Greywater Treatment with a Submerged Membrane Sequencing Batch Reactor

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Outline

List of Abbreviations

Abbreviations:

ASM	activated sludge model
ASP	activated sludge process
BNR	biological nutrient removal
BW	blackwater, i.e. wastewater from the toilet
CAPEX	capital expenditure
CASP	conventional activated sludge process
CW	constructed wetland
E.Coli	Escherichia Coli
FC	faecal coliforms
FS	Faecal Streptococci
GW	greywater, i.e. domestic wastewater except from the toilet
HSSF	horizontal type subsurface flow
IAWPRC	international association on water pollution research and control
INWRDAM	inter-islamic network on water resources development and management
IWA	international water association
LAS	linear alkylbenzene sulfonates
MBR	membrane bioreactor
NTU	nephelometric turbidity units
OECD	organisation for economic co-operation and development
OPEX	operational expenditure
PRR	phosphate release rate
PUR	phosphate uptake rate
RBC	rotating biological contactor
S	soluble constituents
SBR	sequencing batch reactor
SLES	sodium laureth sulfate (or sodium lauryl ether sulfate)
SLS	sodium lauryl sulfate (or sodium dodecyl sulfate)
SM-SBR	submerged membrane sequencing batch reactor
SSHF	subsurface horizontal flow constructed wetland
SWM	sustainable water management
TC	total coliforms
TDC	training and demonstration centre
VSSF	vertical subsurface flow constructed wetland
WWTP	wastewater treatment plant
X	insoluble constituents

List of Symbols

Symbols:

BOD_5	$[g_{O2}\ L^{-1}]$	biochemical oxygen demand in 5 days
COD	$[g_{O2}\ L^{-1}]$	chemical oxygen demand
f_d	$[g_{VSS}(g_{VSS})^{-1}]$	fraction of biomass as cell debris
HRT	[d]	hydraulic retention time
k	$[g_{substrate}\ (g_{biomass}d)^{-1}]$	maximum specific substrate utilisation rate
k_{DO}	$[d^{-1}]$	dissolved oxygen rate constant
k_d	$[d^{-1}]$	decay coefficient
k_d	$[g_{VSS}(g_{VSS}d)^{-1}]$	endogenous decay coefficient
k_h	$[d^{-1}]$	maximum specific hydrolysis rate
k_La	$[s^{-1}]$	mass transfer coefficient
$k_{m,S}$	$[m^{-3}d^{-1}]$	constant maintenance energy coefficient
k_{orgN}	$[d^{-1}]$	specific ammonification rate of organic nitrogen
k_{STO}	$[d^{-1}]$	specific storage rate
K_S	$[mgL^{-1}]$	half saturation coefficient or Monod constant for heterotrophic biomass
K_N, K_{NH}	$[mgL^{-1}]$	half-saturation constant for NH_4-N
K_{NO3}	$[mgL^{-1}]$	half-saturation constant for NO_3-N
K_{NO2}	$[mgL^{-1}]$	half-saturation constant for NO_2-N
K_{NOx}	$[mgL^{-1}]$	half-saturation constant for NO_x-N
K_O, K_{DO}	$[mgL^{-1}]$	half-saturation constant for DO
k_{orgN}	$[mgL^{-1}]$	half-saturation constant for ammonification of organic nitrogen
K_{STO}	$[mgL^{-1}]$	half-saturation constant for storage of X_S and S_S
K_X, K_h	$[mgL^{-1}]$	half saturation coefficient for hydrolysis of slowly biodegradable substrate
MLSS	$[gL^{-1}]$	mixed liquor suspended solids
MLVSS	$[gL^{-1}]$	mixed liquor volatile suspended solids
OUR	$[mg_{DO}\ (L\ h)^{-1}]$	oxygen uptake rate
oTS	$[gL^{-1}]$	organic total solids
pH	[-]	- log (concentration of H+)
$\dot{Q}$	$[m^3d^{-1}]$	volumetric flow rate
r_{AUR}	$[mg_{NH4\text{-}N}\ (g_{oTS}\ h)^{-1}]$	ammonium utilisation rate
r_g	$[g_{VSS}m^{-3}d^{-1}]$	rate of net biomass production
r_{NUR}	$[mg_{NO3\text{-}N}\ (g_{oTS}\ h)^{-1}]$	nitrate-nitrogen utilisation rate
r_{su}	$[gm^3d^{-1}]$	rate of substrate change due to oxidation
r_{su}^{g}	$[gm^3d^{-1}]$	rate of substrate change related to growth
r_{su}^{m}	$[gm^3d^{-1}]$	rate of substrate change related to maintenance

$r_{S,s}$	$[g_{VSS}m^{-3}d^{-1}]$	rate of soluble substrate change
$r_{X,s}$	$[gm^{-3}d^{-1}]$	rate of biomass production due to rbCOD
$r_{X,\,VSS}$	$[g_{VSS}m^{-3}d^{-1}]$	rate of total VSS production
S	$[gm^{-3}]$	growth limiting substrate concentration
S_I	$[mg\ L^{-1}]$	soluble inert organic matter
SRT	[d]	solids retention time
S_S	$[mg\ L^{-1}]$	soluble readily biodegradable substrate
S_{STO}	$[mg\ L^{-1}]$	stored readily biodegradable substrate
SS	$[gL^{-1}]$	suspended solids
t_c	[h]	total cycle time
TKN	$[gL^{-1}]$	total Kjeldahl nitrogen
TMP, Δp	[bar]	transmembrane pressure
TOC	$[gL^{-1}]$	total organic carbon
TS	$[gL^{-1}]$	total solids
V	$[m^3]$	volume
VSS	$[gL^{-1}]$	volatile suspended solids
X_B	$[gL^{-1}]$	biomass concentration
X_{BH}	$[gL^{-1}]$	active heterotrophic biomass
X_{BA}	$[gL^{-1}]$	active autotrophic biomass
X_I	$[gL^{-1}]$	particulate inert organic matter
$X_{o,\,i}$	$[g_{VSS}m^{-3}d^{-1}]$	influent non-biodegradable VSS concentration
X_S	$[gL^{-1}]$	particulate slowly biodegradable fraction
Y^g	$\left[\frac{g_{VSS,\ produced}}{g_{substrate,\ removed\ via\ growth}}\right]$	true growth yield
Y_A	$[g_{COD}\ g_{COD}^{-1}]$	yield coefficient for autotrophic biomass
Y_H	$[g_{COD}\ g_{COD}^{-1}]$	yield coefficient for heterotrophic biomass
Y_{obs}	$\left[\frac{g_{VSS,\ produced}}{g_{substrate}}\right]$	observed yield

Greek symbols:

μ	$[d^{-1}]$	specific growth rate
μ_{max}	$[d^{-1}]$	maximum specific growth rate
$\mu_{x,AUR}$	$[d^{-1}]$	specific growth rate of nitrifying bacteria
$\mu_{x,AURmax}$	$[d^{-1}]$	maximum specific growth rate of nitrifying bacteria
$\mu_{x,NUR}$	$[d^{-1}]$	specific growth rate of denitrifying bacteria
$\mu_{x,NURmax}$	$[d^{-1}]$	maximum specific growth rate of denitrifying bacteria
η_{AX}	[-]	anoxic factor
τ	[h]	hydraulic retention time

Indices:

H	heterotrophic
A	autotrophic

Suffixes:

rb	ready biodegradable
sb	slowly biodegradable
nb	non-biodegradable
nbp	non-biodegradable particulate
nbs	non-biodegradable soluble

List of Tables

List of Figures

1 Introduction and Objective

The work presented in this thesis has been carried out within the frame of the project "Zer0-M: Sustainable Concepts Towards a Zero Outflow Municipality", which intended to develop concepts for a sustainable water and wastewater management in the four Mediterranean countries: Morocco, Tunis, Egypt and Turkey. Work on water supply and sanitation often implies modifications to living habits and a new view on wastewater. It is no longer considered as something to be disposed of, but as a valuable resource, which should be treated accordingly. Therefore the project has a strong part of information transmission, awareness rising aimed at local authorities and water consumers.

The main issue and one of the important components of the development and dissemination strategy of the Zer0-M project is the erection of Training and Demonstration Centres (TDCs), including support and research with the assembling of a greywater treatment MBR at the chair of Chemical Engineering at the Technische Universität Berlin. The TDCs shall allow adapting existing techniques to local conditions, to test them and to show them to attendants of the training courses.

Sustainable water management (SWM) in the context of this project means the consideration of the in-house water-cycle beginning at the water consumption, going on with the separate collection of different wastewater fractions which allows a cost-efficient treatment according to their specific characteristics. Treated greywater (household wastewater not coming from toilet flushing) can be reused for irrigation or for domestic use (car washing or toilet flushing) without health hazards for farmers and consumers. The environmental and economic damage can be limited when reducing water abstraction (from surface water or aquifer) and when improving the quality of receiving bodies through a better water management. In pilot and real scale applications the project has implemented technologies for sustainable water and wastewater management in the MEDA partner countries, demonstrating and using water saving devices, greywater reuse schemes, constructed wetlands and other appropriate technologies for wastewater treatment and urine separation with the purpose of capacity building through know how exchange, transfer between the partners and erection of those SWM installations. Against this background, the work presented here focuses on greywater treatment for reuse.

Health hazards and social problems are often caused by the lack of water in sufficient quality and quantity and the reuse of wastewater without sufficient treatment for irrigation purposes. SWM can therefore be an option not only for peri-urban areas and small communities, so far without functioning sewer system and wastewater treatment, but also for isolated facilities, especially tourism facilities with a high demand for independent but high-quality water. The use of membrane technologies can be suitable exactly under these conditions, because tourism is of great economic importance in Mediterranean countries with a high return on investments, and so the Zer0-M project contributes to the economical enforcement of MEDA

partner countries.

Furthermore, the decreasing availability and quality of conventional water sources together with the increasing demand for high quality freshwater forces everybody independent of its social, cultural, and academic background to think, propose, and implement alternative and sustainable solutions for the management of the valuable resource water. One of the strategic assets to close the gap between supply and demand for water as well as to meet economic considerations is to treat and reuse domestic greywater on-site. Greywater is generally defined as low polluted wastewater originating from bathtubs, showers, hand washing basins and washing machines excluding wastewater from the kitchen and the toilet flushing system (Nolde, 1999). Greywater contains impurities and micro-organisms derived from household and personal cleaning activities and it shows a wide range of pathogenic and other liquid waste materials, which people normally want to eliminate from the inside of their homes (Birks et al., 2004; Friedler, 2004; Ottoson and Stenstrom, 2003; Veneman and Stewart, 2002). Those varieties in greywater quality, partly due to different regional and cultural user behaviour, should be taken into consideration when setting appropriate risk-based standards for the reuse.

Lately, the greywater treatment and reuse option have been widely studied, especially in Europe, Australia, Japan and California. Still, long term investigations are rare. Nolde (1999) reported a ten year experience in greywater reuse for a multi storage building, however only a few full-scale plants are currently in operation to draw enough conclusions out of their operation (Friedler, 2004). Further studies and process optimisation are therefore essential to understand the implications of this technology on public health as well as to be consistent with the principles of ecological sustainable development, which does not decrease the amenity of the local community.

Greywater reuse has been implemented from simple approaches such as bucketing wash machine greywater for cleaning stone floors, as done in Tunisia in private households, up to more advanced technologies, like constructed wetlands (CW) or membrane bioreactors (MBRs) for the treatment of bathing water in the hotel sector. Still, reuse is often practiced without a clear understanding of public and private health risks that may be caused without properly designed land application systems for disposal of greywater. This implies the installation of suitable treatment systems with respect to the reuse option, including properly addressed cost calculations for installation, operation and maintenance.

Recently more in-depth MBR studies have been conducted on greywater because of their inherent benefits, namely: compactness and the complete retention of micro-organisms by either microfiltration (MF) or ultrafiltration (UF) membranes (Lesjean and Gnirss, 2006; Melin et al., 2006b). The thesis shall therefore compare the different possibilities of greywater treatment with special emphasis on membrane technology. Experiences and results presented herein are gained mainly from a Submerged Membrane Sequencing Batch Reactor (SM-SBR), which were then compared to the project partner plants (CW, MBR) within the Zer0-M

framework, and among literature findings with the focus on the differences in influent characteristics, effluent quality and technology of greywater treatment.

Only a short description on biological, chemical and technical information is given here in order to give a better understanding of the particularities of the different treatment options. Nevertheless the experimental set-up, the methods to determine kinetic parameters of aerobic heterotrophic biomass and the used analytical methods are described in detail. In addition different membranes are characterised and tested for their suitability in greywater treatment.

An intensive literature review has shown that there is enough data for the design of municipal wastewater treatment plants (WWTP), but a huge lack of information for biokinetic parameters for the design of greywater treatment plants, especially if treated with membrane bioreactors. These biokinetic values are needed as key parameters for the design and process optimisation. The development and validation of a mathematical model to describe the biological process of the microorganisms in greywater sludge is conducted against the background of treatment in a membrane bioreactor and with reference to the existing models of ASM 3.

2 Greywater Treatment

2.1 Greywater Treatment and its Importance for Sustainable Water Management

Greywater treatment and reuse is part of sustainable water management (SWM). The dictum SWM involves two important concepts with respect to water: sustainability and management. To understand the approach behind SWM, both these concepts must be defined and understood.

Sustainability stands for a process or a state which can be maintained indefinitely. One of the first definitions of sustainability is the one created by the Brundtland Commission, led by the former Norwegian Prime Minister Gro Harlem Brundtland. The Commission defined sustainable development as that which "meets the needs of the present without compromising the ability of future generations to meet their own needs." (Brundtland, 1987) This refers to the potential longevity of vital human ecological support systems, such as the planet's climatic system, systems of agriculture, industry, forestry, fisheries, human communities in general and the various systems on which they depend.

A resource should be allocated in such a way that all, including the environment, have an adequate share without discrimination, both now and in the future. Next to this qualitative definition as an ethical/ ecological proposition, sustainability can be defined quantitatively in terms of system life expectancy. Communities have to know whether their efforts to achieve sustainability goals are successful or not and they need tools and knowledge to measure, monitor and maintain them. The definition of basic needs, like clean water and sanitation for everybody, is perhaps the greatest challenge to adopt sustainable practices in our daily lives.

Management can be understood as directing and controlling a group of people or entities to coordinate and harmonise them towards accomplishing one goal. Management often comprises the deployment and manipulation of human, financial, technological, and natural resources. In recent years there has been a shift from the traditional ‘top-down’ approach to a more open, small hierarchical management system, where all levels give input into the allocation and use of resources. This ensures that the needs and concerns are addressed by the group most affected by the use of the resource, without the lose of wider issues concerning the whole community. Efficient management can be only implemented with a clear understanding of the needs of the stakeholders and the knowledge of possibilities and limitations of the resource.

With an understanding of sustainability and management, it is now easier to understand the purpose of SWM, as displayed in Figure 2-1. Potable water which comes from the local water supplier is segregated. The faeces can be used to produce biogas during the process of anaerobic digestion, while the urine can be used as fertiliser. Treated greywater and rainwater are suitable for irrigation or domestic reuse. Water circulates locally and can be used more

than once with an adequate treatment.

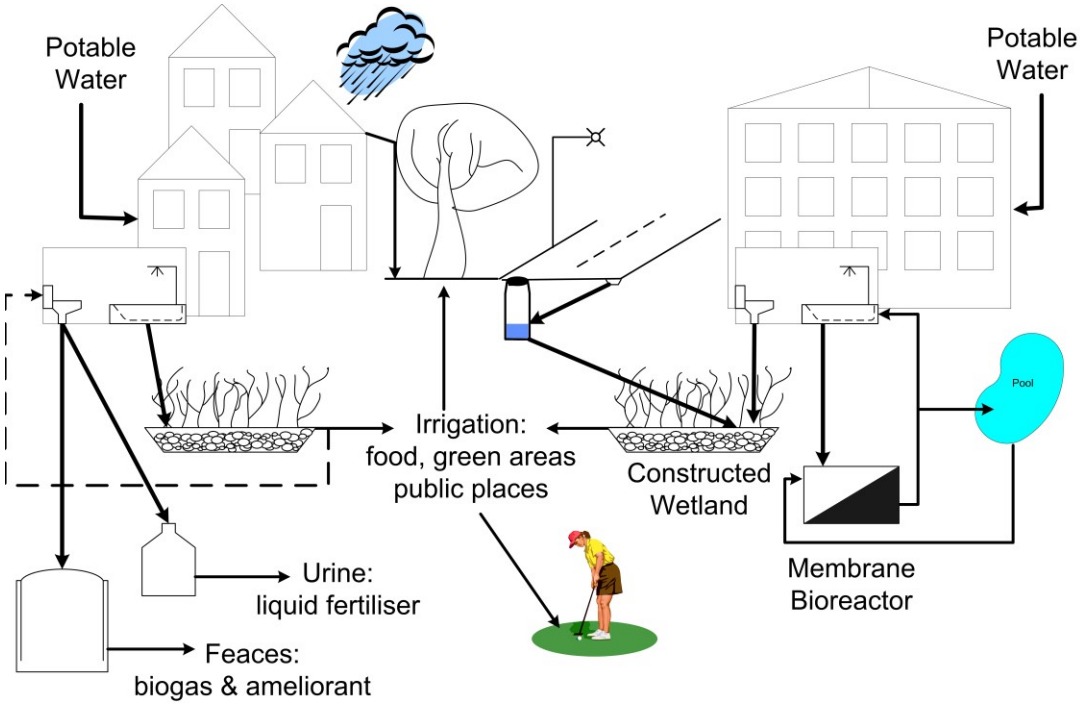

Figure 2-1: Principle of SWM

Greywater reuse involves a whole new look at the usage of precious water resources. Water problems cannot be solved only by technical solutions, but they require the consideration of cultural, educational, communicational and scientific aspects.

2.2 Greywater: Composition, Treatment and Reuse

2.2.1 Greywater Composition

To improve the current situation of wastewater treatment in most small communities new approaches like water segregation, on-site treatment and internal water reuse are desirable, especially in water scare regions. On a small scale this involves the collection and treatment of greywater (Lazarova et al., 2003). Greywater is generally defined as low polluted wastewater originating from bathtubs, showers, hand washing basins and washing machines excluding wastewater from the kitchen and the toilet flushing system (Nolde, 1999). Erikson *et al.* (2002) suggested that greywater characteristics pertaining to the accumulation of xenobiotic organic compounds were particularly important when considering adequate treatment and reuse. The variation observed in greywater quality should be used to set appropriate treatment, health and reuse standards.

The main components of greywater are solved substances in the form of surfactants, fats and oils from personal care products; the matrix can be further characterised by low amounts of

suspended solids and low turbidity (Al-Jayyousi, 2003). Greywater can further contain low concentration of hair, skin particles and dandruff, as well as impurities and micro-organisms derived from household cleaning activities. Greywater may include a wide range of pathogens (Birks et al., 2004; Eriksson et al., 2002; Friedler, 2004; Ottoson and Stenstrom, 2003; Veneman and Stewart, 2002).

The reason for the variation can be found in different user behaviour due to cultural and regional differences. It is important to know the exact source of greywater. The incorporation of kitchen effluent leads to higher COD concentration and higher amount of oil and fat, which must be separated before treatment, whereas the usage of shower effluent results in a very low COD concentration (Merz et al., 2007).

Surfactants

Surfactants (surface active agents, also known as tensides or detergens) are wetting agents that lower the surface tension at the liquid-liquid interface. They are organic compounds with a hydrophilic and a hydrophobic fraction and are extensively used in households as well as in industrial processes. Biodegradation and environmental impact of ionic and non-ionic surfactants has been the subject of substantial research for many years, e.g. Jönson (1991), Levine et al. (2001), Liwarska-Bizukojc et al. (2008), and Oschmann et al. (2005) with different results in terms of membrane and sludge behaviour, as well as COD removal. The later varied from 47% for TritonX-100 and 74% for Rhamnolipid (both non-ionic surfactants) after 10d of aerobic operation in an experimental degradation set-up (Mohan et al., 2006) up to complete carbon degradation in a greywater treatment system with a hydraulic retention time (HRT) of 2.75h (Konopka et al., 1997). Four primary groups of surfactants exist: amphoteric (dual charge), anionic, cationic and non-ionic. The hydrophobic, non-polar part of the surfactants is always an alkyl group. Thermodynamics of the surfactants systems are of great importance because surfactant systems may be presented in both ordered (micelles) and disordered (free surfactant molecules and/or ions in the solution) phases.

Surfactants in greywater are from detergents, cleaning products and personal care products, where they act as emulsifiers and washing substances. About 80% of the usage of anionic and non-ionic surfactants are in personal care and cleaning products (IKW, 2005). The oil and water solubility of surfactants depends on the relation between the hydrophobic and the hydrophilic part.

Anionic surfactants are mostly sodium salts with interfacial active anions (e.g., sodium lauryl sulfate (SLS) or sodium laureth sulfate (SLES), the two most common anionic foaming agents). The functional group is composed of salts of carboxylic acids ($R\text{-}COO^{-}\text{-}Na^{+}$), sulphuric acids ($R\text{-}SO_2O^{-}\text{-}Na^{+}$) and sulphuric acid ester ($RO\text{-}SO_2O^{-}\text{-}Na^{+}$). Soaps belong to the group of carbon acid salts. Non-ionic surfactants are free of ions; in general eudermic (skin friendly) and therefore, they can be found more in detergents and cosmetics. The functional group is polyglycol ether ($RO(CH_2\text{-}CH_2\text{-}O)_nH$).

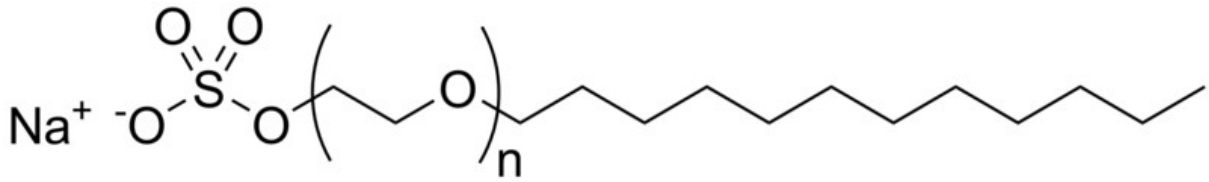

Figure 2-2: Structure of the anionic surfactant SLES

The alkyl group of surfactants exist either as a single row (cf. Figure 2-2) or as a more or less branched form. However, the level of branches does affect the biodegradability of the substances. The higher the degree of branches the worse they can be eliminated by micro-organisms. The 2004 adopted European detergents regulation No. 648/2004/EC requires a high biodegradability of surfactants, thus it can be expected that only single row or minimally branched hydrocarbon chains are introduced in the molecules.

Within the group of anionic surfactants, the linear alkylbenzene sulfonates (LAS) make up the majority and are generally regarded to be biodegradable. The aromatic ring of LAS can resist biological degradation, transfer into the environment and finally turn back into the drinking water. Therefore, several intensive studies have been carried out. (Kosswig and Stache, 1993).

Swisher (1987) stated that a large number of surfactants have relatively low biodegradability. Due primarily to economic reasons, it is impractical to replace those low biodegradable surfactants in all household and industrial applications. Pretreatment methods like ozonation and other advanced chemical oxidation of surfactants in wastewater needs to be developed which allow safe uses of low biodegradable surfactants (Lin et al., 1999). Surfactants have become almost universal in household and industrial products, due to the ability to influence interfacial tension at low concentrations. Synthetic produced surfactants with improved quality have replaced soaps made from natural plant extracts. Although surfactants are so ubiquitous, they are normally present only at low concentrations in domestic wastewater. This is also true for greywater from shower effluent where LAS concentration in a range between 0.3-1.2 mgL^{-1} where detected (Konopka et al., 1997; Merz et al., 2007).

Hygienic Risk / Pathogens

Pathogenic microbes, bacteria, and viruses are derived from human sources (typically blood, urine or excreta). Although, excreta are usually absent in greywater, pathogen are observed in greywater. The assumption that greywater is relatively unpolluted has strengthen the idea that greywater recycling may be more acceptable to users than recycling all the domestic sewage. Nevertheless, Lazarova *et al.* (2001) found a high level of organic matter and microbiological pollutions in dark greywater, which is comparable to those in domestic sewage. Sources of these micro-organisms may be from diaper washing, hand washing after toilet usage, receiving bacteriological infected urine from shower misuse, or from cleaning uncooked vegetable and raw meat. Several other authors validated the pathogenically risk of greywater,

with high faecal coliforme (FC) concentration of nine tenfold (Lazarova et al., 2003; Rose et al., 1991). The whereabouts of possible contamination in a greywater system is of high importance in order to guarantee public health when it comes to reuse of the treated greywater. Thus a disinfection step is potentially appropriate prior to subsequent re-use.

Suitability for Biological Treatment

Investigation made by Jefferson et al. (2001) showed that greywater, compared to sewage, has a low organic load, combined with a high COD:BOD ratio and a nitrogen and phosphorous deficiency. To overcome these limitations these authors added macronutrients to the greywater and thereby improving the potential for biological treatment. Merz et al. (2007) reported a greywater composition with no limitation in nitrogen and phosphorous, as well as a COD:BOD ratio of around 1.8, favourable for easy biological degradation. The work by Scheumann and Kraume (2009) was carried out with synthetic greywater, although the COD:BOD ratio was approximately 4, nutrient limitation was not observed. In fact, the treatment success was more dependent on SRT and HRT than on greywater composition. A summary of different greywater characteristics is given in Table 2-1 showing the dependency of the greywater composition on their source. Feedwater composition has to be considered carefully, when treatment possibilities are evaluated.

Table 2-1: Characteristics of greywater originated from different sources

	average values ± standard deviation									
	(Christova-Boal et al., 1996)	(Christova-Boal et al., 1996)	(Atasoy et al., 2007)	(Jefferson et al., 1999)	(Nolde, 1999)	(Friedler, 2004)	(Hernández Leal et al., 2007)	(Masi et al., 2007)	(Merz et al., 2007)	(Liwarska-Bizukojc et al., 2008)
source of origin	bathroom	laundry	mixed	hand basin	bath and shower	kitchen sink	mixed	camping site	shower	synthetic
pH	6.4 - 8.1	9.3-10	7.1			6.48±0.6		7.6±0.4	7.6±0.4	7.5±0.3
BOD_5, mgL^{-1}	76-200	48-290	90	109	50-100*	890±480	215±102	53±16	53±16	50±11
COD, mgL^{-1}			245	263	100-200	1340±1076	425±107	502	122±21	209±80
TN, mgL^{-1}				9.6	5-10		17.2±4.7			17.3±6.7
TKN, mgL^{-1}	4.6-20	1.0-40	9.0					2.5	11.9±2.4	
NH_4-N, mgL^{-1}	0.1-15	0.1-1.9	1.3			0.6±0.81	7.2±3.7	1.7	6.6±2.5	7.3±5.4
NO_3^-N, mgL^{-1}	0.05-0.2	0.1-0.31						0.32		0.9±0.9
TP, mgL^{-1}	0.11-1.8	0.062-42	7.3	2,58	0.2-0.6		5.7±2.6	6.6	0.98±0.53	
PO_4^{3-}P, mgL^{-1}						22±27	2.3±1.3		1.0±0.4	0.74±1.6
Conductivity, µs cm^{-1}	82-250	190-1400	401						855±191	
Faecal Coliform, $100mL^{-1}$	170-$3.3*10^3$	110-$1.09*10^3$	3565		10^{-1} - 10^1	$1.2*10^6$ ± $2.4*10^6$			$2.48*10^5$ ±$1.2*10^5$	

* measured as BOD_7

2.2.2 Process Options for Greywater Treatment

Compared to the conventional water and wastewater distribution system (drinking water supply → single use for cooking, personal care and toilet flushing in the household → wastewater disposal to a central WWTP) the onsite treatment technologies and water reuse dissemination schemes (drinking water supply → use for cooking and personal care → onsite treatment → reuse for toilet flushing → wastewater disposal to a decentralised WWTP) are more complex, but may become a viable alternative. They incorporate pumps, recirculation piping, aeration, and other features that require ongoing or periodic monitoring and maintenance in order to guarantee stable operation.

Nowadays many different greywater treatment plants are in operation, but a comparative review of experiences and results is still lacking. The strong regional and seasonal fluctuations in the quality of the produced greywater at its source make it difficult to create binding universal treatment pattern as best available technique. Inclusive of this variation is the specific reuse objective, which needs to be considered if an assessment is carried out. Together with more stringent discharge requirements (cf. chapter 2.3), the design of treatment technologies has improved in order to achieve high performances in interaction with size, soil, ground water, and landscape limitations. Greywater recycling systems do not have a uniformly regulated specification in the international context. Nevertheless, all systems should accomplish four basic criteria (Al-Jayyousi, 2003):

- hygienic safety
- aesthetics,
- environmental sustainability
- technical and economic feasibility

Most alternative treatment technologies applied today treat wastes from septic tanks, which retain settleable solids, grease and oils (cf. Figure 2-3). This pre-treatment provides an environment for partial digestion of settled organics. Post treatment can include aerobic or anaerobic biological treatment in suspended or fixed-film reactors, combined with soil infiltration or fixed-media filtration, and disinfection. Each treatment technology has its benefits and limitations, which are explained later in this chapter. Nevertheless, technical problems are often encountered in the recycling system due to insufficient maintenance (Asano et al., 2007; Nolde, 2005).

Occasionally, the pre-treated greywater is directly used for irrigation purposes. The water moves through the soil down to the groundwater and eventually drains naturally into an aquifer.

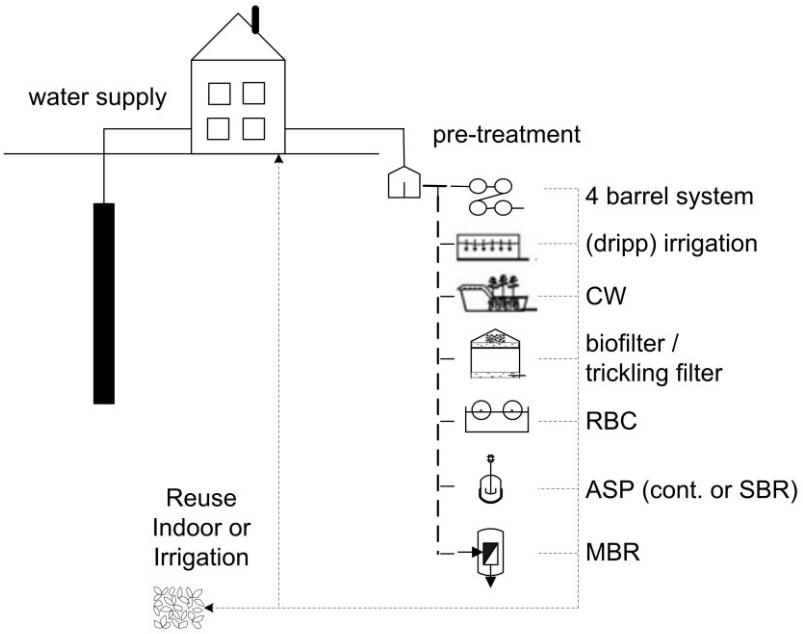

Figure 2-3: Overview of possible greywater treatment options

Established biological processes typically applied to domestic sewage treatment may be insufficient for greywater due to the lack of bacterial retention. Thus additional measures are required (e.g., post UV or chemical disinfection) to disinfect the treated water before reuse (Birks et al., 2004). Advanced physical methods, such as nano-filtration (NF) or the combination of ultra-filtration (UF) and reverse osmosis (RO), may be an appropriate solution, where space is a limiting factor. However, such processes incur a cost penalty due to the higher energy demand. Simple filtration with micro-filtration (MF) membranes may consume less energy and eliminate bacteriological contamination, but usually not the BOD_5. This will lead to the formation of slime, bacterial re-growth and odour issues because of anaerobic conditions in the service water distribution system.

A practical example as an overview of different treatment options is applied at the Training and Demonstration Centre (TDC) in Turkey (cf. Figure 2-4). These pilot plants are operated to promote knowledge of the different technologies suitable for sustainable water management. Low technology plants, like the rotating biological contactor (RBC) or a constructed wetland (CW) are used as well as the more advanced technologies like sequencing batch reactor (SBR) and membrane bioreactor (MBR). In the later, kitchen effluent can be included without troubling the treatment performance and effluent quality (Murat et al., 2007).

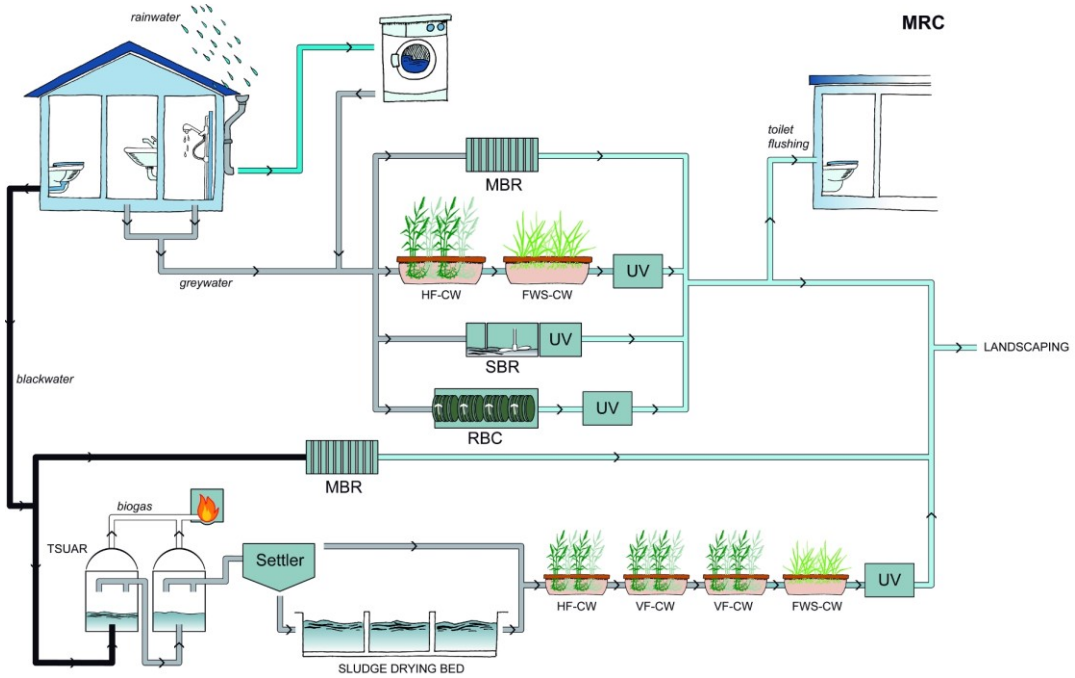

Figure 2-4: Treatment and reuse scheme for grey- and blackwater at MRC, Turkey (www.zer0-m.org)

4-Barrel System

The treatment with the four plastic barrel system, as promoted from the Inter-Islamic Network on Water Resources Development and Management (INWRDAM) in Jordan (Al-Beiruti, 2003), is very simple and is specifically designed for low income households to reuse treated greywater as irrigation water. The first barrel (160L capacity) is a grease, oil and solids separator and thus requires occasional de-sludging, manually done by the users. The second and the third barrels (220L capacity) are filled with gravel (2-3 cm graded diameter) to treat the settled effluent from the first barrel. The water passes through the gravel from top to bottom in the second barrel and vice versa in the third barrel, from where the overflow goes into the fourth to store the treated greywater. Anaerobic treatment is accomplished in the gravel filters. The clarified water has been observed to meet World Health Organisation's guidelines for *restricted* irrigation, e.g. irrigating trees or fodder crops. The only data reported were the BOD_5 with an average value of 350 mgL^{-1} and the TSS with a value of 114 mgL^{-1} (Al-Beiruti, 2003).

Figure 2-5: 4-barrel system for greywater treatment in Jordan (Al-Beiruti, 2003)

Rotating Biological Contactor (RBC)

The RBC is a fixed biological film reactor and consists of a series of plastic circular disks mounted on a horizontal shaft and is rotated perpendicular to the direction of the waste flow. In a conventional RBC unit, approximately 35–40% of the total disk surface area is submerged in the wastewater. Organisms in the wastewater attach on the rotating media until they form a thin layer of biomass. RBC units are widely used in the treatment of municipal and industrial wastewater because it is possible to obtain high performance at low energy consumption. RBCs have also shown to be effective for greywater treatment, reducing the inlet BOD_7 from 250 mgL^{-1} down to below 5 mgL^{-1} (Nolde, 1999). A number of similar processes have been in operation for several years, one of them a 400-bed hotel with a six-stage RBC process, is in operation since 1996. As with SBR, the water quality is difficult to guarantee with regard to suspended solids and pathogens and so additional stages must be implemented including sedimentation and UV disinfection. Friedler (2006) has shown a pilot RBC to yield good quality effluent with a removal of 98% and 95% of turbidity and BOD_5, respectively. This RBC consisted of two basins a 15 L, each equipped with 13 discs, and a sedimentation basin of 7.5L. The HRT was 2h in average with manually excess sludge removal. The velocity at the outer edge of the disc was set to 0.15 ms^{-1}.

Constructed Wetland (CW)

CW use the natural degradation processes to take up nutrients. They are operated either as horizontal flow (HF), vertical flow (VF) or as (FWS). The high degree of biodiversity present

in these systems allows multiple usages for several different classes of compounds. The vegetation (roots, stems and leaves) in a wetland provides the condition upon which microorganisms can grow as they break down organic materials. Together with chemical processes in the soil filter, approximately 90 percent of pollutants, measured as BOD_5 and COD, are removed under central European climate conditions.

