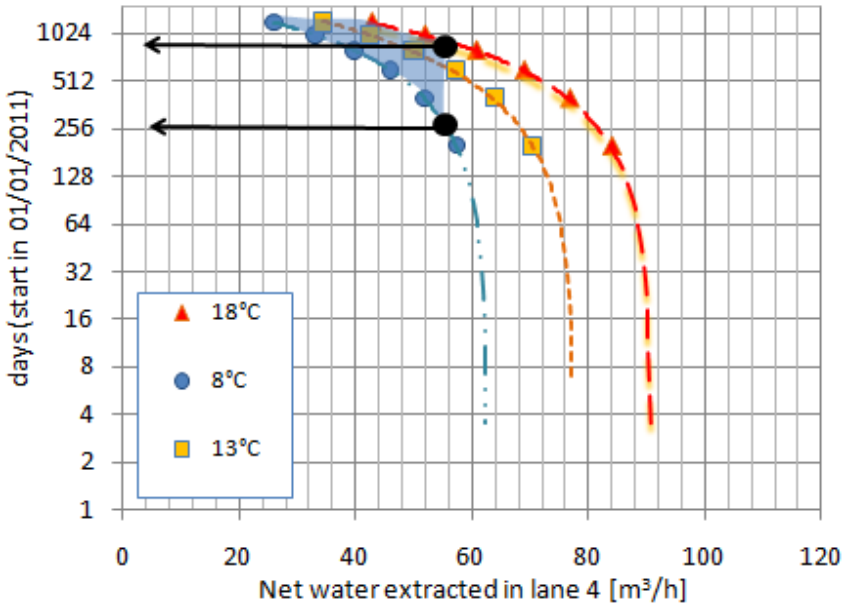

Figure 7.4: The X axis is the net permeate flow rate; the Y axis is the time of operations (past and future). In this chart, day 2710 is the 01.1.2011. In light blue, a time-temperature region with insufficient hydraulic capacity for MBR lane 4. The black dots are the T_{life} *achievable while delivering the necessary hydraulic capacity at 8°C and at 18°C.*

The blue region in Figure 7.4 represents the region where the future performances will not allow to process the necessary hydraulic capacity. It is defined by the following conditions : (i) every MBR lane should at least produce 55 m^3/h (=220/4 m^3/h) in any season or condition; (ii) a proper sludge-water temperature range is used. By excluding this region from the future scenario, the T_{life} is in a range between 8.1 years at 8°C and 9.97 years at 18°C (black dots in Figure 7.4), instead of 10.8 years as determined throughout the end-point of operations.

7.3.3 T_{life} *concept based on chlorine contact*

T_{life} can also be evaluated from a chemical (oxidative aging) standpoint. Membrane module suppliers suggest not to overcome a maximum cumulated chlorine contact over its life-time. In the case of Zenon, a maximum exposition of 500000 ppm*hours is recommended.

Tables 7.1-7.2 and Figure 7.2 report the cleanings performed in the history of Schilde MBR for the different lanes. Cleanings were carefully planned in the past years to minimize as much as possible the chlorine contact. The cleaning protocol was generally the same with the exception of October-November 2007. The average permeability recovery reduced over time (9° column in Table 7.2), while the

contact time increased up to 36 hours soaking per chemical. During recovery cleaning RC-9 and RC-10, several backwashes were enforced.

Table 7.1: Cleaning modes in full-scale Schilde MBR.

Cleaning	Mode	Chemicals	frequency	Time	Conc.
				h	
Mantainance	In - Out	NaOCl	Weekly	0.5	0.6 g/l NaOCl
Recovery	Out - In	2-3 steps	TMP > 0.4-0.5	4-64	0.6 g/l NaOCl

Table 7.2: List of the results for the 4 MBR lanes, from 2004 to 2010. CA=HCl; Ch=NaOCl.

mm/yy	RC	Step1	Step2		Recovered Permeability [LMH/bar]				
				MBR-1	MBR-2	MBR-3	MBR-4	Avg	Time
				LMH/Bar	LMH/Bar	LMH/Bar	LMH/Bar	LMH/Bar	H
08/2005	1	2.75 g/l CA		83	70	84	56	66	2
10/2006	2	0.60 g/l Ch	3.9 g/l CA - pH2	15	60	94	53	50	2+2
10/2007	3	0.60 g/l Ch		0	0	0	0	0	18
11/2007	4		0.7 g/l CA - pH2	0	0	0	0	0	18
05/2008	5	0.60 g/l Ch	2.2 g/l CA - pH2	35	40	71	7	39	18+18
01/2009	6	0.60 g/l Ch	2.2 g/l CA - pH2	NA	NA	NA	NA	NA	18+18
07/2009	7	0.60 g/l Ch	2.2 g/l CA - pH2	47	65	65	35	49	18+18
03/2010	8	0.60 g/l Ch	2.2 g/l CA - pH2	36	32	38	18	29	18+18
04/2011	9	0.60 g/l Ch	2.2 g/l CA - pH2	70					24+24
01/2012	10	0.60 g/l Ch	2.2 g/l CA - pH2	34	32	30	25	30	36+36

End-of-life scenario is known to reflect in more frequent RCs (Cote *et al*., 2012). From 2003 to 2011, the MBR exposition to chlorine was 250000 ppm*hours and the empirical trend in Schilde's chlorine contact is in fact exponential, (Figure 7.5). The threshold of cumulated chlorine contact in lane 1 will be reached in 2018 with a T_{life} of 15 years, and in lanes 2-3-4 with an T_{life} of 16 years.

The increase in cleaning frequency as an indicator of the estimated T_{life} (as in Cote *et al*., 2012) was not applicable to the MBR Schilde: the aging reflected in longer contact-time rather than in higher cleaning frequency. This because the loss of performances was mostly visible in autumn-winter, and as a consequence, recovery cleanings were mostly operated in that yearly period.

In conclusion, the T_{life} determined due to permeabilities decay is shorter than that one reached by chlorine exposition. Same results were achieved by Cote *et al*. (2012). From an investment cost perspective, it appears thus more convenient to force RCs rather than to let the MBR foul to avoid chlorine exposition.

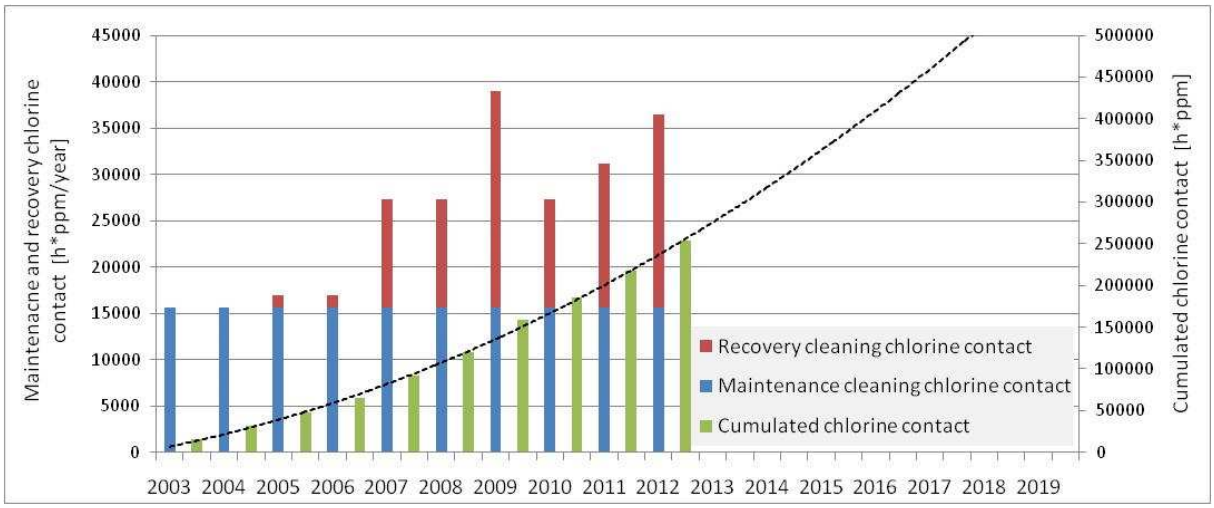

Figure 7.5: Yearly and cumulated chlorine contact during operations of lane 1.

7.3.4 T_{life} concept based on a financial standpoint

The T_{life} concept was rephrased into a realistic option where permeate flow throughput is still possible. In the case of flux decline instead, the specific energy costs will increase with the lower extracted permeate. Is it possible to define a T_{life} on the basis of feasible energy costs?

A biological activated sludge model (ASM) study of Schilde MBR allowed a calculation of the energy costs (Fenu *et al.,* 2010), quantifying it in 0.63 kWh/m^3 with a net permeate extraction of 55 m^3/h per lane, i.e. for an yearly average permeate production of 220 m^3/h, and an energy cost of:

55 m^3/h * 24 h/days * 365 days/year * 0.63 kWh/m^3 * 0.08 euro/kWh = 24282 euro/year.

The coarse bubble aeration, the compressors, the warming of the permeate for the cleanings, the mixing energy and the pre-treatment are run at constant energy consumption, regardless of flows, i.e. they accounted respectively for 35.2%, 3.1%, 6.6%, 7.0% and 2.6%, for a total of 54.0% of the total energy when the system is operated with 220 m^3/h (Fenu *et al.,* 2010).

The ASM model allows to determine the energy consumption of all devices in case of lower hydraulic flows to the MBR, through modelling of controls. Fine bubble aeration, influent and recycle pumps were found to adapt to lower loads without influencing energy costs. The energy consumption in function of the permeate flow was computed in Figure 7.6 (trend noted in kWh/m^3).

Figure 7.6 allows now to look at the net permeate flow in function of temperature and forecasted scenarios. The black arrows indicate a possible use of this chart. Starting with foreseen time and temperature, permeate flow and related energy cost can be obtained. The minimal permeate production

corresponding to end-point of lane 4 is 23.9 m^3/h at 8°C degrees. The related energy cost can be accounted in 1.07 kWh/m^3 permeate (Figure 7.6). Yearly energy cost at end-point of operations is:

23.9 m^3/h * 24 h/days * 365 days/year * 1.07 kWh/m^3 * 0.08 euro/kWh = 17921 euro/year.

This is to be summed up to the energy costs provided for the flow that the MBR lane cannot treat anymore:

31.1 m^3/h * 24 h/days * 365 days/year * 0.63 kWh/m^3 * 0.08 euro/kWh =13730 euro/year.

The energy necessary to treat 55 m^3/h at end-point raises from 24282 to 31651 euro/year when coming to end-point scenario. In conclusion, though the energy consumption per m^3 doubles, operations are still economically feasible. Given these figures, energy cost is no end-of-life trigger for membranes replacement.

Finally, considering the market price of Zenon ZeeWeed500 fibers and a minimum 8 years T_{life} , it can be concluded that the energy gained by operating at design flow cannot counteract the yearly investment cost. From an economical standpoint, in the MBR Schilde is best to bring the membranes as closely as possible to the end-point of operations. However other factors overrule this aspect: (i) providing the necessary permeate flow throughput in a standalone MBR; (ii) providing the necessary effluent water quality flow in a hybrid MBR parallel to a CAS process, where influent can partially be diverted to the CAS process.

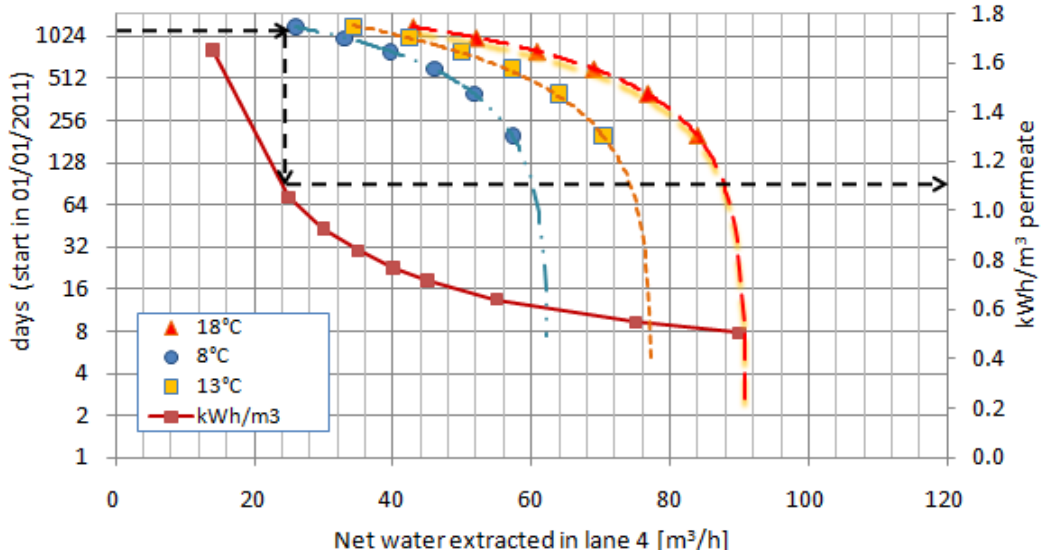

Figure 7.6: The X axis is the net permeate flow rate; the Y axis is the time. In this chart, day 2710 is the 01.1.2011. Prediction of the flux decline in the MBR lane 4 over time. The arrow shows how, starting from a day, both "net water extracted per lane" and "specific energy consumption" can be derived for a past/predicted scenario.

7.3.5 T_{life} *concept based on membranes mechanical stability*

The mechanical failure was reported from Ayala *et al.* (2011) as a dominant factor to replace membranes (flat sheets in this specific case). In Schilde, a reduced capability to stand high TMPs was observed. While in the past the maximum TMP (500 mbar) was well tolerated, since 2009 high pressures coincided in at least 4 events with increased turbidity of the backwash (BW) water. This fact pointed to the potting resin weakened by the chlorine exposure. Fibers' connection appears the weakest point of an MBR.

Recently, after reparation and partial substitution of some fibers bundles, the problem wasn't frequently encountered anymore. Thus, despite the alarming signals, a full lane membrane replacement cannot be determined by mechanical stability problems.

Yet, this fact has an important consequence in operating at T_{life} scenario. Operators may for safety reasons lower the maximum TMP, reducing the maximum permeate water flow.

7.4 *General applicability of the study*

The method based on "permeability decline" forecasted a decline in the full-scale permeate production of the Schilde MBR. This has in fact occurred. This was mainly visible during cold climate, and far from cleaning events. In 2015, the MBR has been replaced with new fiber, expanding the flow capacity up to 350 m^3/h.