The process takes place without input of energy as e.g. needed for oxygen supply with blowers in a conventional activated sludge system (CAS). In addition, there is no production of excess sludge, because there is a balance of biomass growth and decomposition. To compensate the low energy demand a higher footprint is needed, but CW have proven to be a good alternative for small and medium sized wastewater treatment plants (Conte et al., 2001; Green and Ho, 2005; Hagendorf et al., 2005; Masi et al., 2007).

Greywater treatment with CW has been carried out in Flintenbreite, Germany, where three vertical constructed wetlands with sizes of 2 m^2 per inhabitant have been constructed. The constructed wetland was equipped with a primary clarifier exhibiting three pits functioning as a grit chamber as well as for solids and grease control (Li et al., 2003). In Sweden, Günther (2000) has reported of a combination of a CW with a soil layer infiltration and a pond system, which has been built and successfully operated at lower cost compared to CAS. Due to long turnover times, the reduction of bacteria and viruses was almost complete. The investigation from Masi (2007) at a camping site in Tuscany, Italy, showed a very good treatment performance of a horizontal flow (HF) wetland system with a hydraulic loading rate of 0.083 md^{-1} and a surface area of 115 m². This systems works only in summer time with a high fluctuation in wastewater production (0.3 to 7 m^3d^{-1}). The entire wetland treatment system is continuously fed by gravity, without energy consumption. Segregation of grey and blackwater allows a better treatment and a safe reuse of the treated grey water, which is pumped back to the buildings for toilet flushing.

Sequencing Batch Reactor (SBR)

Sequence Batch Reactors are often used in areas without sewer network for primary or secondary treatment as small wastewater treatment plants (Teichgräber et al., 2003) and in industrial applications (Flapper et al., 2001). The SBR has demonstrated good removal efficiency, but cannot be guaranteed for suspended solids and pathogen removal and so their implementation into re-use operation is potentially limited unless coupled with subsequent treatment (Shin et al., 1998). Messalem et al. (2000) reported of a two-stage pilot scale system comprising an SBR treatment and tertiary micro-filtration, operated at the Beer-Sheva municipal wastewater treatment plant, by incorporating sidestream microfiltration unit (Memcor, Australia) to treat the supernatant of the SBR process. The treated effluent resulted in 6 log bacterial removal and a very low BOD_5 <5 mg L^{-1}; turbidity was also low (0.2 NTU). Messalem et al. (2000) concluded that the resultant treated effluent was suitable for reuse for agriculture. Detailed information on SBR will be given in chapter 3.2.

Membrane Bioreactors (MBR)

The solid-liquid membrane separation bioreactors employ either UF or MF modules in a submerged/ immersed or sidestream configuration for the retention of biomass. Since an MBR is used in this study, more information will be given in chapter 3.1. The MBR has the potential for complete pathogen removal, high solids retention (therefore no secondary settlement required) and an increased loading capacity coupled with a reduced footprint (Judd, 2006; Stephenson et al., 2000). Gildemeister et al. (2005), Nolde (2005) and Oschmann et. al. (2005) reported on successful applications of MBR in greywater treatment and pointed out that there are some specific characteristics, e.g. fouling to be considered. Some MBR applications have also been successfully commercialised for decentralised usage in single or double family houses with 4-8 person equivalents. The greywater is collected in a first tank for preliminary sedimantion and coarse filtration by a 3mm screen. The water is pumped into the second tank with the activated sludge and the membrane incorpoarated. Due to aeration, the fluid is moved perpendicular to the membrane surface, where the treated water passes through the membrane plate, while the sludge stays in the tank. (cf. Figure 2-6)

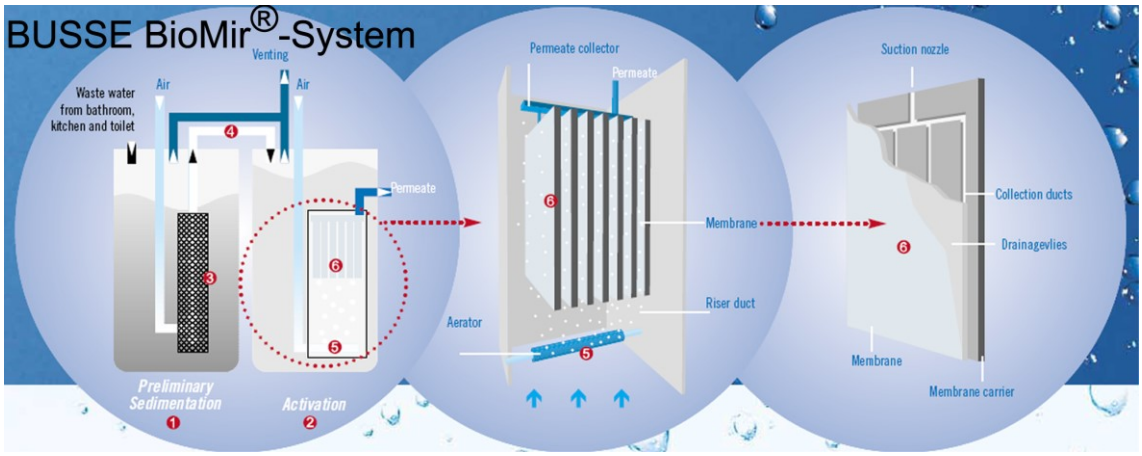

Figure 2-6: Scheme of a small MBR by BUSSE (http://www.busse-gmbh.de)

Summary

The advantages and disadvantages of the different treatment option for greywater are summarised in Table 2-2. In Germany, 300 to 400 greywater recycling systems are actually operating, involving a number of different treatment concepts (Nolde, 2005). Surveys suggest that between 60 and 80% of onsite single household GW treatment systems were not maintained appropriately and did not produce adequate quality greywater effluent (Jeppesen, 1996). The current management programs typically do not include routine operation and maintenance activities. Reuse is often practiced without a clear understanding of public and private health risks, as well as the environmental degradation that may be caused with the application of insufficiently treated greywater to land. A need for suitable re-use treatment systems exists, including properly addressed costing and scheduling for installation, operation and maintenance.

Table 2-2: Advantage and disadvantage of different GW treatment systems

technology	advantages	disadvantages
4-barrel system	▪ low cost technology (CAPEX) ▪ level of self-sufficiency ▪ simple technology with almost no expertise ▪ low operational costs OPEX	▪ low effluent quality ▪ contact with sludge from the first barrel and with untreated GW possible
RBC	▪ short contact periods due to large active surface → short HRT ▪ capable of handling a variation in flows ▪ low operational costs ▪ little skills for plant operation ▪ low power requirements ▪ low sludge production ▪ good process control	▪ requirement for covering RBC units in northern climates ▪ shaft bearings and mechanical drive units require frequent maintenance
CW	▪ excellent removal of BOD_5 and TSS ▪ good removal on nutrients ▪ ability to handle daily or seasonally variable loads ▪ low energy and maintenance requirements	▪ sensitive to high ammonia levels ▪ large land area requirement ▪ potential for mosquito production
SBR	▪ equalisation, biological treatment and secondary clarification in a single reactor vessel ▪ operating flexibility and control ▪ minimal footprint	▪ higher level of maintenance → more sophisticated controls and time units ▪ potential of discharging floating or settled sludge during the draw or decant phase
MBR	▪ good effluent quality with high hygienic standards ▪ high biomass concentration and higher sludge age compared to ASP ▪ reduced reactor volume and footprint ▪ reduced net sludge production	▪ complex and costly pre-treatment of the incoming wastewater ▪ membrane integrity (failure detection, lifetime) ▪ high CAPEX (membrane modules) and OPEX

2.2.3 Greywater Reuse

Greywater may be reused on-site for irrigation purposes, toilet flushing, and laundry use depending on the type of greywater and its level of treatment. In single house systems, the

favourable option for reuse of greywater is the toilet flushing, because the amount of water required equals the amount of greywater produced for hygiene purposes such as washing, showering and bathing (Birks et al., 2005). It reduces the demand of high quality drinking water of around 35%. Although lately, the greywater treatment and reuse option have been widely studied, especially in Europe, Australia, Japan and California, still, long term investigations are rare, even though Nolde (1999) reported of a ten year experience in greywater reuse for a multi storage building. He came to the conclusion that a biological treatment is indispensable to avoid technical problems and public health risks. The tested multistage RBC had an energy demand of 1.5 kWh m^{-3} and produced greywater with an BOD_7 below 5 mgL^{-1}. Only a few full-scale plants are in operation to draw enough conclusions out of their operation (Friedler, 2004). It is therefore essential to gain more knowledge on greywater treatment and reuse to understand the implications on public health as well as to be consistent with the principles of sustainable development. Many studies have focused on different treatment options without considering costs. Friedler and Hadari (2006) performed a feasibility study on newly built multi-storage houses where the greywater reuse system was installed during construction of the building. Taken a water price of 1.16 US$/$m^3$ and sewage charges of 0.3 US$/$m^3$, the RBC-based system became economically feasible with a building of seven storeys (28 flats), and a return period of 15 years was calculated.

When greywater is returned to the groundwater, it should be treated with tested and reliable methods. The water percolates through the ground in an unsaturated zone of one metre or more. The subsoil should consist of sand (or smaller grain size). Safety zones around water extraction wells need to be established and a long enough retention time in the saturated zone must be secured before water extraction (i.e. reuse of groundwater).

Treated greywater is most suitably for subsurface irrigation of non edible landscape plants and crops, where leaves or stems are not eaten directly, such as fruit trees or berry bushes, because it does not only conserve treated tap water, but greywater may also benefit plants because it often contains nutrients such as nitrogen or phosphorus. The benefits of grey water recycling include:

- Lower fresh water use
- Less strain on failing septic tank or treatment plant
- Greywater treatment in topsoil is highly effective
- Ability to build in areas unsuitable for conventional treatment
- Less energy and chemical use
- Groundwater recharge
- Plant growth
- Reclamation of otherwise wasted nutrients

Greywater reuse may offer financial savings to each household as well as to the community, because greywater use diminishes sewer flows, thereby lessening the need to expand e.g. WWTP in growing communities. Other benefits from greywater reuse are the decrease in

quantities of wastewater drained to the septic tank and the contribution to the development of home garden agriculture, which means a contribution to household food security and income.

2.3 Legislation for Water Reuse

Integrated water resources policies and regulations have to save and conserve water quantity and quality, while at the same time protect the environment as well as people from water-related hazards. So, regulation promotes and encourages the reuse of waste- and greywater in terms of the above mentioned manners. New scientific achievements and a broad public discussion have found their way into the legislation, establishing requirements for the reclamation of grey and other wastewaters, e.g.:

- the World Health Organisation (Guidelines for the safe use of wastewater, excreta and greywater. 3rd edition (WHO, 2006))
- the European Commission (Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for community action in the field of water policy. (EuropeanParliament, 2000))
- the U.S. Environmental Protection Agency, Municipal Support Division Office of Wastewater Management Office of Water Washington, DC (EPA/625/R-04/108 - Guidelines for Water Reuse. (US-EPA, 2004))
- the Australian Health Ministers' Conference, (National Guidelines for Water Recycling. (Australian-EPA, 2006))

These new regulations set risk based reuse standards on the basis of the socio cultural background with variations in the selecting of suitable parameters, as can be seen in

Table 2-3.

Several investigations show an increasing interest from the authorities to think anew on the reuse of treated greywater not only in remote areas but also in urbanised regions (Anderson, 1996; Bingley, 1996; Friedler, 2004; Nolde, 2005) due to increasing shortage of drinking water. The above mentioned guidelines shall be taken as help for setting effluent standards for greywater reuse. Australia has already included the greywater reuse in their national guidelines.

Table 2-3: Water quality criteria for irrigation and other urban uses in various countries

	Chemical Parameters					Microbiological Parameters
	BOD_5 at 20ºC [mgL^{-1}]	COD [mgL^{-1}]	TSS [mgL^{-1}]	TP [mgL^{-1}]	TN [mgL^{-1}]	Escherichia coli [cfu/100 mL]
WHO (2006) Volume 4: Excreta and greywater use in agriculture						restricted irrigation[a]: $<10^{5;\ b}$ unrestricted irrigation[a] of crops eaten raw: $<10^3$
The Urban Waste-water Treatment Directive (91/271/EEC) (1991)	25[c]	125	$< 10^4$ p.e.: 60[d] $> 10^4$ p.e.: 35[d]	$< 10^5$ p.e.: 2[e] $> 10^5$ p.e.: 1[e]	$< 10^5$ p.e.: 15[f] $> 10^5$ p.e.: 10[f]	
The Bathing Water Directive (2006/7/EC) (2006)						excellent quality [g]: 500[i]; 250[j] good quality [g]: 1000 [i]; 500 [j] sufficient [h]: 900 [i]; 500 [j]
Australian EPA (2006); National Guidelines for Water Recycling	20[n;p]		30[n;p]			1000[n] 100[p] < 1[o]

[a] For greywater reuse
[b] These values are acceptable due to the regrowth potential of E. coli and other faecal coliforms in greywater.
[c] Without nitrification; The parameter can be replaced by another parameter: total organic carbon (TOC) or total oxygen demand (TOD) if a relationship can be established between BOD_5 and the substitute parameter.
[d] This requirement is optional.
[e] Discharge into sensitive areas;
[f] Discharge into sensitive areas; Total nitrogen means the sum of total Kjeldahl nitrogen, nitrate-nitrogen and nitrite-nitrogen.
[g] Based upon a 95-percentile evaluation.
[h] Based upon a 90-percentile evaluation.
[i] For inland waters
[j] For coastal waters and transitional waters
[n] Landscape irrigation — trees, shrubs, public gardens, etc
[o] Commercial food crops consumed raw or unprocessed
[p] Commercial food crops

Table 2-3 (cont.): Water quality criteria for irrigation and other urban uses in various countries

		Chemical Parameters					Microbiological Parameters
		BOD_5 at 20ºC [mgL^{-1}]	COD [mgL^{-1}]	TSS [mgL^{-1}]	TP [mgL^{-1}]	TN [mgL^{-1}]	Faecal Coliforms [cfu/100 mL]
NAWQAM, Egypt (2004) Operational Drainage Water Reuse Guidelines, DR-TR-0103-006-DR		40[k]				30[k;l]	1000[k]
US.EPA/625/R-04/108 (2004) Guidelines for Water Reuse	Unrestricted Urban Reuse	5-30		5-30			Average: 2.2-20 Maximum: 23-75
	Restricted Urban Reuse	20-30		5-30			Average: 23-200 Maximum: 240-800
	Agricultural Reuse	5-30		30			Average: 2.2-200 Maximum: 23-800
	Unrestricted Recreational Reuse	5-30		30			Average: 2.2-20 Maximum: 23-75
	Restricted Recreational Reuse	20-30					Average: 2.2-200 Maximum: 23-800
China; (2002) GB/Tt18920-2002, GB/T18921-2002, GB3838-2002	Unrestricted Reuse	<6			0.5	15 <5[s]	500
	Toiltet flushing	<10				<10 [s]	3
	Irrigastoin of green	<20				<20 [s]	3

[k] Water quality standards for drainage water reuse
[l] Measured as Nitrate (NO_3^-), not as TN
[m] Irrigation water quality guidelines
[s] Measured as Ammonia-N (NH_4^+-N), not as TN

3 Technical and Biochemical Background

3.1 Membrane Bioreactor (MBR)

An MBR couples biological wastewater treatment and solid liquid separation by incorporating membrane technology. The first use of an MBR was in 1969 by Dorr Olivier Inc. (Le-Clech et al., 2006), where an UF membrane was used to separate activated sludge from the final effluent of a biological wastewater treatment system and the sludge was recycled back into the aeration tank. Since then, the MBR system has evolved, and research on MBR technology has increased significantly, particularly in the last 5 years (Ng and Kim, 2007). In wastewater treatment MBR is now a commonly applied technology with an increasing number of installations. Up to the year 2005 about 300 references of industrial applications (> 20 m^3d^{-1}) and about 100 municipal wastewater treatment plants (WWTPs > 500 p.e.) were identified in a study undertaken by Lesjean and Huisjes (2007). The capacity for applications in industries is smaller compared to municipal applications (median flow of 180 m^3d^{-1} and 2500 m^3d^{-1} respectively) (Iversen et al., 2007).

Stringent discharge standards have promoted this development. Early MBR installations were mostly constructed in external, so called “sidestream configuration” (Figure 3-1), however nowadays, the “immersed module configuration” is dominant in the commercial environment (Figure 3-2) (Judd, 2006).

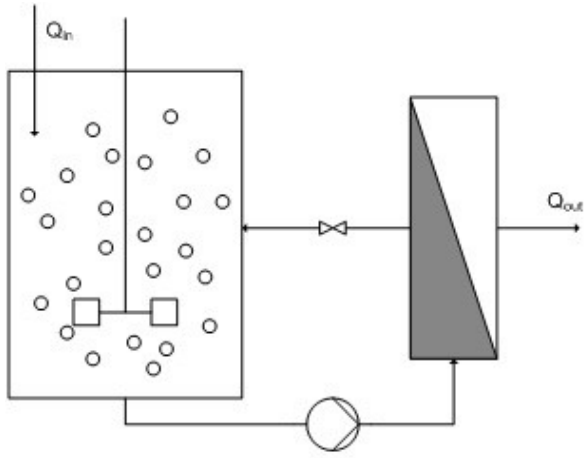

Figure 3-1: Sidestream MBR configuration

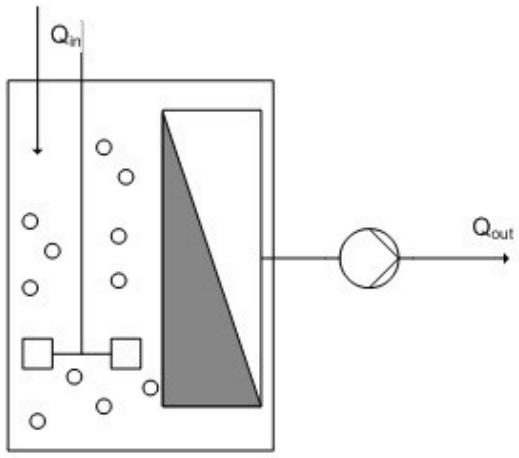

Figure 3-2: Immersed MBR configuration

In side-stream configuration, the membrane module is sited outside the bioreactor and biomass is re-circulated through a filtration pump. In immersed configuration, the membrane is submerged into the activated sludge tank and permeate is withdrawn either via a pump or via gravity flow. Membranes are either micro filtration (MF, >50 nm) or ultra filtration (UF, 2-50 nm) and the module construction categorised as (Judd, 2006):

- plate and frame (PF)
- hollow fibre (HF)
- multi tubular (MT)
- capillary tube (CT)

In the commercialised membrane technology market, the dominant players are the plate and frame (PF) modules, e.g. produced by Kubota (0.4 µm) and the hollow fibre (HF) module, mainly produced by Zenon/ GE Water (0.04 µm).

The immersed vertically oriented HF unit is connected with pump on the permeate side to create a vacuum to remove the treated water out of the reactor. The typical filtration capacity is in the range of 40-70 $L(m^2h)^{-1}$ with a TMP of 100 to 500 mbar. The sheer stress is provided by coarse bubble aeration. Periodic backflushing and occasional chemical cleaning of the membranes helps to control the fouling tendency of the membrane. MLSS concentrations between 15-20 kg m^{-3} are typically (Judd, 2006).

The flat sheet membrane consists of a solid support plate with a space layer in between to withdrawal permeate from both sides of the bulk fluid by a partial vacuum applied within the membrane plate matrix. Several plates are assembled to a single module, which can be staked into racks. The system can be operated either by gravity; with a head of 1 to 1.5 m above the membranes or by a pump introduced TMP usually below 200 mbar. Compressed air, a mixture of coarse and fine bubbles, is introduced through a distribution manifold at the base of the membrane module to avoid sludge blocking and fouling. The MLSS is maintained within the range of around 12-15 kg m^{-3} (Judd, 2006).

3.1.1 Main Operational Parameters

Flux

Operational flux depends upon a number of interrelationships among the TMP, the crossflow velocity on the membrane surface, pore size and material of the selected membrane material and biomass characteristics. Due to the development of a specific biocenosis in dependency of the wastewater, each installed MBR will differ from the one before. The flux is responsible for the membrane area to be installed, the footprint of the MBR, cleaning regime, in case of the SM-SBR also for the HRT, and not to forget costs. Standard operational fluxes for MBR in municipal wastewater treatment range from 10 to 40 $L(m^2h)^{-1}$, typically 20-25 $L(m^2h)^{-1}$.

Sub-Critical Flux Operation

To design the MBR at its best, the determination of the critical flux is indispensable (Ognier et al., 2004). Howell et al. (1995) described a theory of a critical flux operation where no apparent fouling could be observed. Howell et al. (1995) stated further, if a clean non-fouling operation could be sustained and low energy consuming operation could be promoted,

membrane technology applications would rapidly increase. This theory was further defined by Field *et* al. (1995) who developed the strong and weak definitions of critical flux. The first form exists when the flux of a suspension refers to the flux of clean water at the same TMP. In the second form the critical flux exists with a linear relationship between TMP and flux, but with a slope of the line different from clean water. In ultra- and micro-filtration processes a flux plateau exists, where an increase in TMP yields in no flux increase, independently of fouling and is mainly due to concentration polarisation (Field et al., 1995). The phenomenon induces both osmotic effects and reduces mass transfer due to the increase in viscosity at the membrane surface (Ognier et al., 2004). Later work by several investigators has shown that despite an initial choice of sub-critical flux operation, fouling would occur over long operational periods (Le Clech et al., 2003; Ognier et al., 2004).

Trans-Membrane Pressure (TMP)

TMP is defined as the difference between the average hydraulic head at the mid point of the membrane module and the pressure applied to the permeate line (Le Clech et al., 2003). Hydrophobicity of the membrane material, variation in the hydraulic head which is of significance in MBR operation, and most significantly fouling can influence TMP, leading to an increase. Therefore it might be necessary to add pumps while desinging an MBR or change the frequency of the chemical cleaning protocol, increasing operational costs. The TMP for flat sheet modules is noticeable lower with a TMP < 0.1 bar compared to the hollow fibre modules with an applied TMP in the range of 0.1 to 0.4 bar (Judd, 2006).

Aeration

Aeration is needed for supply of oxygen for the microorganism, degradation of carbon, and nitrification (Chiemchaisri and Yamamoto, 2005) as well as to deliver the desired crossflow on the membrane surface to limit fouling, increase fluid transfer through the membrane and reduce sludge blocking at the membrane surface (Le Clech et al., 2003). The crossflow velocity can be put into a function of membrane configuration, reactor design, aeration intensity, and sludge characteristics (viscosity). It needs to be pointed out that an increasing aeration may result in no additional shearing effect beyond a certain point at the membrane surface (Prieske et al., 2008). Membrane manufactures have recommended using coarse aeration rather than fine aeration for a good scouring effect, although they have low oxygen transfer efficiencies, but then again Sofia et al. (2004) presented higher values for fine air bubbling. This might be due to the low induced air-bubble resistance leading to higher velocities up to an attained plateau level (0.69 ms^{-1}) at an aeration intensity of 0.017 ms^{-1} on the membrane surface. Further increase in crossflow velocity was insignificant (Sofia et al., 2004).

Fouling

Next to flux, the second most important parameter to take into consideration for the operation of MBR is fouling. It causes a declining flux (where TMP is constant), or an increasing TMP (where flux is constant) and is one of the increasing operational costs factor, by premature pumping intervention and increasing chemical cleaning frequency. At today's stage of research the membrane community says that both the higher sludge and the lower sludge concentration in submerged operated MBR are responsible for fouling.

Two very recent published detailed reviews show the complexity of fouling in activated sludge processes. Operating parameters such as SRT, HRT, dissolved oxygen (DO) or the food to microorganism ratio (F/M) are responsible for the sludge characteristics and therefore have an indirect effect on membrane fouling; aeration and cleaning my control fouling, whereas the sludge determines fouling (Meng et al., 2009). The interaction between proteins, polysaccharides, and the suspended colloids within the cake layer and the mixed species environment in the ASP make it difficult to understand and to determine the mechanism behind fouling and its grade of responsibility (Le-Clech et al., 2006).

The soluble microbial products (SMP), extracellular polymeric substances (EPS), and the amount of proteins and polysaccharides may be considered as the main fouling agents (Cho et al., 2004; Drews et al., 2008a; Drews et al., 2008b; Iversen et al., 2007; Jefferson et al., 2004; Lee et al., 2004; Nghiem and Schafer, 2006; Ognier et al., 2004; Oschmann et al., 2005). However, Ishiguro *et al*. (1994) showed no significant effect on the flux by either dissolved organic carbon (DOC), sugar, and protein.

In operating a special type of MBR, the so called Submerged Membrane Sequencing Batch Reactor (SM-SBR) , Kang *et al.* (2003) found that mixing intensity and oxygen concentration proved to have a major influence on the membrane performance regardless of the SBR phase. A higher oxygen concentration resulted in a slower rise in TMP, corresponding to less membrane fouling. The higher oxygen concentration influenced a lower specific resistance of cake layer due greater particle size and a higher porosity. In addition Shin and Kang (2002) found that fouling affected the biological performance in an SM-SBR due to declining flux: HRT increased and consequently caused endogenous respiration of microorganisms.

Cleaning

Various chemical and mechanical methods have been reported in literature and from membrane manufactures. A simple mechanical cleaning can be achieved by introducing a relaxation period during operation. Cleaning with compressed air, cohesive with membrane backfluching is typically used for HF modules and is considered as mechanical cleaning. If diluted NaOH, citric acid, or NaHOCl is added to the backwashing solution then chemical cleaning is applied. A circulation of that chemical solution through the membrane and pipe system is needed for cleaning, which can be undertaken in place or outside in a separate tank.

Cleaning is applied when the operational flux declined under a limit set by the operator to remove the reversible fouling and to restore the primordial flux. The cleaning protocols vary from application to application and consist of maintenance cleaning, usually applied once or twice a week, and intense cleaning once every one to three month, depending on the wastewater and plant operation. Chemical cleaning in most cases tends to recover flux and prevent microbial degradation of the membrane (Shin et al., 1998). However, where an increase in initial pressure after chemical cleaning is noted, it can be postulated that permanent, irrecoverable fouling has occurred.

3.1.2 Summary

To summarise, the crucial point is to find and maintain the best overall permeate flux, where as the flux depends on the (Judd, 2006):

- membrane resistance
- operational driving force
- hydrodynamic conditions
- fouling and cleaning of membrane surface
- sludge characteristics

Although several thousand MBRs operate under good conditions with long membrane life times, still many open questions exist, especially to understand the fundamentals of fouling and to gain detailed information of gas-liquid hydrodynamics at the membrane surface; both to overcome inefficiencies in the operation of MBRs. This will lead to the adoption of the membrane technology for communities and for other reuse purposes at a reasonable price. Compared to the conventional activated sludge process the MBR attends with some principle advantages:

- independent of filamentous sludge bulking and other sludge settling characteristics
- mixed liquor suspended solids (MLSS) concentration three times higher
- high carbonaceous conversion and nitrification rates together with short hydraulic retention times (HRT)
- reduced footprint
- higher sludge age (SRT) favourable for slow-growing microorganism and resulting in a low sludge yield combined with partially sludge stabilisation
- permeate with high quality in terms of turbidity, solids and colloidal matters
- rejection of bacteria and viruses

These benefits approach the main objective in biological wastewater treatment, which is to remove the maximum of pollutants at a minimal HRT with an excess sludge production as low as possible. Recently MBRs for greywater treatment have been studied more deeply because of their compactness and superior water reuse potential due to the complete disinfection achieved by the micro- or ultra-filtration membranes (Lesjean and Gnirss, 2006; Melin et al., 2006a; Scheumann et al., 2009). Further investigations are the basis of this thesis.

3.2 Sequencing Batch Reactor (SBR)

The Sequencing Batch Reactor (SBR) has proven to be a viable alternative to continuous-flow systems in carbon and nutrient removal from domestic and industrial wastewaters (Artan et al., 2001). Originally designed as simple treatment technology for COD and phosphorous removal, the SBR has undergone different modifications to achieve nitrification and denitrification along with COD and phosphorous removal (Kargi and Uygur, 2003). The process offers several advantages over other types of activated sludge reactors, particularly the flexibility of cyclic phasing and operating times. The cycle time can be easily modified at any time to adopt changes in process conditions, influent characteristics or effluent objectives, increasing process control and efficiency. SBR application has been proven successful in the treatment of both domestic and industrial wastewaters. (Brenner, 2000; Dangcong et al., 2005; Furumai et al., 1999; Peters et al., 2005; Teichgräber et al., 2003)

While aeration and settling are simultaneous but in spatial sequence in the continuous-flow systems, they are carried out in the same reactor but in temporal sequence in the SBR systems. The technology provides the ability to modify process conditions dependent upon influent characteristics or effluent objectives, operating in a single tank and having an improved process control due to an easy change of HRT, either by changing the volme of wastewater added to the tank or by changing the process time (Andreottola et al., 2001). While mechanically simpler and often less expensive than continuous flow systems, the SBR requires careful monitoring and optimisation when applied to the biological treatment of wastewater. The operational parameters for each SBR process therefore tend to be very site specific. All over the cycle time should be as short as possible to achieve optimum exploitation of the volumetric capacity of the plant and to push down the cost to its minimum. However, a balance between cycle time and treatment performance has to be identified.

3.2.1 Main Operational Parameters

The SBR process has a cyclic nature, each cycle consisting of several phases (cf. Figure 3-3). In the fill phase the wastewater is fed into the reactor. After filling, time is given in the react phase, including (intermittent) aeration, for the biological conversion to further progress. The microorganisms settle to the reactor bottom in the settle phase, the clear treated wastewater is discharged in the draw phase, and than the reactor is left idle in the idle phase, until the fill phase of a new cycle starts. The total cycle time (t_c) is the duration corresponding to the sum of these five phases (Artan et al., 2001). In literature, the cycle time for SBR operation varied from t_c=3h, municipal wastewater, (Shin and Kang, 2002) over t_c=4h, municipal wastewater, (Innocenti et al., 2002) and t_c=6h, municipal sewage, (Artan et al., 2002) to t_c=12h, synthetic wastewater, (Kargi and Uygur, 2003).

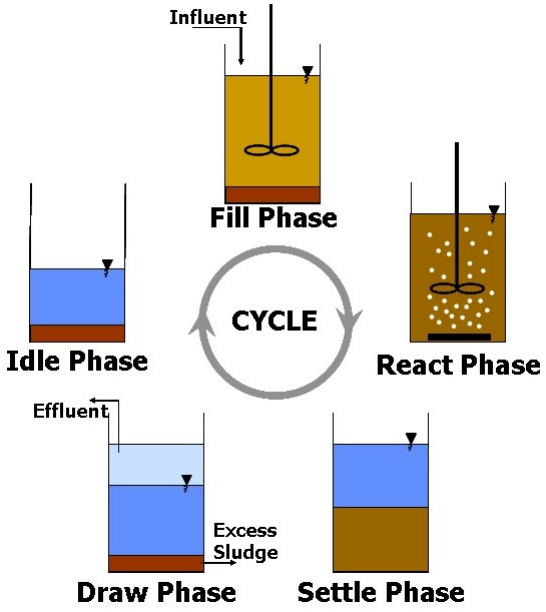

Figure 3-3: SBR principle of operation

Fill Phase

In the fill phase, influent wastewater is filled into the SBR, depending on the influent wastewater composition and biodegradability, the concentration of toxic organics in the wastewater, the volumetric exchange ratio (VER, defined as volume added to the overall hydraulic volume), and the treatment requirements (e.g., enhanced nutrient removal) (Artan and Orhon, 2005). Teichgräber (2003) found that a VER=0.5 is typically for SBR in Germany, whereas Krampe and Krauth (2001) reported a VER=0.1 for a nitrogen removal efficiency of 86.6% compared to 67.1% for a VER=0.3.

The feeding time can range from a very little time of the total cycle time up to the whole duration of cycle. In the static fill mode the wastewater is fed to the reactor at once at the beginning of one cycle with no mixing of sludge. Depending on the fill pattern, the SBR can be compared to either a plug flow or a completely mixed reactor (Morgenroth et al., 1998).

Anaerobic/ anoxic fill mode is generally adopted as it has a number of advantages, including the simultaneous removal of organic carbon, nitrogen and phosphorous, effective prevention of filamentous bulking of activated sludge. Nevertheless, a relatively large fraction of influent TN is converted to N_2O during anoxic filling (Park et al., 2001).

The mixed fill mode (the total amount of wastewater to fill the reactor is neither fed static nor continuous, but divided into several smaller portions) results in a good denitrification, and when desired, in a subsequent reduction of oxygen demand and energy input, as well as providing the anoxic or anaerobic conditions required for biological phosphorous removal. Aerated filling results in the beginning of aerobic reactions, a reduction of cycle time, and holds substrate concentration low, which may be important if biodegradable constituents exist which are toxic at high concentrations. (Ketchum, 1997)

React Mode

During settle, draw and idle phase, it is assumed that no biological conversion occurs. The biodegradation of the wastewater pollutants takes place during the process time, which corresponds to the sum of fill and react phases unless the static fill is applied. The process time can be further divided into the aerated period, and the mixed period, which is either anoxic or anaerobic, depending on the presence of nitrate (Artan et al., 2001).

The react period is system specific, because of its dependence upon biological composition of the wastewater and the required effluent quality. The simple treatment with only an aerated reaction phase results in carbon removal and bio solid reduction, if aeration is extended (Ketchum, 1997). If a biological nutrient removal (BNR) process is desired, anaerobic or anoxic stages are incorporated into the react period. The order, length, number and type of phases used in the react period can therefore vary broadly.

Kargi and Uygur (2003) carried out investigation with a five-step SBR (total volume of 5L) in order to determine the most suitable ratio of COD/N/P to maximise nutrient removal. The SBR process consisted of anaerobic, anoxic, aerated, anoxic, and aerated phases (2/1/4.5/1.5/1.5 h respectively with 0.5 h allowed for settling) treating synthetic wastewater. The COD/NH_4^+-N/PO_4^{3-}-P ratio best suitable was determined to be 100/2/0.54 yielding 95, 94 and 99% removal respectively.

Similar experiments carried out by Chang *et al.* (2000) in a 30L laboratory scale SBR with synthetic wastewater illustrated the importance of varied HRT and process times on the best nutrient removal strategy. Unfortunately, no information was given concerning the VER. The selection of 1-3-2 h of anaerobic-aerobic-anoxic phases yielded in a maximum removal efficiencies for TN and TP with final effluent concentrations of less than 2 mgL^{-1}.

Andreottola *et al.* (2001) achieved a 91% COD and 95.2% total Kjeldahl nitrogen (TKN) removal from industrial wastewater (plywood factory) when implementing a process as follows: immediate filling of 0.25L, 1h 50min anoxic reaction, 1h 50min aerobic reaction, immediate filling of 0.25L, 1h 50min anoxic reaction, 1h 50min aerobic reaction, immediate filling of 0.25L, 1h 50min anoxic reaction, 1h 50min aerobic reaction, 1h settling, and discharge. The total cycle time in the 3.5L reactor added to 12h with a VER of 0.25.

An alternative strategy for complete denitrification in the treatment of greywater was carried out by Shin *et al.* (1998) with a 1000L SBR system. The total cycle time of 12h was arranged in a constant change of 60min aeration and 60min anoxic conditions. The cyclic SBR operation resulted in a more effective nitrification and denitrification compared to conventional SBR operation methods under low organic concentration, to be observed in greywater.

Further work of treating greywater with SBR is not reported in literature, although some producers like PONTOS use this technology successfully.

Settle/ Decant/ Idle

During Settle the activated sludge is separated from the supernatant. The importance and difficulty of this stage is to withdraw a turbidity free effluent without disturbing the settled sludge. This is the key element in operation of SBR since this process operates with no return sludge (Shin et al., 1998). The time needed for settlement depends strongly on the method of decantation, the height of supernatant, and sludge rheology. Typical durations range from 0.5 to 2 hours. At last, the idle phase, with no function for the operation of the SBR cycle is simply due to uncertainty in the design data, and is used as a reserve time that can be added to any phase or period, as need arises. Therefore, the effective cycle time may be 1 to 4 hours less than the total cycle time (Ketchum, 1997).

3.2.2 Summary

As mentioned in the introduction of this chapter the SBR process has a broad application in wastewater treatment and can be considered as a viable alternative to continuous-flow systems in nutrient removal as well as in carbon and suspended solids removal. The development of a unified design will help to understand the process better and hence, will remove obstacles in hindering the wider application of the SBR. In nutrient removal, the SBR can offer a great deal of operational flexibility, because it allows adjustment of aerobic, anoxic and anaerobic periods through temporal control of aeration and filling and its cyclic nature.

3.3 Submerged Membrane Sequencing Batch Reactor (SM-SBR)

The possibility to treat wastewater with a Submerged Membrane Sequencing Batch Reactor (SM-SBR), as described in Figure 3-4, goes one step further. It overcomes the restriction of the simple SBR process and its dependency on sludge behaviour for the process of decantation. Compared to the conventional SBR process no sedimentation phase is needed. The biological degradation proceeds during the withdrawal phase and therefore shortens the cycle time compared to the conventional SBR process. Substantially higher solid concentration in the biological reactor reduces the reaction volume. In accordance to lower SRT it is also possible to minimise the excess sludge production. All these points are further investigated in this work and compared to the few existing articles, dealing with this technology. The combination of the MBR process with the SBR operation leads to a procedural advantage.

In general, membranes require higher aeration rates than needed for the biological activity resulting in an increased dissolved oxygen (DO) concentration in the filtration chamber. In the conventional MBR, the return sludge transports oxygen into the denitrification chamber, inhibiting the process there. To overcome this problem, usually a degassing chamber is needed. This is not the case in an SM-SBR, because the inflow during the filling phase guarantees a fast reduction of DO. In addition, the membrane facilitates a complete retention

of sludge and particulate matter. To ensure the cross-flow at the membrane surface during the withdrawal phase aeration is needed responding in further biological activities and biodegradation. So, on a small footprint hygienically acceptable, germ-free water is produced due to the integration of micro-filtration membranes into the treatment process. (Krampe and Krauth, 2000; Scheumann and Kraume, 2007)

The advantages of the SM-SBR can be outlined as follows:

- Reduction of the cycle time through partly simultaneity of biological degradation, solids settlement, and withdrawal;
- Increase of the MLSS concentration and thus reduction of the reactor volume;
- Improvement of the effluent quality through complete solids retention;
- Simple modification of process conditions dependent upon influent characteristics or effluent objectives, but additional controlling needed;
- Possible reduction in operational cost;
- Improved process control leading to good nutrient removal;
- No entrainment of oxygen from pre-denitrification (as in continuous MBR).

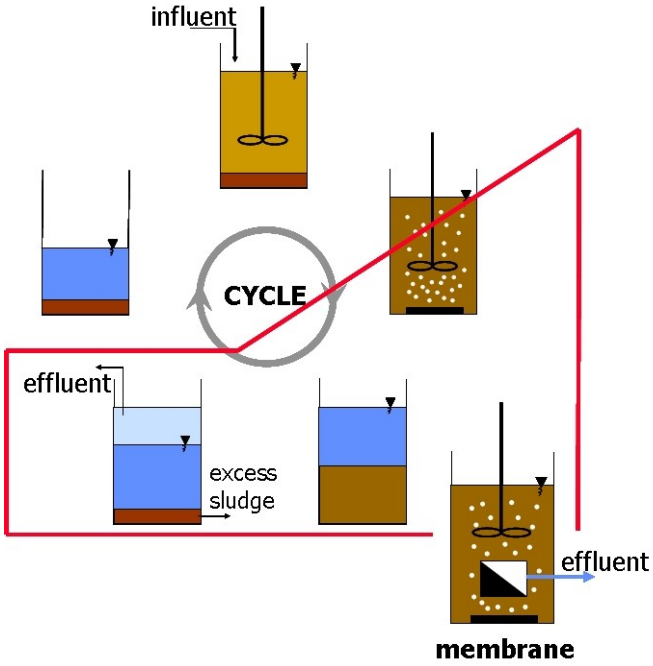

Figure 3-4: SM-SBR: principle of operation of the hybrid system

Shin and Kang (2002) used a 3h cycle for complete nutrient removal treating municipal wasterwater. The operating conditions for the SM-SBR with a working volume of 1.7 m³ and a submerged HF membrane module with a total area of 18m² were as follows: 40min fill and anoxic, 30min anoxic/anaerobic, 100min aerobic, 10min anoxic, and a permeate withdrawal time of 130min, required by the membrane. Despite varying influent characteristics, COD

removal was always higher than 95% and TN removal reached a maximum of 85% after a few weeks. Even though the SM-SBR system is theoretically a high rate processes (due to the complete retention of biomass), the cycle times, phase times (except for settle, decant and idle) and HRT are similar to the one observed in normal SBR operation possible of good nutrient removal. The flux was between 0.3 and 0.35 md^{-1} at stable operation, leading to an HRT of 12 h.

Compared to a conventional MBR, the SM-SBR shows a better stability in nitrogen and phosphorous removal when the wastewater shows a high variation in the COD/TN ratio. Furthermore the sequencing batch operation can reduce the fouling of the membrane, although higher EPS existed (Zhang et al., 2006). However, due to the implementation of a membrane, the treated effluent is suitable for reuse, irrigation, and direct infiltration (Messalem et al., 2000). The SM-SBR application can be seen in hotels of water scare tourism areas to save valuable drinking water due to the reuse of greywater from showers, and everywhere else where high effluent quality standards are needed. The SM-SBR therefore can be technically viable for application to greywater reuse. (Andreottola et al., 2001; Scheumann et al., 2009)

3.4 Biological Nutrient Removal

Biological carbon, nitrogen, and phosphorus removal from wastewater is an established process in wastewater treatment. Despite the broad knowledge and practical experience that has been accumulated over the decades, there are still certain aspects of biological nutrient removal, which require further research. Especially new adopted technologies like the SM-SBR or the MBR draw the attention of the scientific community.

Biological nutrient removal copies in a concentrated form the self-cleaning process of microorganism in natural water bodies. The wastewater pollutants serve as food for the microbes and they are then metabolised for energy and growth. Each wastewater creates an adopted biocenosis in the treatment plant, which can be manipulated by operational parameters for the most effective treatment performance.

3.4.1 Important Operational Biological Parameters

The most significant adjustment for the optimisation of the biological performance is the appropriate selection of aerobic, anoxic and anaerobic stages. Other parameters like HRT, SRT, MLSS, and F:M are also used to optimise the biological operation within the wastewater treatment plant, like in an SM-SBR.

Hydraulic Residence Time

The hydraulic retention time (HRT or τ) is defined as follows:

$$\tau = \frac{V}{\dot{Q}} \qquad \textbf{(3-1)}$$

where τ = hydraulic detention time, s
V = volume of the reactor, m^3
$\dot{Q}$ = volumetric flow rate, m^3s^{-1}

Operational cycle time has been reported to vary from very low τ = 1.5h in greywater treatment for carbon removal (Hu, 2002), over τ = 2.5h for an SM-SBR (Shin and Kang, 2002) and τ = 12h for an SBR plus additional micro-filtration (Shin et al., 1998) up to τ = 24h, when flow rates are highly variable and enhanced biological nutrient removal is required (Ketchum, 1997). The HRT is then related to the VER. A maximum VER of 50% has been recommended in the literature (Teichgräber et al., 2003).

It is reported that for wastewater treatment in MBR, the performance is relatively insensitive to HRT of certain length (Stephenson et al., 2000) and can vary widely in a range from τ = 7.6h to τ = 22h (Judd, 2006). However, for the application of an SM-SBR the HRT is potentially more significant, since all biological processes (aerobic, anoxic, anaerobic) are incorporated into a single tank. So, in order to optimise the biological performance, HRT must be primarily taken into consideration.

Mixed Liquor Suspended Solids

Mixed Liquor Suspended Solids (MLSS) concentrations are typically in a range from 3.0 to 5.0 gL^{-1} in an ASP (Metcalf and Eddy, 2003), depending strongly on the settling ability and velocity. Nevertheless, they are equivalent to the MLSS concentration in an MBR treating greywater in Morocco, where a submerged membrane is incorporated into the SBR resulting in complete retention of biomass in the reactor and a high SRT > 360 d. In municipal wastewater treatment biomass concentrations can reach up to 40 gL^{-1} for zero sludge wastage processes (Stephenson et al., 2000). In greywater treatment the MLSS concentration is low, starting as little as 1.3 gL^{-1} (Merz, 2006), over 3.6 gL^{-1} (Shin et al., 1998) and reaching finally 8 gL^{-1} after one year operation with complete biomass retention (Scheumann and Kraume, 2009). This is mainly due to the reason that the influent greywater has a low concentration of COD and nutrients.

Food to Microorganism Ratio

The food to microorganism ratio (F/M) is a commonly used parameter in wastewater treatment to characterise process design and operating conditions with values in a range from

0.04 to 0.1 for SBR (Metcalf and Eddy, 2003). The reduction of F/M is the result of the higher applied MLSS concentration in applied membrane couples activated sludge processes. This is advantageous, because the sludge production is therefore reduced. Stephenson *et al.* (2000) observed a F/M of 0.15 (based on a BOD/ MLVSS basis), typically for MBR operation, but Gildemeister *et al.* (2005) found only half that value with an F/M of 0.074 for greywater treatment.

Shin and Kang (2002) showed that the COD/TN ratio does not have any effect on the organic matter removal in SM-SBR, because the complete retention of microorganisms by the membrane minimised the effect of washout, and because the membrane was also a barrier to the high molecular weight compounds.

Solids Retention Time

The solid retention time (SRT) represents the average time during which the sludge remains in the reactor and is the most critical parameter for the design of activated sludge processes. SRT influences treatment process performance, aeration tank volume, sludge production, and oxygen requirements. Values from 1-2 days for BOD_5 removal in domestic wastewater up to 5-40 days for sludge stabilisation can be taken as typical (Kargi and Uygur, 2003; Metcalf and Eddy, 2003; Moussa et al., 2005). However, low sludge production rates observed in membrane coupled activated sludge processes treating greywater mean that long solids retention times approaching infinity are possible (Scheumann and Kraume, 2009). Long SRT may be important for the stabilisation of nitrifying bacteria, which may become abundant upon the extension of SRT (Shin and Kang, 2002).

The SRT is the operational parameter that can be used to control and stabilise the MLSS concentration within the reactor, interacting with the performance of membrane flux. Shimizu *et al.* (1996) discovered a linear relationship between a declining flux and an increasing MLSS up to 8 gL^{-1}, but a significant non linear decrease of the flux with a MLSS concentration from 8 to 18 gL^{-1}.

Aeration

The dissolved oxygen (DO) concentration in wastewater treatment plants is of central importance in determining the biomass activity and the corresponding BOD_5 or COD elimination. To estimate the needed amount of aeration or aerators, the DO in is measured in clean water, before the start up of the wastewater treatment plant, according to a standardised ASCE procedure (Gillot et al., 2005). Nevertheless, the prediction of oxygen transfer may be relatively inaccurate with clean water, as it fails to take into account all the parameters affecting mass transfer, like geometry, sludge viscosity and the performance of the aeration system under operating conditions. To better characterise the aeration system, and therefore the DO concentration, several authors defined a transfer number N_T, which has the same

physical meaning as the specific standard oxygen transfer efficiency and can be used as a scale up factor for oygen transfer (Gillot et al., 2005):

$$N_T = \frac{k_L a}{U_G} \cdot \sqrt[3]{\left(\frac{v^2}{g}\right)} \qquad \textbf{(3-2)}$$

where g: gravitational acceleration, ms^{-2}
$k_L a$: mass transfer coefficient, s^{-1}
N_T: transfer number
U_G: gas superficial velocity, ms^{-1}
v: kinematic viscosity of the water, m^2s^{-1}

However, where membrane technology is combined with a biological process, often the airflow rate is adjusted to optimise the performance of the membrane rather than to apply the optimum DO concentration for the microorganism. Theoretically, the amount of oxygen that must be transferred in the aeration tanks equals the amount of oxygen required by the microorganism in the activated sludge system to oxidise the organic material. In practice, the transfer efficiency of oxygen from gas to liquid is relatively low, which means that only a small amount of oxygen supplied is used by the microorganism (Metcalf and Eddy, 2003). To meet the DO requirement of the activated sludge process, the dissolved oxygen concentration in the aeration tank should be maintained at about 1.5 to 2 mgL^{-1} in all areas of the aeration tank. This is confirmed by Kargi and Uygur (2003), who reported a successful operation of an SBR for nutrient removal by maintaining an oxygen concentration in the aerated phase above 2 mgL^{-1}, while the DO during the anaerobic and anoxic phases must be around zero. Higher DO concentrations (>2.0 mgL^{-1}) may improve nitrification rates in reactors with high BOD_5 loads, but exceeding 4.0 mgL^{-1} does not enhance this process, but increases the aeration costs considerably (Metcalf and Eddy, 2003).

3.4.2 Characterisation of Wastewater Constituents

Important for the design of a functioning treatment plant it is indispensable to know the wastewater constituents as best as possible. They can be grouped into the following categories:

- carbonaceous substrate,
- nitrogenous components,
- total and volatile suspended solids, and
- alkalinity.

Each group can then be further subdivided into parameters, which are of importance for the design of biological nutrient removal processes.

Carbonaceous Components

The carbonaceous components are measured as BOD_5 or COD, where the latter gains more and more popularity for the characterisation of wastewater, especially in the most current computer simulation models (Henze et al., 2000). A COD mass balance is easier to understand concerning the balance of the carbonaceous material which is oxidised and incorporated into cell mass. The rate at which COD can be oxidised in a reactor is i.a. limited by the rate at which DO is transferred from the air to the liquid phase. Other than BOD_5, the COD constitutes of a non-biodegradable and biodegradable fraction. Together with the biomass in the feed, the carbonaceous compounds can be divided into biodegradable COD, non-biodegradable COD (inert material) and biomass, as described in Figure 3-5.

The biodegradable COD is further divided into readily biodegradable substrate (S_S or rbCOD) and slowly biodegradable substrate (X_S or sbCOD). The readily biodegradable substrate consists of simple soluble molecules that can be readily absorbed by the organisms and metabolised for energy and synthesis, whereas the slowly biodegradable substrate is made up of particulate, colloidal, and more complex organic molecules that require enzymatic breakdown prior to absorption and utilisation. The rbCOD fraction has a direct effect on the activated sludge kinetics (oxygen consumption in the reactor) and on the denitrification rate in preanoxic zones in biological N-removal, where it will be consumed before the aeration zone (Metcalf and Eddy, 2003). On the other hand, a study carried out by Vocks *et al.* (2005) showed that a post-denitrification without C dosing applied in an MBR is a reliable technology. There, storage compounds within the cells of an EBPR process possibly act as C-sources for denitrification, leading to denitrification rates above endogenous rates.

The non-biodegradable COD is divided into soluble (S_I or nbsCOD) and particulate (X_I or nbpCOD) material. Both are considered to be unaffected by the biological action in the system. The inert soluble material leaves the system by the secondary clarifier effluent, whereas the inert particulate material is enmeshed in the sludge mass and accumulates as inert volatile suspended solids. The inert particulate material will be removed from the system by the removal of excess sludge and to some extent be present in the settler effluent as well. Moreover, the active biomass is divided into two types of organisms: heterotrophic biomass ($X_{B,H}$) and autotrophic biomass ($X_{B,A}$).

Orhon *et al.* (1994) identified in his undertaken study of a domestic wastewater sample a soluble fraction of 48.7% (sCOD=19 0mgL^{-1}) of the total COD (tCOD=390 mgL^{-1}), which can be further subdivided into the readily biodegradable COD with 44.9% (S_S=175 mgL^{-1}) and inert soluble COD with 3.8% (S_I=15 mgL^{-1}). The particulate fraction makes up the remaining 51.3% (pCOD=200 mgL^{-1}) of the total COD (tCOD=390 mgL^{-1}). This fraction, in analogy, is then divided into the slowly biodegradable, particulate COD with 22.6% (X_S=88 mgL^{-1}) and non-biodegradable particulate COD with 28.7% (X_I=112 mgL^{-1}).

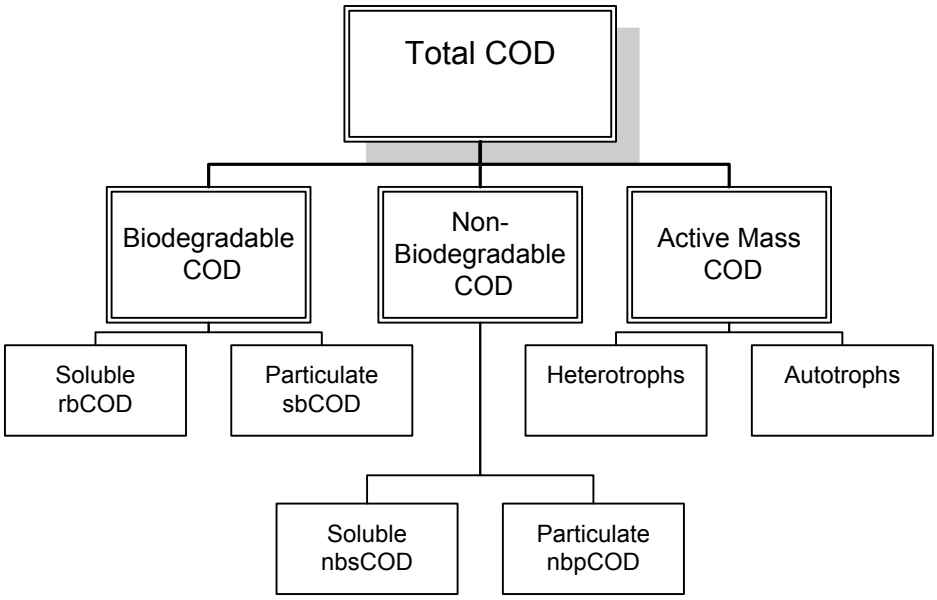

Figure 3-5: COD fraction for wastewater characterisation

COD is fast degraded during the aerobic conditions, but in rivalry required for both the biological phosphorus removal and the denitrification. Therefore, the optimal supply and utilisation of the COD is critically important and constitutes the major challenge in a single-tank SBR, because the conditions (aerobic or anoxic/anaerobic) can only be changed for the entire reactor. However, the settling and decant phases provide differing conditions in the supernatant and the sludge blanket and the method of influent feed provides an additional option to obtain different conditions in parts of the tank. (Keller et al., 2001)

In an SBR, the DO concentration remains low for the beginning hours of the react phase by application a static fill, where most probably the BOD_5 is oxidised. This is the 'feast' part of the reaction period as there is a relatively high concentration of BOD_5. Eventually, the rate of oxygen uptake decreases and the DO concentration recovers. This recovery period is important, because the scarcity of food favours the utilisation and oxidation of recalcitrant organics by the biomass. Sludge in the SBR system, when subjected to proper feast and hunger cycling, can accommodate rapid changes in component concentrations and degrade slowly reacting compounds (Scheumann et al., 2007a).

Nitrogenous Components

The total nitrogen (TN) composition is illustrated in Figure 3-6. The nitrate and nitrite is near zero due to anaerobic conditions in the sewer system. 60-70% of the influent total Kjeldahl nitrogen (TKN) will be as NH_4-N in domestic wastewater (Metcalf and Eddy, 2003), low as 20% in high strength organic wastewater from the production of ABS (Acrylonitrile-polyButadiene-Styrene) (Cho et al., 2001), and high as 80% in shower effluent greywater from a sports ands leisure club (Merz et al., 2007).

NH_4-N can be easily incorporated in bacterial cell synthesis or directly used for nitrification, whereas the organic fraction needs to be hydrolysed by enzymes. The particulate non-biodegradable nitrogen will be captured in the sludge floc, similar to the nbpCOD, and removed from the system with the excess sludge and to some extent over the settler effluent. The non-biodegradable soluble organic fraction in domestic wastewater is found to be 18-38% (average: 25%) of the total inlet soluble organic nitrogen, which can range from 4.5 to 5.5 mgL^{-1} measured as nitrogen (Parkin and McCarty, 1981).

In this thesis, the TN is measured from a filtered sample and represents only the soluble fraction, which is not captures in the sludge flocs.

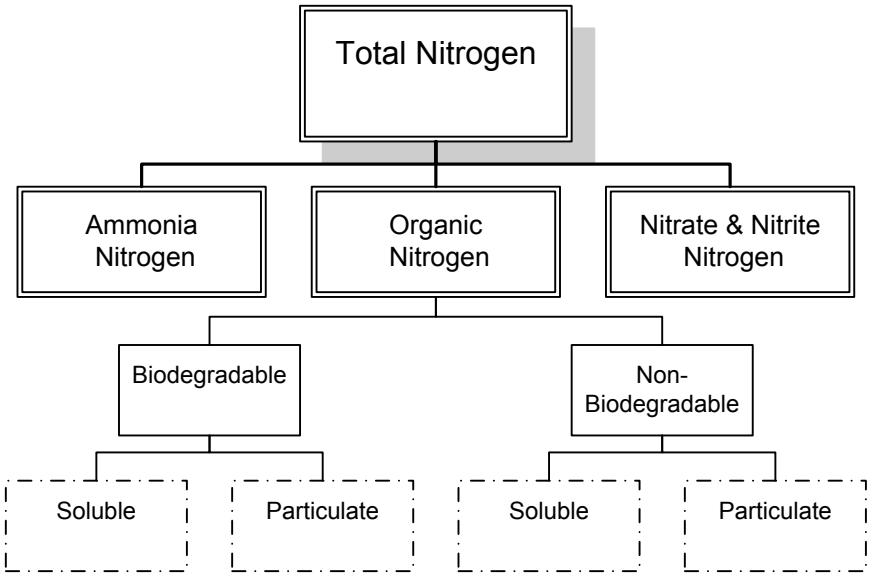

Figure 3-6: Nitrogenous constituents in wastewater

3.4.3 Kinetics and Removal Mechanisms

Mass balances and mass transfer are required for the design of treatment plants to determine process performance and reaction rates (which include reaction rate coefficients) via modelling of treatment kinetics, removal mechanism, and hydraulic conditions within the reactors. To find the optimum conditions for the biological performance in an SBR for example, it should be of priority to select a react phase, which tends to incorporate aerobic, anoxic, and anaerobic periods in interaction with the most suitable feeding pattern, depending on influent wastewater composition to achieve the needed effluent requirements.

Knowledge on microbial growth, on the rates at which biological reaction and conversions occur and the degree of their degradation, generally both a function of the constituents involved, will be used to characterise, optimise and adjust the process of biological nutrient removal. Scientifically substantiated mathematical models present the basis in the design today.

Microbial Growth

Cells need energy in order to grow or to maintain their vital cell functions via metabolism of the delivered substrate. Growth may be defined as the orderly increase in all cellular constituents, either in mass of a single cell or in size of a population, and results from the biosynthetic and energy generating processes. This requires macro elements like carbon, nitrogen, oxygen, hydrogen, phosphorous, sulphur, and iron, as well as trace elements like manganese, cupper, molybdenum, etc. Depending on the organism, different portions are transformed into biomass, metabolites, and carbon dioxide. Each microbial population undergoes a growth curve with several distinct phases, called the lag-, exponential-, stationary-, and death phase (cf. Figure 3-7), where substrate and nutrients are present in excess. In the lag phase the organism adapts to the changing surrounding condition with a delay in growth activity, e.g. when sludge is taken from the WWTP into batch reactors to carry out additional experiments. During the exponential phase the organism grows at its maximum rate, before it goes into the stationary phase as soon as inhibition or limitations occur. No net increase or decrease in cell number is visible. However, many cell functions continue including energy metabolism and biosynthesis processes. It might even be that there is cryptic growth – some cells grow while others die. The two processes are balanced and no net increase is visible. Finally, the cell concentration decreases, the death phase is reached, accompanied by cell lysis. (Brock, 1997)

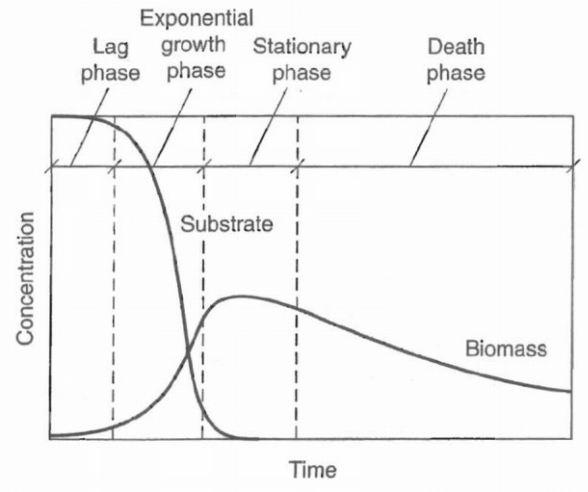

Figure 3-7: Batch process biomass growth with changes in substrate and biomass concentration (from Metcalf&Eddy, 2003)

In activated sludge systems autotrophic and heterotrophic bacteria form a complex ecosystem with active cells at different levels in different growth phases. The SRT may be used to control the dynamic of those bacteria, because it is the reciprocal of the microbial net specific growth rate at steady state (Ni and Yu, 2007). Over a wide range of growth rates, the biomass yields can be expected to be constant. For very low growth rates, found in greywater sludge

(Scheumann and Kraume, 2009), other phenomena must be considered. In those cases, part of the substrate is used for cell survival and not for reproduction, yielding energy only for maintenance (Drews and Kraume, 2007).

Microbial Growth Parameters

The kinetic of microbial growth controls the substrate oxidation (i.e., utilisation) and the production of biomass, yielding in the amount of total suspended solid concentration (TSS) of the activated sludge processes. The process of transformations can be set equal to the depletion of the electron donor. For the heterotrophic bacteria the electron donors are the organic compounds during aerobic oxidation and for the autotrophic, nitrifying bacteria it is mainly ammonia. The specific substrate utilisation rate r_{su}, the specific net biomass production rate r_g, and the production rate of volatile suspended solids (VSS) $r_{X,\,VSS}$ estimate the amount of sludge produced in the process and is known as the observed yield (cf. equation 3-3 to 3-7).

specific substrate utilisation rate r_{su}:

$$r_{su} = -\frac{k \cdot X \cdot S}{K_S + S} \qquad \textbf{(3-3)}$$

specific net biomass production rate r_g:

$$r_g = -Y \cdot r_{su} - k_d \cdot X$$

$$r_g = Y \frac{k \cdot X \cdot S}{K_S + S} - k_d \cdot X \qquad \textbf{(3-4)}$$

specific biomass growth rate μ:

$$\mu = \frac{r_g}{X}$$

$$\mu = Y \frac{k \cdot S}{K_S + S} - k_d \qquad \textbf{(3-5)}$$

where k_d = endogenous decay coefficient, $g_{VSS}(g_{VSS}d)^{-1}$
k = max. specific substrate utilisation rate, $g_{substrate}(g_{biomass}d)^{-1}$
K_S = half velocity or Monod constant, gm^{-3}
r_{su} = rate of substrate change due to oxidation, $gm^{-3}d^{-1}$
r_g = rate of net biomass production, $g_{VSS}m^{-3}d^{-1}$
S = growth limiting substrate concentration, gm^{-3}
X = biomass concentration, gm^{-3}
Y = yield, $g_{VSS,\,produced}(g_{substrate,\,removed})^{-1}$
μ = specific biomass growth rate, $g_{VSS}(g_{VSS}d)^{-1}$

production rate of volatile suspended solids $r_{X, VSS}$:

$$r_{X,VSS} = -Y \cdot r_{su} - k_d \cdot X + f_d \cdot k_d \cdot X + \dot{Q}\frac{X_{o,i}}{V} \text{ with } r_{su} = r_{su}^g + r_{su}^m \quad \textbf{(3-6)}$$

observed biomass yield:

$$Y_{obs} = -\frac{r_{X,VSS}}{r_{su}} \quad \textbf{(3-7)}$$

where f_d = fraction of biomass as cell debris, 0.1-0.15 $g_{VSS}(g_{VSS})^{-1}$
$\dot{Q}$ = influent flow rate, m^3d^{-1}
r_{su}^g = rate of substrate change related to growth, $gm^{-3}d^{-1}$
r_{su}^m = rate of substrate change related to maintenance, $gm^{-3}d^{-1}$
$r_{X, VSS}$ = rate of total VSS production, $g_{VSS}m^{-3}d^{-1}$
V = reactor volume, m^3
$X_{o, i}$ = influent non-biodegradable VSS concentration, $g_{VSS}m^{-3}d^{-1}$
Y_{obs} = observed yield, $g_{VSS, produced}(g_{substrate, removed})^{-1}$

For substrate depletion, the cell must be in contact with the biodegradable COD, which is infiltrated through sorption and finally because of enzymatic reactions decomposed.

The above mentioned basic equations describe the interaction between microbial growth and substrate utilisation in activated sludge processes and are based on the Monod kinetic (cf. equation (3-8)), directly derived from the Michaelis-Menten formalism (Liu, 2006):

$$enzyme + substrate \underset{k_1}{\overset{k_1}{\Leftrightarrow}} enzyme - substrate - complex \overset{k_2}{\Rightarrow} enzyme + product$$

$$\mu = \mu_{\max}\frac{S}{S + K_S} \quad \textbf{(3-8)}$$

where μ_{max} = maximum specific growth rate, d^{-1}

The Monod equation is linked to microbial growth and has been widely used to describe the process. However, it has no mechanistic basis since it is purely empirical, developed from a curve fitting exercise. It shows a functional relationship between the specific growth rate and the essential substrate concentration; furthermore it is accepted by the IAWPRC (now IWA) task group as the fundamental basis for the development of the activated sludge models and for the determination of the biokinetic coefficients (Al-Malack, 2006). The Michaelis-Menten equation was derived from the mechanism of enzyme reactions, where the reactive material is held constant and although it gives a mechanistic meaning to the constants involved, none can be applied to a substrate-cell system as described by the Monod equation. Because of this

difference, the Michealis-Menten kinetic is used to describe nongrowth linked biodegradation, whereas the Monod kinetic is used for growth linked processes (cf. Figure 3-8).

Since the publishing of the empirical Monod kinetic equation, 50 years ago, the rational mechanism with its simplest hyperbolic form, has tried to be derived mathematically. Moreover, due to the poor theoretical understanding of the Monod equation, for decades it has been argued about the physical meaning of the Monod constant K_S, as well as about the large variation observed of this constant (Liu, 2007). At the time, when the microbial growth rate is half the maximum specific growth rate, then it is defined that the substrate concentration reaches the half velocity constant K_S.

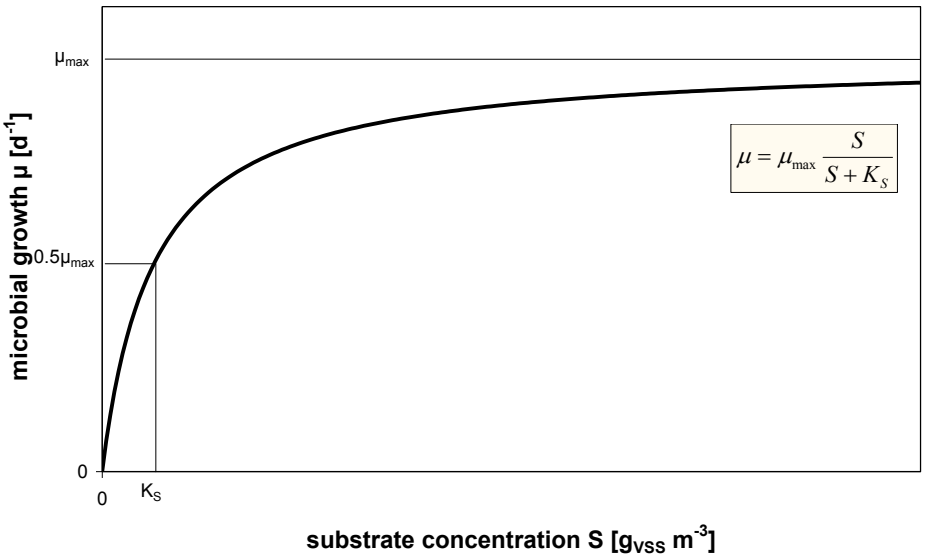

Figure 3-8: Monod based growth

The rates of microbial growth and substrate depletion are coupled via the yield coefficient as described in equation (3-7). If all the carbon could be transferred into biomass the theoretical yield would be calculated to 0.78 (Drews, 2004), but due to the production of carbon dioxide during aerobic respiration of heterotrophic bacteria the maximal value is reduced. Biomass yield can be estimated with a simple COD mass balance and stochiometry. Assuming glucose as substrate and $C_5H_7NO_2$ as new cell the aerobic biological oxidation of organic matter can be written as follows:

- $3\ C_6H_{12}O_6 + 8\ O_2 + 2\ NH_3 \rightarrow 2C_5H_7NO_2 + 8\ CO_2 + 14\ H_2O$

The yield based on the glucose consumed equals to 0.42 $g_{cells}\ g_{glucose}^{-1}$ (Metcalf and Eddy, 2003).

Over a wide range of growth rates, biomass yields from substrate uptake can be considered constant; still other phenomena must be taken into account when reaching either steady state conditions (low growth rate), or when substrate limitations occur.

Phenomena under Substrate Limitations

The maintenance concept, introduced by Pirt (1965), can be used to describe the phenomena under substrate limitation, like the reduced sludge production noticed in ASP with growing sludge age or substrate limited wastewater, e.g. greywater (Jefferson et al., 2001). Substrate is partially used for cell survival and not for reproduction, therefore the corresponding substrate uptake rate only yields the energy needed for maintenance (e.g., renewal of the cell membrane) and depends on the type of the limiting substrate and on temperature (Drews and Kraume, 2007). Now, if the maintenance energy would be assumed to be zero, than equation (3-7) reduces to the true growth yield Y^g:

$$Y^g = \frac{r_{X,VSS}}{r_{su}^g} \qquad \textbf{(3-9)}$$

where Y^g = true growth yield, $g_{VSS,\ produced}(g_{substrate,\ removed\ via\ growth})^{-1}$

But, if the maintenance energy is not zero, then the part of energy used for maintenance will increase with decreasing growth rates, which means the observed yield is a function of μ. On the assumption that the maintenance energy is constant and independent of the growth rate, the substrate uptake rate can be expressed as follow:

$$-r_{su} = \frac{r_{X,VSS}}{Y^g} + k_{m,S} \cdot X \qquad \textbf{(3-10)}$$

where $k_{m,S}$ = constant maintenance energy coefficient, $m^{-3}d^{-1}$

The maintenance coefficient $k_{m,S}$ and the true yield Y^g permits modelling of the process, including final biomass concentration at steady state. Limiting nutrient concentrations hinder nutrient diffusion and subsequent transport into the cell. The availability and the transport of substrate to the cell surface and then through several cell layers is the central problem under nutrient-limited conditions. The demands for energy and biosynthesis can only be satisfied by physiological adaptations, i.e. to maximise the limited nutrient transport by increased synthesis of membrane-bound permeases or initiating synthesis of high-affinity transport systems is a common response to nutrient limitation. (Konopka, 2000)

Later studies have shown that $k_{m,S}$ is not constant, especially when growth is limited by other sources than the energy substrate. In a literature review undertaken by Drews and Kraume (2007) only a few variations of $k_{m,S}$ have been observed in the operation of MBR, with no reported valid correlation for the influence of hydraulic residence time, specific growth rate or sludge age. Bouillot *et al.* (1990) and Wisniewski *et al.* (1999) (both cited in Drews and Kraume (2007)) suggest for MBR in wastewater treatment a maintenance coefficient

$k_{m,S}$ = 0.04 mg_{COD} $(mg_{VSS}\ h)^{-1}$ and a true yield of Y^g = 0.36 mg_{VSS} $(mg_{COD})^{-1}$.

Under sufficient energy substrate supply, the formation of energy storage substances (e.g., glycogen) is presented by Pirt (1982) via a growth dependent term in his maintenance concept. Still, this growth dependent term is seldom considered in practise:

$$-r_{su} = \frac{r_{X,VSS}}{Y^g} + k_{m,S} \cdot X + \frac{k'_{m,S}}{X} \cdot \left(1 - \frac{\mu}{\mu_{max}}\right) \quad \textbf{(3-11)}$$

Herbert (1958) postulated in his investigation of continuous flow culture the concept of endogenous metabolism where at net zero growth (e.g., cryptic growth) the substrate uptake is explained by lysis of existing cells. Similar to the maintenance concept, the endogenous metabolism takes place in parallel to anabolism and can be neglected in processes with sufficient substrate supply. If the cell tissue is not completely used for reuse in new cell synthesis, then the lysis rate is named as the decay coefficient k_d.

Nitrogen Removal Mechanism

Nitrogen is increasingly important in wastewater management because of the many effects of nitrogen on the environment, e.g. eutrophication. Nitrogen exists in various forms, depending on the oxidation states, and can readily change from one form to another. The principal forms of nitrogen are organic nitrogen, ammonia, nitrite, and nitrate. Ammonia is extremely toxic to fish and many other aquatic organisms and in addition it consumes the DO in water, increasing the potential of fish die-off. All forms of nitrogen are taken up as a nutrient by photosynthetic blue-green bacteria and algae, which then excessively grow and resulting in the so called algal bloom. Although nitrate itself is not toxic, its conversion to nitrite is a concern to public health, because of its hazardous effects in water consumed by infants. In the body, nitrite can oxidise the iron (II) and form methemoglobin, which binds oxygen less effectively than normal haemoglobin. The resulting decrease in oxygen levels in young children leads to shortness of breath, diarrhoea, vomiting, and in extreme cases even to death.

The biodegradation of nitrogen in a wastewater treatment consists of two processes: Nitrification under aerobic conditions and denitrification under anoxic conditions. Sequence batch reactor systems have been successfully applied throughout the world for carbon removal, nitrification and denitrification (Artan et al., 2001; Bernardes and Klapwijk, 1996; Kargi and Uygur, 2003; Peters et al., 2005). Where membrane technology is applied, complete retention of micro-organisms can encourage the growth of specialised microorganisms, potentially improving the performance further. However, Manser *et al.* (2005) has concluded that the membrane separation neither enhances the nitrification performance nor improves the safety against overloading or wash-out compared to a CAS system, because both systems exhibited a similar maximum nitrification rate with average values of 33±5 and 36±5 mg_N $(g_{COD}\ d)^{-1}$ at 20°C, respectively.