This study focuses on the data analysis of a full-scale MBR, and concludes on end-of-life triggers and different T_{life} estimation methods. Five conditions are necessary to understand the general applicability of this research study:

(i) The method applied in 7.3.2 provides an empirical forecast of the T_{life}. According to this method, the higher the top points of Figure 7.3 are the longer is the estimated T_{life}. Since these points are expression of successful cleaning (or low fouling events), the quality of the cleaning procedure considerably influences the final result. For what regards this study, RC8-RC10 were performed with considerable care and aggressiveness so to be considered representative (Table 7.2). Chlorine contact was assured on both sides of the fibers, and all along its height;

(ii) The conclusions proposed in paragraph 7.3.4 can be generalized in MBRs where: (1) a decline in hydraulic flow is possible, as in a hybrid MBRs where part of the influent flow can

be diverted to the CAS lane; (2) coarse bubble flow and major energy consumers are controlled independently from fouling events or from extraction flow. Only in these cases, a decrease in permeate flow is reflected in a higher specific energy consumption;

(iii) The conclusions proposed in method 7.3.3 and 7.3.5 are definitely specific of the Schilde MBR;

(iv) The Schilde MBR is a hybrid installation. Due to this reason, a stable loss in hydraulic capacity does not necessarily imply the membrane replacement. Nonetheless, this study tries to generalize the results by offering two possible targets of the method proposed in 3.2: the T_{life} at end-point of operations; the T_{life} while maintaining the permeate flow throughput;

(v) Operational conditions are specific in any full-scale MBR. Data analysis of different MBRs would thus give more robustness to the proposed research approach. Nonetheless this research offers through method 7.3.2, according to us, a representative estimate of the T_{life} of full-scale Zenon submerged membranes operated in municipal applications.

7.5 ***Conclusions***

This study critically looks at the T_{life} concept by analyzing full-scale data from different perspectives. The full-scale MBR T_{life} was assessed on: (i) maintaining the permeate flow throughput; (ii) the permeability decline; (iii) aging by chemicals; (iv) energy cost; (v) aging by mechanical stress.

- A method based on permeability decline and TMP provides an T_{life} estimate incorporating total permeability decay. The method was further elaborated inherently to operations with no long-term flux decline. The T_{life} of the least performing lane of Schilde MBR was estimated in an interval ranging from 8.1 to 10.0 years.
- The increase in operating pressure remains the main end-of-life trigger for deciding when to replace membrane modules;
- Mechanical and permeate flow throughput analysis of the data do not provide a clear estimate of the T_{life} ;
- T_{life} estimation based on chlorine contact was found optimistic, suggesting how MBRs age due to irreversible fouling before they would do due to chlorine contact.
- At end-of-life operations, the energy cost appears high but affordable, i.e. 1.07 kWh/m^3 permeate. Earlier membrane replacement thus can never be counterbalanced by energy costs saving.

*7.6 **Financial comparison of MBR and CAS technology***

From the list of the WWTP projects realized by Aquafin (Flemish operator for wastewater treatment), the latest projects have been extracted from a database and subdivided according to costs categories. When looking at Table 7.3, investment costs are splitted in electromechanics/building and related to the type of technology as well as the design load.

A look at the data allows to see how stand-alone MBRs are more expensive than CAS systems when designed for the same load, i.e. cost per P.E. of Tervuren is 0.61. This fact can be explained by three major points:

(i) a stand-alone MBR is confronted with huge flow variations. Expecially when it has to tackle a $6Q_{14}$ design. In this case, as to reduce the membrane surface, buffer tanks are build in front of the installation. Therefore the clarifiers volume saved by the MBR concept is "re-invested" in buffer tanks for the influent flow;

(ii) MBR filtration tanks are overdesigned as to accommodate hypothetical additional membrane surface.

(iii) The membrane cost has only recently significantly dropped. Several Chinese industries can nowadays offer a retrofit of membranes for any sort of configuration (flat sheet or hollow fibers). Membranes surface cost could be nowadays re-calculated with a reduction of 1/3 in investment costs.

A financial comparison between CAS and stand-alone MBRs has in fact no meaning, since investment costs in MBRs in stand-alone configuration are already more expensive than CAS systems. With the operational costs also being higher, MBRs in stand alone configuration are out-competed.

In case of hybrid MBRs, according to the information provided in Table 7.3, some further discussion is possible. The Schilde MBR is compared to the average investment cost of a CAS system of similar size (0.44 €/P.E.) .

As to do this exercise, the following conditions have been applied:

(i) all investment costs have to take replacement costs into account. According to operators experience (Aquafin database) electro-mechanic works have a replacement time of 15 year; building constructions have a replacement time of 30 years; membrane investment cost is to be complemented by replacement costs based on the results achieved in this chapter;

(ii) when looking at CAS/MBR, energy and sludge production costs have to considered, according to what is calculated by aid of the ASM model (chapter 4).

(iii) the cost of the MBR can be recalculated on the basis of cheaper supplier which are able to retrofit a similar membrane configuration, i.e. hollow fibers in the case of Schilde. According to the information available at Aquafin, the fibers purchase costs can drop to 1/3th.

(iv) An interest rate of 2.6%/year is considered, as to compare assets in different years of operation and investment.

When summing all this information up, the results are computed in Figure 7.7 for different parameters input. Results show that the energy consumption in MBR outcompetes the technology. Membrane replacement is not a sufficiently sensitive parameter to compensate for the operational costs.

Table 7.3: Investment database of some latest projects in Aquafin. All costs are expressed in 1000 euro's. Loads are calculated on a P.E. BOD basis. "E-M" stands for electro-mechanics asset. The column "Others" represent costs that have been accounted in the database besides "Building" and "E-M" costs.

WWTP	Type	Year	Load	E-M	Building	Others	Membrane	Total cost	Actualized cost	Cost per P.E.
			P.E.	€	€	€	€	€	€	€/P.E.
Langemark	CAS	2009	4200	500	1800	500		2800	3214	0.77
Oosterzele	CAS	2008	4200	423	2000	277		2700	3186	0.76
Pittem	CAS	2010	5000	600	1400	200		2200	2525	0.51
Messelbroek	CAS	2006	6500					2950	3480	0.54
Beernem	CAS	2003	6799	450	1100	950		2500	3400	0.50
Schilde	MBR	2003	7000	533	1067		500	1600	2228	0.32
Wingene	CAS	2007	7300	500	1000	500		2000	2450	0.34
Asse	CAS	2009	8200					3700	4250	0.52
Berendrecht	CAS	2010	8700	800	1800	300		2900	3238	0.37
Merchtem	CAS	2009	15300					5000	5740	0.38
Tervuren	MBR	2003	17000	3150	2650	700	1000	7500	10446	0.61
Sint-Pieters	CAS	2001	20000	1700	3367	2933		8000	12000	0.60
Ruisbroek	CAS	2005	33000					9100	11670	0.35
Beveren	CAS	2008	43000					9100	10740	0.25
Grimbergen	CAS	2002	80000	3500	14500			18000	26000	0.33

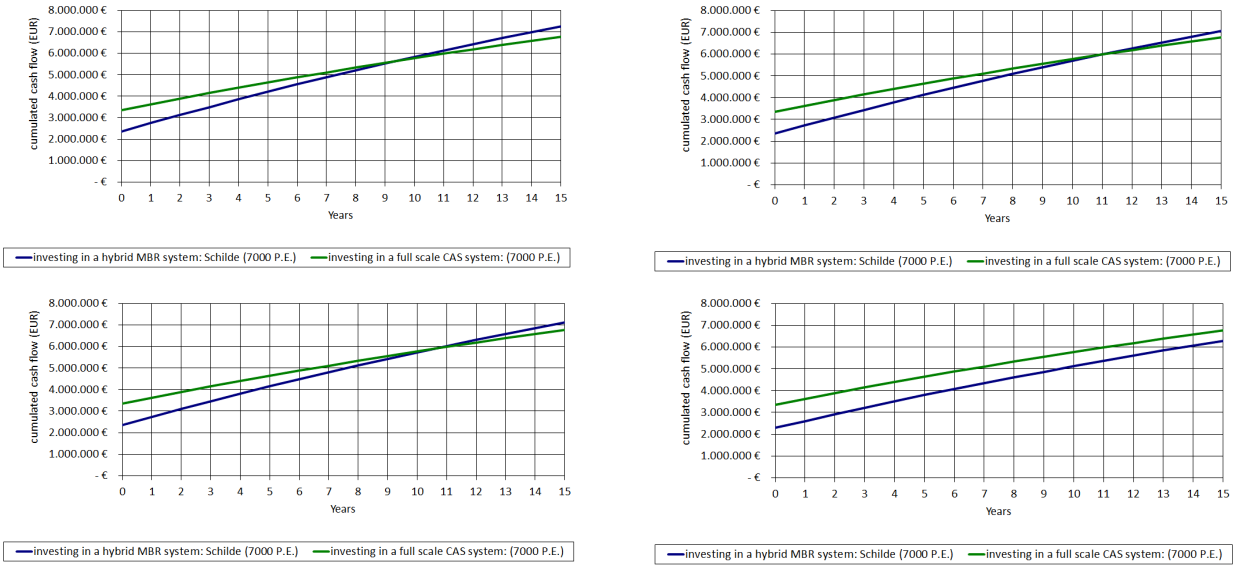

Figure 7.7: Financial analysis of MBR vs CAS systems. At the top left, membrane replacement time is 11 years and MLSS concentration in the biology is 10 g/l. At the top right, membrane replacement time is 20 years and MLSS concentration in the biology is 10 g/l. At the bottom left, membrane replacement time is 11 years and MLSS concentration in the biology is 15 g/l. At the bottom right, membrane replacement time is 11 years, MLSS concentration in the biology is 10 g/l, and energy costs are equal for MBR and CAS systems.

MBRs appear to be a costly application. However these calculations forget that the MBR technology is primarily an application for water re-use. And therefore the production of water for agricultural uses should be accounted in the financial analysis. Moreover this work promotes the use of MBRs for alternative applications: in chapter 6, the MBR sludge is continously inoculated in a CAS system, improving the effluent performances of the CAS system; in chapter 9, a fungal MBR proves to be able to degrade known recalcitrant compounds when applied for municipal waste-water treatment.

In this sense the possibilities an MBR configuration can offer are far more wide than a CAS system. And it is in this sence that a true financial analysis should be framed. However a typical western misconception brought MBRs to be applied only for effluent concern, forgetting that water re-use was its main field of application. Only when MBRs are conceived for their multiple applications possibilities, the application is to be considered pioneering and financially rewarding.

*7.7 **References***

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Chapter 8

Evaluating the application of Microbacterium sp. strain BR1 for the removal of sulfamethoxazole in full-scale MBRs

Re-drafted from: Fenu A., Donckels B., Beffa T., Bemfohr C., Weemaes M., (2015), Evaluating the application of Microbacterium so. Strain BR1 for the removal of sulfamethoxazole in full-scale MBRs. Water Science & Technology, 72, 10, 1754-1761.

Abstract: Microbacterium sp. strain BR1 is a bacterial strain that recently received attention for its capability to mineralize sulfamethoxazole (SMX) and other sulfonamides. In this study, the survival of Microbacterium sp. in municipal sludge waters was tested in batch experiments to explore optimal process conditions. Inoculation of Microbacterium sp. was subsequently performed in a pilot MBR operated in two configurations: treating full-scale MBR permeate (post-treatment) and treating raw municipal wastewater. SMX removal by Microbacterium sp. could not be proved in any of the configurations, except for SMX concentrations far higher than the ones normally found in municipal wastewater. By use of molecular tools (FISH analysis) a scarce capability to survive in activated sludge systems was assessed. After inoculation, Microbacterium sp. was reduced to a small fraction of the viable biomass. The observed growth rate appeared to be many times lower than the one of typical activated sludge micro-organisms. Possibilities of application in full-scale municipal wastewater treatment are scarce.

8.1 ***Introduction***

Sulfamethoxazole (SMX) is widely used as an antibiotic (Kümmerer, 2009). Although conventional wastewater treatment technology has shown to significantly reduce the impact on the environment in terms of eco-toxicity (Muñoz *et al.*, 2008), many pharmaceutical compounds, such as SMX, are poorly degradable and are therefore not fully removed in wastewater treatment plants (Clara *et al*., 2005; Joss *et al.,* 2005). Moreover, state-of-the-art post-treatment technologies such as sand filtration, coagulation, flocculation and flotation, fail to completely remove SMX because of its hydrophilic nature (Nakada *et al*., 2007).

As a consequence, SMX is still present in WWTP effluent and concentrations up to 1.7 and 1.9 µg/L have already been reported by Loos *et al*. (2013) and Miao *et al*. (2004), respectively. In surface waters, SMX has been detected at concentrations of µg/L which is in line with other antibiotics (Sim et al., 2011). In addition, the presence of SMX in water bodies can promote the development of antibacterial resistance (Cooper *et al*., 2008).

Novel technologies are developed that allow a better removal of micro-pollutants, including SMX, from wastewater. One such technology is bio-augmentation, i.e. the addition of specialized microbial strains to enhance or enable the degradation of certain compounds. Bouju *et al.* (2012) demonstrated that Microbacterium sp. strain BR1, a gram-positive bacteria isolated from a MBR treating effluent contaminated with several pharmaceuticals, was able to grow on SMX as main source of carbon and energy. This was later confirmed by Ricken *et al.* (2013), who also discovered the metabolic pathway that enabled the degradation of sulphonamide antibiotics.

In this study, the applicability of Microbacterium sp. strain BR1 to degrade SMX in full-scale operation was tested and evaluated. More precisely, the objectives were (1) to investigate whether Microbacterium sp. was able to survive when inoculated in an activated sludge culture and under realistic, non-

optimal conditions and (2) to evaluate to which extent SMX could be removed in activated sludge systems.

Table 8.1: Operational parameters in full-scale and pilot MBR

Operating parameter	Full-scale MBR	Pilot MBR 2° treatment	Pilot MBR Post-treatment
HRT [h]	7	22	48
Influent COD concentrations [mg COD/L]	196±55	196±55	22±8
Inflow [m^3/h]	220±10	0.045±0.005	0.020±0.005
Total Volume [m^3]	1200	1	1
Anoxic to aerobic volume ratio [L/L]	500/650	550/450	550/450
pH	7.9±0.4	7.0±0.2	7.1±0.3
T [°C]	8-19	22.9±1.4	22.6±1.9
Dry solids concentration range [g/L]	9.75±0.75	3.1±0.9	0.75±0.3
Recirculation/influent flow ratio	6:1	6:1	6:1
Inoculated weight per MLSS weight [%]	0	1	45
Membrane Type	GE ZW 500	GE ZW 10	GE ZW 10
Membrane Surface [m^2]	10000	2	2
Membrane Pore Size [µm]	0.04	0.04	0.04

*8.2 **Materials and methods***

*8.2.1 **Bacterial strain cultivation and detection***

Microbacterium sp. cells were acclimatized to SMX by growing them in 25% (vol/vol) Standard I medium, consisting of 3.75 g/L peptones, 0.75 g/L yeast extract, 1.5 g/L NaCl and 0.25 g/L D (+) glucose at pH 7.2-7.4, enriched with 0.5 mM SMX. The cultures were cultivated on a rotary shaker (130 rpm) at a controlled temperature of 28 °C until an optical density (at 600 nm) of 1.2 was reached. This typically occurred after approximately 40 hours.