Nitrification

The biological oxidation of ammonia with oxygen into nitrite followed by a further oxidation into nitrate is called nitrification and a central position within the global nitrogen cycle. Nitrifying bacteria are the only organisms capable of converting the most reduced form of nitrogen, ammonia, to the most oxidised form, nitrate and also carry out a range of other important processes within the nitrogen cycle. The first step is done mainly by *Nitrosomonas*, and the second step (oxidation of nitrite into nitrate) is done mainly by *Nitrobacter*. Nitrifying organisms are chemoautotrophic, and use carbon dioxide as their carbon source for growth.

Nitrification proceeds usually through the transformation of ammonia to nitrate:

- Nitritation: $NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + H_2O + 2\ H^+$
- Nitratation: $NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$

Complete nitrification has been demonstrated in MBR at sludge ages of 5-72 days and organic loading rates of 0.05-0.66 $kg_{BOD}\ m^{-3}\ d^{-1}$ (Stephenson et al., 2000). Sludge age has been shown to have an influence on nitrification in MBR. Stephenson et al. (2000) reported an increase of the ammonia removal efficiencies from 94 to 99% on doubling the sludge age from 5 to 10d, and Innocenti *et al.* (2002) showed an increase in the ammonia uptake rate (AUR) from 0.13 to 2.51 $mg_{NH4\text{-}N}\ (g_{VSS}\ h)^{-1}$ coupled to a change in SRT from 10d to 190d.

Bacteria, capable of nitrification, show generally a low specific growth rate of about 1/day (Henze et al., 1987), therefore process operations have to prevent a wash out of biomass, meaning a minimum sludge age of > 5 days is necessary in order to ensure complete nitrification (Fan et al., 2000).

Under optimal conditions the oxidation rate of nitrite is higher than the one of ammonium, so no accumulation of nitrite occurs. By accepting the stoichiometry, the nitrification process requires 3.43 $g_{O2}\ g_N^{-1}$ and 1.14 $g_{O2}\ g_N^{-1}$ for the two reaction steps.

In order to characterise the nitrification process, one of the most used parameters is the nitrification rate also known as ammonium utilisation rate (AUR). The kinetics of nitrification can be modelled by zero-order and first-order reactions, or as done in most nitrification studies by a Monod type equation. It expresses the effect of substrate concentration on the growth of nitrifying bacteria. The effects of ammonia and dissolved oxygen on the growth rate are described in equation (3-12):

$$\mu_{X,AUR} = \mu_{X,AUR_{\max}} \cdot \frac{c_{NH_4^+-N}}{K_N + c_{NH_4^+-N}} \cdot \frac{DO}{K_O + DO} \cdot \frac{c_S}{K_S + c_S} \quad \textbf{(3-12)}$$

where DO = dissolved oxygen, mgL^{-1}
K_N = half-saturation constant for NH_4-N, mgL^{-1}
K_O = half-saturation constant for DO, mgL^{-1}
$\mu_{x,AUR}$ = specific growth rate of nitrifying bacteria, d^{-1}
$\mu_{x,AURmax}$ = maximum specific growth rate of nitrifying bacteria, d^{-1}

Typical kinetic coefficients for activated sludge are K_N = 0.2-5 $mg_{NH4}\ L^{-1}$, and K_O = 0.3-1.3 $mg_{DO}\ L^{-1}$ (Metcalf and Eddy, 2003). AUR can then be calculated according to this equation:

$$r_{AUR} = \frac{dc_{NH_4^+-N}}{dt} \cdot \frac{1}{oTS} \quad \textbf{(3-13)}$$

where oTS = organic total substances, mgL^{-1}
r_{AUR} = ammonium utilisation rate, $mg_{NH4\text{-}N}\ (g_{oTS}\ h)^{-1}$

Generally this rate is measured at 20°C without substrate limiting conditions. Many experimental data of different specific AURs are quoted in Kraume *et al.* (2005). It has been demonstrated that the nitrification activity in an MBR can be twice as high as in a normal ASP plant, with 2.28 $mg_{NH4\text{-}N}\ (g_{oTS}\ h)^{-1}$ for an MBR compared to 0.96 $mg_{NH4\text{-}N}\ (g_{oTS}\ h)^{-1}$ for the normal ASP process (Zhang et al., 1997).

Denitrification

The reduction of nitrate and nitrite into gaseous nitrogen is called denitrification. The process is performed by heterotrophic bacteria (such as *Paracoccus denitrificans*, *Thiobacillus denitrificans*, and various pseudomonads) under special conditions in both terrestrial and marine ecosystems. In general, it occurs when oxygen (which is a more favourable electron acceptor) is depleted, and bacteria have to turn to nitrate in order to deplete organic matter. Denitrification proceeds through the transformation of nitrate to nitrogen gas:

- Substrate + 4 NO_3^- + 4 H^+ → 5 CO_2 + 2 N_2 + 2 H_2O

The denitrification process requires electrons donors, such as organic substances or hydrogen. It has been demonstrated that under electron donor limitations the formation of intermediates can occur easily. This means that heterotrophic bacteria need an external organic carbon source to accomplish their life functions; therefore the available carbon source influences the denitrification process. For example easily degradable substrates, like acetate or glucose,

allow a higher denitrification rate. This parameter is used to characterise the denitrification process and is also known as the nitrate-nitrogen utilisation rate (NUR). The growth of denitrifying bacteria is influenced by the substrate and by nitrate concentration and can be described as written in the following equation:

$$\mu_{X,NUR} = \mu_{X,NUR_{\max}} \cdot \frac{c_{NO_3^- - N}}{K_{NO_3} + c_{NO_3^- - N}} \cdot \frac{c_S}{K_S + c_S} + k_d X \qquad \textbf{(3-14)}$$

where K_{NO3} = half-saturation constant for NO_3-N, mgL^{-1}
$\mu_{x,NUR}$ = specific growth rate of denitrifying bacteria, d^{-1}
$\mu_{x,NURmax}$ = max. specific growth rate of denitrifying bacteria, d^{-1}

Biological denitrification studied by Dangcong *et al.* (2005) in an SBR to investigate the performance showed that a removal efficiency of more than 99% can be achieved with a granular sludge of high activity and good settling ability exposed to high nitrate loading rate (0.48 $kg_{NO3\text{-}N}$ m^{-3} d^{-1}). Peters *et al.* (2005) could confirm a simultaneous nitrification denitrification because of very low NO_x values of 1.93 mgL^{-1} in the effluent, which can be attributed to the design of the reactor for the maximisation of carbon storage for subsequent denitrification, as well as to the effective aeration control which ensures no over-aeration during the air-on cycle. In opposite, Wilderer *et al.* (1987) showed lower denitrification rates due to the accumulation of nitrite in the medium. The author proposed that a brief aerobic reaction period can be helpful to promote rapid uptake of organics in order to avoid the production of nitrite.

The kinetic reaction rate for denitrification in activated sludge processes can be expressed by equation (3-15), where the value is calculated as the sum of nitrite and nitrate over time. This should be used where the nitrite production during the denitrification process is visible.

$$r_{NUR} = \frac{d\left(c_{NO_2^- - N} + c_{NO_3^- - N}\right)}{dt} \cdot \frac{1}{oTS} \qquad \textbf{(3-15)}$$

where r_{NUR} = nitrate-nitrogen utilisation rate, $mg_{NOx\text{-}N}$ $(g_{oTS}\ h)^{-1}$

Different data are reported in literature, depending on the kind of available C-source. Easily degradable substrates, such as acetate allow rates of 1.1-4.3 $mg_{NO3\text{-}N}$ $(g_{MLVSS}\ h)^{-1}$ (Kristensen et al., 1992) or such as synthetic feed allow rates of up to 11.4 $mg_{NOx\text{-}N}$ $(g_{MLVSS}\ h)^{-1}$ (Soriano et al., 2003). Vocks *et al.* (2005) showed in an MBR for enhanced nutrient removal that even without dosing of an external carbon source in post-denitrification systems the denitrification rates (NUR) in average of 2.2 $mg_{NO3\text{-}N}(g_{MLVSS}h)^{-1}$ are significantly over endogenous rates. The anaerobic reactor for the enhanced biological phosphorous removal (EBPR) located ahead of the process had a positive impact on the DNR.

3.4.4 The Activated Sludge Model (ASM)

Reliable mathematical models, balance equations for the individual parameters (substrate, biomass, nutrients), and valid bio-kinetc parameters are needed as key parameters for design, monitor and control of an optimal process performance. Therefore it is part of this work to develop model equations validated by experimental results, to design future greywater treatment ASP.

In 1962, the first rational kinetic theory of the activated sludge process was introduced by McKinney, pronouncing the importance of sludge age, F/M ratio and the division of the sludge into an active, an endogenous and an inert fraction (Marais and Ekama, 1976). Since then, numerous models describing the kinetic behaviour of microorganism, the removal of carbon, nitrogen and phosphorous in activated sludge processes have been developed. The most commonly used and still up to date is the activated sludge model (ASM), with its different specifications (ASM No. 1, 2, 2d, 3) (Henze et al., 2000). The work of the group that developed these models promotes the structural presentation of biokinetic models via a matrix format, which is easy to read and understand, and contains much of the existing knowledge on the activated sludge process. To illustrate the functional depth of the model, a simple matrix is erected for growth of heterotrophic organism in Table 3-1.

Table 3-1: ASM model for heterotrophic growth in aerobic conditions; taken from: (Henze et al., 2000)

← Mass Balance	Continuity →					
	Component i		1	2	3	Process Rate, ρ_j
	j	Process	X_B	S_S	S_O	$[ML^{-3}T^{-1}]$
	1	Growth	1	$-\frac{1}{Y}$	$-\frac{1-Y}{Y}$	$\frac{\mu \cdot S_S}{K_S + S_S} X_B$
	2	Decay	-1		-1	$k_d \cdot X_B$
	Observed Conversation Rate $ML^{-3}T^{-1}$		$r_i = \sum_j r_{ij} = \sum \nu_{ij} \rho_j$			Kinetic Parameters:
	Stochiometric Paramters:		Biomass $[M(COD)L^{-3}]$	Substrate $[M(COD)L^{-3}]$	Oxygen as neg. COD $[M(-COD)L^{-3}]$	Maximum specific growth rate: μ Half-velocity const.: K_S Specific decay rate: b
	True growth yield Y^g					

First, all relevant components must be identified. In the above given example, this would be biomass (X_B), substrate (S_S) and dissolved oxygen (S_O). The index i counts the components, in this case i=1;2;3. Second, all biological processes that occur in the examined system shall be determined and will be counted by the index j. In the example there are only two processes: heterotrophic growth and decay, which means that j = 1 or 2. It needs to be mentioned that the nomenclature of the ASM is taken for this work to be conform. The symbol X means the insoluble, particulate components and the index S is defined for soluble components. The subscripts then specify the individual components to distinguish between

different fractions in the observed system.

The kinetic rate equations are written in the rightmost column and denoted as ρ_j, whereas the stoichometric coefficients are defined in the lower left corner. Now, the matrix can be read in two directions: for mass balance purposes - downwards in a column presenting a component and for continuity check - across the matrix with the sum of the stoichometric coefficient equal to zero. In the given example, the specification for a mass balances would lead to the following process rates:

$$r_{X_B} = \frac{\mu \cdot S_S}{K_S + S_S} X - k_d \cdot X \qquad \textbf{(3-16)}$$

$$r_{S_S} = -\frac{1}{Y} \cdot \frac{\mu \cdot S_S}{K_S + S_S} X \qquad \textbf{(3-17)}$$

where k_d = endogenous decay coefficient, $g_{VSS}(g_{VSS}d)^{-1}$
$r_{X,s}$ = rate of biomass production due to rbCOD, $gm^{-3}d^{-1}$
$r_{S,s}$ = rate of soluble substrate change, $g_{VSS}m^{-3}d^{-1}$
$r_{X,\,VSS}$ = rate of total VSS production, $g_{VSS}m^{-3}d^{-1}$
S_S = soluble substrate concentration, gm^{-3}
Y = biomass yield, $g_{VSS,\,produced}(g_{substrate,\,removed})^{-1}$

Please read the book on the activated sludge models from the IAWQ task group on mathematical modelling (Henze et al., 2000) for further information.

The growth rate of both heterotrophic and autotrophic organisms in the model is described by the Monod relationship. COD is selected as the suitable parameter for defining the carbonaceous material as it provides a link between electron equivalents in the organic substrate, the biomass and the oxygen utilised, and furthermore, mass balances can be made in terms of COD. The introduced bisubstrate hypothesis states that the biodegradable COD in the influent wastewater consists of two fractions: readily and slowly biodegradable COD. The rbCOD are made of simple molecules able to pass through the cell wall immediately. The sbCOD, which consists of larger complex molecules, is enmeshed in the sludge. After extracellular enzymatic breakdown (often referred to as hydrolysis) the substrate is released to the bulk liquid and transferred through the cell wall and used for metabolism. The death-regeneration hypothesis is the attempt to single out the different reactions that take place when organisms die. The decayed cell material is released through lysis: One fraction being non-biodegradable and adding to the inert residue, while the other, remaining fraction is slowly biodegradable, able to return to the process and be used by the remaining organisms as substrate through hydrolysis.

The assumptions made in the ASM concerning the aqueous environment are valid for most municipal wastewaters, because of their sufficient buffer capacity and low concentration on

C, N, and P (Sotemann et al., 2005). The authors stated also that there are exceptions to be made, when wastewaters outside the average range are investigated (e.g., low COD pollution, or a weak acid-base-balance), resulting in sludge characteristics with variations in growth rate and substrate consumption behaviour. However, experimental determinations of qualitatively different parameters and investigation of identifiability of applied data provide the basis for a successful application of all models.

Key features and assumptions of the model

- Heterotrophic bacteria are the main group for COD depletion under both aerobic and anoxic conditions, with the only difference in the use of nitrate as electron acceptor under anoxic conditions (Henze et al., 2000). Furthermore, the kinetic expressions in the model are based on switching functions (Monod equations), which means they are either active (=1) or inactive (= 0).
- Growth, maintenance and decay processes can be best described as suggested by (Beeftink et al., 1990). Substrate (NH_4, NO_2 , S_S) is utilised for growth and maintenance of the ammonia oxidisers, nitrite oxidisers and heterotrophic bacteria.
- Nitrification is a two-step process, carried out by two types of nitrifying biomass. Therefore nitrite accumulation must be taken into account (Brouwer et al., 1998).
- The decay rates can be subdivided into the aerobic decay, which occurs when the bacteria starve in the presence of oxygen, as well as the anoxic decay, which occurs when the bacteria starve in the absence of oxygen and in the presence of nitrate.
- A predation mechanism is considered in the model by introducing predators as active biomass, as proposed by van Loosdrecht and Henze (1999). The predation rate is a function of the bacterial concentration and squeezed into one decay process. This process represents the sum of all decay and loss processes of the predators like lysis due to phage infection and predation by metazoa. This decay and predation processes result in the generation of inert biomass that is not further metabolised.

Data Determination with the Help of Respirometry Measurements

The measurement of the biological oxygen consumption, directly associated with biomass growth and substrate removal, under defined experimental conditions and the interpretation of the obtained data is know as respirometry (Spanjers et al., 1998). With this method, it is possible to estimate wastewater characteristics in the context of the ASM. Next to the oxygen uptake rate (OUR) measurements, titrimetric (cumulative production), or a combination of both experiments are also common methods to estimate biokinetic parameters for heterotrophic and autotrophic process for the mathematical models, e.g. (Cokgor et al., 1998; Corominas et al., 2006; Dircks et al., 1999; Ekama and Marais, 1979; Gapes et al., 2004; Kappeler and Gujer, 1992; Kristensen et al., 1992; Petersen et al., 2003; Sollfrank and Gujer, 1991; Sozen et al., 1998; Vanrolleghem et al., 1999; Wentzel et al., 1995).

The combination of respirometric and titrimetric data obtained from aerobic oxidation of different carbon sources have been used by Sin and Vanrolleghem (2007) for the enhancement of ASM No.1, in order to describe the nonlinear carbon dioxide transfer rate behaviour with a simple calibration procedure of the CO_2-model, only using titrimetric data. Gernaey *et al.* (2001) used also a combined respirometric–titrimetric set-up to monitor the degradation processes during batch experiments with activated sludge, where the cumulative amount of added acid and base serves as a complementary information source on the degradation processes.

4 Material & Methods

4.1 Synthetic Greywater

For this study synthetic greywater (Table 4-1) is used and the receipt is designed according to Jefferson et al. (2001), Komschuvara (2002), and Kuhn and Mujkic (2003). On the one hand it represents the greywater of a 4-person household. On the other hand the composition is comparable to real greywater from the shower effluent of a Moroccan sports club, which was investigated within the Zer0-M project (Merz et al., 2007) and greywater of other studies where kitchen effluents are not included (Jefferson et al., 2000). Chemicals, like urea and ammonia are added to investigate the performance of nitrogen removal with water of low carbon concentration. Urea (carbamide) ($(NH_2)_2CO$) is the diamid of carbon acid, with an nitrogen amount of 46%. Urea is easily water soluble, colourless, odorless, and neither acidic nor basic. Urea is the end product of the protein metabolism of mammals and beside water the main component of urine. Furthermore urea is part of the human skin and is used in small amounts in cosmetics and pharmaceutics because of its healing effects in the dermatologic context.

Table 4-1: Recipe of synthetic greywater and its resulting feed concentration

ingredients	**approx. daily amount p.P.**	**feed concentration** ($mg\ L^{-1}$) or ($mL\ L^{-1}$)
tooth paste	1.2 g	6.0
shower gel	10 mL	0.05
cleaner	20 mL	0.1
shower oil*	1.0 mL	0.05
shampoo	2.5 mL	0.013
bubble bath	7.0 mL	0.035
urea	4.0 g	20.0
NH_4Cl	2.5 g	12.5
K_2HPO_4	0.5 g	2.5
BOD_5		**50±11 mg O_2 L^{-1}**
COD		**209±80 mg O_2 L^{-1}**

* with 50% ricinus oil

4.2 Experimental Set-up of the Treatment Plants

As mentioned earlier, the SBR process allows the change of operation conditions, depending on the influent concentration as well as the effluent discharge criteria. Mainly three options are easy to perform:

- changes in feeding pattern,
- changes in VER and
- changes in cycle time, including the variation of each phase.

The cycle times were chosen according to values found in literature, where SBR have been

operated with cycle times varying from t_c=3h (Shin and Kang, 2002) over t_c=4h (Innocenti et al., 2002; Kang et al., 2003), and t_c=6h (Artan et al., 2002) to t_c=12h (Bae et al., 2003; Kargi and Uygur, 2003).

Three different reactors were operated at the Technische Universität Berlin, Chair of Chemical Engineering:

- Set-up A: 29L lab scale reactor, configured as a membrane loop reactor
- Set-up B: 1000L commercially available MBR for the treatment of domestic wastewater (4-8pe)
- Set-up C: 500L pilot scale reactor, first with storage tank (= set-up C_{stor}) and later with direct feeding of greywater concentrate and drinking water into the biological tank (= set-up C_{direct})

The first trials were carried out with a small 29L lab scale reactor in order to verify the possibility of greywater treatment. In parallel, a commercially available system with a tank volume of 1000L was operated to scale-up and transfer results from the lab scale into real technical applications. Unfortunately the low flux of the membrane did not allow sufficient changes in the set-up B. Therefore, after two years, a third SM-SBR with a tank volume of 500L was built and put into service. New membrane modules and the elimination of the storage tank have been practised there. The step by step approach resulted in a constant improvement of performance and decrease of HRT. An overview of the different operational process conditions is given in Table 4-2.

Table 4-2: Operating conditions

Parameter	set-up A	set-up B	set-up C_{stor}	set-up C_{direct}
SRT, d	> 250	> 360	>360	>400
HRT, h	13-60	33-100	33 and 24	12 and 8
Cycle time (t_c), h	4-6	4-12	3-8	2-3
$TS_{reactor}$, gL^{-1}	1.5 - 3.5 (start-up) 1.5 - 4.5	0.8 - 1.2 (start-up) 2.0 - 3.1	2.5-4.5	4.5-13.0
$oTS_{reactor}$, %TS	65-70	60-70	70-80	80-90
F/M, $g_{COD,in}(g_{oTS,reactor}\ d)^{-1}$	0.124	0.074	0.06	0.05
aeration rate, $Nm^3(m^2h)^{-1}$	not measured	not measured	4	4
L_{org}, $g_{COD}(Ld)^{-1}$	/	0.049±0.010	0.076±0.034	0.076±0.034
VER	0.1-0.5	0.12	0.25	0.25
flux, L $(m^2h)^{-1}$	7.0-13.0	8.5-12.5	5.0-12.0	35.0-15.0
TMP, bar	0.1-0.4	0.1-0.15	0.1-0.4	0.08-0.12

It needs to be pointed out that all configurations were operated with very long sludge ages to minimise the excess sludge production for an easier handling in remote areas and with and low fluxes to obtain long maintenance intervals.

4.2.1 Set-Up A: The 29L Lab scale Reactor

The 29L rectangular bioreactor (cf. Figure 4-1) was equipped with one submerged PF module (A3 GmbH) comprising twelve elements with a total microfiltration membrane area of 0.38 m². Permeate was removed using a peristaltic pump sited in the permeate line. The reactor volume and the TMP was measured by pressure transducers located at the base of the reactor and in the permeate line respectively. A fine bubble membrane diffuser was used to supply air for both biological aeration and membrane air scour. Airflow was controlled via a needle gauge and a motor driven stirrer was used to ensure complete mixing during the anoxic phase. The variations of VER was set by a pressure transducer at the bottom of the tank. The Siemens programmable logic controller (PLC) controlled the single SBR phases, the feed mode, as well as stirrer speed and aeration intensity via electrically actuated solenoids.

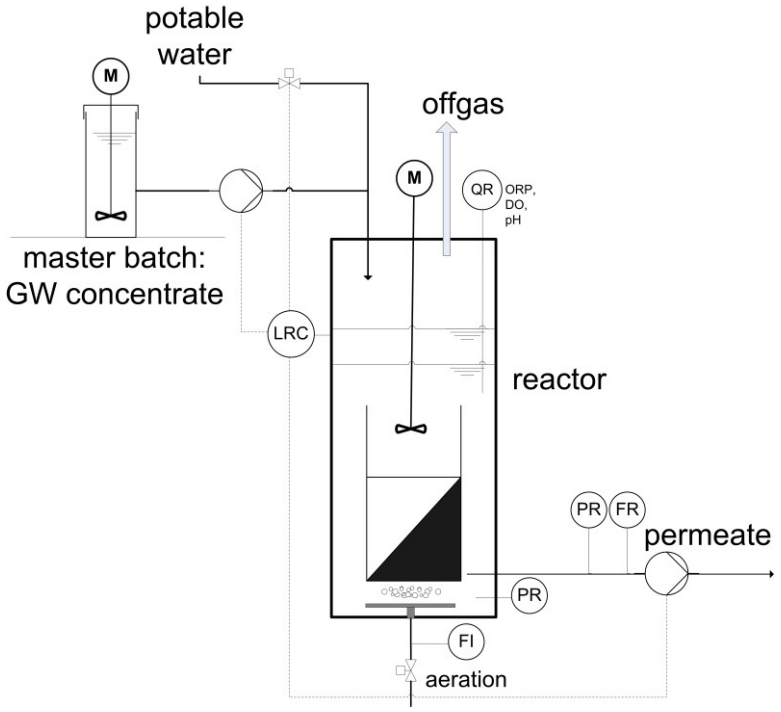

Figure 4-1: Scheme of the 29L lab scale reactor

Run Mode of the Reactor

The time was varied for the anoxic phase from 60 to 120 min and for the aerated phase from 180 min to 270 min. The static filling took about 2 min at the beginning of the anoxic phase. The VER was set in the range of 0.2 to 0.5. Experiments started with investigations on the membrane behaviour with VER=0.5, and were followed by investigations with VER=0.3-0.2 to assess the treatment performance under changing conditions and to validate simulations based on microbial kinetics. The permeate withdrawal started usually 5 min after the beginning of the aerated phase. The reason for the short waiting period was owned to the

reachability of short HRT with membrane modules of low permeability.

The following run modes, illustrated in Table 4-3, have been applied to set-up A.

Table 4-3: Run modes of set-up A: The Lab scale reactor

run mode	HRT [h]	VER	anoxic phase [min]	aerated phase [min]
I	12	0.5	90	270
II	9	0.5	90	180
III	20	0.3	120	240
IV	15	0.3	90	180
V	13	0.3	90	150
VI	13	0.3	60	180
VII	30	0.2	150	210
VIII	22.5	0.2	90	150
IX	40	0.1	90	150

4.2.2 Set-Up B: The 1000 L Reactor

A 1m^3 reactor was utilised as a small wastewater treatment application (4-8pe) for research purposes in the field of greywater treatment. The commercially available BioMir® reactor system by BUSSE Engineering (cf. Figure 4-2) consisted of two 1 m^3 tanks, one for storage and the second for biological treatment. A fine bubble membrane diffuser was used to supply air for the biological aeration and a coarse bubble aerator was used to supply air for the membrane air scour. Airflow was set constant at a rate of 60 $Lmin^{-1}$ with an air compressor and a PLC controlled and operated the single SBR phases (feed, reaction and withdrawal).

In the first phase (until day 300) one submerged plate and frame module (A3 GmbH) was introduced into the biological reactor, comprising 22 elements with a total MF-membrane area of 3.9 m² and permeate was removed by gravity. In the second phase the membrane area was doubled by adding a second module of the same specifications. Permeate was removed by a suction pump. The volumetric exchange ratio was set with the level controller at constant VER = 0.12. The informations from the probes (DO and OPR), as well as from the pressure transducer for the fluid level in the biological reactor were directly recorded in the computer.

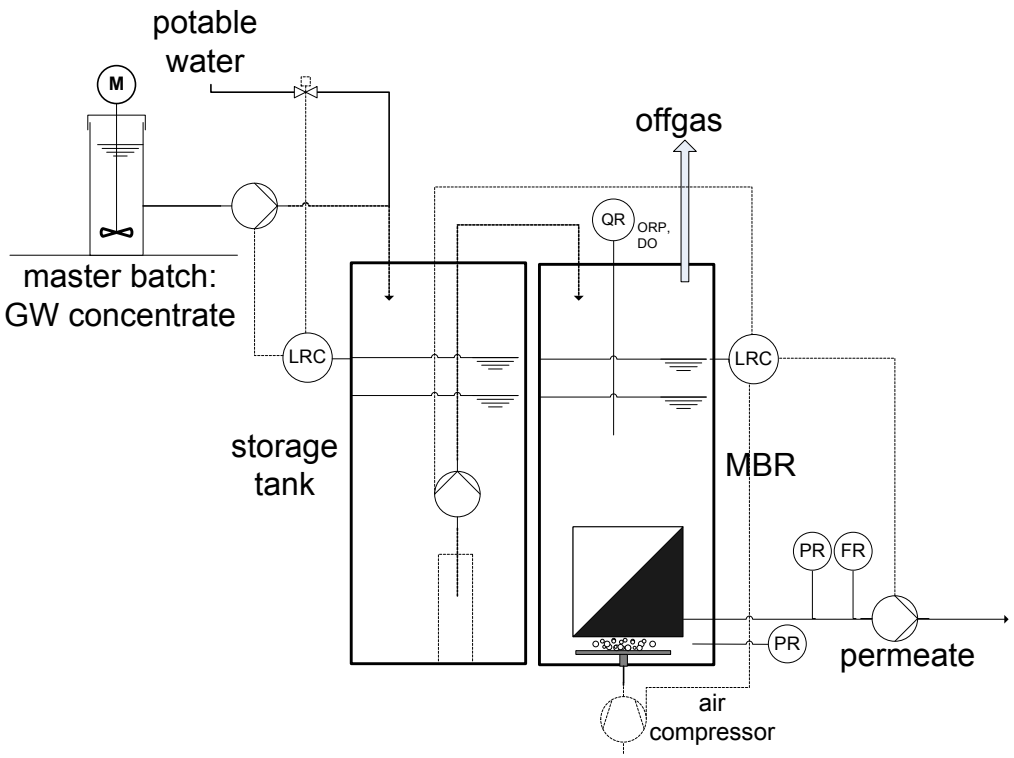

Figure 4-2: Scheme of the 1000L reactor

Run Mode of the Reactor

Set-up B was operated at three different cycle time setting, but with a constant VER. The first run was set to a cycle time of 12h (240 min for the anoxic phase and 480 min for the aerated phase). Due to very long HRT, the cycle time was reduced by half to t_c=6h (180 min for the anoxic phase and 180 min for the aerated phase) during run II. After introducing a second membrane module into the reactor, the cycle time was shortened further more in run III to t_c=4h, reducing the anoxic phase to 90 min and the aerated phase to 150 min. Still, the permeate withdrawal was started shortly after the beginning of the aerated phase. The reason was owned to the reachability of short HRT with membrane modules of low permeability. The VER was held constant at 0.12 for all set-ups. The following run modes, illustrated in Table 4-4, have been applied to set-up B.

Table 4-4: Run modes of set-up B: The 1000L BUSSE reactor

run mode	HRT [h]	anoxic phase [min]	aerated phase [min]
I	100	240	480
II	50	180	180
III	33	90	150

The solids retention time can be assumed to be greater than 360 days, because no biomass was taken out, except for sampling of around 200 mL per week out of the biological reactor.

The theoretical SRT can be calculated and equals 35,000 d for the known conditions: The reactor volume V_R is 1000 L, the TS concentration is 4.5 gL^{-1} after 300 days of operation. The amount of daily excess sludge production equals the sampling volume and is 0.03 Ld^{-1}.

4.2.3 Set-Up C: The 500 L Pilot Scale Reactor

The 500L pilot scale SM-SBR was operated in two different set-ups, with a constant VER of 0.25 for all different configurations. A medium bubble aerator was used to supply air for both biological aeration and membrane air scour. Airflow was controlled via a needle gouge and a PLC controlled and operated the single SBR phases (feed, reaction and withdrawal). The data from the probes (DO and OPR) and the pressure transducers (indicating the fluid level) as well as TMP were directly recorded on a computer. The solid retention time is >360d (set-up C_{stor}) and >400d (set-up C_{direct}), respectively, because no biomass was taken out except for sampling of around 200 mL per week out of the biological reactor. The theoretical SRT can be calculated in analogy to set-up B and equals 17,500 d for the known conditions: The reactor volume V_R is 500 L, the TS concentration is 6.7 gL^{-1} after 300 days of operation. The amount of daily excess sludge production equals the sampling volume and is 0.03 Ld^{-1}.

Set-up C_{stor} (cf. Figure 4-3) consisted of two tanks, the first for storage of the synthetic greywater, and the second for the biological treatment and worked with a HRT of 33h, 24h, and 12h. Two submerged polyphenol resin plate and frame modules ($A_{membrane}$ = 7.8m²) were introduced into the biological reactor, taken from the 1000L reactor for the long HRT of 33h and 24h. For HRT = 12h, the membrane modules were replaced by new ones, all identically in size, but made of different membrane materials (PVDF for the MF module; PES for the UF module). Permeate is removed using a peristaltic pump and the reactor volume is controlled by a level controller.

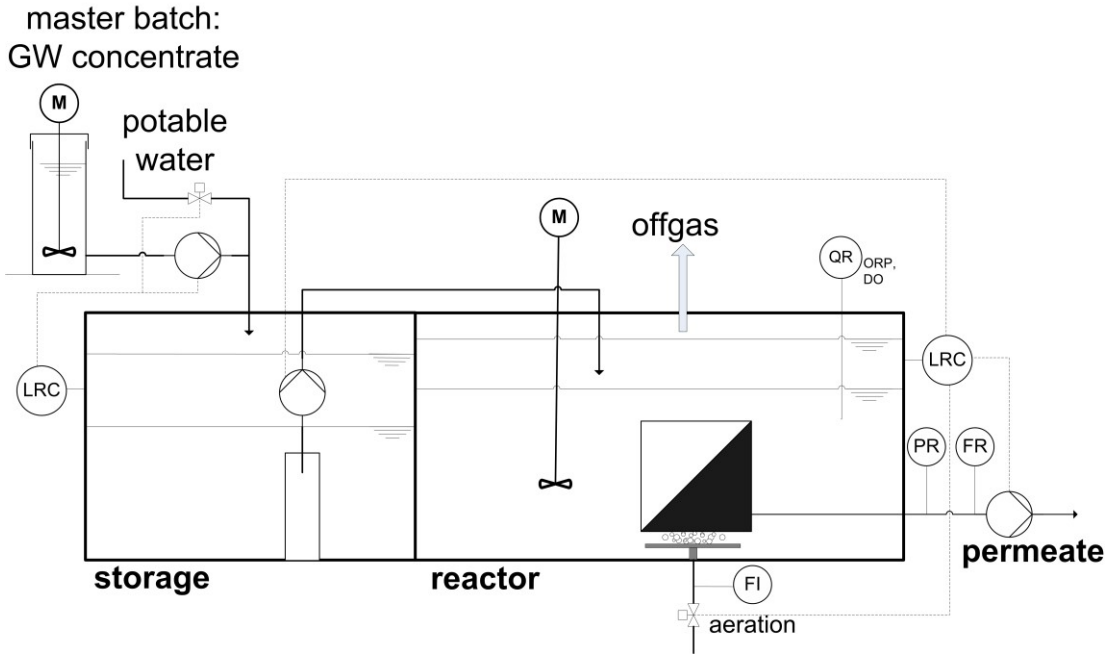

Figure 4-3: Scheme of the 500L set-up C_{stor}

For set-up C_{direct} the greywater concentrate and potable water was mixed directly into the biological chamber (cf. Figure 4-4). The HRT was now 12h and 8h. The last reduction was done togehter with the change of the withdrawal of permeate by gravity flow. The hydraulic head was set to 80 cm. The reactor volume is controlled by a level controller.

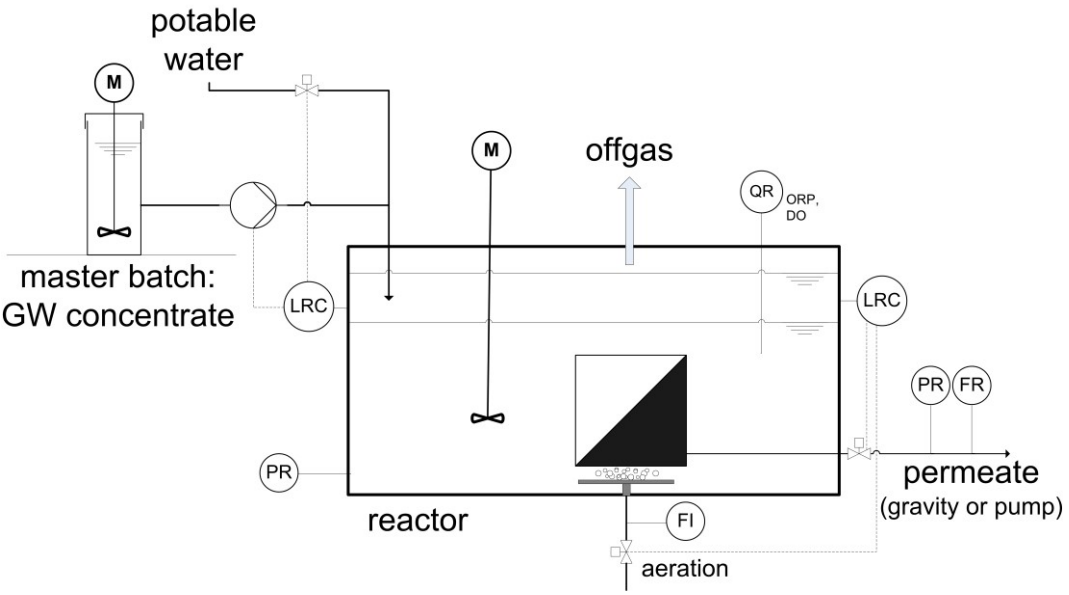

Figure 4-4: Scheme of the 500L reactor set-up C_{direct}

Run Mode of the Reactor

Set-up C_{stor}: The reactor was operated with a constant volumetric exchange ratio of 25% and with a total cycle lengths of 8h, 6h, and 3h. With this set-up, the SBR cycle began with a fill phase of approx. 20-25min, which was included in the anoxic phase. The aerated reaction phase consisted then of a period from 110-300 min, incl. the idle phase. The permeate withdrawal via the peristaltic pump started with begin of the aeration.

Set-up C_{direct}: The reactor was operated also with a constant VER of 25%, but with shorter cycle times of 3h and 2h, compared to set-up A. With the latest set-up, the SBR cycle had only a static fill phase of 5min, which was included in the one hour anoxic phase. The aerated reaction phase consisted then of a period of 60 min, incl. the idle phase. The permeate withdrawal via gravity started with begin of the aeration, because of comparability reasons with the other set-ups.

The following run modes, illustrated in Table 4-5, have been applied to set-up C.

Table 4-5: Run modes of set-up C: The 500L reactor

Set-up	run mode	HRT [h]	anoxic phase [min]	aerated phase [min]
C_{stor}	I	33	180	300
	II	24	150	210
	III	12	70	110
C_{direct}	IV	12	60	120
	V	8	60	60

4.3 Membrane Test Cell Applications

One of the major problems associated with membrane separation processes, which hinders the widespread application of the process, is the reduction in permeability, commonly known as 'membrane fouling'. For the design of a membrane process the characterisation of the suspension is needed for prediction of required membrane area and optimal operating conditions.

Therefore, filtration tests with a test cell were applied to investigate the fouling potential of greywater sludge from the SM-SBR. In addition, nanofiltration (NF) membranes were tested for the physical greywater treatment as an alternative to the membrane coupled biological process. The obtained data were analysed and compared with the membrane behaviour in the pilot plants, and with data from other test cell investigations undertaken with sludge from different MBR processes in wastewater treatment.

Next to the test cell application, critical flux investigations have been performed within the 29L lab scale reactor. The method will be described next, before coming to the two test cell assembles.

4.3.1 Critical Flux Determinations within the Lab Scale Reactor

In all tests permeate was returned to the top of the reactor to maintain practically a constant head on the retentate side of the membrane, which means that changes in TMP were assumed to be solely due to fouling. TMP was taken to equate to the difference between the average hydraulic head at the mid-point of the membrane module and the permeate pressure. The permeate flux was calculated by collecting a volume of filtrate over a defined time period and was then repeated three times and an average calculated. The reactor was allowed a minimum of 24h to recover between the tests.

Between each run, the small module was removed from the reactor, chemically cleaned and tested with clean water to detect signs of permanent fouling prior to the next test. The cleaning involved an initial 1h circulation with a pH adjusted 0.5% wt. sodium

dichlor-isocyanurat solution through the module followed by a 12 hour soaking period. The module was subsequently mechanically washed with clean water followed by a throughput of clean water for 1h prior to use.

4.3.2 Aerated Test Cell

In the aerated test cell, all experiments were carried out in a cross flow filtration module, which was designed specifically for biological sludge. The module was operated at a channel heights of 5 mm, variable cross flow velocities, variable aeration rates and in different operating mode (either ΔP=const or J=const). It has an effective membrane area of 0.0088 m².

Around 3-5L of the sludge sample is filled into a double wall storage container (1) where a constant temperature is maintained. The sludge suspension is fed via a peristaltic pump (2) through the pulsation damper (3) into the test cell (4) for membrane investigations. The permeate is collected in a small container on a digital scale (5), where the permeate flow can be quantified. The retentate is returned into the storage container. The test cell allowed a cross flow velocity of 0.02 ms^{-1}. All values of the experiments are recorded with the software "Visual Designer®" to a PC.

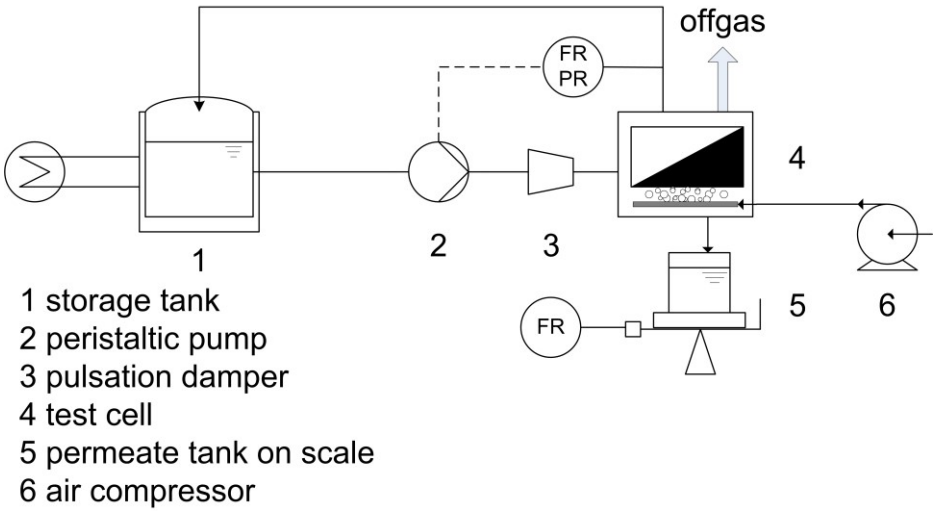

Figure 4-5: Scheme of the aerated test cell

4.3.3 The Amafilter Test Cell for Nanofiltration of Greywater

The scheme of the Amafilter test cell is illustrated in Figure 4-6, which is used for the treatment of greywater with nanfiltration (NF) membranes. As storage container (1) serves a 10-liter-milk jug of stainless steel. In the lower part of the vessel, a pump (2) sucks the feed out of the storage over the feed valve to the test cell (Type UTZ 944; (3)). The permeate is collected in a small jar on a digital scale (4), while the retentate is pumped over the bypass back to the storage tank. The temperature of the feed is kept constant.

The pressure and the cross flow velocity inside the test cell were set and regulated with the PC program "Visual Designer®" via the pressure valve, the bypass valve and the frequency of

the pump. The test cell itself was cylindrical with a flat flow channel across the membrane surface to guarantee a permanent contact with the feed solution. A circular membrane piece with an area of 0.0044 m^2 was laid on the channel, and supported by a fine wire network. The Permeate was removed perpendicular to the membrane.

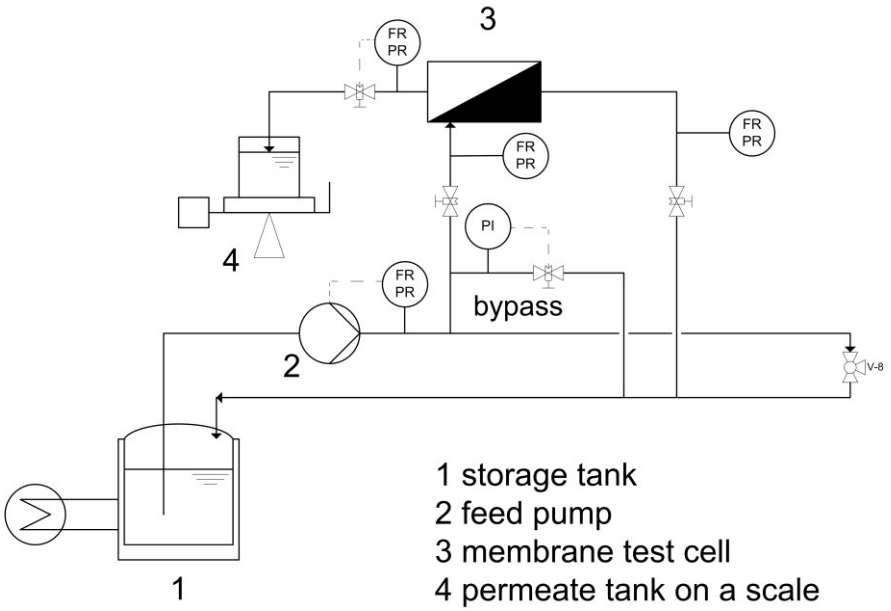

Figure 4-6: Scheme of the Amafilter test cell

Data Collection

The transmitted signals were converted on a PC with the software Visual Designer®. The conversion was controlled by user equations, implemented in the program. The transmembrane pressure (TMP) was calculated from the difference between permeate and retenate pressures. The permeate flow was calculated from the slope of the time depending scale values. The flux was calculated from the permeate flow divided by the membrane surface area of 0.0044 m^2. The cross flow velocity on the membrane surface was calculated out of the channel area and the retentate volume flow.

Membrane Preparation

Before the start of each experiment, the membrane was cut and immersed for two hours in deionised water before transferred to the test cell. The hydraulic resistance of each membrane was determined individually by measuring the flow of pure water through the membrane. This hydraulic resistance served as comparison among the different membranes.
The synthetic greywater in the storage tank had a COD with a concentration of approximately 250 mgL^{-1}. The cross flow velocity was to a defined speed; and at the same time, the TMP was regulated at a constant value. For the membrane screening, the pressure difference was chosen according to the manufacturers' recommendations and the temperature was set to

25°C. The trials started 10min after the desired temperature was reached.

24h batch experiments were carried out to judge the separation capacity in terms of COD of the tested membranes, in which the greywater circulated in the system; both permeate and retentate where returned into the storage tank. Every five seconds TMP, permeate flow, temperature and the cross flow velocity were recorded. Every two hours for the first 8h a sample of 20mL from permeate and feed was taken, as well as after 22h at the end of each experiment, to investigate a time dependency.

Influence of Operational Parameters

For the interpretation of membrane systems the separation characteristic for the specific membrane wastewater is of significant importance. Therefore, the effects of various operating parameters have been investigated in the Amafilter test cell.

At the beginning of the experiments, the water flow was measured for 30min together with the later used TMP, which ranged from 5 to 25bar. The influence of the feed concentration on the membrane behaviour was determined by changing the concentration by the factor of 2 and 4. By increasing the concentration in the feed concentrate, only ammonia is held at the same low value as used in the screening test to see the effect of monovalent ions on the NF membrane. The concentrate was stored at 4°C to produce freshly 10L feed solutions for the test cell investigations. The experiments were at a constant temperature (25°C or 35°C) and at a constant cross flow velocity of 2 ms^{-1}. The sampling started after one hour of establishing constant operating conditions to measure the following parameter: BOD5, COD, TN and NH_4.

Cleaning

After each test, the Amafilter test cell apparatus was cleaned for 2 hours with distilled water. Once a week, a 0.2% citric acid was used for maintenance cleaning, and afterwards rinsed again with distilled water until the retentate was neutral again.

The membranes were rinsed for the first 30min with deionised water at 25°C, before cleaning with a 0.1% P3 Ultrasil 60A solution at 35°C. Finally, a 30min rinse with deionised water at 25°C was carried out to close the cleaning procedure.

4.4 Batch Tests for Determination of Biokinetic Parameters

Batch tests are used in order to determinate kinetic parameters of microbial activity like oxygen uptake rate (OUR), denitrification or nitrate-nitrogen utilisation rate (NUR), nitrification or ammonia utilisation rate (AUR), phosphate release rate (PRR), and phosphate uptake rate (PUR). These tests are also valuable instruments for characterisation of substrates in wastewater and of biomass in wastewater treatment plants. Furthermore it is useful to characterise these paramters on different days, because biomass behaves as a dynamic system that varies with time. In this work only the first three parameters were calculated, because the

design of the different MBR treating greywater did not incorporate biological phosphorous removal.

In literature, several different methods are established for the determination of kinetic parameters as well as for the COD fractioning of the feed. Most common is the use of respirometry as a tool to measure the activity of microorganism via the usage of DO over time. The advantage of this method is its robustness and its sensitivity. The results of these investigations find their response in dynamic modelling of the activated sludge process, e.g. ASM 1 (Henze et al., 1987), since the kinetic and stoichiometric relationship for COD removal and bioactivity acts on mass balances, which is affected by (Vanrolleghem et al., 1999):

- process rates, depending on kinetic, stoichiometry, and concentration of involved components, such as soluble carbon sources, ammonia, etc.
- transport terms of nutients, depending on concentrations.

The methods in Table 4-6 have been identified to fit best to achieve the goals set in this study.

Table 4-6: Used methods for the determination of kinetic parameters

method	purpose	estimation of:	information needed:
Ekama *et al.*, (1986)	determination of the COD fraction X_s in the influent experimental method for μ_{max} of heterotrophic bacteria	X_S, k_h, K_X, μ_{max}	X_H, Y_H
Kappeler and Gujer, (1992)	simple method to estimate kinetic parameters of heterotrophic biomass determination of COD wastewater fractions also usable for the determination of kinetic parameters of nitrifying bacteria	X_S, X_H, μ_{max}, K_S, k_H	Y_H, k_d
Sollfrank and Gujer, (1991)	stoichiometric parameters necessary for the description of heterotrophic growth and hydrolysis of slowly biodegradable organic matter	Y_H	S_I
Spanjers and Vanrolleghem, (1995)	respirometric measurements at low substrate concentrations for estimation of biokinetic parameters for autotrophic and heterotrophic microorganism simultaneous assessment of decay coefficient	X_S, S_{NH}, Y_A, $\mu_{max,H}$, $\mu_{max,A}$, K_S, b_H, b_A	X_H, Y_H

Sludge from the SM-SBR (in most cases from set-up C, except for some AUR and NUR measurements with set-up B) and synthetic greywater are introduced into a vessel of 3L and 1L at different F/M ratios to carry out the respirometry batch tests for the determination of the OUR. The sample volume was set to 5 mL in order to constant operational conditions during one batch run. The measuring system, as illustrated in Figure 4-7, is adapted from Kappeler and Gujer, (1992) and consists of a closed batch reactor with a volume of either three or one

litre. The biomass respiration rate is assumed to be independent of oxygen input over the liquid surface. The temperature is set to 20°C by a thermostatic water bath, stirring is maintained between 170 and 200 rpm, and the aeration device provides compressed air. The DO sensor is connected with a transmitter to a data registration system and maintained between 4 and 6 $mg_{DO}L^{-1}$.

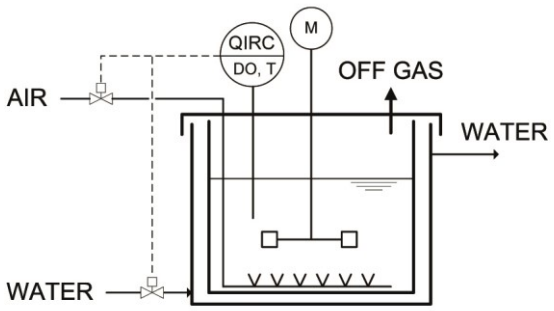

Figure 4-7: OUR batch assembly

Although one run with addition of ammonium chloride did not reveal any activity of the nitrifying bacteria, allylthiourea (ATU) was added to inhibit autotrophic organism, e.g. nitrifiers, activity at a dose of 2 mgL^{-1}, which was adequate for batch of less than 24 hours.

Several runs were undertaken with the addition of sodium acetate at different concentrations as an easy biodegradable C-source for determination of a carbon balance and also for the determination of $\mu_{max,H}$ on a single C-source. In these runs, micro nutrients were added to avoid nutrient limitation other than carbon.

Experiments in a 1L stirred vessel, in analogy to the OUR batch assembly, were undertaken to determine the ammonium utilisation rate (AUR) and the nitrate-N utilisation rate (NUR) by obtaining first aerobic conditions and then anoxic conditions. For some batch runs, acetate was added as an easily degradable C-source to determine the NUR without substrate limitations. The batch was filled with a sample and left idle for 20 minutes. During the run the temperature was maintained at 20°C by a thermostatic water bath and stirred at low 130 rpm all along the experiences. Each run contained two phases, the first started with 90 minutes under aeration with a DO between 8 and 9 $mg_{O2}L^{-1}$, and the second with N_2-gas providing anoxic condition with a DO below 0.3 $mg_{O2}L^{-1}$. Samples were taken every 10 to 20 minutes and filtered through a 0.2 µm cellulose acetate filter to be subsequently analysed using ion chromatography.

4.5 Analytics

4.5.1 Online Parameters

Dissolved Oxygen (DO) and Oxidation-Reduction Potential (ORP) were measured online via calibrated probes (WTW Sentix 41 and Mettler Toledo P14805 respectively for the Lab scale and the batch reactor, whereas WTW Ecoline Oxi 170 and Ecoline pH 170 respectively for the other plants) and recorded directly onto the computer.

4.5.2 Physical Parameters

The electric conductivity (indicates indirectly the salt concentration in the reactor) was measured with the Conductivity Meter LF 340 by WTW, whereas the pH was measured with the pH-Meter 765 Calimatic. The turbidity of the permeate was analysed with the help of the photometer SPECORD 200, by Carl Zeiss Technology, at a wave length of 520 nm, directly after sampling.

The mean particle size was determined with a Mastersizer S (Malvern Instruments GmbH, Herrenberg, Germany) with sample presentation unit, pump, stirrer and UV for a more homogenous mixture of the sample. The 300RF lens was used, allowing the measurement of particle sizes ranging from 0.05 – 900 µm.

4.5.3 Chemical Parameters

All samples were analysed directly after sampling, but if not possible for a maximum of 72h stored at 4°C. Samples preparations were done by the filtration with a cellulose acetate filter (pore size: 0.2 µm, Sartorius), before measuring NO_2-N, NO_3-N, NH_4-N, PO_4-P, according to standardised methods from DIN (1996; 1999) with ion chromatography (DIONEX, DX-100 Ion Chromatograph). The samples for the COD and TN measurement were filtered with a 0.45 µm glass fibre filter by Sartorious, before they were analysed by Dr. Lange kits and spectrophotometry (Dr. Lange, ISIS 9000 MDA Photometer). Later, NO_3-N, NH_3-N, PO_4-P was also measured with the usage of Dr. Lange kits.

4.5.4 Biomass Measurement

The biomass was determined as total volatile suspended solids. The sample was dried for 24 h at 105°C, in order to obtain the total dried weight (TS), before the heating to 550°C for 2 h in a muffle furnace scales the organic fraction of the sludge suspension.

5 Results and Discussion

The results from the investigations are presented and discussed in the following chapter. The gained results and knowledge of the operation and maintenance of the different reactors are used for comparison with the results from the real greywater treating MBRs located at the Zer0-M partner institutes and with the data given in literature. The influence of different HRT on carbon and nutrient degradation, sludge development and permeate quality is investigated with detailed cycle analysis. The rate for degradation of nitrogen compounds in terms of ammonium uptake rate (AUR) and nitrate nitrogen uptake rate (NUR) can be analysed directly out of the SM-SBR operation and validated with batch experiments.

The question arising from the slow biomass growth, whether it was due to the used synthetic feed or whether similar observations were made in greywater treatment with MBR, shall be clarified. The batch experiments for further analysis of biokinetic parameters helped to solve the questionable points and to understand better the characteristica of greywater sludge. These obtained parameters were essential for the description of sludge properties. Furthermore, to understand the treatment concept completely, the COD fractioning of the feed was necessary to set the single fractions into relation with the biokinetic parameters. The incorporation into valid mathematical models like the activated sludge model ASM 1 (Henze et al., 2000) were meaningful for future design of MBR treating greywater.

Next to the evaluation of the biological parameters, it was also of great importance to analyse the membrane behaviour. Therefore, critical flux investigations and determinations of fouling tendencies were carried out. The first runs were done in the lab scale reactor; whereas later experiments were done with the aerated test cell. The obtained results were set in contrast to the online data from operation of the SM-SBR.

In some cases, e.g. treatment and reuse of water in cruise ships, a separation of surfactants and other pollutants from the greywater via nanofiltration membranes may come into action. Therefore first investigations with the Amafilter test cell were carried out. The results are given in chapter 5.3.3.

5.1 Greywater Characteristics

Greywater (cf. Table 5-1) was characterised regarding the proportion of biodegradable COD (expressed as the ratio BOD_5/COD) and the nutrient fraction (expressed as the ratio COD/NH_4 N/PO_4-P). In the literature the ratio BOD_5/COD varied between 0.25 for greywater (Jefferson et al., 1999) and 0.44 for domestic low strength wastewater (Metcalf and Eddy, 2003). The high concentrations of detergents in grey water are known to be slowly biodegradable, explaining the difference to the low strength wastewater. The BOD_5/COD ratio of greywater has a value of 0.24 for the studies done with the SM-SBR. The average ratio of COD/NH_3/TP has been reported typically with 100/5/1 for domestic wastewater

(Metcalf and Eddy, 2003). Kargi and Uygur (2003) calculated an optimum COD/NH_3/PO_4-P for a maximum nutrient removal in the activated sludge process for synthetic wastewater with a five-step SBR of 145/5.87/1, whereas Jefferson et al. (1999) measured a COD/NH_3/TP ratio up to 1030/2.7/1 for greywater, indicating a macro-nutrient limitation. The synthetic greywater used in these investigations have a COD/NH_3/PO_4-P ratio of 121/5.69/1, which is very close to the optimum ratio found by Kargi and Uygur. For the highly diluted greywater from studies done with shower effluent from a sports club the ratio of COD/NH_3/TP is determined at 100/14/1.5, favourable for biological treatment with no limitation concerning the macro nutrients (Merz et al., 2007).

Table 5-1: Greywater characteristics

	average values ± standard deviation				
	own studies	Merz *et* al. (2007)	Masi *et* al. (2007)	Jefferson *et* al. (1999)	Nolde (1999)
pH	7.5±0.3	7.6±0.4			
BOD_5, mgL^{-1}	50±11	59±13		104±45	50-100*
COD, mgL^{-1}	209±80	109±33	502	207±115	100-200
TN, mgL^{-1}	17.3±6.7			9.6	5-10
TKN, mgL^{-1}		15.2±4.5	2.5	3.91±4.72	
NH_4-N, mgL^{-1}	7.3±5.4	11.8±4.2	1.7		
NO_3-N, mgL^{-1}	0.9±0.9		0.32		
TP, mgL^{-1}		1.6±0.53	6.6	3.67±3.88	0.2-0.6
PO_4-P, mgL^{-1}	0.74±1.6	1.0±0.4			
BOD_5/COD	0.24	0.54			
COD/NH_3/TP	121/5.7/1**	100/14/1.5		1030/2.7/1	
Conductivity, µs cm^{-1}		645±67			
Faecal Coliform, $100mL^{-1}$		$1.4*10^5$ ±$1.1*10^5$			10^{-1} - 10^1

* measured as BOD_7 **as COD/NH_3/PO_4-P

5.2 Experiences from Operation of the SM-SBR

The SM-SBR was operated in three different set-ups as described in chapter 4: Set-up A was the 29L lab scale reactor, set-up B was the 1000L pilot scale reactor and set-up C was the 500L reactor. Each configuration was operated for at least a year. The usage of synthetic feed allowed a better comparison of different operational conditions, e.g. change of VER or change in cycle time/phases time. The results were compared among each other with the research emphasis on the evolution of biomass. The trials were complemented with additional batch investigations to gain knowledge of kinetic parameters such as μ_{max}, OUR and other rates like DNR etc. The goal of this study was to identify the feasibility and the design parameters of the SM-SBR to treat greywater with the purpose of reuse (indoor or irrigation).

The membrane was mainly used as a tool, as the separation device and was not in the focus of this study. Nevertheless, some test cell, critical flux, and permeability investigations were conducted (cf. chapter 5.3).

5.2.1 Development of Biomass

The sludge contains mainly particles of a size between 10 and 100 µm as can be seen in Figure 5-1. The half logarithmic illustration shows a curve, similar to a Gaussion distribution between the particle sizes of 1 to 300 µm, meaning that the particles between 20 - 60 µm should be the greatest fraction on a quantity basis. This is not the case. A look into Figure 5-2 indicates that 50% of the sludge particles are smaller than 30µm for the SM-SBR as well as for the MBR with the high SRT of 140 d. The mean particle size distribution of the MBR operated with the low SRT of 25 d has its maximum at the particle size of 65 µm.

The sludge with the higher volume fraction of small particles comes from set-up C and the MBR feed with synthetic wastewater and a SRT of 140d. This may build a denser layer of biomass on the membrane surface and therefore influence the permeability negatively. Under the microscope the sludge of the SM-SBR in set-up C shows a dense floc structure, cf. Figure 5-3, mainly composed out of bacteria, as well as a few protozoa and metazoa (cf. Figure 5-4).

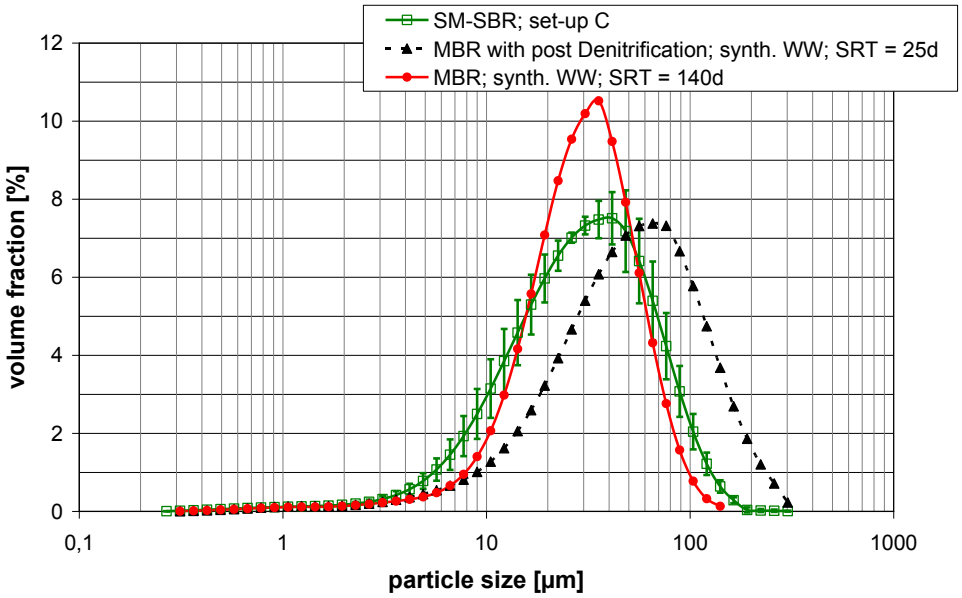

Figure 5-1: Particle size distribution of greywater sludge as volume fraction

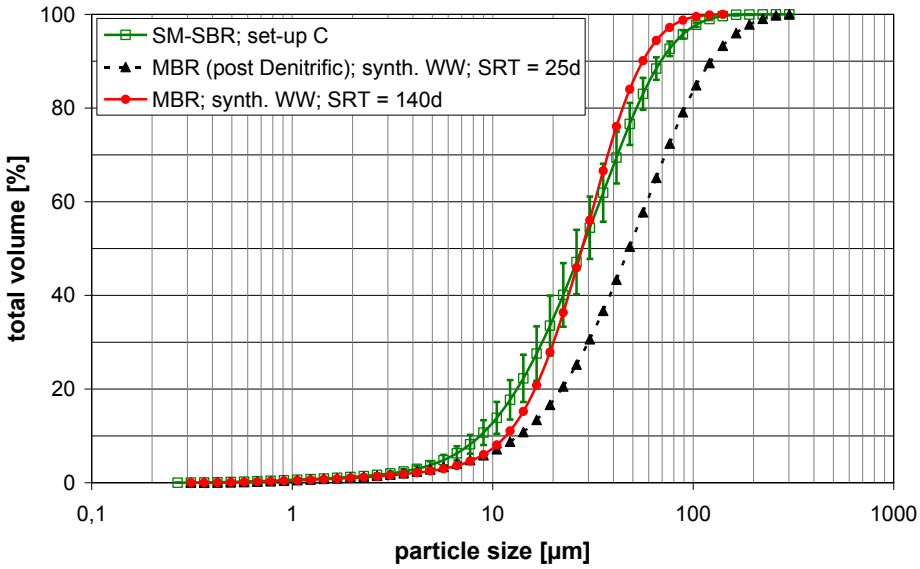

Figure 5-2: Total volume of the particle size distribution of greywater sludge

Figure 5-3: GW sludge under the microscope

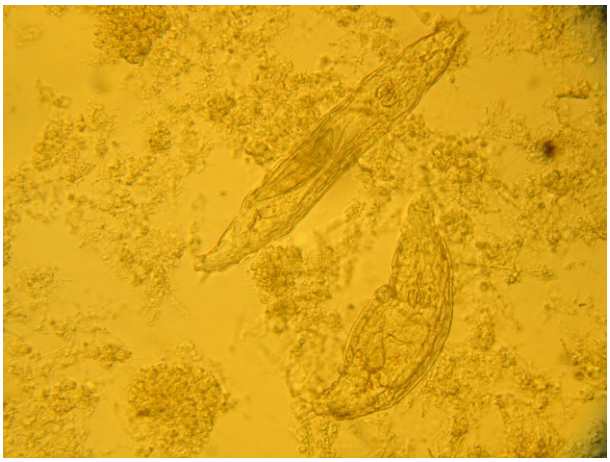

Figure 5-4: *Rotaria* in GW sludge

The quantification of biomass can be carried out by measuring the suspended solids (MLSS) concentration and the volatile suspended solids (MLVSS) concentration. Another possibility is the measurement of total solids (TS), which includes the biomass, as well as other soluble organic and inorganic compounds. The organic total solids (oTS) is calculated from the TS minus the inorganic fraction, which remains in the cup after heating up to 550°C. The inorganic fraction mainly composed out of salts and inert particles inserted by the feed leaves the system either with the soluble phase during permeate withdrawal or adsorbs on the sludge.

The Figure 5-5 shows the evolution of biomass of all three set-ups. Set-up A shows the highest fluctuations. This may be the result of the various changes in opearion (VER, HRT), necessary for the determination of the critical flux of the small membrane module. Set-up B

and C show a similar behaviour in growth although set-up B was operated under very long HRT of 50h from day 220 until day 300 whereas set-up C was operated with a HRT of 24h in the same period. This may indicate that both HRT allow a growth of the biomass only under nutrient limited conditions. The VER was set to 0.12 for set-up B and to 0.25 for set-up C.

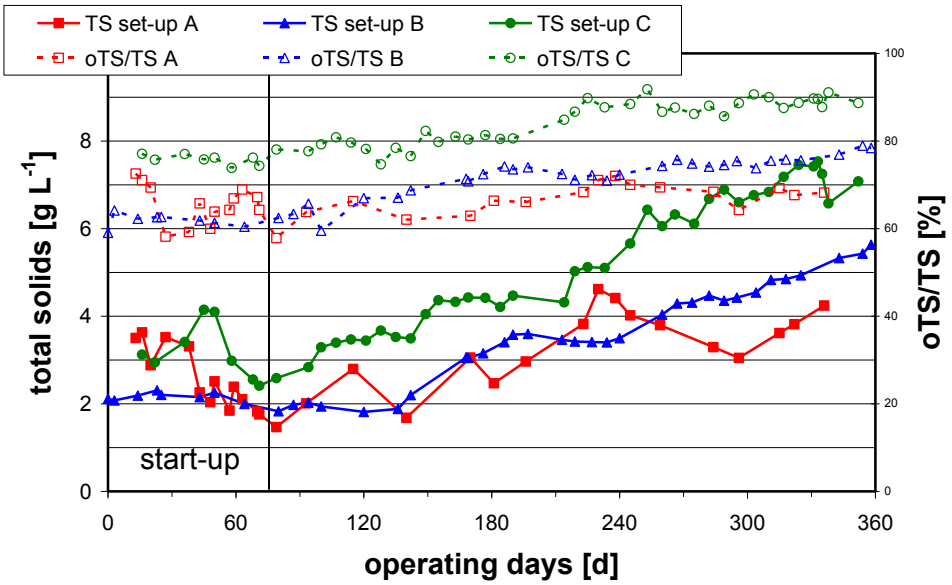

Figure 5-5: Evolution of biomass for all three set-ups

The Figure 5-6 shows the biomass evolution of set-up C over the whole operating time of two years. Although the HRT was reduced four times, no significant change in the growth rate can be seen. The total solids concentration was between 2 gL^{-1} and 4 gL^{-1} in the start-up phase with an HRT of 33h. After the first reduction to HRT = 24h at day 80 (first point in the left corner of the diagram), the TS started at 2.5 gL^{-1} and reached the maximum concentration of 14.6 gL^{-1} at day 737. The low sludge production rate of the activated sludge with $r_X = 0.019\ g_{TS}\ (L\ d)^{-1}$, which equals to a specific growth rate of 0.002 d^{-1}, is independent of the cycle time and may be a result of the low loading rates of 0.15…0.65 $kg_{COD}\ (m^3\ d)^{-1}$. The same r_X was determined with synthetic feed at a ratio of C/N/P = 150/15/1 and a loading rate in the middle of the ones from set-up C with a value of 0.41 $kg_{COD}\ (m^3\ d)^{-1}$ (Heran et al., 2008). Another explanation could be minor nutrient limitations of the greywater feed, which has not been investigated. The macro nutrient balance was close to an optimum as shown before (cf. chapter 5.1). Towards the end, it seems that the measured TS concentration levels to a plateau, fluctuating between 12 and 15 gL^{-1}. If this is the case, than the maximum TS concentration in the SM-SBR is reached for an organic loading rate of 0.65 $kg_{COD}\ (m^3\ d)^{-1}$. But to validate this proposal, more experiments (e.g. an additionally increase in the organic loading rate) and an even longer operation time should be undertaken.

The almost constant and high organic fraction within the TS concentration of around 90% after the HRT reduction to 12h in set-up C shows that, although their was no excess-sludge

removal, no accumulation of inert anorganic substances occurred. Heran *et al.* (2008) reported similar values with a VSS/TSS ratio in the range from 0.80 to 0.89, when the influent does not contain particulate solids. Comparing these results with values for set-up C with the HRT of 24h and a low biomass concentration between 2.5 and 4.5 gL^{-1}, the organic fraction was only around 70%, it can be said that the continuous reduction of cycle time and therefore of HRT led to an improvement concerning the biomass structure in favour of a more abundant fraction.

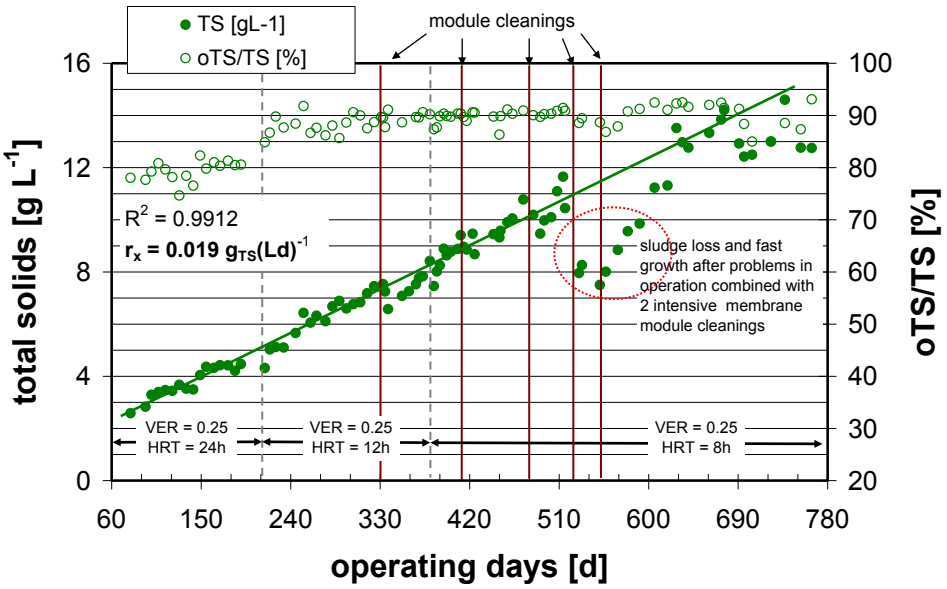

Figure 5-6: Biomass development over operation time, set-up C

The problems during the operation of the SM-SBR between day 530 and 560 occurred from membrane failure. The membrane surface was ripped from its plate during the process of cleaning and caused a leakage of sludge. After fixing the module, the biomass grew faster compared too the period before. This was enhanced because the feed pump dosed more concentrate into the reactor. With a normalisation of the process, biomass growth slowed down and was within the same rate as before the membrane and feed pump failure.

The reductions of HRT during the operational period resulted in an increase of the organic loading rate L_{org}. The organic loading rate is defined as the amount of COD or BOD_5 applied per day to the micro-organism in the aerated tank. For the SM-SBR, the reactor was started with a low value of 0.08 g_{COD} $(Ld)^{-1}$ in set-up B with a HRT of 50 h and reached an average L_{org} of 0.65 g_{COD} $(Ld)^{-1}$ during the shortest HRT of 8 h (cf. Table 5-2). The maximum organic loading rate was at 1.09 g_{COD} $(Ld)^{-1}$ due to a failure of the concentrate feeding pump, which resulted in a higher feed concentration of $360mgL^{-1}$. Writing the data into a diagram as described in Figure 5-7 with data from literature (Stephenson et al., 2000) and data from other investigation carried out at the Chair of Chemical Engineering, TU Berlin, a trend is visible. A low L_{org} enforced a low biomass concentration and a high L_{org} resulted in a high biomass

concentration. Nevertheless, the specific L_{org} of 0.07 ± 0.03 d^{-1} remained more or less unchanged for all configurations.

Table 5-2: L_{org} [d^{-1}] for different HRT in GW treatment compared to municipal WW

reactor configuration	L_{org} [g_{COD} (L d)$^{-1}$]
set-up B, HRT = 50 h	0.008 ± 0.01
set-up B, HRT = 33 h	0.16 ± 0.02
set-up C, HRT = 24 h	0.32 ± 0.16
set-up C, HRT = 12 h	0.50 ± 0.25
set-up C, HRT = 8 h	0.65 ± 0.26
GW - MBR, HRT = 13h (Merz et al., 2007)	0.19 ± 0.08
WW - MBR (Vocks et al., 2005)	2.83 ± 1.50

The very low contaminated greywater from shower effluent of a sports and leisure club which was treated in a 3L lab scale MBR (Merz et al., 2007) lies in the bottom left corner, whereas the municipal wastewater from a pressurised separation sewer in the outskirts of Berlin (Vocks et al., 2005) is to be found in the upper right corner. In the middle of the imagined diagonal are the values for the SM-SBR.