The growth of Microbacterium sp. was monitored using a commercial FISH kit (VIT® Microbacterium sp. BR1 Kit). Probe design and in-silico specificity testing was carried out using the ARB software package. For FISH analysis, fresh activated sludge was fixated by dilution 1:1 (vol/vol) in pure ethanol in 15 ml sterile vials stored at -20°C prior to the analysis. The probe mix EUB labelled with 6-FAM was used for viable bacterial cell counts. Total cell count was performed by DAPI (4',6-diamidino-2-phenylindole) DNA staining.

8.2.2 ***Preliminary batch experiments***

Prior to the experiments with the pilot MBR (see below), two series of dedicated batch tests were performed. In a first series of batch experiments (noted as A), the ability of the microbial community already present in the full-scale MBR ("activated sludge") to degrade SMX was tested and compared with the removal efficiencies observed on the full-scale MBR. During this experiment, dissolved oxygen, temperature and pH were respectively controlled at 5 ± 0.2 mg O_2/L, 20°C and pH 6.5 ± 0.1. The experiment was performed in a 3 L vessel for a duration of 4 days and mixing was carried out at 300 rpm. The activated sludge concentration was 4 g MLSS/L, a typical concentration in WWTPs.

A second round of experiments (B) was conducted to study the survival of *Microbacterium sp*. in non-sterile conditions, *i.e.* raw influent wastewater. The experiment was conducted under controlled conditions (pH 6.5 ± 0.1 and 5 ± 0.1 mgO_2/L) and at different temperatures (10-15-20-25-30°C). The survival of *Microbacterium sp*. was evaluated after four and eight days by measuring total bacterial cell count and *Microbacterium sp*. through FISH analysis.

8.2.3 ***Full-Scale and pilot MBR***

The experiments were performed at the full-scale WWTP of Schilde (Schilde, Belgium), operated by Aquafin NV, treating 5500 m³/day of municipal wastewater.

It consists of an anoxic tank, an aerobic tank and a MBR unit equipped with hollow fibre membranes. Fine bubble aeration in the aerobic tank is provided through diffusers and controlled on a fixed dissolved oxygen (DO) set-point.

Two inoculation experiments were performed using a pilot MBR (Figure 8.1) composed of two separated biological compartments (anoxic and aerobic) with total volume of 1000 L. A submerged membrane was placed into the aerobic compartment and air scouring was provided (1.8 Nm^3/h) to prevent clogging of the membranes. Fine bubble aeration was provided through plate diffusers and pH was controlled by automatic dosing of concentrated NaOH and HCl solutions. Temperature was controlled by three heat resistances placed inside the reactor.

The *Microbacterium sp.* bacteria were inoculated in the pilot MBR, which treated full-scale MBR effluent (post-treatment) and raw municipal wastewater in respectively the first and second experiment. The operating conditions of the pilot MBR were optimized based on the results of the batch tests and the limitations for practical application (see discussion).

Grab samples were taken on a regular basis and these were analysed for NH_4-N, NO_2-N, NO_3-N, COD and MLSS according to APHA standards (1999). Both MBRs were equipped with the on-line dissolved oxygen, nitrate (effluent), pH and temperature sensors. More details on the operating conditions of both MBRs are given in Table 8.1.

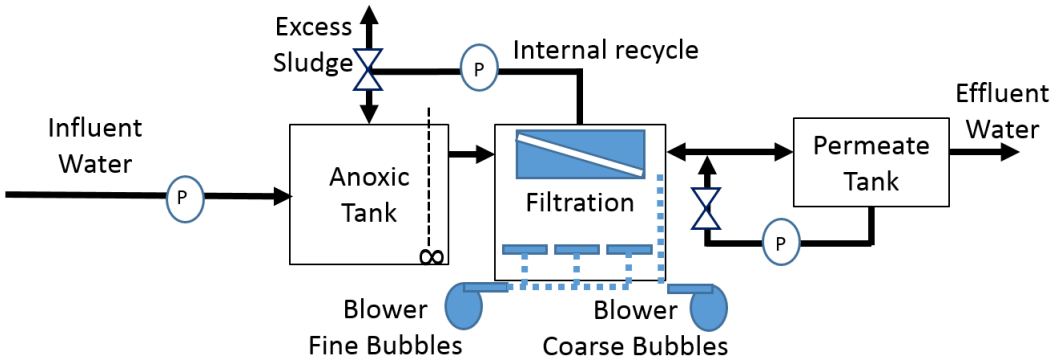

Figure 8.1: schematic representation of the Pilot MBR used for the experiments.

*8.2.4 **Micro-pollutant sampling and analysis***

Influent and effluent samples of the MBRs were taken by flow composite automatic samplers in glass containers and stored at -20°C. For SMX analysis in the water phase, samples were filtered through 0.45 µm glass-fibre filter and the pH was adjusted to 7.5. Samples were concentrated on pre-packed Oasis HLB cartridges (200 mg, 6 mL) (Waters, Eschborn, Germany) that were preconditioned with 1 x 2 mL heptane, 1 x 2 mL acetone, 3 x 2 mL methanol and 4 x 2 mL non-carbonated mineral water (pH 7.5). Percolation was performed at a constant rate of 10 mL/min. Then, cartridges were completely dried with nitrogen stream (200 mbar) for 1 hour and the eluate was diluted with 1 mL of high performance liquid chromatography (HPLC) mobile phase. The HPLC was equipped with a column Zorbax SB C18 (150x3.0mm, 3.5µm particle size, Macherey-Nagel) and operated with a flow of 0.350 mL/min, using methanol and HPLC-H_2O + 0.1% formic acid solvents. SMX-d4 was used as an internal standard. For SMX analysis in the sludge phase, sludge water was stored at -20°C. The analysis of the samples was carried out by a commercial laboratory (Omega Lab), with HPLC (Agilent 1200) on a C18 column with gradient elution and detection by tandem mass spectrometry (MS/MS).

*8.3 **Results and Discussion***

*8.3.1 **Preliminary batch experiments***

In batch experiments B, *Microbacterium sp*. was inoculated in raw influent wastewater and the ability to grow on this medium was evaluated using FISH analysis. Apart from investigating whether the microorganisms were able to survive, optimal temperature and minimum required inoculation ratio, defined as the ratio (weight/weight) between inoculated biomass and activated sludge, were determined.

From the results, depicted in Figure 8.2, one can clearly see that *Microbacterium sp*. do not survive for temperatures below 20 °C. Eight days after inoculation, only negligible amounts of *Microbacterium sp*. were observed, regardless of the applied inoculation ratio. Since the temperature in a typical central European activated sludge plant fluctuates between 7 and 19 °C (winter/summer), these results indicate that *Microbacterium sp.* will not survive when inoculated in a full-scale installation treating municipal wastewater.

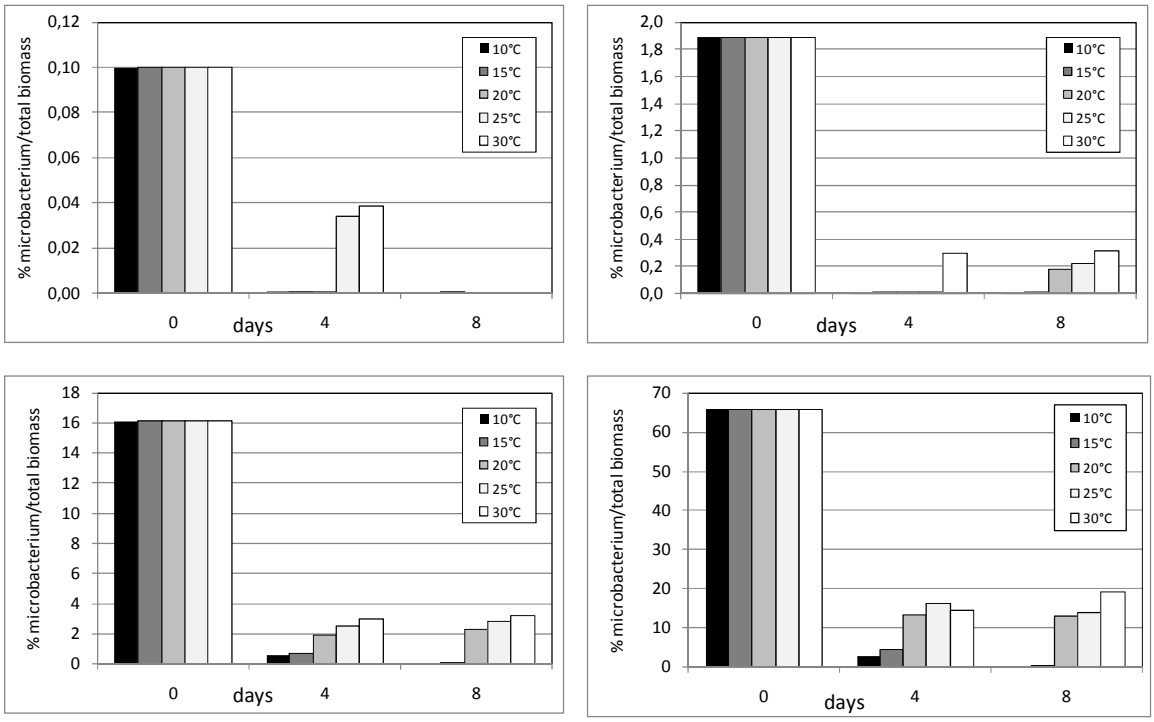

Figure 8.2: Results of the batch tests where the effect of temperature and inoculum ratio was investigated. Microbacterium and total (viable + dead) biomass (DAPI) are measured by FISH analysis.

Figure 8.2 also shows that even for higher temperatures, significant amounts of Microbacterium sp. can only be maintained in the activated sludge community when high inoculation ratios are applied. However, because the growth rate of Microbacterium is very low, it is not realistic to produce Microbacterium sp. cultures in quantities that allow such high inoculation ratios for full-scale applications.

*8.3.2 **Removal of sulfamethoxazole by full-scale MBR activated sludge***

Prior to discussing the results obtained with the pilot MBR, the removal efficiencies of the full-scale MBR were determined by measuring the SMX concentration in the influent and effluent during a sampling campaign of four months (Figure 8.3, right). The average concentrations of SMX in the full-scale MBR influent and permeate were 120 ± 62 ng/L and 58 ± 54 ng/L, respectively, and an average efficiency of approximately 52 % was observed. One can also see that the removal efficiencies fluctuate

considerably, often dropping to very low values. This variation could not be fully explained, but dilution of the influent and the occurrence of peak loads (so-called first-flush phenomena) during rain events, may have strongly influenced the observed removal rates. Nevertheless, these observations provide a reference to compare the removal efficiencies obtained when *Microbacterium sp.* is inoculated (see further).

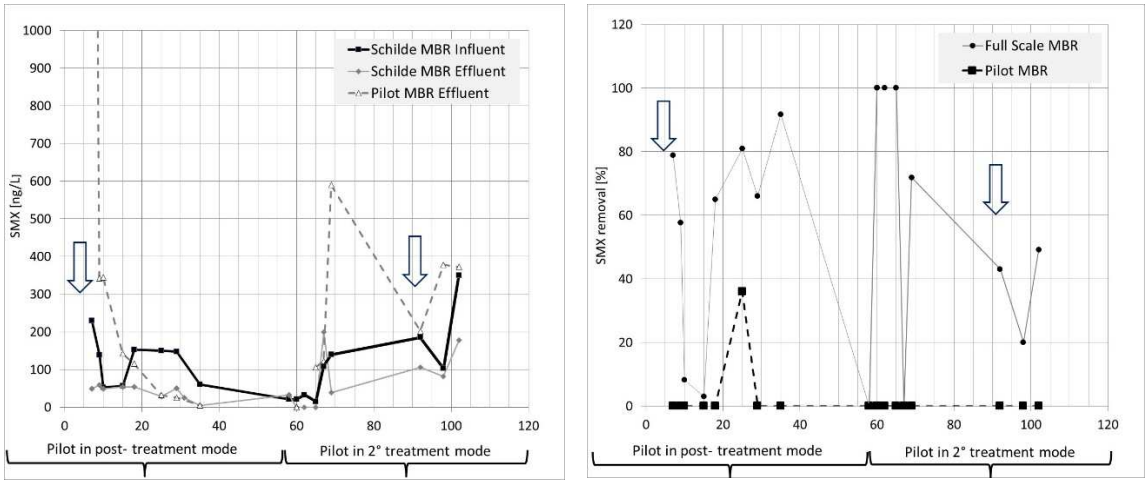

Figure 8.3: On the Y axis full-scale MBR influent, full-scale MBR effluent, pilot-scale MBR effluent concentrations & removals of SMX. The arrows represent the inoculation of Microbacterium in the pilot MBR waters. On the X axis, the days of operations. In post-treatment configuration, the pilot MBR receives full-scale permeate. In secondary treatment configuration the pilot MBR receives full-scale influent waters.

The observed removal efficiencies are in agreement with literature. Göbel *et al.* (2007) investigated the performance of a CAS system and observed removal efficiencies of 50 to 90%, whereby less than the 5% could be attributed to sludge sorption processes. Suàrez *et al.* (2010) observed 20% removal and no sorption onto the sludge for an activated sludge system with SRT of 20 days. Also in our case, no SMX was measured on the activated sludge phase.

The removal of SMX was also evaluated in batch experiments (A) using activated sludge from the full-scale MBR. These experiments confirmed the results obtained from the full-scale MBR, *i.e.* that SMX can be degraded by the activated sludge community. Indeed, SMX was removed from the liquid phase with an efficiency of 92.5 ± 2.5%. The higher removal efficiency can be explained by the fact that the hydraulic retention time (here, equal to the duration of the experiment) was 4 days, whereas the average HRT in the full-scale MBR was about 7 hours.

8.3.3 ***Removal of sulfamethoxazole in pilot MBR treating full-scale MBR permeate***

Based on the results of the batch experiments, one could easily conclude that the operating conditions of the full-scale MBR did not allow survival of *Microbacterium sp.* when inoculated. Therefore, it was decided to operate the pilot MBR under more favourable, yet practically realistic conditions as to promote *Microbacterium sp.* survival (see Table 8.1). As expected given the low COD content of the permeate, the MLSS concentration remained very low during the experiment (Table 8.1) and the application of a high inoculation ratio was feasible.