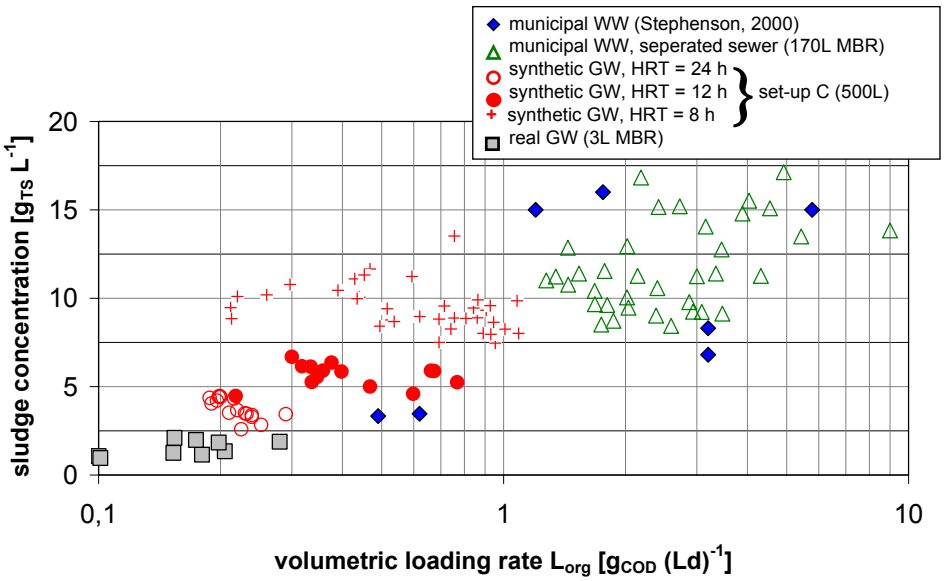

Figure 5-7: Correlation of sludge concentration and volumetric organic loading rate L_{org}

High loading rates induces a high concentration of total solids (sludge), whereas at low loading rates a low sludge concentration can be expected. Now asking the question, if L_{org} has an influence not only at the total sludge concentration, but also at the sludge production the answer is no. Figure 5-8 shows that no tendency of the different loading rates on the sludge production is visible. The sludge production is between 0.05 $kg_{TS}(kg_{COD})^{-1}$ and 0.5 $kg_{TS}(kg_{COD})^{-1}$ for most measured points of set-up C with the corresponding range of L_{org} between 0.2 $g_{COD}(Ld)^{-1}$ and 0.9 $g_{COD}(Ld)^{-1}$. The sludge production of the MBR treating

municipal wastewater is with values between 0.07 $kg_{TS}(kg_{COD})^{-1}$ and 0.7 $kg_{TS}(kg_{COD})^{-1}$ slightly higher, although the corresponding range of L_{org} is by a factor of 10 higher with values between 1 $g_{COD}(Ld)^{-1}$ and 6 $g_{COD}(Ld)^{-1}$. The difference in sludge production would mean that the specific biomass growth in the SM-SBR should be higher than in the MBR operated with municipal wastewater. Increasing the L_{org} may yield in a considerable higher biomass yield and thereby reduce the HRT further more. On the other hand the low L_{org} may be more sustainable for the operation of a membrane coupled system, since a higher L_{org} usually results in a higher TS concentration. The oxygen transfer rate may become limited and a higher aeration rate is needed, which then costs more energy because of greater blowers or compressors.

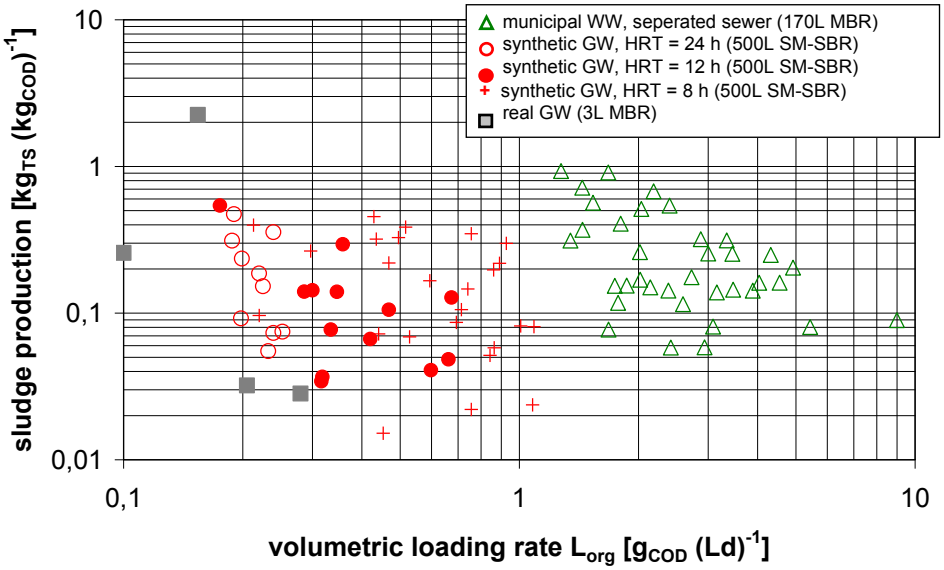

Figure 5-8: Correlation of sludge production and volumetric organic loading rate L_{org}

As a process parameter, the food to micro-organism ratio (F/M ratio) can be used to characterise operating conditions. Typical for activated sludge processes is a value of 0.04 kg_{BOD} $(kg_{TS}\ d)^{-1}$ and for high rate processes like MBR a value of 1.0 kg_{BOD} $(kg_{TS}\ d)^{-1}$ (Metcalf and Eddy, 2003).

In set-up C the F/M ratio oscillated at the end at around 0.05 kg_{COD} $(kg_{TS}\ d)^{-1}$ as shown in Figure 5-9. The value is lower than the ones found by (Rosenberger et al., 2002) for MBRs. There the reported F/M ratio ranged from values of 0.1 kg_{COD} $(kg_{TS}\ d)^{-1}$ for synthetic wastewater, which is doubled compared to the ones in this study, to 0.021 kg_{COD} $(kg_{TS}\ d)^{-1}$ for domestic wastewater, which is half the F/M ratio in synthetic greywater. The various ratios may be due to different feed compositions and microbial populations. Low net sludge production can be linked to low loading rates and low F/M ratios. The low amount of substrate per unit biomass leads to a competition among microorganisms. At the beginning there was a low concentration of biomass and a high feed concentration resulting in a higher

F/M ratio. During the operation, the feed concentration was kept constant, but the TS concentration grew. So, with no excess sludge removal, the feed concentration led to a corresponding sludge concentration, which is specific for each wastewater.

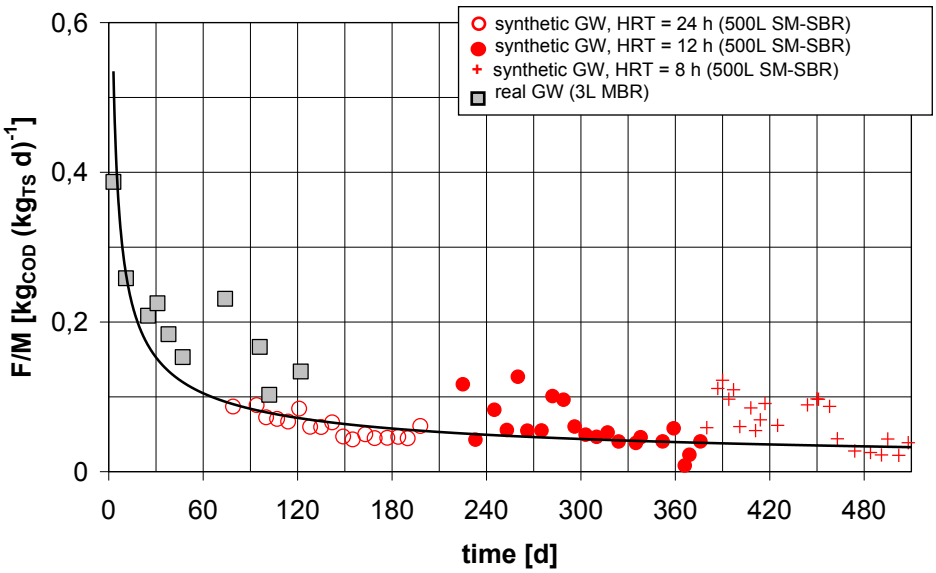

Figure 5-9: Development of F/M ratio over time of GW sludge with no excess sludge removal

5.2.2 Cycle Analysis

For all set-ups, cycle analyses were carried out. Investigations of COD and nitrogen removal within one cycle, combined with the online measurements of DO, ORP and flux of the membrane module showed possible optimisation potentials in terms of time reduction for the aerated and anoxic phase. A short HRT is desirable to build treatment plants with a low footprint and to minimise their operational costs. Hu (2002) investigated the effect of different HRT (between 0.25 to 3.85 h) on biological greywater treatment and found that the optimal retention time in terms of COD, BOD_5 and SS removal rates is 1.5 h. In this study, the optimum cycle time, which correlates to the HRT, had to be determined while taken the following parameters into account:

- TS concentration in the reactor,
- membrane permeability,
- removal rates of COD, BOD_5, nitrogen compounds, and
- maintenance intervals for the application in remote areas.

The obtained profiles from the cycle analysis helped to identify the weak points of each configuration as shown in Figure 5-10. The blue line of the left-hand graphic shows the concentration of dissolved oxygen (DO) within the biological reactor. The dots represent the flux through the membrane. It can be seen that the decline of DO during the anoxic phase is very slow, while the uptake to saturation concentration is fast. The flux is measured with

8 $L(m^2h)^{-1}$.

The sludge settled fast in the anoxic phase in set-up B, because the apparatus did not allow a mixer to be integrated. This resulted in a poor oxygen uptake by the microorganisms during this phase, since only over the interface water/sludge an oxygen mass transfer was possible. Furthermore this led to the avoidance of denitrification (cf. Figure 5-10b). The nitrate-nitrogen uptake rate (NUR) was only 0.38 $mg_{NO3\text{-}N}$ $(g_{oTS}\ h)^{-1}$, which lay in the middle of the rates found by Kujawa and Klapwijk (cited in Kraume et al. (2005)) between 0.2 and 0.6 mg_N $(g_{MLVSS}\ h)^{-1}$ for endogenous denitrification. The biomass was completely mixed only during the aerated phase.

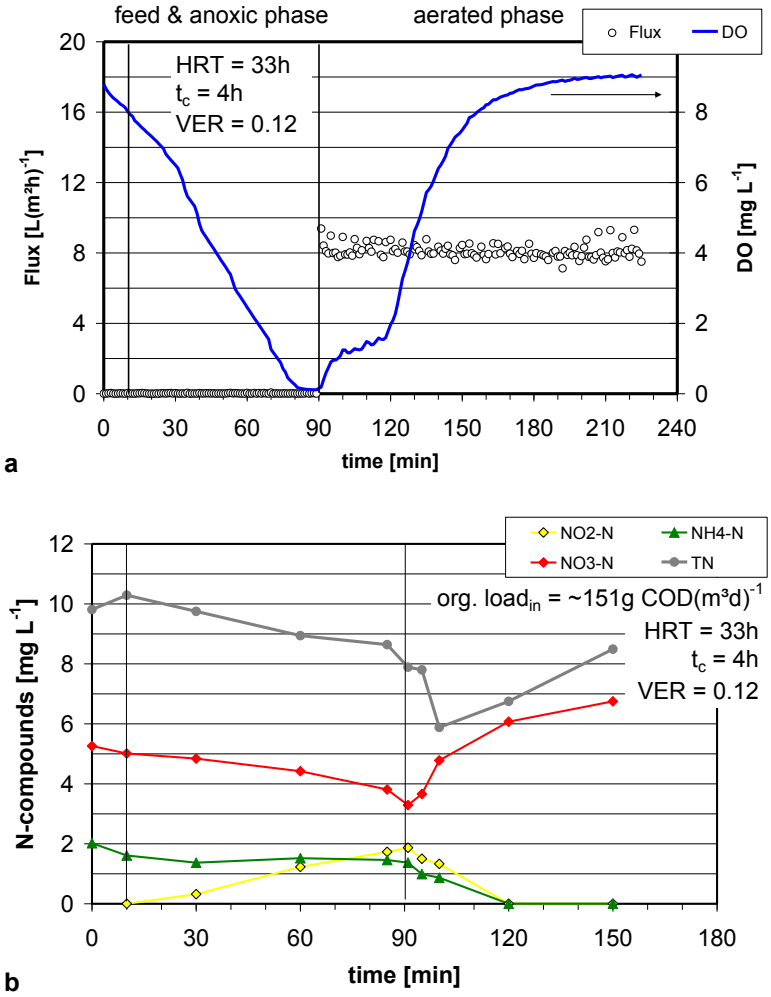

Figure 5-10: Cycle of Set-up B; a: Online cycle measurement b: Cycle analysis of nitrogen compounds

Another example can be seen in the description of the cycle analysis of set-up C in Figure 5-11. It illustrates the results of one cycle for different HRT in terms of the parameters gained from online measurements (Figure 5-11: a-d) and the evolution of the nitrogen compounds (Figure 5-11: e-h). The cycle analyses indicate that the denitrification – nitrification process works under all different HRT and still indicate a small optimisation potential in reduction of

the cycle time (t_c) down to 90 min, meaning a further decrease of the HRT to 6 h. After 80 days the HRT in set-up C was reduced to 24 h and has been since reduced in consecutive steps down to 8 h.

A complete denitrification was achieved mostly; only for an HRT of 33h complete denitrification was not attained. This might be explained by the still remaining DO of up to 1 mgL^{-1} throughout the anoxic phase together with the long hunger period. The stirrer speed of the mixer was too high and oxygen got over the water surface into the bulk of the liquid. In Figure 5-11 b the oxygen curve shows that after nearly 60 min the biological activity (degradation of ammonia) has ended, indicated by oxygen saturation. This is validated by the corresponding nitrogen cycle analysis (cf. Figure 5-11 f). A similar evolution is recognisable in Figure 5-11c, where the oxygen concentration starts to increase to saturation after 20 min. But this observation is contradicted by the cycle analysis, which shows that only 45 min after the beginning of aeration the nitrification process was finished (Figure 5-11g). With the shortest HRT of 8h, 30 min aeration reveal a complete nitrification and 30 min of anoxic condition a complete denitrification. Giving each phase 50% safety buffer time the total cycle time could be reduced to 90 min. In order to achieve this modification more membrane area should be introduced into the reactor. With an HRT = 8 h and gravity flow the flux equals to 25 $Lm^{-2}h^{-1}$ for the UF-module and 35 $Lm^{-2}h^{-1}$ for the MF-module. In studies on municipal and domestic wastewater flux values for submerged membrane modules between 5 and 40 $Lm^{-2}h^{-1}$ have been found (Stephenson et al., 2000).

5.2.3 Removal Efficiencies

The overall removal efficiencies for COD, TN and NH_4-N for the different reactor configurations are shown in Table 5-3, as well as the average feed and permeate concentrations over the operation period. The samples have been taken 15 min after the beginning of each cycle phase. It should be mentioned that the influence of time was neglected during the sampling. The variation in feed concentrations can be explained on the one hand with a first biodegradation of COD in the storage tank, and on the other hand by the variation of pumping, due to the dead zones in the elbows of the short flexible hose in front of and behind the peristaltic feed pump, the greywater concentrate directly into the reactor.

Table 5-3: Average concentrations ± standard derivation in feed and permeate and removal efficiencies

	Feed	Permeate	Removal efficiency					
	[mg L^{-1}]	[mg L^{-1}]	set-up A	set-up B	set-up C 33h	24h	12h	8h
COD	203 ± 69	19.2 ± 6.1	0.73	0.89	0.91	0.91	0.91	0.91
TN	18.4 ± 6.7	5.8 ± 4.0	0.37	0.53	0.73	0.75	0.82	0.78
NH_4-N	9.4 ± 6.1	0.38 ± 0.70	0.98	0.96	0.93	0.99	0.96	0.98
NO_3-N	0.66 ± 0.78	4.0 ± 3.7	/	/	/	/	/	/

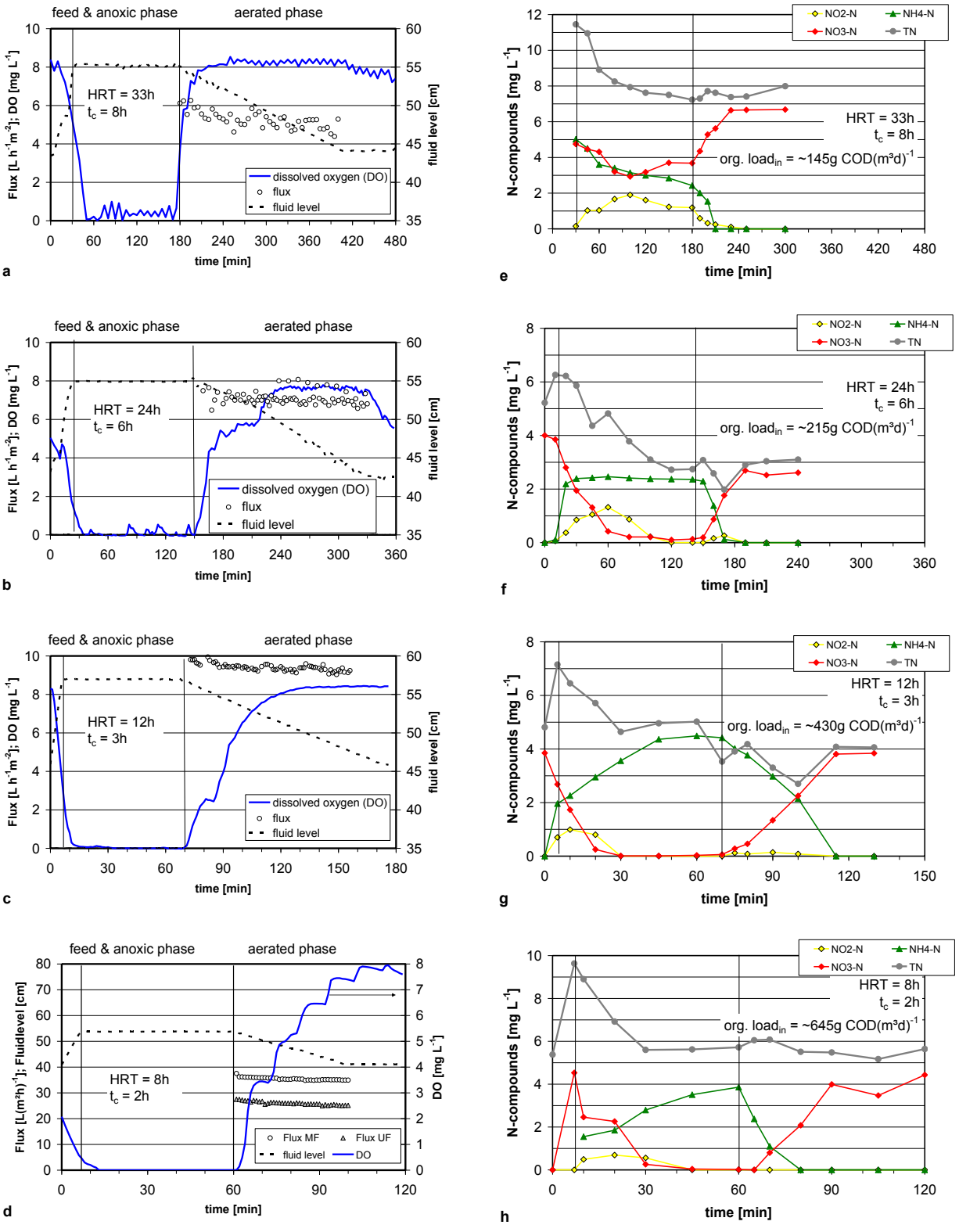

Figure 5-11: a-d: Online cycle measurement of set-up C; e-h: Cycle analysis of nitrogen compounds of set-up C

It is visible in Figure 5-12 that the poorest performance in COD and TN removal was maintained by the 29 L lab scale reactor from set-up A. The various changes in HRT and

VER for the membrane studies caused an unstable biocenosis (sludge population) during the time of operation. A biological steady state was not reached, which might be a reason for the poor performance in COD and TN removal. Another problem was the partly heavy foaming of the greywater sludge due to the surfactants in combination with fine aeration diffuser and the non existing adaptation of the microorganism at the beginning. The ammonia elimination was, on the other hand, in average above 98%, indicating a very good nitrification. This may be the possible result, without further discussion, of a good oxygen transfer into the liquid due to the fine bubble aeration with aeration intensity of 0.017 m^3 $(m^2s)^{-1}$.

In set-up B, the 1000 L reactor showed a deviance in TN removal, although a long period without aeration was established. The geometry and construction of the reactor did not allow the assembly of a mixer. The sludge settled fast and easy, avoiding a complete denitrification. Most of the settled sludge could not participate on the mass transfer, because of the absence of turbulence. In the above liquid pahse, the dissolved oxygen concentration was over 1.0 mgL^{-1}. The long HRT of 50 h, or even 100 h in the beginning, forced the biomass mainly into an endogenous respiration mode. The available carbon was used up very fast at the beginning of the aerated phase.

Set-up C showed the best removal performance. The COD was removed in average of around 91%, indicating a soluble inert fraction of around 9%. The nitrogen removal was near or even over of the maximum theoretical removal capacity of 0.8, according to equation (5-1):

$$S_{N,effluent} = \frac{\frac{V_{reactor}}{V_{fill}}}{1+\frac{V_{reactor}}{V_{fill}}} \cdot S_{N,\mathrm{inf}\,luent} = \frac{1}{VER+1} \cdot S_{N,\mathrm{inf}\,luent} \qquad \textbf{(5-1)}$$

where $V_{reactor}$ = reactor volume, m^3
V_{fill} = volume of influent, m^3
$S_{N,effluent}$ = nitrogen concentration in the effluent, mgL^{-1}
$S_{N,influent}$ = nitrogen concentration in the influent, mgL^{-1}

In all different set-ups the ammonia removal was above 96%, except for set-up C with a HRT of 33h. It must be mentioned that the permeate removal started directly with the beginning of the aeration period where ammonia was not yet degraded. From the results of the cycle analysis a 100% removal could have been reached with an aeration period of 30 min prior the membrane filtration.

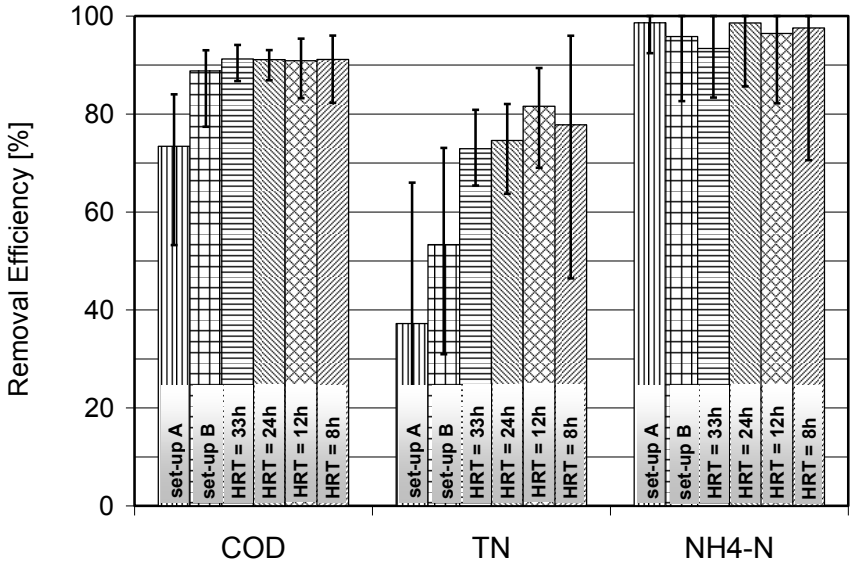

Figure 5-12: Average removal efficiency and its min/max values for the different configurations

5.3 Membrane Performance

The membrane helps to reduce the cycle time since the operation becomes independent of sludge settling ability and the withdrawal can start already during the reaction phase. Nevertheless the reactor performance is next to a proper function of the biological degradation of pollutants limited by the membrane permeability and stability. It is therefore indispensable to secure a high grade of membrane functionality to receive a permeate of very good quality, reusable in-house for toilet flushing or in agriculture, e.g. agriculture by enclosed cultivation in greenhouses (Howell, 2004).

The widespread application of membrane technology in the municipal and industrial wastewater treatment is limited due to the reduction in permeability, which is known as ‘membrane fouling’. The membrane has to be cleaned frequently to stay in economical operation. Membrane fouling “occurs due to the following mechanisms: (1) adsorption of solutes or colloids within/on membranes; (2) deposition of sludge flocs onto the membrane surface; (3) formation of a cake layer on the membrane surface; (4) detachment of foulants attributed mainly to shear forces; (5) the spatial and temporal changes of the foulant composition during the long-term operation (e.g., the change of bacteria community and biopolymer components in the cake layer). In other words, the membrane fouling can be defined as the undesirable deposition and accumulation of microorganisms, colloids, solutes, and cell debris within/on membranes” (Meng et al., 2009). A sustainable operation is possible when operating the membrane below critical flux conditions (McAdam et al., 2005), which depend on the transport of sludge over the membrane surface initiated by turbulence generated through aeration as well as generated by the specific solute–membrane interactions, affected by charge and hydrophobicity (Le-Clech et al., 2006). The theory of critical flux was

first introduced by Field et al. (1995) who stated that "there exists a flux below which a decline of flux with time does not occur; above it, fouling is observed". Although several other authors, like Le-Clech et al. (2003) or Ognier et al. (2004) stated that the permeability decreases even under these circumstances as well it is helpful to determine the critical flux since operation above this flux fouling becomes severe. The use of constant flux and monitoring of resultant TMP rise have proved to be particularly useful in the context of monitoring fouling in complex fluids and is currently the mode of choice in many MBR applications (Le-Clech et al., 2006).

Unlike in a continuous MBR process, in a typical SBR the fill and withdrawal phase are separated from one another dependent upon the treatment objective (Artan and Orhon, 2005), creating a variation in the hydraulic head by up to 50% of reactor volume dependent upon the VER. As a consequence, while the withdrawal continues and the hydraulic head decreases, biomass concentration will increase. The effect of biomass concentration on MBR fouling is not as obvious as aeration effects, mainly because of the complexity and variability of the biomass components (Le-Clech et al., 2003). Therefore even if initially operating at subcritical flux, concentration of the biomass may lead operation into a 'supra-critical state', which cannot be maintained for a long time (Defrance and Jaffrin, 1999a). This could mean an increased chemical cleaning frequency, greater potential of irreversible fouling and an increase in pumping costs due to the variability in available hydraulic pressure and increased TMP, or declining flux dependent upon control adopted (McAdam et al., 2005).

5.3.1 Investigations with the 29 L Lab Scale Reactor

Critical Flux

The critical flux can be identified by using the step method, introduced by Field *et al.* (1995) either with a fixed TMP (TMP is increased stepwise and change in flux monitored) or with a fixed flux (flux is increased stepwise and change in TMP monitored). The fixed flux method as can be seen in Figure 5-13 was adopted to avoid overfouling of the membrane in the initial stage and since it is more advantageous for MBR operation (Defrance and Jaffrin, 1999b). The critical flux was determined only for the membrane module in set-up A.

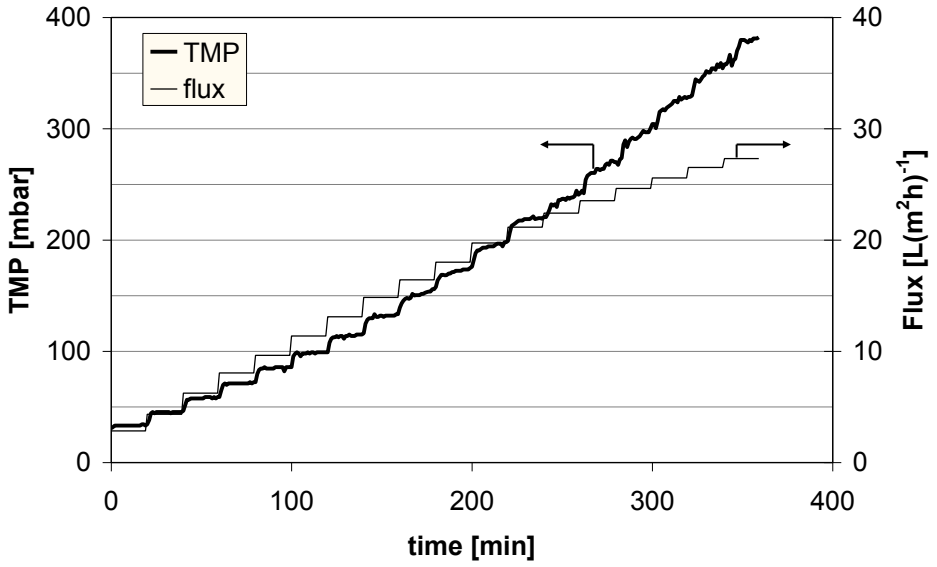

Figure 5-13: Critical flux determination at a TS concentration of 3.5 gL^{-1}

In this investigation the critical flux was defined as the final flux step at which TMP stabilises. Below critical flux, TMP rose slowly and stabilised in less than 15 minutes, which agreed with a similar investigation conducted by Defrance and Jaffrin (1999b). Several runs were done to determine the critical flux. Between each run chemical cleaning was conducted and followed by a clean water critical flux test to identify the presence of permanent fouling, which could not be removed by chemical cleaning (Shin and Kang, 2002).

The threshold point to identify the critical flux was approximately 13.5 $L(m^2h)^{-1}$, when the TS concentration was stable at 3.5 gL^{-1} (cf. Figure 5-13). This flux was used in the later applications as a guide value to operate the membrane modules of the SM-SBR in moderate conditions.

Although there was evidently some ambiguity amongst investigators like Ognier *et al.* (2004), Pollice *et al.* (2005) or Su *et al.* (2008) on the influence of biomass concentration on the fouling mechanism at the membrane surface, the experimental data of this study showed that an increase in biomass concentration within this reactor led to an increase in the operational TMP (corresponding to a reduction in operating flux under hydraulic pressure operation). This would mean the critical flux measured was valid only for a total solids concentration of 3.5 gL^{-1}. The critical flux should not be applied to operate a membrane coupled wastewater treatment process with almost no excess sludge removal.

Membrane Performance Analysis

The influence of increasing biomass concentration during withdrawal on membrane performance was investigated by comparing two testing protocols each with identical settings

in cycle time of 4.5 h (anoxic: 90min, aerated: 180min), an HRT of 9 h, and a flux of 13.5 $L(m^2h)^{-1}$ over a seven day operation period. The only difference was the fill and withdrawal method as written in Table 5-4.

Table 5-4: Applied protocol for membrane performance analysis

	protocol I 'continuous head'	protocol II 'falling head'
fill strategy	replacing the withdrawn permeate with fresh feed in the reactor when a water level drop of 0.03m occurred during the aerated phase	instant fill at the beginning of anoxic phase
withdrawal		continuous intermittent withdrawal during aerated phase
$\frac{h_{fluid,start}}{h_{fluid,end}}$ in the reactor	~ 0	0.5, leading to an increase of biomass by the factor 2

The withdrawal with a permeate pump of the first cycle for the two protocols is given in Figure 5-14. In both cases the TMP recovered to the recorded prior to the intermittent break within the first few minutes of operation. In the case of continuous filtration TMP appeared to stabilise after approximately 4 minutes until the following intermittent break, with only a negligible increase throughout the withdrawal phase. In the case of the reducing hydraulic head, once TMP has recovered, it continued to climb without a period of stabilisation. The instability of the reducing hydraulic head system indicated that flux operation may be supra-critical from the beginning of the cycle (Defrance and Jaffrin, 1999b). An approximate linear TMP increase was observed with time. This may be directly attributed to the linear increase in biomass concentration during permeate withdrawal.

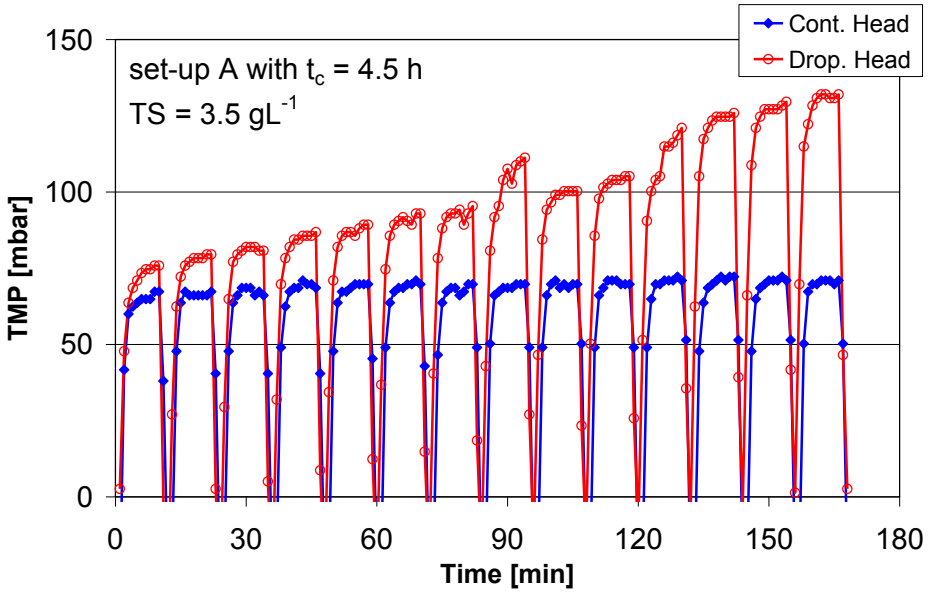

Figure 5-14: Increase in TMP during 1st withdrawal in continuous and dropping head operating mode

Although the experiment started with a similar initial TMP of approximately 70 mbar the slope differed strongly with the beginning of permeate withdrawal, because

- of the supra-critical operation, which resulted from the reducing hydraulic head operation and
- of the conversely quasi-steady state operation, achieved under continuous hydraulic conditions.

This tendency was evaluated with a long term investigation of several days (cf. Figure 5-15). To simplify the long term data for the visualisation, only the final peak from each withdrawal phase (=the last point of one cycle, before the new cycle starts again) was plotted in the graphic. The break in the data of the reducing hydraulic head test between hour 42 and 88 is due to a fault on the programmable logic controller (PLC) where the membrane underwent complete aeration without permeate withdrawal. In order to complete the data set, operation was allowed to continue further to ensure a minimum of seven days with usable operational data from this point. Examination of the full data indicates a linear increase of TMP with time as a consequence of progressive fouling and agrees with a trend observed by Tardieu *et al.* (1998).

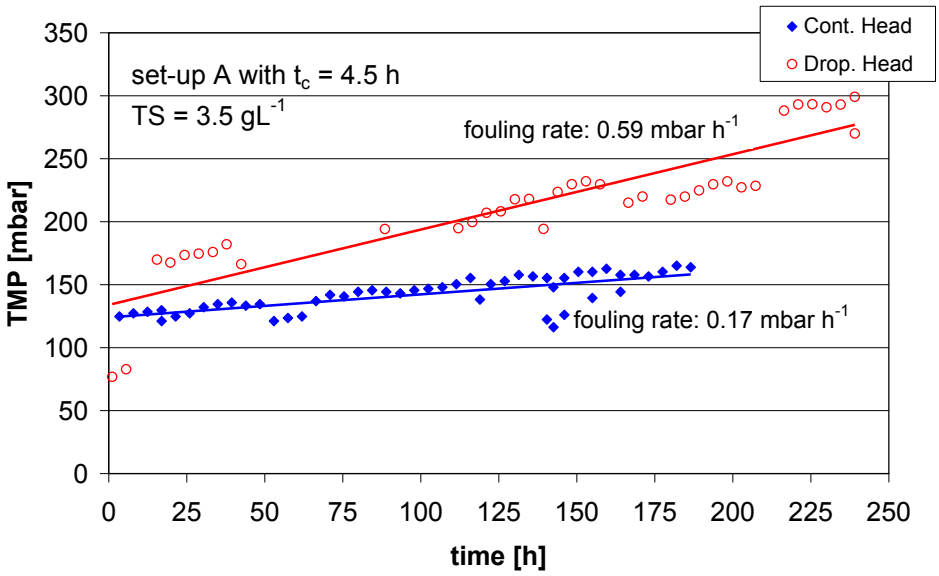

Figure 5-15: Long term effect on TMP of the two different operating modes

It is generally recognised that fouling of the membrane is most critical at the start of the filtration run, or when the change in pressure or flux is most rapid. Therefore by operating with reducing hydraulic head conditions it is evident that fouling will continually occur throughout each cycle. This development of fouling at the membrane surface is also thought to lead to a greater risk of irreversible fouling. (Bacchin et al., 2006)

5.3.2 Membrane Module Performance in the SM-SBR

Many authors have reported the use of intermittent filtration in order to prolong the operation period between chemical cleaning intervention (Drews et al., 2006; Judd, 2006; Psoch and Schiewer, 2005; White and Lesecq, 1993). According to White and Lesecq (1993) the most suitable intermittent operating mode for submerged MBRs is to maintain constant superficial liquid velocity on the membrane surface and to vary applied flux or TMP, which can be done by employing a cyclic on – off filtration mode . The technical handicap of membrane filtration is the maintenance of a sufficiently high shear stress on the membrane surface in order to erode the top layer of cake formed during permeate withdrawal. However, it has been shown that cake formation cannot be reversed by lowering the TMP unless the fluid velocity is high enough to reach the critical erosion stress for the particles in the cake (Kwon and Vigneswaran, 1998). The recovery of flux with no increase of TMP after each relaxation during the intermittent mode, as described exemplary in Figure 5-16, is similar to a study undertaken by Defrance *et al.* (1999b), where the TMP rises rapid initially followed by a gradually rising plateau. Partial cake breakage occurs when filtration stops and aeration continues, but by restart of filtration the cake layer is reformed resulting in a slow pressure increase.

The same behaviour was found during gravity operation as shown in Figure 5-16. The TMP decreased during the aerated phase of one cycle. The withdrawal of permeate resulted in an increasing biomass concentration, which was in addition responsible for the TMP rise. Therefore the declining TMP under gravity flow in Figure 5-17 is the result of the dropping water head of around 15 cm and the increase in TMP due to linear increase of sludge concentration; hence visible is a reduction of TMP of less than 15 mbar. The horizontal TMP devolution after the 110^{th} minute is because filtration has stopped. The SM-SBR is in the idle phase.

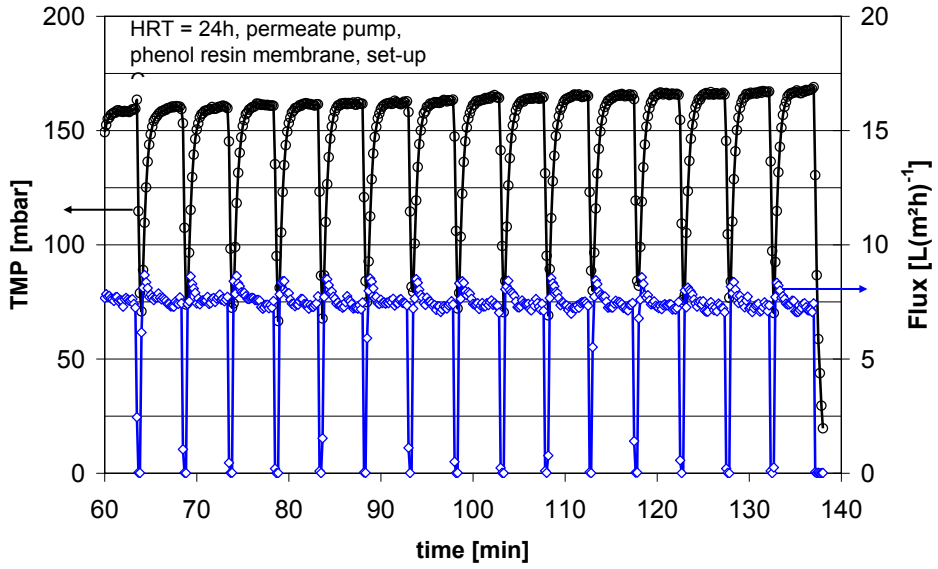

Figure 5-16: TMP evolution with intermittent aeration (4.5min on & 0.5min break) and suction pump

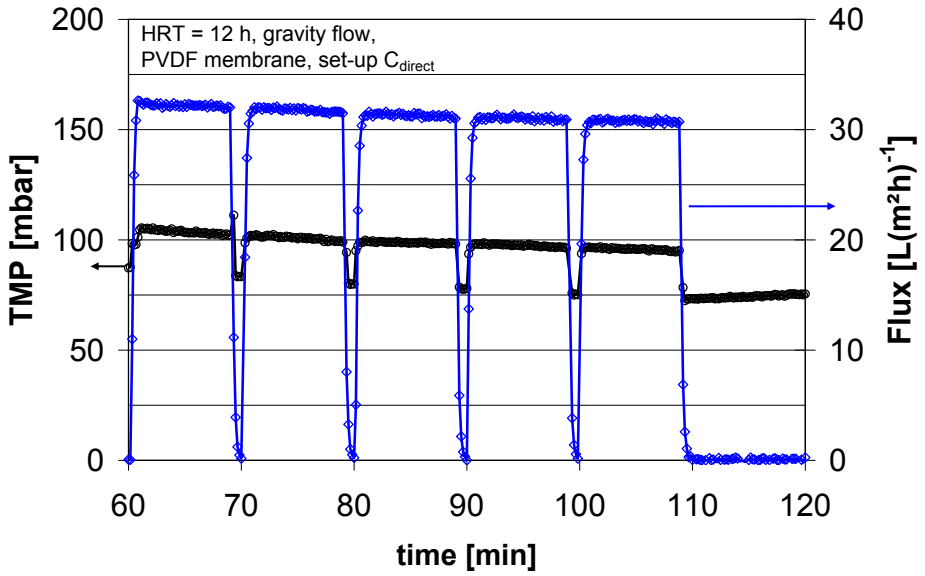

Figure 5-17: TMP evolution with intermittent aeration (9min on & 1min break) at gravity flow

Figure 5-16 shows that the flux stays more or less constant in one cycle at low values of 5-7 $L(m^2h)^{-1}$ for the polyphenol resin membrane. These values lie at the lower end of reported literature data. In studies on municipal and domestic wastewater values for submerged membrane modules between 5 and 40 $Lm^{-2}h^{-1}$ have been found (Stephenson et al., 2000). The TMP was 190 mbar on average, corresponding to a permeability of J = 38 $L(hm^2bar)^{-1}$. To operate the membrane far below the critical flux of 13.5 $L(hm^2)^{-1}$ (McAdam et al., 2005) had the advantage that the process could be run over a period of 120d continuously. Due to the mentioned low flux, chemical cleaning outside the reactor was necessary at an interval of

6 month only. Still, a better membrane performance could enhance the SM-SBR performance in terms of cycle time reduction or HRT reduction.

The change of membrane modules in set-up C led first to a reduction of HRT to 12h, by an increase of permeability to 150 $L(m^2hbar)^{-1}$ at the beginning and an operating flux of 9-12 $L(m^2h)^{-1}$. The permeate withdrawal was set to 9.0 min of permeation and 1.0 min of relaxation with an aeration rate of 4 Nm^3 $(m^2h)^{-1}$. Still the results concerning the membrane behaviour were not sufficient, because already after 30 days of operation, the permeability declined to ~60 $L(m^2hbar)^{-1}$. Therefore, the operation of the SM-SBR was changed from suction pump to gravity flow. With this modification, the membrane modules showed a higher flux of 35 $L(m^2h)^{-1}$ (cf. Figure 5-18). Due to this optimisation of permeate withdrawal, the HRT was than reduced to 8 h, which corresponds to a cycle time of 2 h. High removal efficiency was achieved, as explained already in chapter 5.2.3. The overall performance of the SM-SBR was limited to the membrane permeability for obtaining a short cycle time. Nevertheless, a continuous decline of flux was noticeable, indicating to undertake a membrane cleaning at least every 3 month in order to keep a low HRT. However longer MBR operating periods have been reported with up to 8 months between cleans (Sofia et al., 2004). The operating time between two chemical regenerations was estimated using the following equation:

$$t_{operation} = \frac{TMP_f - TMP_i}{\frac{dP}{dt}} \qquad \textbf{(5-2)}$$

where TMP_i = initial pressure, mbar
TMP_f = membrane manufacturers recommended maximum operating pressure, 400 mbar
dP/dt = gradient of the TMP line

Using the equation (5-2), the operating time between chemical cleans were calculated to be 175 d for the MF membrane and 207 d for the UF membrane for operation under gravity flow. Still, the implementation of a more sustainable membrane cleaning protocol, e.g. cleaning at shorter intervals to avoid such a visible drop in permeability (cf. Figure 5-18), could maintain a high level membrane performance and would therefore enhance the SM-SBR performance further more in terms of cycle time reduction (cf. Figure 5-11).

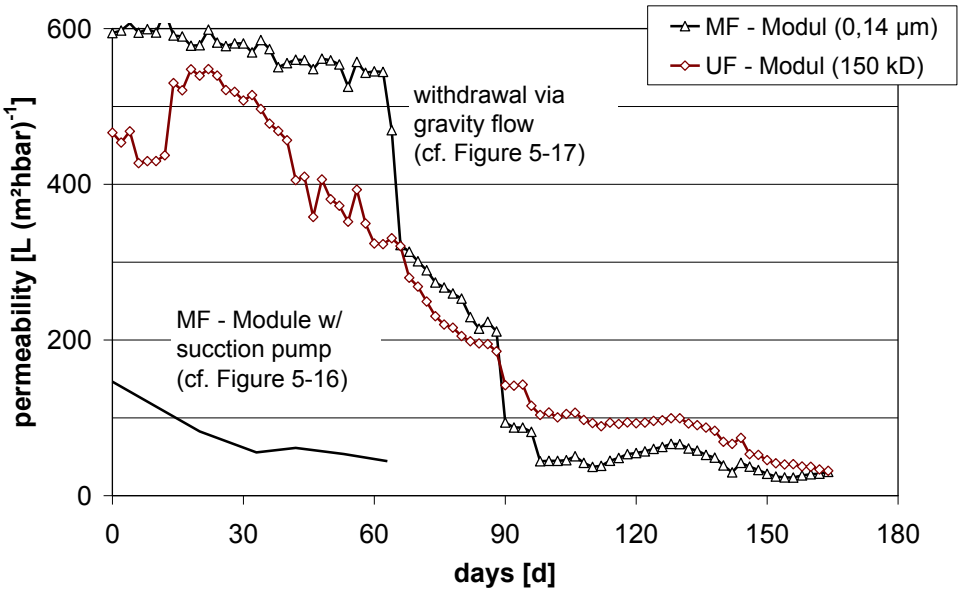

Figure 5-18: Permeability of two different membranes modules (UF and MF) during operation of set-up C, treating GW sludge

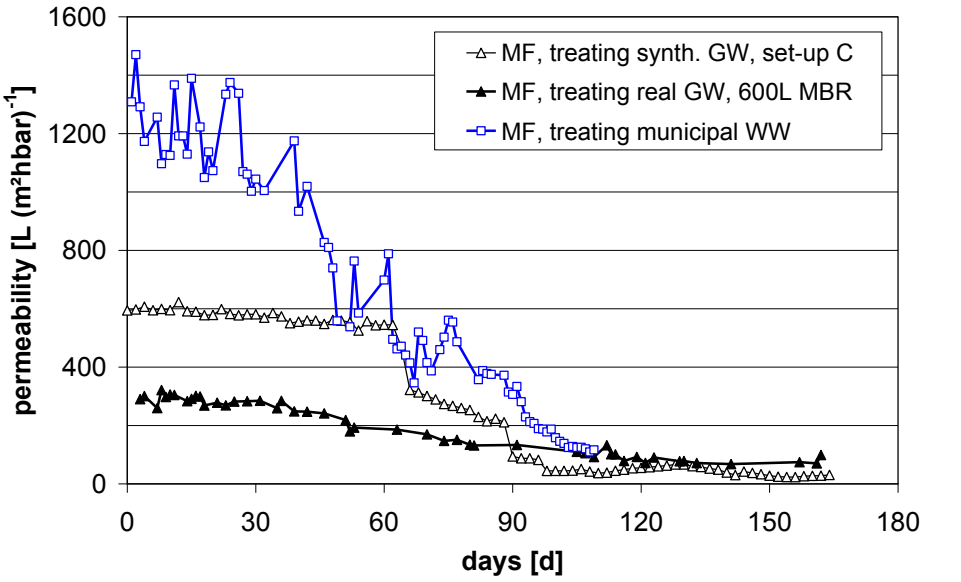

Figure 5-19: Permeability of MF membranes in different WW

In comparison to other wastewater as shown in Figure 5-19, the permeability was between an MBR treating real greywater (Atasoy et al., 2007) and an MBR treating municipal WW, which was operated at the chair of Chemical Engineering at the Technische Universität Berlin. The permeate withdrawal in the MBR treating real greywater was also carried out at gravity flow (constant TMP), but without relaxation pause during permeate withdrawal, i.e. the membrane module had only one relaxation phase after 30 - 40min of constant permeation until the cycle with a total time of 3 h started again. The permeability dropped continuously

over a period of 4 month from 300 to 100 L(m²hbar)$^{-1}$ (Scheumann et al., 2007b). For all three applications, the TMP rose proportional to the flux decline. After around 90-100 days, the permeability reached a stable low value of near 50 L(m²hbar)$^{-1}$, independent of the wastewater treated and of their configuration.

Many different factors can be held responsible for the drop in permeability, such as fouling, membrane blocking, membrane material, mixed liquor, and feedwater characteristics, or system operation (Chang et al., 2002). The complexity and importance of module design (i.e. membrane material, type and module configuration), and process operation (including aeration rate, hydraulic and sludge residence times) make it difficult to understand the mechanism behind fouling.

Nevertheless, in order to evaluate fouling in the absence of sludge viscosity data, the rate of change in TMP was used (ΔTMP/Δt). The filtration period was periodical due to operating an SBR cycle, with the filtration time used for Δt. For the operation under gravity flow the results in Table 5-5 were calculated.

Table 5-5: Fouling rate under gravity flow treating synthetic GW (MF and UF membrane), set-up C

days of operation	TS [g L^{-1}]	microfiltration membrane		ultrafiltration membrane	
		Δ TMP [mbar]	ΔTMP/Δt [mbar min^{-1}]	Δ TMP [mbar]	ΔTMP/Δt [mbar min^{-1}]
10	8.01	4.01	0.075	13.81	0.256
70	12.77	1.78	0.033	10.39	0.192
110	12.92	1.31	0.015	9.43	0.106

The fouling rate decreased, which meant that after chemical cleaning the cake formation on the membrane surface is predominant with particles able to block pores. After a certain time, the tendency to form new sludge layers on the membrane surface is limited, a stable cake or gel layer avoids the deposition of new particles. Compared with the fouling rate from previous investigation of 0.17 mbar min^{-1} (McAdam et al., 2005), the fouling rate with the new MF membrane module was much lower, whereas the UF membrane showed a higher fouling rate.

Another parameter to judge the membrane is a look at the permeability decline for subcritical conditions. The fouling rates are low and either the TMP rises or the permeability declines over a period of time (*dTMP/dt* or *dK/dt*, respectively). Pollice *et al.* (2005) reported that very low permeability decline rates are reported for large pilot plants operated with relaxation, i.e. with intermittent zero permeate flow to allow the aeration to scour the membrane surface. This can be validated by the results of the pilot scale SM-SBR (cf. Figure 5-20). Although the trend is similar, the curves for both modules lay above the data found by Pollice *et al.* (2005) reported. For the UF module, the gradient is much steeper compared to the MF module or the data from Pollice *et al.* (2005). This is the result of the low distance between membrane bottom and aeration unit with its effect on the shear stress on the membrane module. Even if the aeration rate is very high with 4 Nm³ (m²h)$^{-1}$ the liquid velocity calculates only to

0.08 ms^{-1}, leading to a faster permeability decline, most probably enhanced due building of flow channels between the membrane plates. For further studies it should be kept in mind that even for pilot reactors some principles in reactor configuration should not be overruled. In the case of set-up C, the reactor geometry led to the placement of the membrane modules next to each other and not to a rack configuration.

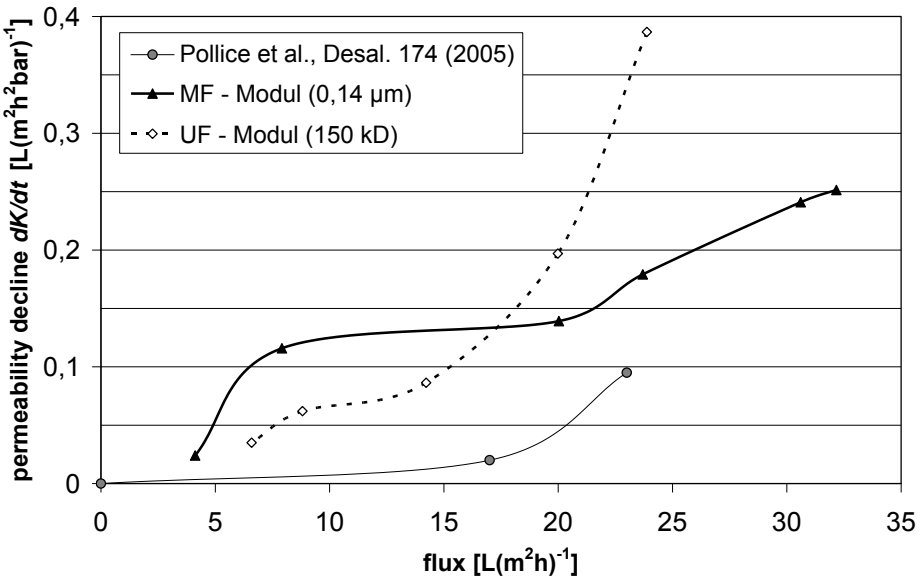

Figure 5-20: Permeability decline *dK/dt* over flux

5.3.3 Nanofiltration as an Alternative?

Greywater treatment can be done not only biological but also with pure filtration over a nanofiltration (NF) membrane. The company ROCHEM uses this principle of operation on cruise ships. The greywater from the showers, hand wash basins and washing machines is collected in a buffer tank, before it is treated with NF membranes. The concentrate goes to the treatment cycle for black water, where it is treated with an MBR, equipped with UF membranes. The filtrate is either reused in the ship or discharged into the ocean (www.rochem.de). The investigations in this study are undertaken with the Amafilter test cell as described in chapter 4.3.3.

Membrane Screening

A preliminary membrane screening, characterised by different molecular weight cut off (MWCO), was undertaken with the following membranes (Table 5-6) and the COD elimination was used as a suitable parameter for measuring the quality of the treated water. In addition the flux was observed in order to assess whether the performance of different membranes were acceptable.

Table 5-6: Suitability test of different membrane materials for greywater treatment

membrane	type	material	MWCO [Da]	TMP [bar]	temperature						
					25°C				35°C		
					COD concentration [mgL^{-1}]						
					0	250	450	900	0	450	900
Osmonics Desal DK	NF	polyamide composite	150-300	5	X		X	X	X	X	X
				10	X	X	X	X	X	X	X
				15	X		X	X	X	X	X
				20	X		X	X	X	X	X
				25	X		X	X	X	X	X
Osmonics Desal DL	NF	polyamide composite	150-300	5	X		X	X	X	X	X
				10	X	X	X	X	X	X	X
				15	X		X	X	X	X	X
				20	X		X	X	X	X	X
				25	X		X	X	X	X	X
Nadir NF-PES-10	NF	permanent hydrophilic polyether sulphone	>500	10	X	X					
Nadir P005F	UF	permanent hydrophilic polyether sulphone	5.000	3	X	X					
Nadir P020F	UF	permanent hydrophilic polyether sulphone	20.000	3	X	X					
Nadir P150F	UF	permanent hydrophilic polyether sulphone	150.000	0,7	X	X					

x = tested combination

The permeate quality and permeability of the tested membranes are illustrated in Figure 5-21. It can be seen that with smaller MWCO the COD retention increases, while the permeability decreases. The only exception comes from the Nadir P020F membrane with a MWCO of 20.000 Da compared to the Nadir P005F with a MWCO of 5.000 Da. The permeate quality of Nadir P020F is better for higher feed COD than for the Nadir P005F membrane, but worse for a low COD feed concentration (cf. Figure 5-22).

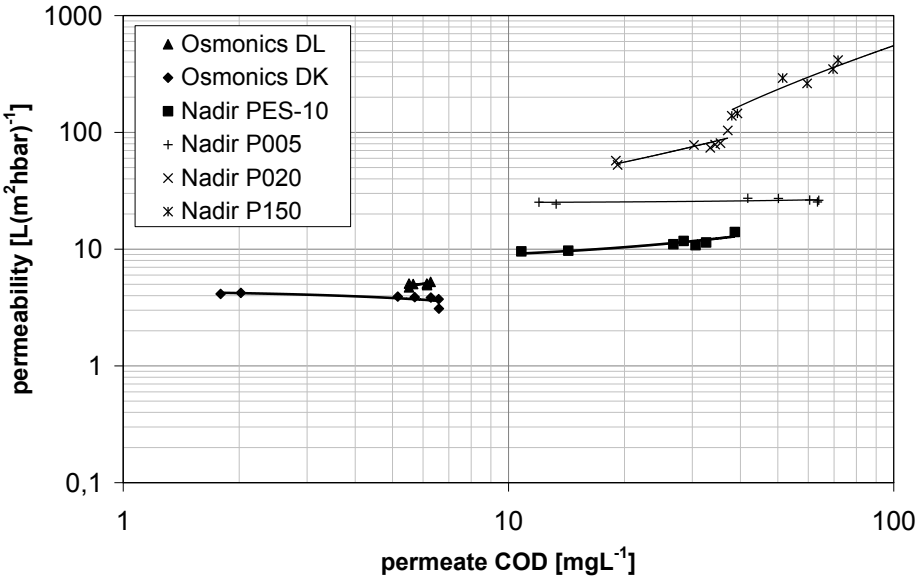

Figure 5-21: Membrane screening for GW filtration: permeability related to the permeate quality

The different behaviour of the two membranes can be explained by the adsorption of surfactants in the pores of the membrane, as Jönsson (1991) describes for UF membranes, and therefore, the MWCO gets smaller than 5000 Da during operation. It is assumed that the fine pores of the membrane P005F are too small for the surfactants to penetrate into the membrane pores, which results in a higher COD concentration of the permeate. The pore size of the Nadir P150F is too big for the adsorption of surfactants and too big for a good COD retention.

The requested permeate quality with a COD concentration of less than 20 mgL^{-1} was given for a COD_{feed} range between 100 and 300 mgL^{-1} only for the Osmonics DL and the Osmonics DK membrane provided. The Nadir PES-10, P005 and P020 membranes achieved the COD threshold only for a feed of low COD inlet concentration. Since it was reasonable to assume that in a real system a concentration significantly higher than the feed concentrations for this test, these membranes were excluded.

The differences of retention and permeability of the DL and DK membranes are likely to be the result of the thinner layer of the DL membrane on top of the same polymer backbone for both membranes. This resulted in a higher permeability but a lower COD retention of the DL membrane. The other membranes showed essentially a significantly higher permeability, but could not provide the desired permeate quality.

Based on an average COD retention of the two Osmonics membranes of more than 97% and a COD concentration of ~5 mgL^{-1} in the permeate, it is expected that in a real plant design a permeate recovery of 70-80% (as standard in RO application for desalination) could be possible and hence the retentate concentration can be enhanced by a factor of 4-5, while the produced permeate stays within the limit of 20 $mg_{COD}L^{-1}$ for reuse purposes. Hills *et al.* (2001) reported that a combination of biological pre-treatment and membrane filtration with

different types of membrane, only the NF membrane produced a reusable permeate with a BOD_5 concentration below 3 mgL^{-1}.

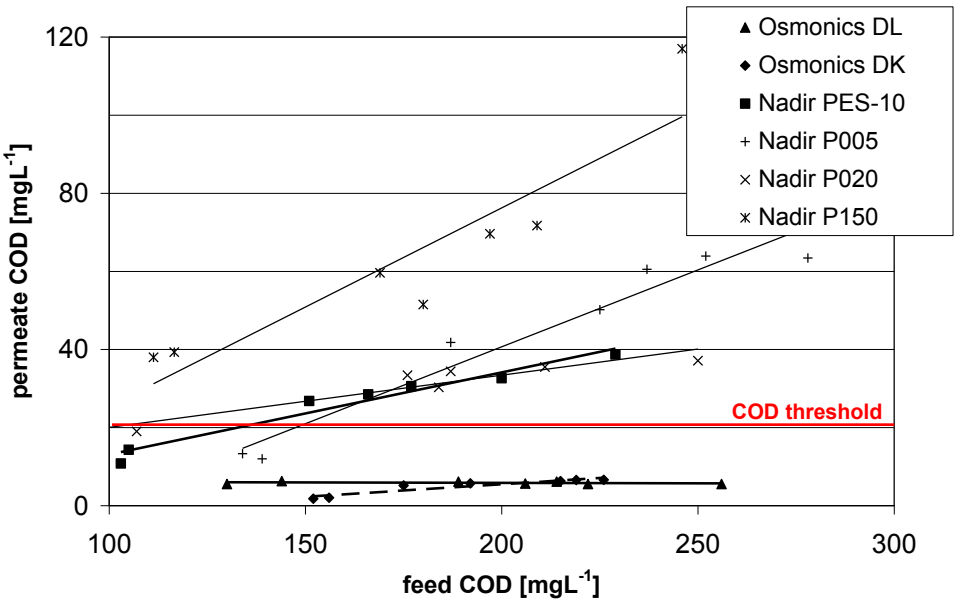

Figure 5-22: Membrane screening for GW filtration: permeate quality related to the feed COD

Critical Flux Determination

As for any membrane filtration process, e.g. MBR or SM-SBR, the filtration of greywater with NF membranes will lead to irreversible fouling if operated over the critical flux. Therefore, a critical flux determination was undertaken for the Osmonics DL membrane as described exemplary in Figure 5-23. The COD concentration was set to 900 mgL^{-1} and the temperature to 25°C and 35°C, since it is expected to receive greywater with temperature above 25°C.

For the trial at 35°C the following observation were made. The flux decreased above the TMP of 15 bar. Therefore it can be assumed that the critical flux of 88 $L(m^2h)^{-1}$ was reached between the TMP of 10 and 15 bar. For the run at 25°C, the flux decline was reached at a TMP of 20 bar. The critical flux was determined at 84 $L(m^2h)^{-1}$. A similar behaviour was measured for the Osmonics DK membrane. In literature, no similar investigations were found in order to compare the measured data.

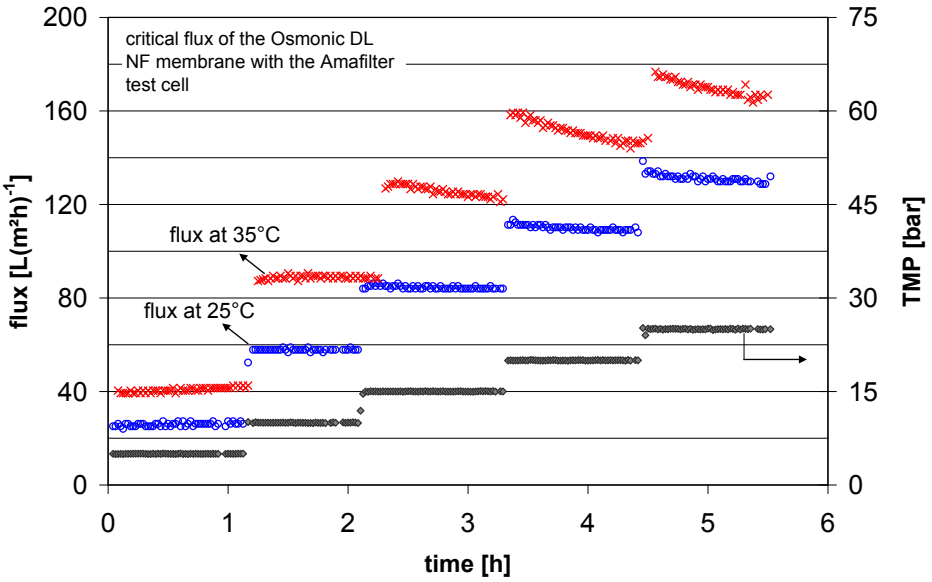

Figure 5-23: Critical flux determination of the Osmonics DL membrane at feed$_{COD}$ = 900 mgL^{-1}

Another method was used to validate the above measured values. The flux was plotted over the TMP for greywater and for deionised water to identify the critical flux. The point at which the greywater curves leave the linear water curve can be identified as the critical flux (cf. Figure 5-24). The difference is given in the graphical analysis, because now the flux values between each step of increase of TMP can be made visible.

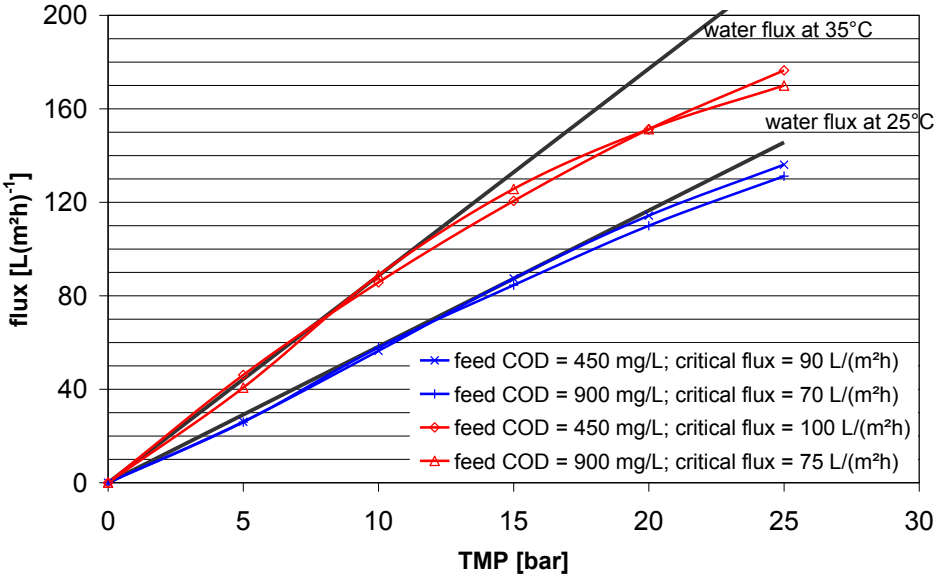

Figure 5-24: Evolution of flux over TMP for the Osmonic DL membrane for COD concentration of 450 and 900 mgL^{-1} in correlation to deionised water at 25°C and 35°C

The behaviour of the greywater curves was nonlinear, as seen in Figure 5-24, and with increasing TMP the flux gradient decreased, i.e. after a certain value was reached, the graph of the greywater measurement slipped of the linear line of the water flux. It can be assumed that the deviation at higher pressure was due to the operation over the critical flux. Nevertheless, a final statement concerning the practical assessment of the achieved critical flux was hardly possible, since the investigations took place at a test cell with a small membrane area. In real application with complete modules the flux might be even higher or lower.

The flux increased with temperature for the same TMP applied to the membrane. The permeability of both Osmonics membranes increased from 15 to 30%, by comparing the water flux at both temperatures (25°C and 35°C). This tendency was validated in literature, were they found that higher temperature led to a higher permeability either due to the fact that the hydrogen bonds between water molecules became weaker and thus more water permeated into the membrane, or that the membrane pores expanded at higher temperatures and therefore a greater convective transport was possible (Toutianoush, 2003; WEF, 2005).

Filtration of synthetic greywater

Real applications are operated with membrane modules, where the retentate is pumped back to the feed tank. The concentration of the feed would increase because the withdrawn permeate has a low COD. In order to see the impact of COD variations different runs with different concentration have been undertaken at the Amafilter test cell.

In average, the flux in the test cell declined nonlinear with 25% as the feed COD was set to 900 mgL^{-1}. Schipolowski *et al.* (2006) investigated the reliability of test cell measurements and found that the membrane behaviour depended on the average properties of a large membrane surface. The variations within the membrane material have a major influence on the test results and made an error of up to 23% for the permeability. Taking this and all other possible sources of error into account, the permeability decline would be in the range between 20-30%. Nevertheless, the use of test cells showed that treatment of greywater with a NF membrane was suitable. Further investigations should be done with a lab scale apparatus.

The influence of temperature on the flux is presented in Figure 5-25, with an increased flux for the higher temperature due to the reasons mentioned above. In the undertaken experiments the COD retention declined slightly with increasing temperature (cf. Table 5-7).

Table 5-7: COD retention of the Osmonics DK membrane at different temperatures

inlet COD concentration	COD retention*	
[mgL^{-1}]	Osmonics DK at 25°C	Osmonics DK at 35°C
450	0.977 ± 0.004	0.965 ± 0.004
900	0.981 ± 0.006	0.973 ± 0.006

*as average value ± standard derivation

Two explanations for the temperature depending flux can be made:

- The solution diffusion model defines the transport of individual components takes place by diffusion along the gradient of the chemical potential. Since the chemical potential increases for rising temperature, retention of the membrane can be reduced.
- The pore blocking model; the aforementioned expansion of the membrane can be assumed, increasing the flow for bigger components through the membrane.

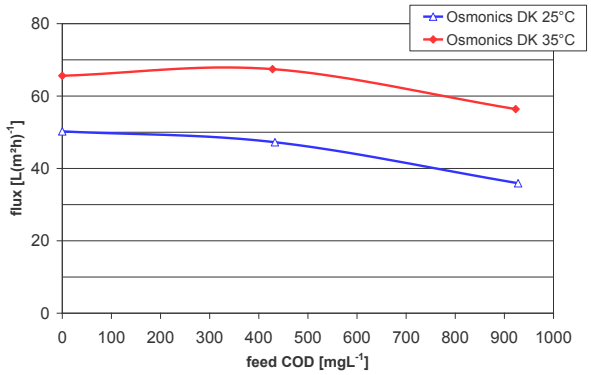

Figure 5-25: Temperature influence on flux for the Osmonics DK membrane

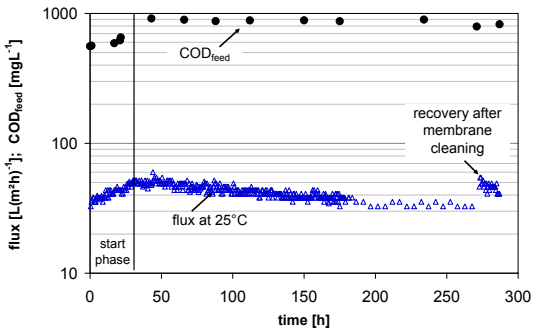

Figure 5-26: Longterm study on permeability decline for the Osmonics DK membrane

In an additional experiment the long term behaviour of an Osmonics DK membrane was tested. This result showed the impact of a high concentration of COD up to 1000 mgL^{-1} (due to a return of the concentrate from greywater treatment to the system) on the flux of a longer operational period of 12 days. At the end a chemical cleaning was undertaken and its success tested. Based on the previous tests results the run was set up with a TMP of 10 bar and a temperature of 25°C to ensure the operation below critical flux.

The flux curve and the feed COD concentration are displayed in Figure 5-26. For the first 30 hours the flux increased from approximately 32 $L(m^2h)^{-1}$ to about 50 $L(m^2h)^{-1}$, most probably because of membrane conditioning to the high greywater feed concentration. It can be assumed that this phase of adaptation could have happened also in the previous experiments, because the test preparation was the same for all.

Although the flux was well below the defined critical value, the permeability of the membrane decreased with time again, relatively linear at the beginning, to 32 $L(m^2h)^{-1}$ at the end. The deterioration of permeability performance was observed by other authors as well. Helmig (1992) and Wendler (2003) found that the molecules of surfactants adsorbed at the membrane surface and contributed largely to decline in flux. The hydrophilic surface of the membrane influenced the adsorption of the surfactants positively. The cationic surfactants and the alkyl group of the anionic and non-ionic surfactants attached easily to the membrane surface. The adsorbed molecules formed a coating with increasing number of layers of small

particles and suspended solids. After reaching the maximum permeability the flux dropped from 50 $L(m^2h)^{-1}$ to 35 $L(m^2h)^{-1}$ by around 30% in a period of seven days (168 hours). After cleaning the flux went up to 55 $L(m^2h)^{-1}$, which indicated no irreversible fouling.

Summary

In a screening, seven membranes with different MWCO were tested for the treatment of synthetic greywater. Only the NF membranes by the company Osmonics were suitable for treatment with the purpose of reuse. The permeate quality was around 5 $mg_{COD}L^{-1}$, significant lower than needed for reuse. The investigated MF and UF membranes did not provide the desired permeate quality. However, in combination with other processes, especially in pre-treatment, a large potential of those membrane application for greywater treatment might be given.

Following the pre-selection of the Osmonics DL and DK membranes, experiments with variation of feed concentration, pressure and temperature were undertaken. The critical flux was measured in the range of 90 and 110 $L(m^2h)^{-1}$. The assumption that a real application would lead to a rising concentration of the feed induced a set of experiments at a feed COD concentration of around 1000 $mg_{COD}L^{-1}$. The flux declined with increasing COD values of less than 30% compared to deionised water. The long time trial significantly below the previously determined critical flux revealed a permeability reduction of 30% from 5.0 $L(m^2hbar)^{-1}$ to 3.5 $L(m^2hbar)^{-1}$ over time as well, mainly contributed to the interaction between membrane surface and surfactants from greywater. Nevertheless the COD retention was stable above 97%.

The experiment with the test cell showed that nanofiltration of greywater is an alternative treatment option. Next to the space-saving construction of a greywater treatment system with a NF membrane process, another advantage is its robustness of the process against fluctuations in feed composition and concentration, which is a major problem for biological treatment systems. Nanofiltration is a simple and efficient way to treat greywater, and therefore an interesting alternative to conventional MBR and advanced SM-SBR, e.g. on cruise ships. Nevertheless, a direct comparison to the SM-SBR cannot be made at this stage. Therefore a laboratory or a pilot plant should be installed and investigated to understand the technology choice better. Only then it is possible to say something about energy consumption, which must be higher than the amount needed by the operation of the SM-SBR.

5.4 Batch Test Experiments for the Determination of Kinetics

Braha and Hafner (1987) stated that the usage of batch-cultures may represent a less expensive and a more helpful proceeding to model biokinetics in activated sludge systems than continuous-flow cultures. Furthermore, lab scale batch investigations reduce the

expenditure for technical devices and the time between operational periods in single runs due to a short transient behaviour. Gaudy and Gaudy (1972) have found out that the adaptation processes of biomass occurs usually during the total reaction time, because the remaining compounds of the mixed substrate may become less available with time due to biodegradation, which may lead to complications in the process of adaptation of biomass. This is also noted by Wentzel *et al.* (1995), who has reported differences between activated sludge system and batch test kinetic constants. These variations have been attributed to the activity of the biomass and the content of COD. However, theses differences should have a lower impact for sludge from SBR operation, since it is already a batch operated system.