Prior to the experiments, two elements were thought to favour *Microbacterium sp.* survival after inoculation when the pilot MBR was operated as a post-treatment. First, the amount of micro-organisms in ultra-filtered MBR permeate is very low, so the competition with other micro-organisms will be limited (Hirani *et al.*, 2013). Second, the COD in the permeate consists mainly of recalcitrant SMPs (Fenu *et al*., 2011), which was confirmed in the two months prior to the inoculation experiments where no biological growth was observed.

Nevertheless, the very low SMX concentrations in full-scale MBR permeate could be limiting for the inoculated biomass. In the experiment, the removal of SMX at higher concentrations was investigated as well, by looking at the period immediately following the inoculation. Indeed, *Microbacterium sp.* was grown in a medium that contains nutrients and relatively high concentrations of SMX.

The COD and NH_4 concentrations of the permeate during the experiment were 22 ± 8 mg COD/L and 0.2 ± 0.1 mg NH_4-N/L, respectively. Elevated concentrations of COD and NH_4 were observed in the effluent for approximately 9 days after inoculation, due to the nutrients present growth media that was added when inoculating. The measurements depicted in Figure 8.4 show that the DO concentration dropped from 9 to 1 mg/L immediately after inoculation, indicating an increased biomass respiration, and reached saturation after approximately 13 days.

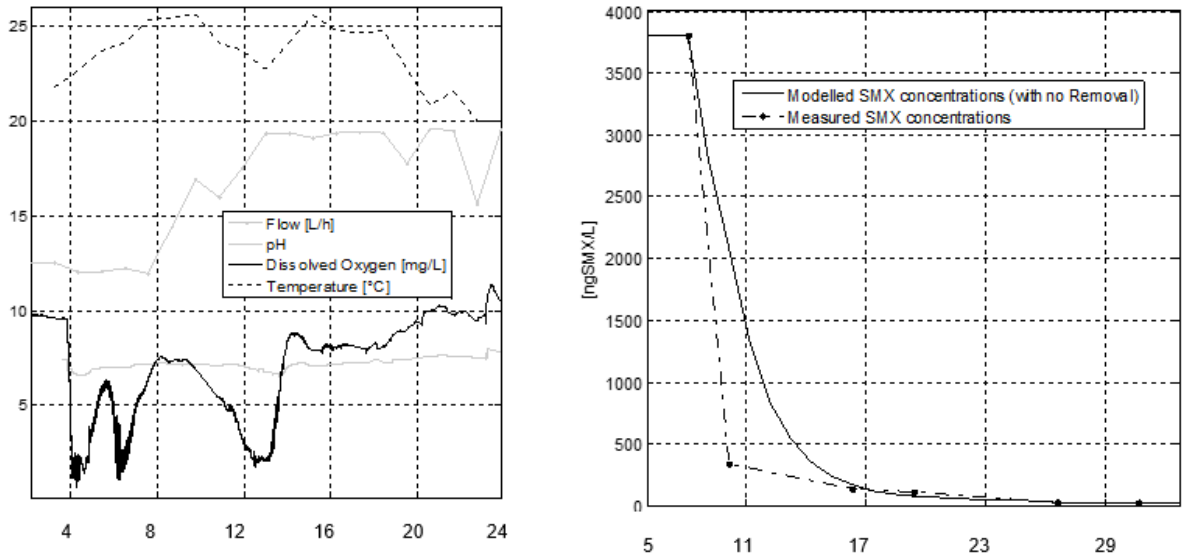

Figure 8.4 (left): on-line sensors data during pilot MBR treatment of the full-scale permeate waters. On the X axis, the days of pilot operations. Figure 8.4 (right): predicted (assuming no removal) and measured SMX concentrations of pilot MBR during post-treatment of full-scale permeate waters. On the X axis, the days of pilot operations.

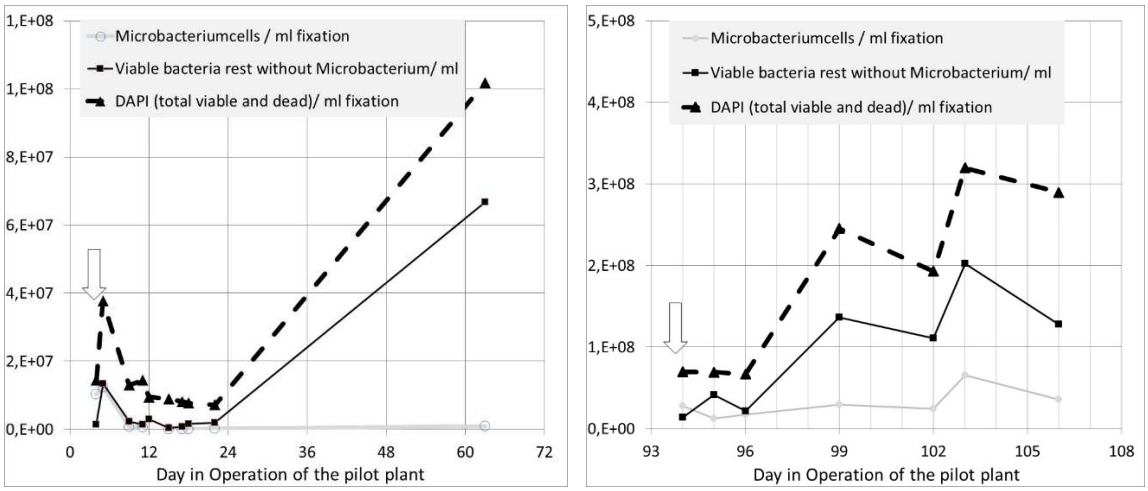

Figure 8.5: Monitoring of biomass according to FISH techniques. The arrows represents the day the Microbacterium sp. was inoculated. At the left side Figure, the pilot treats full-scale permeate waters. At the right side Figure, the pilot treats full-scale influent waters. On the X axis, the day of operations. On the Y axis, the cell count.

After inoculation, the concentrations of SMX were significantly higher than the average concentrations in raw municipal wastewater (120 ± 62 ng SMX/L) and MBR permeate (see Figure 8.4). To investigate the removal of SMX by *Microbacterium sp.*, one has to distinguish between dilution and removal or breakdown. For this, a simple degradation model was built based on mass-balances. In Figure 8.4, the measured SMX concentrations in the pilot MBR are compared to the ones predicted without degradation (only dilution). These results confirm that SMX is removed at high SMX concentrations. Ricken *et*

al. (2013) concluded that high, non-inhibitory SMX concentrations, might still drive selection for utilization as carbon and energy source, but in their work, the removal efficiency of *Microbacterium sp*. was evaluated for higher concentrations (100 µM sulphonamides) that were significantly higher than the municipal range concentrations. The present experiment suggests that the actual challenge of such strain is to have it working in the municipal SMX range.

These results are also confirmed by FISH analysis. The concentration of both viable biomass and *Microbacterium sp*. dropped with time after inoculation, but the latter dropped faster (Figure 8.5, left). The observed drop in the viable biomass concentration can be explained by the low COD load and the fact that it consists mostly of recalcitrant SMPs. One can also see that the percentage of *Microbacterium sp.* on total cells dropped to about 1 - 3% in 20 days. This indicates that *Microbacterium sp.* could not cope with the autochthonous bacterial growth, and full-scale application as a post-treatment of MBR permeate is practically not feasible.

8.3.4 ***Removal of sulfamethoxazole in pilot MBR treating raw municipal wastewater***

In this section, the results obtained when the pilot MBR was used to treat raw influent wastewater are discussed. Although the composition of the wastewater is the same as for the full-scale MBR, a comparison between both systems is difficult because, as discussed above, the operating conditions of the pilot MBR (Table 8.1) were chosen such as to promote survival of Microbacterium sp. after batch experiments showed that survival in the conditions at which the full-scale MBR was operated was very unlikely.

The measurements performed during this inoculation experiment are shown in Figure 8.4. The COD concentration of the influent wastewater was 196 ± 55 mg/L and a COD removal of 55% was established by the pilot MBR. Ammonia was fully removed and the nitrate concentration in the effluent fluctuated between 1 and 4 mgNO_3-N/L, resulting in an overall nitrogen removal of approximately 93%. During the time of the experiment, the operation of the full-scale MBR was monitored as well (see Section 8.3.2) and it was found that SMX was removed by the activated sludge (Figure 8.3). From the measurements in the pilot MBR, on the other hand, one could conclude that no removal of SMX occurred in the pilot MBR since the effluent concentrations were not significantly different from the influent concentrations (Figure 8.3). The sludge phase of the pilot MBR was also analysed and no SMX was detected, meaning that no significant sorption onto sludge occurred.

An explanation for the inability of the inoculated *Microbacterium sp.* bacteria to survive is found in the fact that they cannot compete with micro-organisms present in activated sludge. This is confirmed by the results of the FISH analysis (Figure 8.5). In the inoculation medium, the viable *Microbacterium sp.*

cells accounted for 40% of the total number of viable cells. However, after inoculation, the viable bacteria in the activated sludge increased from 1.4E7 cell/ml to 1.3E8 cell/ml, whereas *Microbacterium sp.* only increased from 2.8E7 cell/ml to 3.6E7 cell/ml (29% increase in 14 days). In other words, the autochthonous cells grew approximately 15 times faster than the inoculated *Microbacterium sp.* cells. As a result, the fraction of *Microbacterium sp*. rapidly dropped to 5-10% of the total cells, despite a the fact that SMX was non-limiting.

The doubling time of the inoculated biomass and the autochthonous biomass has been experimentally estimated. This has been done by considering that all of the experimental curves in Figure 8.5 (right side) have a common trend of upside-downside points. For all of these curves, a line in between top and bottom points has been drown. All the lines, determined this way, have a growing trend. The growing trend represents the bacterial cell count growth over time. And we refer to it as rough doubling time estimation.

The experimental doubling time of *Microbacterium sp.* in the pilot reactor, proved to be exceptionally long, *i.e.* around 45 days. Since, municipal MBRs are operated with SRTs in the range of 10-25 days, *Microbacterium sp.* would have no chance of survival in realistic applications. An adjustment of municipal MBRs design to allow the survival of *Microbacterium sp*. would involve either filtration operations at very high MLSS concentrations or increased design volumes. In both cases, operational and financial feasibility of such adaptation is a clear objection.

8.4 ***Conclusions***

In this study a pilot MBR was inoculated with Microbacterium sp. strain BR1 to investigate the potential for SMX removal in full-scale applications. From the results, one can conclude that high wastewater temperatures were necessary to increase the chance of Microbacterium sp. survival in raw municipal wastewater. When fed with full-scale MBR permeate, SMX removal was only observed for concentrations that were several times higher than typically found in municipal wastewater. When fed with raw influent wastewater, no SMX removal was observed either. The doubling time of Microbacterium sp. was found to be far higher than the SRTs of municipal MBRs. Application of bio-augmentation with Microbacterium sp. in full-scale applications is unrealistic.

8.5 ***References***

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Chapter 9

Evaluating the application of Phoma sp. UHH 5-1-03 for the degradation of Carbamazepine and Diclofenac in full-scale MBRs

Abstract: In this study, the survival of an aquatic ascomycetous fungus, Phoma sp. UHH 5-1-03, was tested in municipal sludge waters. By employing a detailed lab scale protocol, the Phoma sp. achieved significant carbamazepine and diclofenac removal rates whereas no sorption mechanisms onto sludge or the fungus were identified. Optimal process conditions and degradation performances were explored in controlled conditions and a minimum water temperature of 20°C was found as an implementation limit. Inoculation of Phoma sp. was subsequently performed in a pilot MBR operated in two configurations: treating full-scale MBR permeate (post-treatment) and treating raw municipal wastewater. Phoma sp. is able to survive in municipal wastewater, in competition with activated sludge, while degrading the target compounds even in very low concentrations. The mechanism of degradation differs for the two targeted compounds. While diclofenac degradation is potentiated by the extra-polymeric laccase induction, carbamazepine is not affected by it. Further investigation is necessary, as to explore Phoma sp. survival as well as the laccase degradation potential in the alkaline range. Applicability of the concept in full-scale is critically discussed within this work.

9.1 ***Introduction***

Pharmaceutically active compounds (PhACs) comprise a wide range of synthetic compounds. PhACs have been detected in secondary treated effluents, surface water bodies, and even in drinking water (Snyder, 2008). PhACs may occur in WWTP effluents due to no or low tendency to adsorb onto activated sludge or because their microbial degradation is not fast enough to be completed within the hydraulic residence time (HRT) of the treatment plants (Groz *et al.*, 2012). CAS treatment was not specifically designed to remove PhACs (Suárez *et al*., 2008), and their removal efficiency by activated sludge can vary significantly (Hai *et al*., 2009). Among them, carbamazepine (CBZ) and diclofenac (DF) were detected most frequently (Zhang *et al*., 2012). Some authors even report an increase in concentration of the latter compounds along the passage through wastewater treatment plants (WWTPs) as a result of enzymatic conversion of related molecules (Vieno *et al.,* 2007; Gros *et al.*, 2010).

Different approaches may target the biological removal of such compounds. Enzymatic membrane reactors tackle the degradation of PhACs but they deal with gradual loss of enzymatic activity due to various physical, chemical and biological inhibitors in wastewater conditions (Nguyen *et al*., 2013). It would be necessary to periodically replenish the reactor with fresh enzyme. By contrast, a whole-cell reactor may bring about the added advantage of continuous enzyme production (Nguyen *et al*., 2013). The latter approach was pursued by Zhang *et al.* (2012) who designed a bioreactor with a white rot fungus grown on polyether foam, achieving effective elimination of CBZ (60-80%) under non-sterile conditions. Another experiment was performed by Nguyen *et al.* (2013), proving a moderate removal of CBZ and DF in MBR using a mixed culture of bacteria and white rot fungi. Removal of CBZ and DF were respectively in the range of 20% and 40%. The mentioned experiments were carried out on full-scale WWTP effluent.

Phoma is a genus of common coelomycetous fungi belonging to the phylum Ascomycota. Ascomycetes are the predominant group of fungi in aquatic habitats. As a consequence of the constraints associated with submersion in water, aqueous fungi, such as those used in this study, likely have adapted and specialized enzymes. Ascomycetes, and through them the *Phoma* sp., produce enzymes, called laccases, that are known to be active and stable at alkaline pHs (Kiiskinen *et al.*, 2005). Such characteristic makes these fungi potentially suitable for wastewater applications. Several tests have investigated the *Phoma* potential (Junghanns *et al.*, 2005), although its survival in influent wastewaters, real environmental conditions, and trace pollutants concentrations, has to the best of our knowledge never been reported before.

In this study, the applicability of *Phoma sp.* to degrade CBZ and DF in full-scale operation was tested and evaluated. More precisely, the objectives were (1) to investigate whether *Phoma sp.* was able to survive when inoculated in an activated sludge culture and under realistic, non-optimal conditions and (2) to evaluate to which extent CBZ and DF could be removed in activated sludge systems.

Figure 9.1: Phoma sp. strain UHH 5-1-03 cultivation on liquid malt extract.

9.2 ***Materials and methods***

9.2.1 ***Organism and cultivation conditions***

Cultivation of *Phoma sp. strain UHH 5-1-03* was performed in liquid malt extract medium at pH 5.6–5.8 (Figure 9.1). The inoculum comprised 100 ml (5%) mycelial suspension. The whole culture was homogenized with an Ultra-Turrax (at 120 rpm) equipped with a previously heat-sterilized dispersing element. The suspension was aerated with sterile-air at a rate of 1 L/min.

9.2.2 ***Micro-pollutants sampling and analysis in the water phase***

Influent and effluent samples of full-scale and pilot MBRs have been collected by flow composite automatic samplers in glass containers. All samples have been stored at -20°C.

For DF analysis, aqueous samples were filtered through a 0.45 µm glass-fibre filter and then adjusted to pH 2.8 with 3.5 mM sulfuric acid. DF-d4 was used as internal standard. The sample was enriched on a pre-packed Oasis MCX cartridge (60 mg, Waters, Eshborn, Germany). Cartridges were pre-conditioned with 1x2 mL heptane, 1x2 mL acetone, 3x2 mL methanol and 4x2 mL non-carbonated mineral water (at pH 2.8). Percolation was performed at a flow rate of 20 mL/min.

For CBZ analysis, aqueous samples were filtered through 0.45 µm glass fibre filter and adjusted to pH 7.5. CBZ-c13 was used as an internal standard. Samples were enriched on a pre-packed Oasis HLB cartridge (200mg, 6 mL, Waters, Eschborn, Germany) that was preconditioned with 1x2 mL heptane, 1x2 mL acetone, 3x2 mL methanol and 4x2 mL non-carbonated mineral water (at pH 7.5). Percolation was performed at a constant rate of 10mL/min.

Afterwards, cartridges were completely dried with a nitrogen flow (200 mbar) for one hour. The final eluent was then diluted with 1 mL of high performance liquid chromatography (HPLC) mobile phase. The HPLC was equipped with a column Zorbax SB C18 (150 x 3.0 mm, 3.5 µm particle size, Macherey-Nagel). Flow: 0.350 mL/min. Solvent A: methanol. Solvent B: HPLC-H2O + 0.1% formic acid.

9.2.3 ***Micro-pollutants sampling and analysis in the sludge phase***

Influent and effluent samples of the pilot MBR have been collected by flow composite automatic samplers in glass containers. All samples have been stored at -20°C.

The solid fraction of the sludge was obtained by filtration through glass-fibre filters. The obtained solid fraction (77.8 mg) was directly spiked with appropriate surrogate standard and extracted successively with 5 ml acetonitrile and 5 ml methanol for each 30 minutes at room temperature. The sludge's were

centrifuged at 19,000 rad/min for 5 minutes. The obtained supernatants were combined and evaporated close to dryness by a gentle nitrogen flow and the residue was subsequently dissolved in 1 ml methanol.

The methanol extract was analysed with HPLC (Agilent 1200) on a C18 column with gradient elution and tandem mass spectrometry detection (MS/MS). The mass spectrometer (Agilent QQQ 6460) was operated in positive and negative ionization modes using an electron spray ionization (ESI) source. The ion with the highest intensity was used for reaction monitoring (SRM) and quantification in MS/MS mode. Product identification is based on the retention times of the analytes and on MS/MS detection. Blank and quality control samples were analysed to check the analytical equipment. The blank background noise was less than 30% of the quantification limit. The analyte recovery in the quality control sample was in the range of 80-120%.

9.2.4 ***Detection of Phoma sp. using FISH***

Inoculated biomass has been fixated by 1:1 dilution in pure ethanol (> 96-99.9 %) in 15 ml vials, and stored at -20°C until analysis.

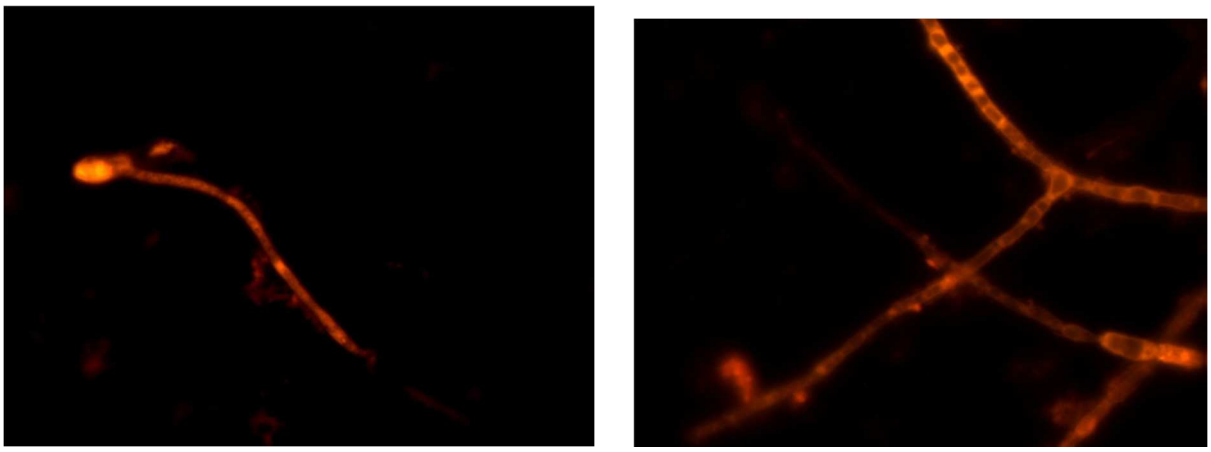

Figure 9.2: Specific detection of viable Phoma.

The presence of Phoma sp. was quantified using the commercial FISH kit VIT® Phoma sp. UHH 5-1-03Kit. Probe design and in-silico specificity testing was carried out by using the software package ARB. A special approach was developed for quantification by FISH techniques. After FISH, a microscopic analysis was carried out (Figure 9.2). Per microscopic view, 100 square areas exist. If Phoma hyphae were found in only 1/100 square areas, a percentage of 1% was given. This procedure was repeated 20 times, resulting in a mean value of Phoma hyphae, which is reported. As it may be expected, standard errors of this measurement were significant and in the range of the 10-20%.

The probe mix EUB labelled with 6-FAM was used for viable bacterial cell counts. Total cell count was performed by DAPI (4',6-diamidino-2-phenylindole) DNA staining of whole fixed cells (Vermicon commercial Kit).

9.2.5 ***Preliminary lab scale tests employing real wastewater***

Prior to the experiments with the pilot MBR (see below), two types of experiments were conducted to study the survival of *Phoma sp*. in non-sterile conditions, *i.e.* raw influent wastewater collected in the full-scale MBR at Schilde.

A first set of experiments (noted as A) was conducted by inoculating *Phoma sp.* in under controlled conditions (pH 5.5 ± 0.2 and 2 ± 0.2 mgO_2/L), at different temperatures (10-15-20-25-30°C), and different inoculation ratios, defined as the weight/weight ratio between inoculated *Phoma sp*. and activated sludge. *Phoma sp.* was inoculated in batches of 1L. The survival of *Phoma sp.* was evaluated after four and eight days by measuring total bacterial cell count and *Microbacterium sp*. through FISH analysis. At 4 and 8 days after incubation start-up, biomass evolution (total biomass and *Phoma sp.*) was cultured in plates.

The degradation mechanism of *Phoma sp.* towards DF and CBZ was investigated with a second set of batch experiments (noted as B). *Phoma sp.* was inoculated in batches of 1L. Each batch was carried out in triplicate, with the following controlled conditions: pH 5.5±0.2; 2±0.1 mgO_2/L; 20 days batch duration. Fungal dry weight was monitored. The following batches were held in parallel:

(B1) a blank batch in absence of *Phoma sp.;*

(B2) a batch where *Phoma* were inoculated but inactivated with 1 g/L NaN_3;

(B3) a batch where *Phoma sp.* were active;

(B4) a batch where *Phoma sp*. was active and extra-cellular laccase production was induced (see later). In batch (B4) extra-cellular laccase production was induced by adding 50 µM $CuSO_4$ and 1 mM vanillic acid in the medium containing the *Phoma sp* (Junghanns *et al*., 2008a). Methanol has been used during preparation to dilute vanillic acid to a final concentration lower than the 0.5% (w/w).

Laccase activity was routinely determined following the oxydation of 2 mM 2,2´-azino-bis-(3ethylbenzthiazoline-6-sulphonic acid) (ABTS) in 0.1 M citrate-phosphate buffer (pH 4.0) at 420 nm [ε420 = 36 mM^{-1} cm^{-1}] (Johannes and Majcherczyk, 2000; Junghanns *et al*., 2008b). Activities are expressed in international units (U), where 1 U is defined as the amount of laccase capable of oxidizing 1 µmol ABTS per minute.

9.2.6 ***Reactors: assembling and monitoring***

The experiments were performed at the full-scale WWTP of Schilde (Schilde, Belgium), operated by Aquafin NV, treating 5500 m^3/day of municipal wastewater.

It consists of an anoxic tank, an aerobic tank and a MBR unit equipped with hollow fibre membranes. Fine bubble aeration in the aerobic tank is provided through diffusers and controlled on a fixed dissolved oxygen (DO) set-point.

Two inoculation experiments were performed using a pilot MBR (Figure 9.3) composed of two separated biological compartments (anoxic and aerobic) with total volume of 1000 L. A submerged membrane was placed into the aerobic compartment and air scouring was provided (1.8 Nm^3/h) to prevent clogging of the membranes. Fine bubble aeration was provided through plate diffusers and pH was controlled by automatic dosing of concentrated NaOH and HCl solutions. Temperature was controlled by three heat resistances placed inside the reactor.

The *Phoma sp.* were inoculated in the pilot MBR, which treated full-scale MBR effluent (post-treatment) and raw municipal wastewater in respectively the first and second experiment. The operating conditions of the pilot MBR were optimized based on the results of the batch tests (A) and the limitations for practical application (see discussion).

Grab samples were taken on a regular basis and these were analysed for NH_4-N, NO_2-N, NO_3-N, COD and MLSS according to APHA standards (1999). Both MBRs were equipped with the on-line dissolved oxygen, nitrate (effluent), pH and temperature sensors. More details on the operating conditions of both MBRs are given in Table 9.1.

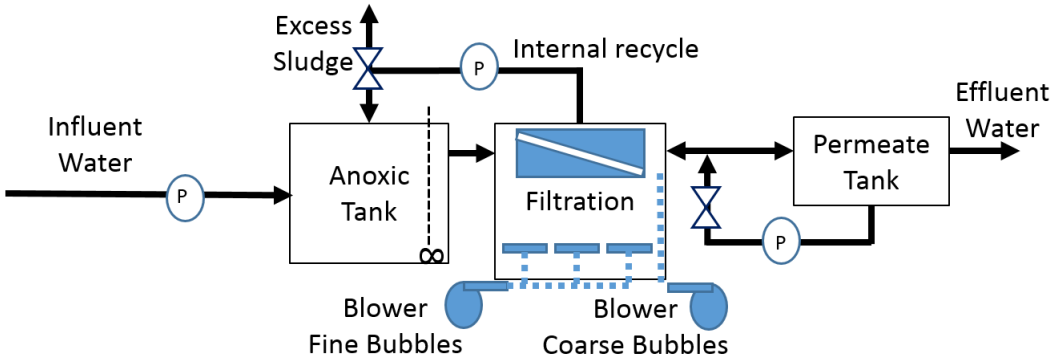

Figure 9.3: schematic representation of the Pilot MBR used for the experiments.

Table 9.1: Operational parameters in full-scale and pilot MBR

Operating parameter	Full-scale MBR	Pilot MBR 2° treatment	Pilot MBR Post-treatment
HRT [h]	7	22	27
Influent COD concentrations [mg COD/L]	196±55	196±55	22±8
Inflow [m^3/h]	220±10	0.045±0.005	0.037±0.005
Total Volume [m^3]	1200	1	1
Anoxic to aerobic volume ratio [L/L]	500/650	550/450	550/450
pH	7.9±0.4	5.5±0.5	5.5±0.5
T [°C]	8-19	22.9±1.4	22.6±1.9
Dry solids concentration range [g/L]	9.75±0.75	3.1±0.9	0.75±0.3
Recirculation/influent flow ratio	6:1	6:1	6:1
Inoculated weight per MLSS weight [%]	0	1	43
Membrane Type	GE ZW 500	GE ZW 10	GE ZW 10
Membrane Surface [m^2]	10000	2	2
Membrane Pore Size [µm]	0.04	0.04	0.04

9.2.7 ***Pilot scale trials***

Inoculation was performed by adding the *Phoma sp.* culture in its media to the pilot tank. A media centrifugation was attempted but, due to the damages to the fungi observed on the microscope, it was avoided. The pilot plant was operated according to two different process schemes:

(i) Post-treatment scheme (01.04.2013 – 27.05.2013): the pilot MBR treated full-scale MBR permeate, according to the conditions specified in Table 9.1. The inoculation was done on 24.04.2013. Sterile liquid malt extract medium has been added up to 0.05 kg BOD/kgMLSS/day as to sustain *Phoma* growth.

(ii) Secondary treatment scheme (27.05.2013 – 17.07.2013): the pilot MBR treated full-scale MBR influent wastewater (Table 9.1). The inoculation started up in 27.05.2013. *Phoma* inoculated in activated sludge, has not been nourished with sterile liquid malt.

The operating pilot MBR conditions, specified in Table 9.1 for both modes of operation, diverged from the full-scale MBR operating conditions. The biomass was found not to survive real field conditions. For this reason, the pilot scale experiments had to be adapted to more favourable conditions (Table 9.1) with regards to temperature, and HRT, as to increase the survival chances (discussed in paragraph

3.2). Only after proving successful CBZ and DF degradation from behalf of the inoculate biomass, the research can be oriented at adapting *Phoma sp*. to CAS process conditions.

In both process schemes, extra-cellular laccase production was induced (Junghanns *et al*., 2008a).

With regards to pH, the fungus operates optimally at slightly acidic conditions. The pilot conditions were likewise applied (Table 9.1).

9.3 ***Results***

9.3.1 ***Removal of the target compounds in the full-scale MBR***

In the period from 01.04.2013 to 17.07.2013, CBZ and DF were sampled in the full-scale MBR. Influent and effluent DF concentrations were respectively 1163±459 ng/L and 989±255 ng/L: by averaging the concentrations in influent/effluent results, DF was removed with an average 15% removal rate. Influent and effluent concentrations of CBZ were respectively 569±345 ng/L and 691±570 ng/L. No significant removal of CBZ was observed in the sampling campaign. On the contrary CBZ was found higher in effluent than in influent MBR wastewater. The increase of CBZ concentration in effluent wastewaters was already demonstrated to occur due to conversion of CBZ glucuronides and other conjugated metabolites to the parent compound by enzymatic processes taking place in the treatment plant (Vieno *et al.*, 2007; Gros *et al.*, 2010).

9.3.2 ***Determination of the optimal activity in function of temperature and inoculum ratio***

The selected strain was inoculated in batches containing full-scale influent wastewater. The purpose was to estimate optimal temperature and inoculation ratio for pilot experiments. In Figure 9.4, the higher the inoculation ratio, the higher the active % of *Phoma sp*. after 4-8 days. An inoculum ratio of 5% is necessary to detect fungal biomass after 8 days of HRT.

Mannan *et al.* (2005) found out that two filamentous fungi species, were dominating almost 95-98% of the existing species in a sludge process with an inoculum dose of 10-20%. However with 5% of fungal inoculum there was no significant dominance of fungi over the existing micro-organisms. Mannan *et al.* reported how the 5% inoculation ratio was found insufficient to adapt fungal biomass in sludge under natural conditions. In the tests performed in Figure 9.4, dominance of fungi is not visible. On the contrary, for any inoculation ratio, the fungal biomass halves its population after 4 days. But for the 5% and 35% inoculation ratio, the decrease in population seems to mitigate.

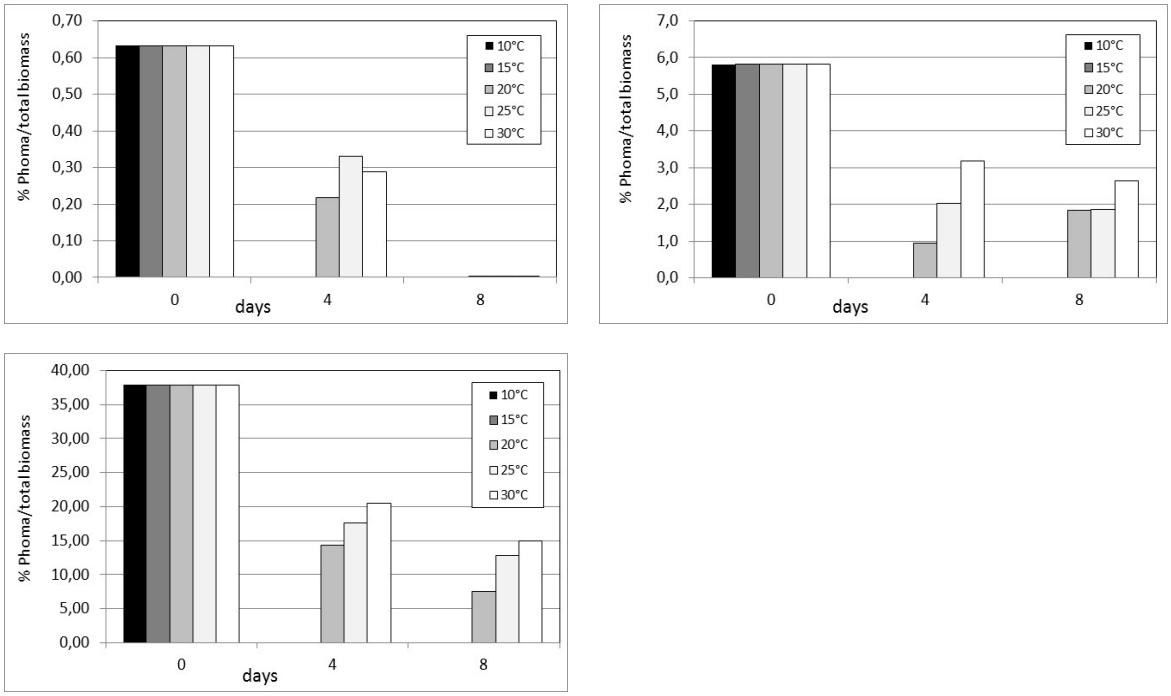

Figure 9.4: Results of the batch tests where the effect of temperature and inoculum ratio was investigated.

No *Phoma sp*. survival was observed for temperatures below 20°C at any tested inoculation ratio. Field wastewater temperatures in Belgium fluctuates amongst 8-19°C along the year. These tests suggested that the survival of *Phoma sp.* in Schilde influent wastewater at field temperatures is unlikely. It was decided to perform pilot scale tests at controlled temperatures (Table 9.1), as to increase the chances of *Phoma sp*. survival.

9.3.3 ***Degradation experiments employing real wastewaters at lab scale***

Batch test experiments (B) were performed in order to assess: the removal rates towards the target compounds; unambiguously investigate the removal mechanism; verify the affinity of *Phoma sp.* towards municipal trace concentrations of the target compounds.

The control batch B1 clearly shows that aerobic conditions in absence of *Phoma sp.* biomass are not sufficient for DF and CBZ removal in municipal waters (Figure 9.5). Nonetheless, batches B1 and B2 indicate that CBZ might have been sorbed, during sampling and conservation, onto the suspended solids contained in the raw wastewater. The inactivated *Phoma* (in batch B2) does not exhibit any continuous and persistent sorption capability towards DF and CBZ. It is concluded that *Phoma* cannot sorb the target compounds.

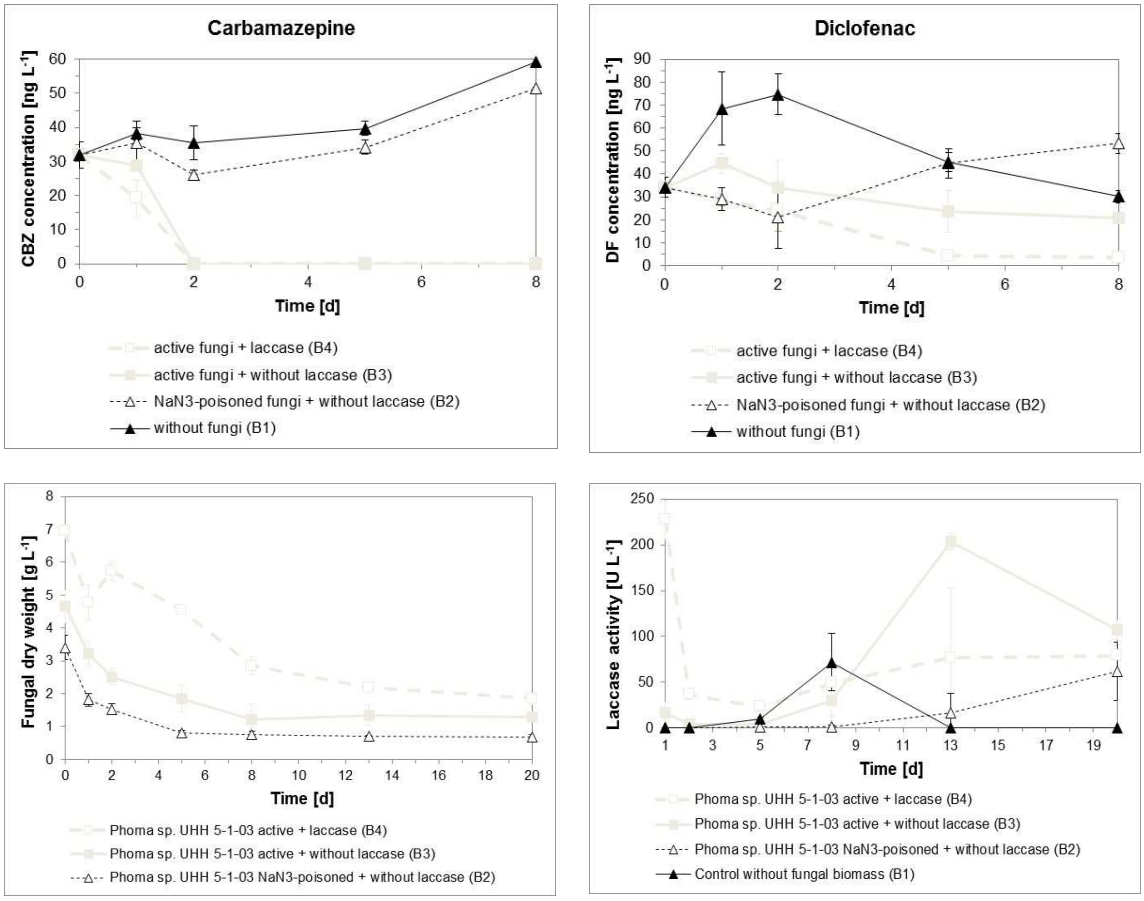

Figure 9.5: Degradation tests in controlled conditions

The monitoring of the laccase activity (Figure 9.5) shows how the induced laccase peak was very unstable by disappearing the second day after laccase induction. Laccase concentrations stayed in a range between 40-80 U/L. On the contrary, active *Phoma sp.* without laccase, as in batch B3, were able to produce increasing laccase concentrations up to 200 U/L. Laccase concentration dropped after day 13, and concurrently DF degradation was limited to a maximum of 5 ng/L (Figure 9.5).

Regardless of laccase induction, CBZ was removed below the detection limit, within two days, i.e. laccase activity (in batch B3) was in fact marginal in days 1-2. CBZ concentration in presence of active *Phoma* was actually removed and likely degraded, without a clear role of extra-cellular laccase induction.

DF was degraded in the batch tests more slowly than CBZ. This result was confirmed also in the pilot tests by comparing the removal rates (read below). But a clear enhancement of DF degradation was obtained when laccase was induced.

In this study pH was controlled at around 5.5-6, both in batch and pilot scale tests. The role of alkaline pH in such application should however be object of further attention. Especially in case of further adaptation to full-scale conditions, i.e. a municipal MBR is operated around pH 7-7.5. Under such conditions, the fungus is able to survive, but laccase released into the wastewater matrix might lose activity.

9.3.4 ***Removal of Carbamazepine and Diclofenac in pilot MBR treating full-scale MBR permeate***

Based on the results of the batch experiments, one could easily conclude that the operating conditions of the full-scale MBR did not allow survival of *Phoma sp.* when inoculated. Therefore, it was decided to operate the pilot MBR under more favourable, yet practically realistic conditions as to promote *Phoma sp.* survival (see Table 9.1). As expected given the low COD content of the permeate, the MLSS concentration remained very low during the experiment (Table 9.1) and the application of a high inoculation ratio was feasible.

Prior to the experiments, two elements were thought to favour *Phoma sp.* survival after inoculation when the pilot MBR was operated as a post-treatment. First, the amount of micro-organisms in ultrafiltered MBR permeate is very low, so the competition with other micro-organisms will be limited (Hirani *et al.*, 2013). Second, the COD in the permeate consists mainly of recalcitrant SMPs (Fenu *et al*., 2011), which was confirmed in the two months prior to the inoculation experiments where no biological growth was observed. Third, being DF and CBZ recalcitrant to activated sludge, they are still present in full-scale permeate waters.

The pilot was operated as post-treatment of full-scale MBR effluent from 1.04.2013 until 27.05.2013 (with conditions specified in Table 9.1). In order to sustain the *Phoma* population, in absence of incoming COD, malt was dosed daily according to the load specified above. *Phoma* inoculum was poured in the pilot MBR on 24 April 2013. Pilot inflow during the testing period recorded 20±2 mgCOD/L and 0.2±0.1 mgNH_4-N/L. DS concentration in the pilot, during the testing period, raised from 0.15 gMLSS/L to 0.53 gMLSS/L.

At beginning of April 2013, CBZ in the pilot effluent was lower than the pilot influent. By diluting the reactor volume with influent wastewaters, influent and effluent concentrations reached the same range in the samples of 14.04.2013 and 19.04.2013 (Figure 9.6). After *Phoma sp*. inoculation, while CBZ concentrations increased at the pilot influent, CBZ effluent concentrations of the pilot MBR raised only moderately resulting in a 40% CBZ removal for about 2 weeks. The positive performance was abruptly lost and no CBZ removal could be further observed. It is difficult to conclude on the instability of the CBZ removal performances in post-treatment configuration. As to ensure maintenance of *Phoma sp.,* metabolic activity has to be ensured and, given the lack of nutrients and BOD in the permeate waters, an additional carbon and energy source has been provided. However, degradation of most xenobiotics (chemicals, pharmaceuticals, etc.) present in wastewater may be a symbiotic process, meaning that the fungus can't stably degrade the target compounds without the activated sludge consortium.

With regards to the DF removal, the initial DF concentration in the pilot was rather high (26.04.2013 in Figure 9.6). DF concentration dropped massively in the pilot reaching MBR effluent concentrations

(Figure 9.6). From 06.05.2013, a net DF removal was established in the pilot (pilot effluent DF concentrations were lower than the MBR effluent DF concentrations).

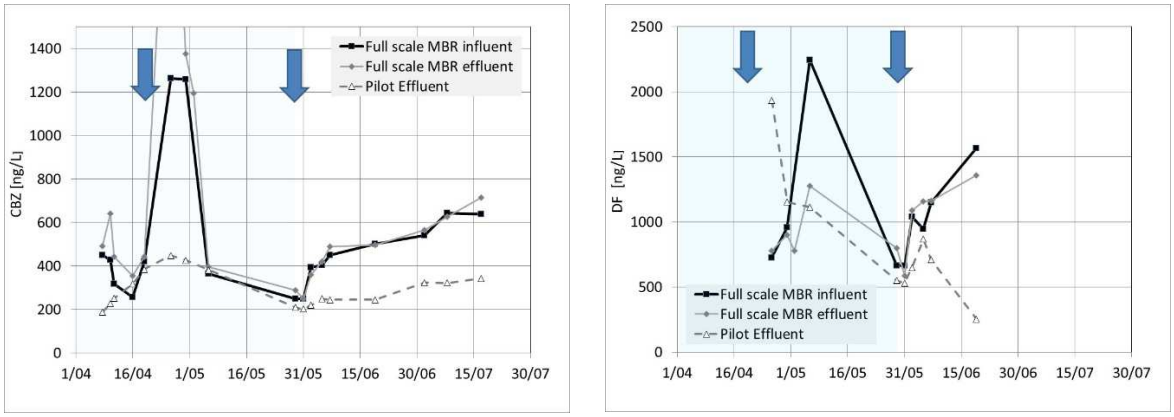

Figure 9.6 (left): On the Y axis full-scale MBR influent, full-scale MBR effluent, pilot-scale MBR effluent concentrations of CBZ and DF. On the X axis, the days of operations. The arrows represent the 2 inoculations of Phoma sp.. In light grey background, the pilot MBR receives full-scale permeate. In white background, the pilot MBR receives full-scale influent waters.

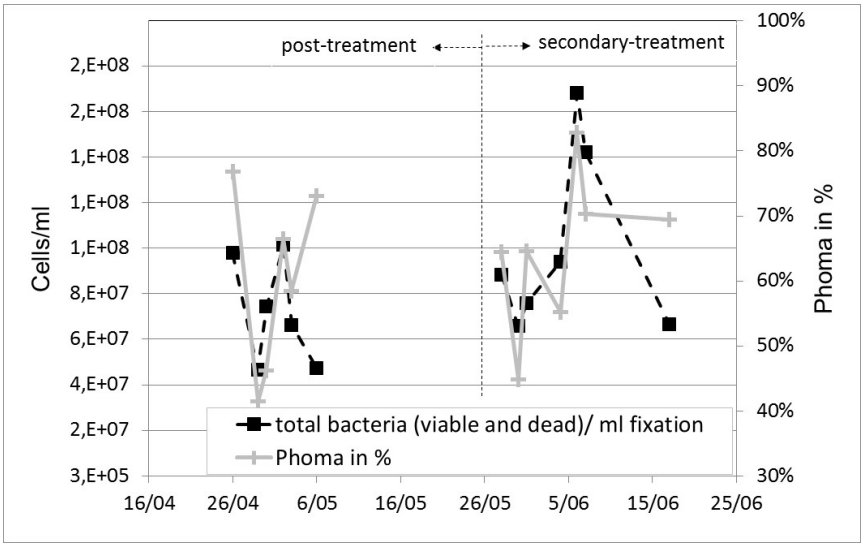

Figure 9.7: Monitoring of biomass according to FISH techniques. The arrows represents the day the Phoma sp. was inoculated. At the left side, the pilot treats full-scale permeate waters. At the right side the pilot treats full-scale influent waters.

The amount of *bacteria* and *Phoma* was monitored by FISH tests (Figure 9.7). The values fluctuate in function of the fixated MLSS concentration in the sample, since it is rather difficult to have constant MLSS in a reactor operated with aquatic fungi (that sticks to surfaces). It is rather difficult to extract useful information. It is noted that fungi prefer to grow in pellet form in suspension, and, thus, monitoring the fungal count in the mixed liquor supernatant sample may not accurately reflect the fungal

concentration in the MBR. Nevertheless, monitoring the fungal count is considered important for confirming the presence of viable fungi in the MBR. The ratio between the total biomass and *Phoma sp*. (viable and dead) remained similar. An exception is drawn in the last measurement point (post-treatment series) where *Phoma sp*. presence increased relative to bacterial mass.

9.3.5 ***Removal of Carbamazepine and Diclofenac in pilot MBR treating raw municipal wastewater***

In this section, the results obtained when the pilot MBR treated raw influent wastewater are discussed. Although the composition of the wastewater is the same as for the full-scale MBR, a comparison between both systems is difficult because, as discussed above, the operating conditions of the pilot MBR (Table 9.1) were chosen such as to promote survival of *Phoma sp*. after batch experiments showed that survival in the conditions at which the full-scale MBR was operated was very unlikely.

The pilot was fed with municipal influent wastewater and operated as a secondary treatment from 27.05.2013, and until 17.07.2013 (with conditions specified in Table 9.1). During all pilot operations NH_4-N was fully removed and NO_3-N was kept between 1-4 mgNO_3-N/L. 93% nitrogen and 55% COD was removed.

Phoma inoculum was introduced on 27.05.2013. At the start, full-scale influent, effluent and pilot effluent had comparable CBZ concentrations (Figure 9.6). While CBZ concentrations increased in the full-scale reactor one week after inoculation, they only moderately raised in the pilot effluent. A 39% CBZ removal was established (average CBZ concentration dropped from 477 ng/L to 262 ng/L).

To check whether any sorption mechanism exists, sludge samples were analyzed. During 15 days of operations, an average influent CBZ concentration of 477 ng/L at 45 L/h resulted in a influent load of 7.7 mg CBZ. The average measured CBZ concentration in sludge (after 15 days of presumed accumulation) was 0.02 mg/kgMLSS. The CBZ sorbed in the sludge was thus about the 0.65% of the CBZ removed during the same period. Therefore, the high CBZ removal were to no extent related to sorption into the sludge fraction as confirmed also in section 3.3.

With regards to the DF concentrations (Figure 9.6), pilot influent and effluent DF concentrations were respectively 1073 ng/L and 593 ng/L. While the full-scale MBR showed occasional removals, the pilot inoculated with *Phoma* sp. achieved 34% removal, which is lower than CBZ removal in agreement with results obtained through in section 9.3.3. As to investigate if any sorption mechanism was involved in the process, an average DF concentration in sludge of 0.03 mg/kgMLSS was measured at the end of operations (in absence of sludge waste). Given the average influent DF concentration at 45 L/h, in 15

days of operations, sorption into sludge did not significantly contribute to DF removal. Once again, DF removal was to no extent related to sorption into the sludge fraction as confirmed also in section 9.3.3.

Bacterial mass was monitored by FISH tests (Figure 9.7). The concentrations fluctuate in function of the amount of suspended solids fixated in the sample. The total *Phoma sp*. (viable and dead) remained in similar ratios with the *Phoma*. An exception is drawn in the last measurement point (secondary treatment series) where *Phoma sp*. concentration increases in comparison with the total bacteria.

At these specific conditions, *Phoma* sp. proves to cope with the autochthonous biomass. In good agreement with a previous study (Yang *et al*., 2013a), the viable fungal and bacterial count in the fungus-augmented MBR supernatant varied over the operating period. Results point however at higher performances of CBZ degradation when *Phoma* is inoculated in activated sludge rather than in permeate water. This result is unexpected and further tests should explain what sort of mechanism can explain higher survival in a more competitive environment.

9.4 ***Concept applicability and drawbacks***

The inoculation of *Phoma sp*. in municipal MBRs with subsequent recalcitrant compounds biodegradation can represent an interesting development that can set MBR technology in a different perspective. It certainly represents a significant development since research has focused frequently on degradation properties of specialized biomass in lab scale, but very seldom has up-scaled the technology. Phoma sp., instead, were proven, although with drastic adaptations, capable to operate in sludge waters.

This study has focused on DF and CBZ, as indicators of well-known recalcitrant compounds present in municipal waters. DF and CBZ are contained in the watch list of the European Water Framework Directives (EU, 2013). But *Phoma sp*. can facilitate the removal of a large range of micro-pollutants. In this study, others compounds' removal have been investigated, as in Figure 9.8. In a very recent publication instead, Hoffman *et al.* (2015) proved how the same biomass can in fact degrade many more pollutants: bisphenol A, 17α-ethinylestradiol, sulfamethoxazole, nonylphenol, and triclosan.

Other aspects however set this type of application in a more critical perspective. And they have to be thoroughly revised before further developing this technology:

(i) Low temperatures may be problematic to selected biomasses. *Phoma sp*. need a temperature of 20°C to survive against autochthonous competition in municipal waters. This is a limit that cannot be overcome in cold climates, unless warming waters up. Therefore some of these technologies might have warm climates as unique potential targets.

(ii) Inoculum amount might have to be substantial. In this case, the cost of the operation might be relevant and it risks to outcompete the technology.

(iii) If bio-augmentation is performed in municipal WWTPs, the process should be combined with regular N cycle process. *Phoma sp.* are for instance operated in slightly acidic conditions and research is conducted at Aquafin facilities to adapt it to more alkaline conditions. This appears to be problematic if the micro-organisms preferentially works in acidic conditions. There is risk that, so to accommodate the inoculated biomass in conventional processes, nitrifiers are washed out. Micro-organisms pH operating range should be considered as a criteria selection.

(iv) Often, the observed growth rate appears to be many times lower than the one of typical activated sludge micro-organisms. In the previous chapter for instance, *Microbacterium sp*. was reduced to a small fraction of the viable biomass. In this case, the cost for adapting a municipal MBR process to accommodating the bio-augmented biomass to steady-state conditions needs to be considered as a selection criteria.

(v) Affinity of the micro-organisms for trace micro-pollutants concentrations is a problem very strongly perceived with real municipal wastewaters. This does not seem to be the case for *Phoma sp*..

(vi) When inoculating biomass in a municipal WWTPs, it should be addressed whether metabolism is performed in aerobic, anoxic, or anaerobic times. There is a risk that prolonged idle times would obstacle the success of the bio-augmentation. This is, for instance, the case of anoxic volumes for *Phoma sp*. since the biomass is strictly aerobic. Several process solutions are possible, but this aspect cannot be ruled out.

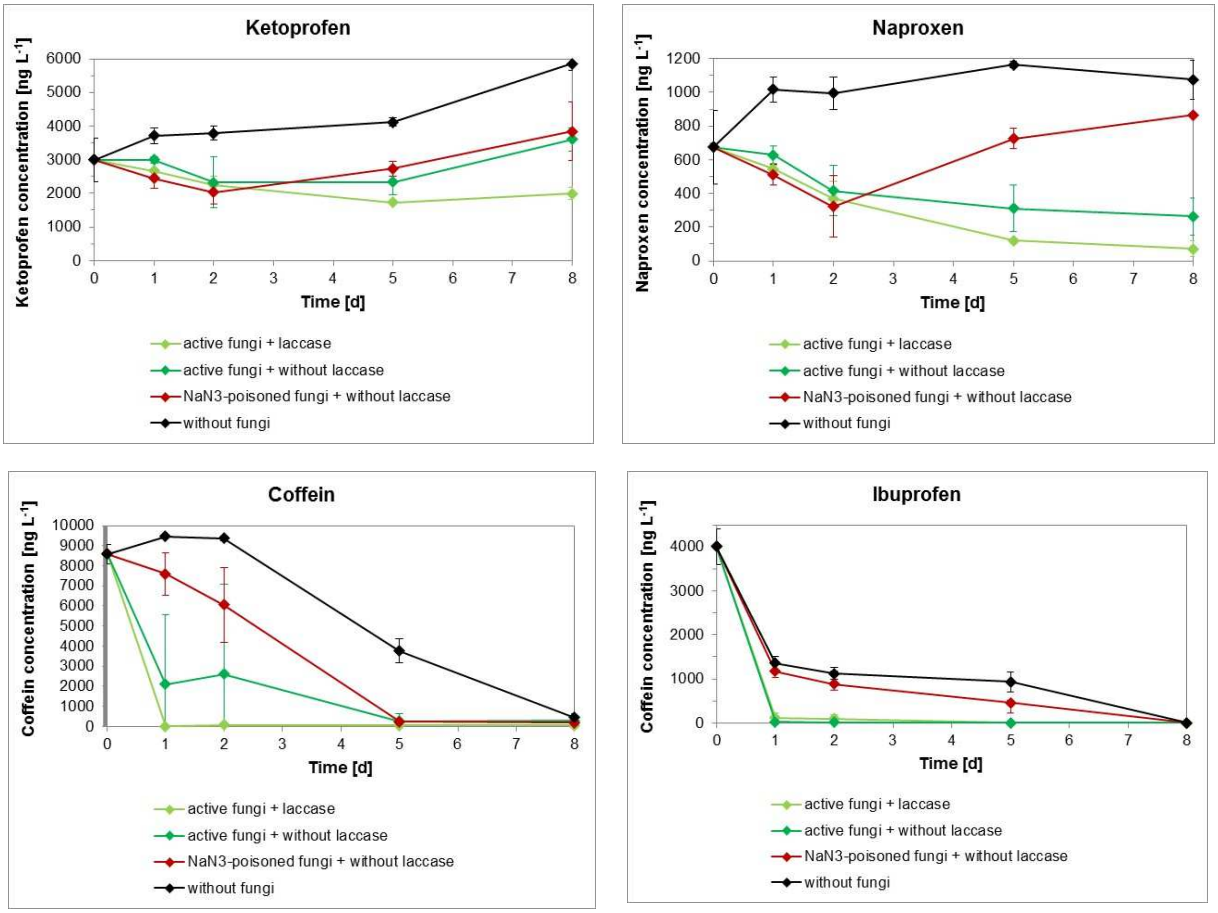

Figure 9.8: Removal of other micro-pollutants from municipal waters when Phoma sp. is operated in controlled lab conditions

9.5 ***Conclusions***

In this study a pilot MBR was inoculated with *Phoma sp. UHH 5-1-03* to investigate the potential for CBZ and DF removal in full-scale applications. From the results, one can conclude that high wastewater temperatures were necessary to increase the chance of *Phoma sp*. survival in raw municipal wastewater. Sufficient proof of CBZ and DF removal was achieved in this study, both in lab and in pilot scale. No sorption on *Phoma* biomass or sludge was detected for CBZ and DF.

The mechanism of degradation differs for the two targeted compounds. While DF is potentiated by the extra-polymeric laccase, CBZ is not. *Phoma* is able to survive in municipal wastewater and in competition with activated sludge. But further adaptation to CAS process conditions is required.

9.6 ***References***

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Chapter 10

Conclusions and perspectives

10.1 ***Discussion***

Scientific research represented through the past years a possible way to valorize the enormous potential of MBR technology. Scientific interest has oriented itself to those aspects mostly discouraging operators from committing into MBRs: fouling and energy consumption.

This thesis tried to answer to the needs, time after time, according to the different MBR era's. In the years 2000-2010, a period of enthusiasm with massive market penetration, the research has accompanied the establishment of MBR technology towards the practitioners' needs. Mathematical modelling of activated sludge systems is necessary to plant design, optimization, and control. ASM Modelling represented an important milestone in modelling of biological treatment processes. But it was initially developed to describe CAS processes under correspondingly typical operating conditions. The logical question we posed was whether all current knowledge about ASM based modelling for CAS is simply transferable to MBR systems, or in other words, how the current MBR process understanding can be merged into the ASM framework. In the years 2005-2010, very few studies were done on the applicability of activated sludge models (ASMs) to membrane bio-reactors (MBRs). This PhD started with the idea of contributing to this subject, by providing an overview of the most recent literature on ASM-based MBR modelling, followed by a critical application of ASM models to a full-scale municipal MBR.

The experience reported in chapter 3 proves that, when modelling purposes do not differ from effluent characterization, oxygen demand and sludge production, ASMs are very relevant to MBR applications. Applicability of ASMs to MBRs therefore has to sum up the above mentioned issues with all the "genetic" limitations of ASMs: they are universally applied in municipal water cases and with very few exceptions; there are very strong remarks on application of ASM platforms to industrial cases.

This study cleared out that the modeller has to evaluate very carefully crucial elements that would reduce the adherence of ASMs to MBR. I highlight here again some crucial aspects: high SRTs influence the hydrolysis of inert material and, as a consequence, the sludge production; high SRTs influences as well the influent characterization procedure; high MLSS concentration will change oxygen transfer rates; all bio-kinetic parameters will have to be revised case by case; particular care needs to be taken since the specific conditions present in MBRs are reflected in important discrepancies when compared to ASM default parameter values.

ASM fractions were increased in numbers as to provide a link between biological reactions and fouling indicators. In cases of ASMs developed for specific purposes related to MBR operations, and with particular care to fouling prediction modelling, the knowledge on SMP and EPS modelling has been critically reviewed on the basis of the literature, including the most recent developments. Research has

not agreed on which modelling platform extension can better simulate SMP/EPS formation or degradation in sludge waters, and there is no consensus on UAP formation and degradation mechanisms, as discussed in chapter 3. The application of the mentioned fouling indicators to the full-scale Schilde MBR has shown how their applicability is not universal. Therefore the driver for this modelling approach should be kept under discussion.

Difficulties in modelling SMPs have been questioned within this work. In Chapter 5, SMPs were fractionated in two species, as universally recommended. The attempt to fit experimentally its kinetics parameters revealed three major difficulties: (i) storage phenomena's in activated sludge are not included in ASM1 and ASM2 modelling platforms. This phenomena was proven to characterize the kinetic steps of UAP fractions; (ii) a distinction into more and less degradable fractions, as PT or PS. This fact would oblige to increase even more the amount of modelled processes; (iii) a membrane rejection mechanism was identified as SMP loading rate dependent, showing the need of a more careful consideration towards this parameter when modelling in full-scale or in a dynamic environment. The fine-tuning of the rejection factor was proven being a necessary adaptation.

Certainly, with regards to the issues raised above on point (i) above, ASM1 and ASM2 platform may appear inadequate to model storage phenomena, and the ASM3 platform may have some peculiarities that could better interpret the SMP processes.

The work in chapter 5 has some merits. Although being a deeply academic type of work, it provides a clear picture of the efforts necessary to transpose literature investigations into dynamic conditions and full-scale environments. And only by implementing this step, it is allowed to estimate the modelling exercise complexity with an accurate list of advantages and drawbacks. In principle, nutrients removal, sludge production and energy fitting did not receive further benefit from the SMP modelling. Since SMPs did not correlate with fouling rates in this full-scale MBR, the main drive for these models was thus not accomplished.
This study quests why should research embark into this complex task and try to answer all the uncertainties that are derived from it? Are there other fouling indicators or other possible fouling mathematical representations?

If SMPs and EPS modelling are not reliable, indicators that may provide a link between fouling mechanisms and biological processes are few. Data driven models are a possible research option, as it were proven by Dalmau *et al.*, (2015) to work better than deterministic models in some specific cases. Modelling and simulation of changes in TMP could be useful to describe fouling through the identification of the most relevant operating conditions. Other groups instead (*inter alia* Cao *et al.*, 2015) pursue their investigations on cake characteristics and particle size distribution. But given the success of ASM

models in modelling water quality and biological processes, the ASM platform should be the base on which the integrated model is built. Therefore, research should not only concentrate on developing predicting fouling indicators, but as well on building an interface that can integrate ASM fractions with promising fouling models.

As we said in the beginning, this study has as well re-oriented itself through the years, according to the different MBR era's. After period of enthusiasm, a strong criticism has come into place whereby the research efforts have not converged into solutions. As mentioned in the introduction, the lack in break-through from research brought some Dutch municipal operators to re-size the interest for this technology. This study has therefore tried to check the possibility to "re-invest" municipal MBRs into less traditional applications that can be still coupled with municipal WWTPs. Here comes the reason for the themes discussed in chapter 6, 8 , 9.

First of all, MBRs are often coupled to CAS systems into what is generally called "hybrid system". When CAS systems are overloaded, parallel MBR lanes can support CAS operations. MBRs can be considered as reserve of nitrification activity that is in function of SRT, temperature and nitrogen load. Several factors, described in chapter 4, procure an advantage to nitrification in MBRs as discussed in the previous chapters. This was illustrated in chapter 6. The help that MBRs can supply to a parallel CAS lane was found proportional to the incoming nitrogen load to the MBR. The study proved that the intuition was true. Yet, an unforeseen difficulty had shown up. The MBR flocs, grown without settling selection pressure, were not embedded in the CAS flocs, and the lower sludge settling properties reflected in deterioration of effluent CAS quality.

A possible valorization of MBRs is the option to guest specialized biomass for the degradation of recalcitrant pharmaceuticals. The MBR environment can in fact retain all biomass and by-pass any complication related to settling of specialized biomass. The targeted micro-pollutants were chosen as specific pollutants belonging to the European Water Framework Directives (EU, 2013). Despite the narrow amount of targeted micro-pollutants, the applicability of the concept is far broader. This was demonstrated in paragraph 9.4, both by research conducted during this work and both by other references that worked on the same micro-organisms.

The experiments with Phoma sp. proved, at least, that the concept is possible and even that degradation can be consistently enhanced of a 40% for CBZ and DF. Degradation mechanisms were partly illustrated unravelling the role of extra-cellular laccase. This study is fact one of the few successful upscaling examples in literature.

Yet, the MBR process had to be adapted to fungal culturing conditions. But in fact, the process conditions should be re-arranged as much as possible to process conditions of conventional activated sludge processes. Phoma should be adapted to alkaline conditions. In this regard, the stability of the laccase activity should be investigated further both in relation to CBZ and DF degradation. *Phoma sp.* should be tested at HRTs and SRTs that resemble more full-scale municipal processes. A future study on the immobilization would even allow to bring the *Phoma sp.* into carriers and let it work in CAS processes.

In fact, the activity of the tested specialised biomass proved to be more favourable to happen as secondary treatment, and therefore in competition to activated sludge, rather than as post-treatment. This fact is rather curious: by growing the biomass at a much slower rate than activated sludge, post-treatment should have been a safe environment for slow biomass growth. Reasons for this fact are to be investigated further. For the moment it could be speculated either that nutrients present in municipal influent water activate the metabolism of the inoculated biomass, or that the synergic effect of the autochthonous biomass is vital to the inoculated micro-organisms survival.

The inoculation of *Microbacterium sp.* was a failure. That chapter is rather an indication of the overall difficulties encountered when embarking on this type of approach. Let us once again look at critically at these difficulties: (i) Low temperatures may be problematic to selected biomasses. Both *Phoma sp*. and *MIcrobacterium sp.* need a temperature of 20°C to survive against autochthonous competition in municipal waters. This is a limit that cannot be overcome in cold climates, unless warming waters up. Therefore some of these technologies might have warm climates as unique potential targets. (ii) Inoculum amount might have to be substantial. In this case, the cost of the operation might be relevant and it risks to outcompete the technology. (iii) Bio-augmentation in secondary treatment should happen contemporaneously with a Nitrification/Denitrification cycle process. This appears to be problematic if the micro-organisms preferentially work in acidic conditions. There is risk that, so to accommodate the inoculated biomass in conventional processes, nitrifiers are washed out. (iv) Often, the observed growth rate appears to be many times lower than the one of typical activated sludge micro-organisms. (v) Affinity of the micro-organisms for trace micro-pollutants concentrations is a problem very strongly perceived with real municipal wastewaters. This does not seem to be the case for *Phoma sp*.. (vi) When inoculating biomass in a municipal WWTPs, it should be addressed whether metabolism is performed in aerobic, anoxic, or anaerobic times. There is a risk that prolonged idle times would obstacle the success of the bio-augmentation. (vii) Overall, activated sludge process adaptations risk to be drastic!

It should not be forgotten how, in wastewater treatment, several approaches are available when targeting micro-pollutants removal. And one of the most widespread methods is the application of granular activated carbon as a post-treatment of effluent water. The latter method was proven to be very effective in removing several compounds from the water phase. Some recent applications have developed robust post-treatment reactors which involve the coupling of a granular activated carbon with a membrane separation (Weemeas *et al.,* 2011; Ganiyu *et al.*, 2015). These approaches are already upscaled in central Europe with interesting and well documented full-scale results. The question one can pose is whether bio-inoculations can compete with a simple granular activated sludge post-treatment. Granular activated carbon post-treatment is easier and a more cost-effective solution to achieve micro-pollutants removal (Katsigiannis *et al., 2015)* . Moreover, by being a physic-chemical approach, it is a robust process with less failure possibilities (*inter alia*: Thole *et al*., 2015; Sperling *et al*., 2015).

Despite the efforts to valorise municipal MBRs, the question whether MBR technology is competitive to CAS technology remains intact. I tried to answer this question by accounting all the experimental data faced in this long and complex work. In chapter 4, the work was carried out by applying the ASM platform to a full-scale MBR. The study revealed how the filtration process was found responsible for the 56 % of the total energy bill. The modelling exercise went through the determination of the kinetic parameters, confirming the reduction of the half saturation coefficients reported in literature. This reduction resulted in a higher TN removal rather than in significant aeration energy savings. The coarse bubbles provided for scouring purposes in the membrane chambers could potentially have a role in the biological process if a different process layout would be used. In fact recent MBR developments brought some innovation that may create a bridge towards these issues: Microdir-Nadyr membrane systems employ fine bubble aeration for scouring purposes, therefore reducing the coarse aeration impact. Kubota and Alfa-Laval for instance deliver gravity assisted membranes, where the cost of permeate pump can be minimized. And last but not least, the cost of membranes is dropping and this is an overall advantage.

The MBR technology was found clearly more energy intensive than a CAS system, when equipped to deliver a comparable effluent water quality. This work was continued in chapter 7, where a more elaborated analysis was carried out, investment & operational costs were summed up, and CAS and MBR systems were compared.

For the definition of the investment costs, an analysis of the life-time of a full-scale MBR was carried out. This concept had never been elaborated in literature before and its impact on the competitiveness of MBR system had to be weighed. The life-time was elaborated on the basis of different approaches:

(i) maintaining the permeate flow throughput; (ii) the permeability decline; (iii) aging by chemicals; (iv) energy cost; (v) aging by mechanical stress.

The permeability decline method was found the most indicative for defining the remaining life-time of a membrane. This is a relevant finding with wide applicability for MBR practitioners, as discussed in paragraph 7.4. It offers as well clear indications on how to manage an MBR when approximating its end. It helps to recognize end-of-life triggers, and to focus interest on what is truly important. For instance, as “permeability decline” occurs quicker than “maximum allowable chlorine contact”, cleaning could be more frequent in full-scale practice. Hybrid MBR systems were found less competitive than CAS system even when considering an unrealistic membrane life-time of 20 years. In fact this parameter is not sufficiently sensitive to counterbalance the energy costs.

Only high SRTs could be so far a solution to the problem of the MBR competiveness. By this way, sludge production could be reduced. However, operating an MBR at high MLSS, was tried in the early times, and it is known to generate increasing fouling problems. Sludge concentration is kept around 10-12 g/L in the filtration tanks for most installations. This approach is recommendable from a financial theoretical point of view, but it is rather problematic from an operational point of view.

The result is unfortunately quite clear: due to its energy consumption, the MBR technology is outcompeted. MBRs appear to be a costly application, mainly due to the high energy requirements. However these calculations forget that the MBR technology is primarily an application for water re-use. And therefore the production of water for agricultural uses should be accounted in the financial analysis. Moreover this work promotes the use of MBRs for alternative applications, as in chapter 6, chapter 8 and chapter 9. And MBR technology remains an easy solution in all situations where space is limited, as it would be the case of many industrial cases.

I do not only imagine a wastewater treatment, but an integrated resource recovery system capable, opposite to a CAS system, to deliver: water for agricultural purposes; effluent whereby the pharmaceuticals load is highly reduced; support CAS retrofit by supplying sludge; an efficient water-reuse solution with a small foot-print.
In this sense the possibilities an MBR configuration can offer are far wider than a CAS system. And it is in this sense that a true financial analysis should be framed. However a typical western misconception brought MBRs to be applied only for effluent concern, forgetting that water re-use was its main field of application. Only when MBRs are conceived for their multiple applications possibilities, the application is to be considered pioneering and financially rewarding.

10.2 ***Overall conclusions***

This thesis presented a step forward in the modelling and operation of municipal MBRs. The most important conclusions arising from the present work are summarized below:

- When modelling purposes do not differ from effluent characterization, oxygen demand and sludge production, ASMs are very relevant to MBR applications. However, particular care needs to be taken since the specific conditions present in MBRs are reflected in some important discrepancies when compared to ASM default parameter values.

- The extension of an ASM model with SMPs and its experimental work impacts on the modelling exercise complexity.

- An MBR augmentation in a hybrid installation is possible. A full-scale experience confirmed by higher seasonal TN removals and higher nitrate formation rates that an advantage was achieved. The advantage in terms of nutrient removal is MBR sludge loading dependent.

- A method based on permeability decline and TMP provides an T_{life} estimate incorporating total permeability decay. The method was further elaborated inherently to operations with no long-term flux decline. The increase in operating pressure remains the main end-of-life trigger for deciding when to replace membrane modules.

- Sufficient proof of CBZ and DF removal was achieved when a pilot MBR was inoculated with *Phoma sp. UHH 5-1-03*.

- The MBR technology is more energy intensive than a CAS system with UF and UV disinfection, a system believe to deliver a comparable effluent water quality. Energy consumption in MBR outcompetes the technology.

10.3 ***References***

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Study Titles

- (2008-2006, UNESCO-Institute for Water Education, Delft, The Netherlands, 2 years, 120 ECTS): “Master degree in Water Treatment Engineering”, with Master thesis title in “Fouling assessment and control in Dutch full-scale MBR”.
- (2001-1995, Cagliari University, Italy, 2 years, 300 ECTS): “Master & Bachelor degree in Structural Civil Engineering”, with Master thesis in "Second order effect Instability Analysis in concrete slender columns".

Scholarships

- (2009-2008), Marie Curie Host Fellowship for Early Stage Research Training. Process optimization and fouling control in membrane bioreactors for wastewater and drinking water treatment. www.mbr-train.org.
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- (2014, Antwerp University, Belgium). Basic principles of statistical data-analysis (40 h).
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