Today, respirometry and batch investigation are an established tool to validate mathematical models, which describe the biological and microbiological activity of biocenosis in activated sludge system (Brenner, 2000; Gildemeister et al., 2005; Moussa et al., 2005; Novák et al., 1995). Examples are given by:

- Ni and Yu (2007), who performed a lab scale SBR experiment involving storage compounds to model the growth of multiple microbial species,
- Vanrolleghem *et al.* (1995), who concentrated on the practical identifiability properties of a mathematical model and on the design of informative experiments for parameter estimations,
- Dircks *et al.* (1999), who used respirometry batch experiments for the yield determination,
- Spérandio *et al.* (2005), who compared sludge characteristics of an MBR with an ASP, and
- Ekama et al. (1986), who determined with this tool different COD fractions in wastewater.

Above all, it is important to be precise when measuring the different kinetic parameters. An exceptional position holds the heterotrophic yield Y_H, because of its high dependency on environmental conditions. That means that for each undertaken batch experiment the yield should be determined separately. Usually, this would go beyond the operating expense.

Nevertheless, the yield was determined for the synthetic greywater with sludge from set-up C in a number of batches and graphically calculated according to the method from Dircks *et al.* (1999) in the form of

$$OU = (1 - Y_H) \cdot slope \qquad \textbf{(5-3)}$$

where OU = accumulated oxygen uptake, $mg_{DO}\ L^{-1}$
Y_H = heterotrophic yield coefficient

meaning that the yield coefficient Y_H equalled to 1 minus the slope of the line in Figure 5-27. With this procedure, the defined Y_H coefficient was assumed to be valid for the whole range of the examined substrate concentrations. The calculated yield with sludge from set-up C was

Y_H = 0.53, which was at the lower end of the range of 0.46 – 0.69 Henze *et al.* (1987) described in their proposed general model on activated sludge (latter known as the ASM 1). Van Loosdrecht and Henze (1999) reported values of 0.45-0.50 calculated from the free energy of the catabolic reaction, i.e. the complete oxidation of substrate, but pointed out that the coefficient should be substantially higher when storing polymers in the cell. The investigations at a very high COD concentration or at a high F/M ratio were difficult to undertake in the batch because of foam production due to the greywater surfactants. Therefore the correlation factor R^2 obtained was only 0.8395. The low yield corresponded well to the nature of greywater with its low biodegradability. The COD/BOD_5 ratio of the synthetic greywater was around 4.

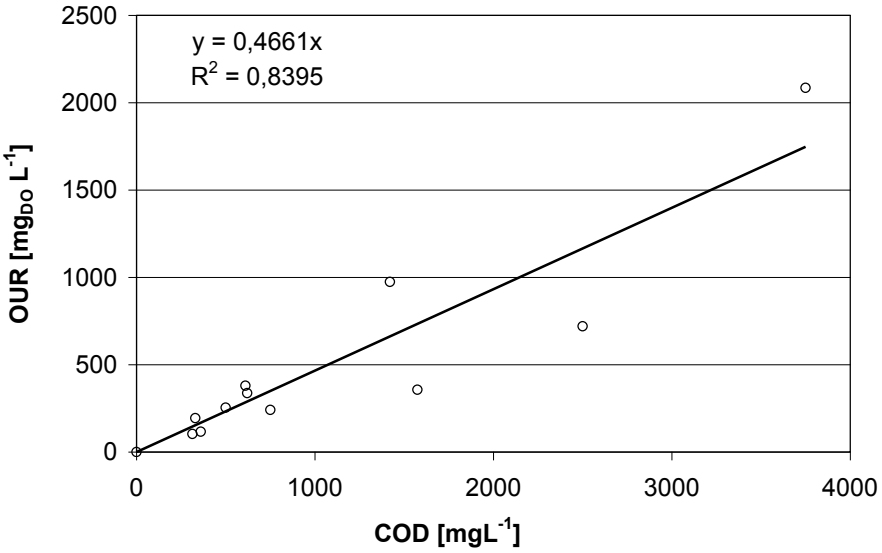

Figure 5-27: Yield determination of sludge from set-up C according to Dircks *et al.* (1999)

Additional batch test with greywater sludge, all from set-up C, in 1L or 3L vessels were undertaken to determine various kinetic parameter and rates. Therefore, the feed fractions were determined firstly, secondly experiments were done to identify the biokinetic parameters such as growth rate etc., and finally on some details of the nitrification and denitrification rate.

The obtained results are later incorporated into a mathematical model for the biological greywater treatment, which delivers valuable information for the comprehension of the treatment process. The development of a mathematical model is of importance to appraise advance developments and operational conditions of the treatment process. Unfortunately, there are only a few kinetic data for greywater sludge in literature to build and compare the mathematical model. The simplified model for the SM-SBR is developed in chapter 6.

5.4.1 COD Fractioning of the Synthetic Greywater

In chapter 3.4.2 an overview was given of the different wastewater constituents as for example carbonaceous components. To determine the COD fractions in the used synthetic greywater, experiments were carried out according to Ekama *et al.* (1986) and Kappeler and Gujer (1992). It was necessary to define the different fractions, because these values were used for later mathematical modelling. For instance, it was important to characterise the true residence time of each fraction in the system in correlation to its associated removal-mechanism and -rate. It was supposed that no particulate matter either biomass or others was presented in the feed, because synthetic greywater is used.

The COD is divided into four fractions: readily biodegradable COD (rbCOD), slowly biodegradable COD (sbCOD), soluble inert COD (nbsCOD), and particulate inert COD (nbpCOD). An example of the OUR batch runs is given in Figure 5-28, where five different phases could be identified.

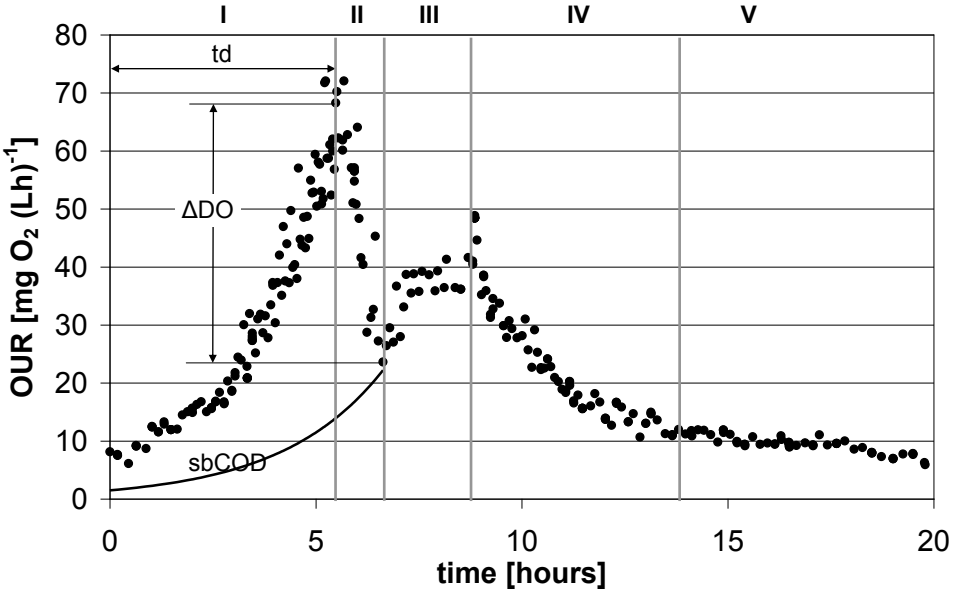

Figure 5-28: Determination of COD fractions via OUR batch test

The first period shows an OUR increase exponentially over time, due to heterotrophic active biomass growth. In the second phase OUR drops (= ΔDO in Figure 5-28) precipitously due to depletion of rbCOD. During the third phase, OUR represents the growth of microorganism on sbCOD followed by saturation due to sbCOD depletion (phase IV) and ultimately the OUR decreases slowly, because of endogenous respiration and decay (phase V). The growth on sbCOD becomes only visible when rbCOD becomes limiting. Despite the fact that wastewater models do not show visible growth on sbCOD in phase I, it is assumed to be the growth on both, the rbCOD and sbCOD utilisation. Nevertheless, the fraction of rbCOD can be calculated using equation (5-4), with t_d as the time from start until the precipitous drop of rbCOD depletion. (Wentzel et al., 1995)

$$rbCOD = \frac{1}{1 - Y_H} \int_{t=0}^{td} (OUR_{total} - OUR_{sbCOD}) \cdot dt \qquad \textbf{(5-4)}$$

where t_d = time from start until precipitous drop, s

In the shown example (cf. Figure 5-28) the amount of the readily biodegradable fraction (S_S) is 264 mgL^{-1}, which is 35.0% of the initial COD concentration and the fraction of sbCOD (X_S) equals to 269 mgL^{-1}, which is 35.7% respectively. Once the decay phase is reached, the residual COD in the batch gives the inert fraction (S_I+X_I) of the COD, which is 29.3% of the initial COD. The nbCOD can be further subdivided in its particulate part, enmeshed in the sludge, and in its soluble part, leaving the reactor with the permeate. The analysis of the reactor shows that the effluent COD concentration is in average around 19 mgL^{-1}. This value corresponds well to the fraction of snbCOD = 9.4%. The average values calculated for the different fractions in comparison to literature values are listed in Table 5-8.

Table 5-8: COD fractions of different wastewaters

type of wastewater	total COD [mgO_2L^{-1}]	S_S [%]	X_S [%]	X_H [%]	S_I+X_I [%]	references
synthetic GW	203 ± 69	25 ± 16	42 ± 9	~ 0*	33 ± 22	this study
raw WW	663	5	38	10	47	} (Ginestet et al., 2002)
settled WW	403	8	51	10	31	
primary effluent (municipal WW)	250	11	53	7	29	(Kappeler and Gujer, 1992)
combined sewer	396	30	35	10	25	(Lagarde et al., 2005)
separated sewer	878	43	19	8	30	ASM1
municipal WW	410	9	77	within X_S	14	(Orhon et al., 1997)
municipal WW		20	40	20	20	(Henze, 1992), in: (Orhon et al., 1997)

*assumed to be zero, because it is synthetic wastewater

The determined values indicate that the composition of the synthetic greywater is within the reported literature values for different kind of wastewaters. (Mehlhart, 2005) reports that the rbCOd from real greywater results mostly from detergents and skin grease and therefore should content more particulate matter (hair, skin, and dandruff particles) than the synthetic greywater used in this study. The particulate matter can account for the fraction of nbCOD or sbCOD. The synthetic feed does not enclose such human wastes, but since the synthetic greywater contains detergents and oil the rbCOD concentration should be comparable, whereas the particulate fraction is most probably underestimated in comparison to real greywater. Still, it is known that the quality of greywater strongly varies depending on the source and on the cultural background. It does not necessarily mean that the values obtained for the synthetic greywater are out of range or at any border compared to other sources of greywater. Unfortunately in literature, no values can be found.

5.4.2 Respirometry for the Determination of Biokinetic Parameters

As mentioned earlier, an intensive literature survey showed the lack of biokinetic parameter in greywater treatment, which is needed for proper plant design. Therefore, batch experiments were carried out, where sludge biomass from the operated reactor and fresh feed was mixed in different F/M ratios to determine μ_{max} and other specific biokinetic data (k_d, k_h K_S, etc.), as shown in Table 5-9.

Table 5-9: Biokinetic parameters of sludge, coming from different wastewaters

Treatments and feeds at ~20°C	COD [mgL^{-1}]	Biokinetic parameters μ_{max} [d^{-1}]	K_S [mgL^{-1}]	k_d [d^{-1}]	k_h [d^{-1}]	references
SM-SBR GW	203±69	22.4	689	1.07	0.42±0.14	this study
SBR domestic WW	200	6.5	5	0.15		(Artan and Orhon, 2005)
immersed MBR synthetic WW		1.28 – 6.46*	289 – 2933*	0.151 – 0.0261*		(Al-Malack, 2006)
ASP municipal WW	250	2 – 7	2.5 - 4.0	0.1 - 0.4	1.5 - 10	(Kappeler and Gujer, 1992)
raw municipal WW	663				8.8±2.3	
settled municipal WW	403				11.6±2.8	(Ginestet et al., 2002)
settleable fraction**					0.63±0.2	
ASP municipal WW	821	5.4 – 7.8		0.62		(Wentzel et al., 1995)

* Investigations were carried out at MLSS concentration from 3.0 to 15.0 gL^{-1}.
** equivalent to very slowly hydrolysable COD

Determination of μ_{max}, K_S and k_d

The maximum growth rate μ_{max} is the most important parameter for carbon removal and nitrification, because it measures the speed of unlimited growth with substrate surplus. The determination of this parameter is essential for every wastewater composition, since it is strongly influenced by several factors such as temperature, pH, DO, inhibitors, organic carbon, substrate, sludge age and so on. It is therefore important to determine the best F/M ratio in order not to be substrate limited or substrate inhibited. Macro and micro nutrients must be added to avoid limitation as well.

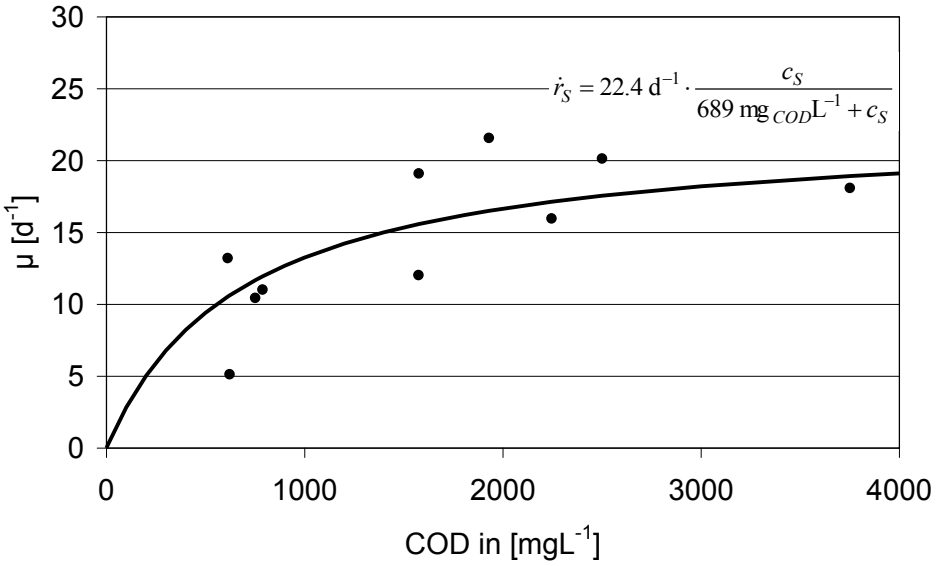

Figure 5-29: Determination of μ_{max} at different substrate concentrations

The maximum specific growth μ_{max} rate of heterotrophic bacteria is determined by iterative curve fitting for different growth rates at different COD concentrations. These rates are calculated according to equation (5-5) with $\mu_{max} \sim 1.05 \cdot (\mu_{max}\text{-}k_d)$ as an approximation for the determination of the decay coefficient (Kappeler and Gujer, 1992). The calculated decay coefficient is then $k_d = 1.07\ d^{-1}$.

$$\ln \frac{OUR_{growth}}{OUR_{t=0}} = (\mu - k_d) \cdot t \qquad \textbf{(5-5)}$$

where μ = growth rate, d^{-1}
k_d = decay coefficient, d^{-1}

The different growth rates μ are plotted over their corresponding COD concentrations. The mechanism for growth of the adapted biomass follows the Michalis-Menten mechanism (cf. equation (5-6)). A curve fitting, assuming a first order reaction is done with the least square method to become the best values for μ_{max} and K_S.

$$\dot{r}_S = \mu_{max} \cdot \frac{c_S}{K_S + c_S} \qquad \textbf{(5-6)}$$

where $\dot{r}_S$ = growth rate on substrate, d^{-1}
K_S = half saturation coefficient, $mg_{COD}L^{-1}$
c_S = substrate concentration, $mg_{COD}L^{-1}$

For μ_{max} determination the F:M ratio had to be high in order to obtain growth without limitations. The added feed concentration (up to 40mL concentrate) can result in inhibition of bacteria growth due to high ammonia concentration of more than 60 mgL^{-1}, (Metcalf and Eddy, 2003), unless biomass is adopted. This is not the case for the sludge from the SM-SBR, because during normal operation bacteria are exposed to a low concentration of ammonia. Therefore, the NH_4Cl concentration in the synthetic greywater was reduced by the factor of 2 for this series of experiments.

Using the above mentioned method yields a μ_{max} of 22.4 d^{-1} and a K_S of 689 mgL^{-1}, respectively (cf. Figure 5-29). K_S corresponds to the value of rbCOD equivalent to the half of μ_{max}. The determined values are very high compared to kinetic studies with municipal wastewater reported in literature. Only Al-Malack (2006) found even higher K_S values for increasing MLSS concentration. Studies done with synthetic wastewater at the Chair of Chemical Engineering, TU Berlin, yielded also high value for K_S (up to 900 mgL^{-1}; an MBR treating synthetic wastewater at long SRT of 50 d). Since all high K_S values are determined with synthetic feed, it might be a hypothesis that the difference to real wastewater lies in the adaptation of biomass to the constant synthetic feed. While feeding a system with real wastewater, the biomass is exposed to changes in its constituents and in COD concentration, especially during rainfall. This is not the case for the operation of lab or pilot scale reactors with synthetic wastewater. The biomass is very well adapted to the substrate and can yield therefore with higher growth rates and higher K_S values.

Although a high growth rate with the batch experiments is calculated, in normal operation of the SM-SBR (set-up C), only a very low specific growth rate of $\mu^* = 0.019\ d^{-1}$ can be found. This might indicate that the HRT, even so it was reduced, is too long for optimal biomass growth during reactor operation. Despite the low COD of greywater, the heterotrophic aerobic biomass shows higher maximum growth rates on either rbCOD and/or sbCOD compared to real wastewaters, whatever treatment process. A justification can be the cumulating effects of a high fraction of rbCOD and the low yield coefficient, which is itself affected by bacteria storage effect due to the long SRT and HRT of the SM-SBR (Dircks et al., 1999). A hypothesis to be validated is that due to the long HRT and SRT, non-storing bacteria are encouraged to utilize sbCOD and recalcitrant substance, such as dead cells, during the famine period.

Determination of k_H

As mentioned above, the growth on sbCOD becomes only visible when rbCOD is totally depleted. Growth becomes limited by the substrate; the OUR is dominated by both, hydrolysis of sbCOD content and by the hydrolysis coefficient k_h, as shown in equation **(5-7**). This latter depends to some extent on the biomass concentration (Henze et al., 2000).

$$\frac{d\,\text{sbCOD}}{dt} = -k_h \cdot \text{sbCOD} \qquad \textbf{(5-7)}$$

where k_h = hydrolysis coefficient, d^{-1}

Hydrolysis makes available all sbCOD by transforming it into rbCOD. Substrate is made cell available by extracellular enzymatic reactions. They are considered to be surface reactions in close contact with the organism and are assumed to be active at all times, independently of the electron donor. For the synthetic greywater $k_H = 0.42 \pm 0.14$ d^{-1}. The data in literature show higher hydrolysis rates (cf. Table 5-9) except for Ginestet *et al.* (2002), who shows similar low rates. It can be said that the higher hydrolysis rates are obtained with batch experiments lower than 24 h, whereas the lower values are deduced from long term experiments >24h. This shows a time sensitivity of the evaluated results from batch experiments. If the slowly biodegradable fraction is not well separated, the hydrolysis rate may include a quantity of the rbCOD. Ginestet *et al.* (2002) explains that higher k_H results mainly from the soluble and colloidal fraction, which are quantified as readily hydrolysable matter.

5.4.3 Rates of Nitrification and Denitrification

The sludge was sampled from the SM-SBR 10 to 20 min after the end of the filling phase. A waiting period of 20 min with a slow mixing speed of 50 rpm was incorporated before the actual measurement of the different nitrogen compounds started. The equations (3-13), (3-15), and the slope from the nutrients concentrations (ammonium, nitrate, and nitrite) versus time (cf. Figure 5-32) were used to evaluate and calculate the different rates. In most batches acetate was added as a source for rbCOD, but for comparison also experiments with greywater concentrate and without any additional carbon source were undertaken. To complete the picture the rates from cycle analysis were likewise calculated.

AUR and NUR results

The ammonium utilisation rate (AUR) was calculated from the slope of ammonia during the aerobic phase, while the nitrate-N utilisation rate (NUR) was calculated from the slope of nitrite and nitrate together during the anoxic phase. Figure 5-30 shows the results from a run as an example for the many batches carried out with acetate as C-source. The sludge was obtained from set-up C with an HRT = 12h.

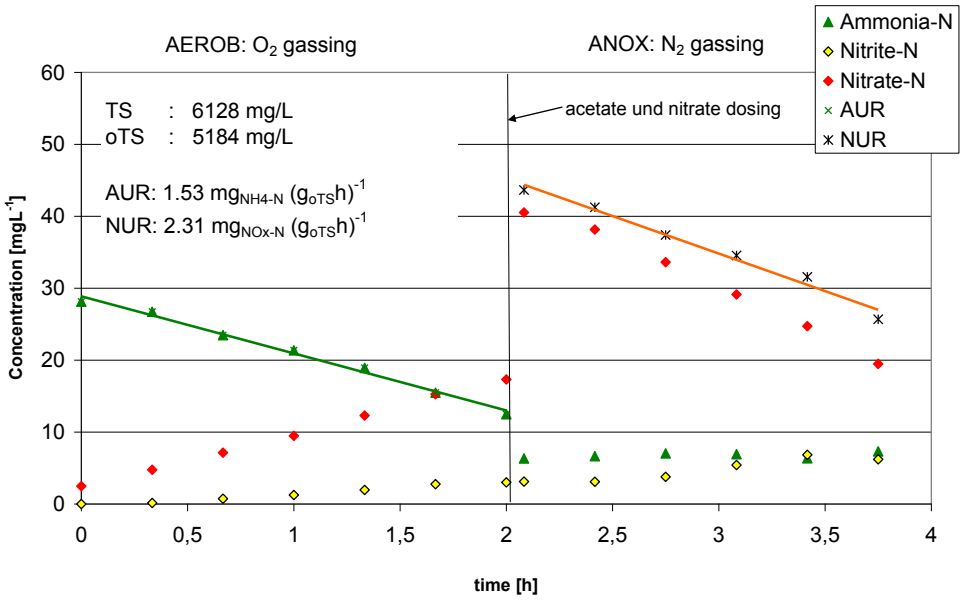

Figure 5-30: AUR und NUR determination with acetate dosing of sludge from set-up C with an HRT=12h

The result obtained from the batch test in Figure 5-30 were AUR = 1.53 $mg_{NH4\text{-}N}$ $(g_{oTS}\ h)^{-1}$ and NUR = 2.31 $mg_{NOx\text{-}N}$ $(g_{oTS}\ h)^{-1}$. A NUR calculated only on the depletion of NO_3-N would result in a minor higher rate of 2.37 $mg_{NOx\text{-}N}$ $(g_{oTS}\ h)^{-1}$. As it can be seen, nitrification and denitrification run linear with time and resulted very often in high R^2 greater than 0.95 for all the undertaken batch experiments. The ammonium depletion as well as the nitrate production occurred with an almost linear trend. During the aerated phase a concentration of nitrite was measured, which increased during the anoxic phase. The nitrite production was visible in all runs, which was an evidence for the strong production of the intermediate product nitrite for the process of nitrification and denitrification due to the high start concentration.

The denitrification process is much quicker with acetate addition, as can be seen by comparing Figure 5-30 with Figure 5-31. This means, in order to improve the denitrification process an external C-source, easy biodegradable like acetate, should be added to achieve a higher NUR and a better total nitrogen removal in greywater treatment processes [Gildemeister, 2005].

Figure 5-32 shows one run with greywater concentrate as the available C-source. The rates for denitrification with AUR = 3.34 $mg_{NOx\text{-}N}$ $(g_{oTS}\ h)^{-1}$ and for nitrification NUR = 2.98 $mg_{NOx\text{-}N}$ $(g_{oTS}\ h)^{-1}$ are higher compared to the batch runs with acetate as the available C-source. The Reason for this might be the adaptation of the sludge to the feed composition, whereas acetate, although know as a source of rbCOD, may need a higher concentration of enzymes for degradation of acetate.

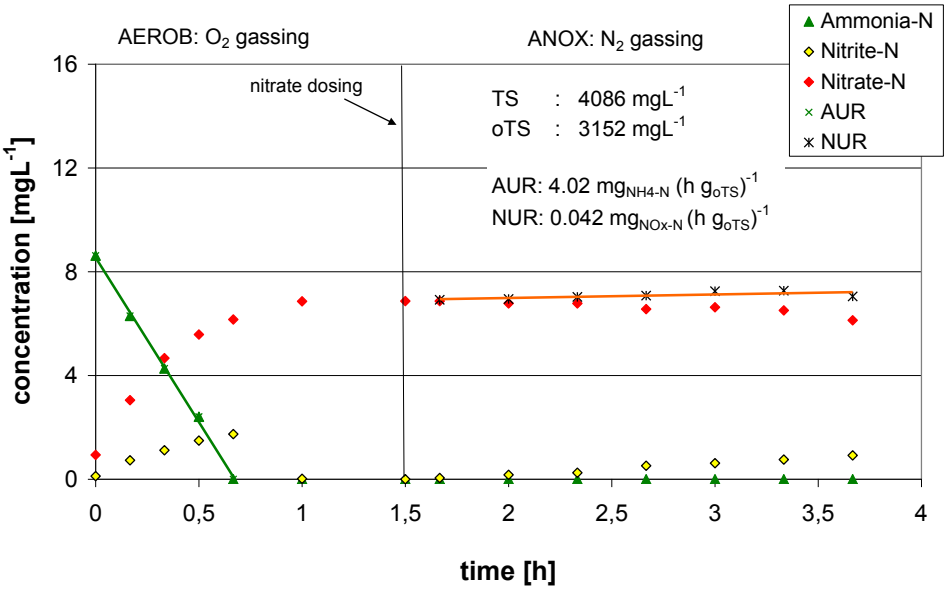

Figure 5-31: AUR & NUR determination without C-dosing

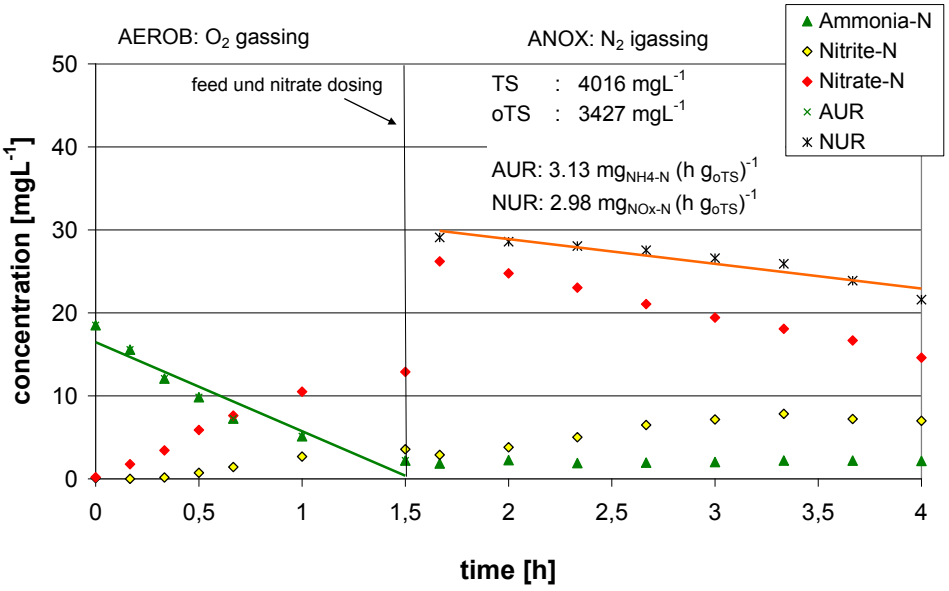

Figure 5-32: AUR & NUR determination with C-dosing in form of GW concentrate

At last, the cycle analysis of the SM-SBR provides further results on the AUR and NUR rates. As shown in Figure 5-33 the rates calculated are lower than in the batch experiments. In the given example the rates are: AUR = 0.78 $mg_{NOx\text{-}N}$ (g_{oTS} h)$^{-1}$ and NUR = 0.84 $mg_{NOx\text{-}N}$ (g_{oTS} h)$^{-1}$. The lower rates are due to the low concentration of COD and nitrogen compounds at the beginning of each cycle.

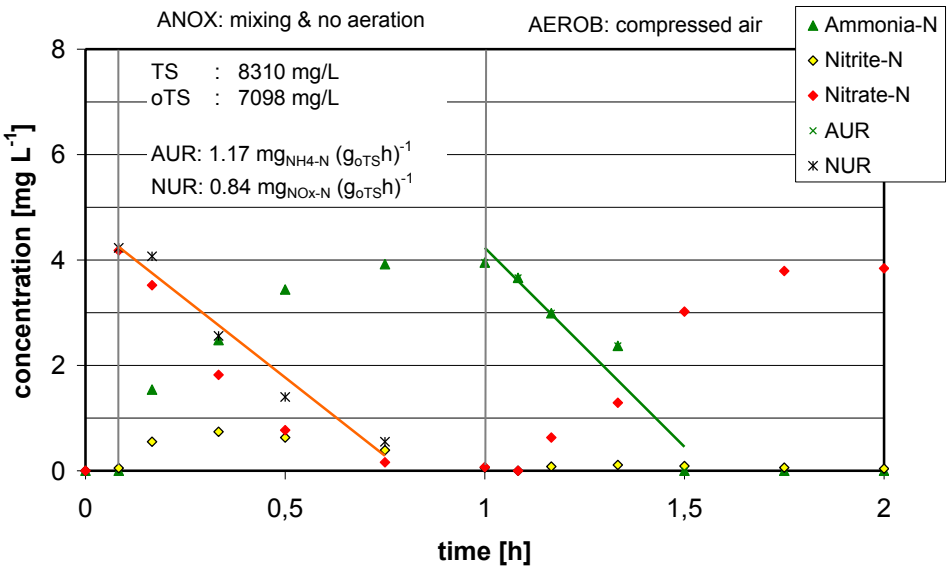

Figure 5-33: Determination of AUR & NUR from cycle analysis (set-up C)

In summary, the results of the nitrate-N utilisation rate (NUR) can be used to assess the denitrification potential of the operating system and hence the resulting N removal efficiency. A comparison of the rates is presented in Figure 5-34.

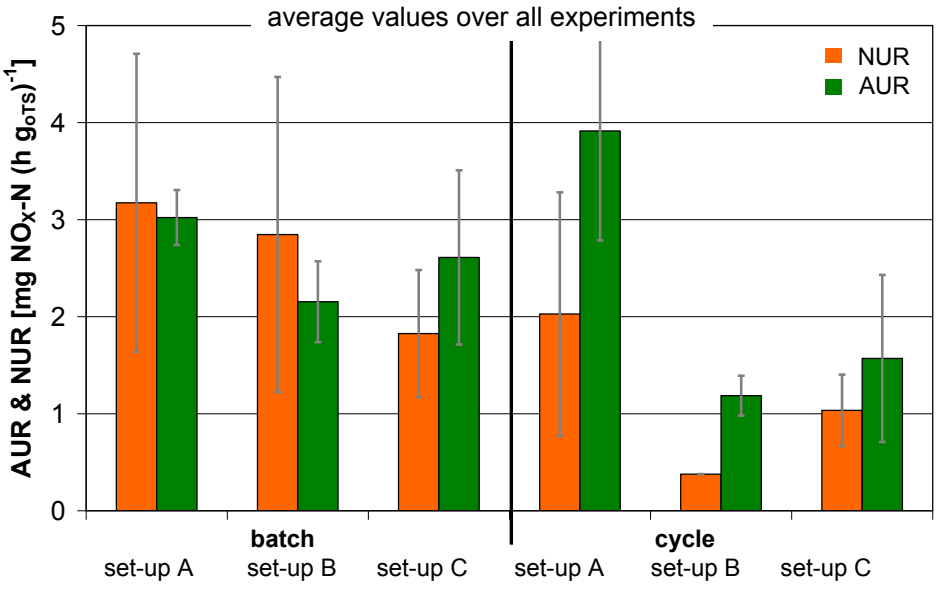

Figure 5-34: Comparison of AUR & NUR for batch experiments and from cycle analysis of all set-ups

It can be seen that the rates have a strong margin of deviation. The reasons are the changing operation conditions, especially in set-up A, as well as the different boundary conditions for the batch experiments (e.g. adding acetate as substrate).

The rates calculated from the cycle analysis for set-up B and C increase with cycle time reduction. Set-up A shows the highest rates during operation, especially AUR. This is mostly attributed to sludge growth in the start-up phase. Ammonia is not only oxidised to nitrate by nitrification, but also incorporated into biomass for cell growth. The highest rate is gained from batch experiments with acetate dosing with the purpose to compare the results to literature data and to analyse the optimisation potential of the performance of the SM-SBR. The value is almost six times the endogenous NUR of 0.52…0.62 $mg_{NOx\text{-}N}$ $(g_{oTS}\ h)^{-1}$, but within the same ratio found in literature (Buckley and Naidoo, 1999).

The range of AUR and NUR is presented in Table 5-10 with special focus on the different HRT for set-up C. The results are gained from cycle analyses of the SM-SBR with its different set-ups and from batch experiments with acetate dosing. The rates show a great variation. The data for specific nitrification rates (AUR) in literature range from 0.78…1.81 $mg_{NO3\text{-}N}$ $(h\ g_{SS})^{-1}$ for synthetic wastewater (Muller, 1995: quoted in (Kraume et al., 2005)) to 1.7…2.0 $mg_{NO3\text{-}N}$ $(g_{VSS}\ h)^{-1}$ for municipal wastewater (Fan et al., 2000: quoted in (Kraume et al., 2005)). A steady increase of AUR, similar to the NUR, could not be found during the reduction of HRT for the operation of the SM-SBR. Nevertheless the values are in the range reported in literature under limiting operating conditions for different MBRs. There, values from 1.0 up to 10.8 $mg_{NOx\text{-}N}$ $(g_{MLVSS}\ h)^{-1}$ are shown (Soriano et al., 2003).

Table 5-10: Range of NUR & AUR from the SM-SBR in comparison with literature

cycle analyses / batch experiments / literature	NUR [mg NO_x-N g^{-1} oTS h^{-1}]	AUR [mg NO_x-N g^{-1} oTS h^{-1}]
set-up A	0.60…4.10	2.07…4.95
set-up A: batch, with acetate dosing	3.97…4.95	1.03…3.14
set-up B	0.38	0.51…0.98
set-up B: batch, with acetate dosing	2.20…5.67	1.66…2.79
set-up C: HRT = 33h	0.71…0.79	0.51…0.98
set-up C: HRT = 24h	0.84…1.53	1.53…3.08
set-up C: HRT = 12h	1.54	0.96
set-up C: all HRT, batch, with acetate dosing	3.44…3.55	
Muller, 1995: quoted in (Kraume et al., 2005)		0.78…1.81
Fan *et al.*, 2000: quoted in (Kraume et al., 2005)		1.7…2.0
(Vocks *et al.*, 2005): EBPR sludge, pre-denitrification	1.2…3.0	
(Vocks *et al.*, 2005): EBPR sludge, post-denitrification	0.47…1.17	
(Soriano *et al.*, 2003): MBR, HRT 10…14h	1.9…11.4	4.6…10.8
(Zhang et al., 2006) : SM-SBR, batch test		0.40 $mmol_{NH4\text{-}N}$ $(g_{VSS}\ d)^{-1}$

5.5 Greywater Treatment with Real Greywater

Alternative treatment options for wastewater reuse were tested and operated within the framework of Zer0-M. Next to constructed wetlands, anaerobic digester and ponds, this was

the advanced technology of membrane bioreactors. A first feasibility study was done with a 3L lab scale MBR at the premises of the Institute Agronomique et Vétérinaire (IAV) in Morocco. The results were used to set the operational conditions for a 600 L pilot reactor installed afterwards. The same type of reactor, one for the treatment of greywater and one for the treatment of blackwater, was also installed from the Turkish partner at the TUBITAK Marmara Research Centre (MRC). Whereas the lab scale reactor was operated in continuous flow mode, the 600L reactors were operated as an SM-SBR. The VER was set at 0.2, meaning an exchange volume of around 120L so that the results were comparable to the results from set-up C in this study.

5.5.1 3 L Batch MBR

A 3 L lab-scale MBR (Figure 5-35) with a hollow fibre UF-membrane, type ZeeWeed by Zenon, was continuously operated for 137 days. The submerged membrane module had a membrane area of 400cm².

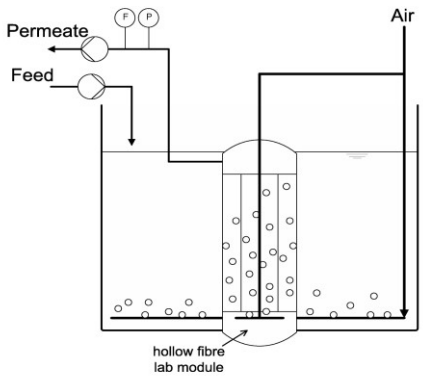

Figure 5-35: 3L lab-scale MBR, operated in the IAV laboratory in Morocco, for feasibility studies

The MBR was operated in a cycle of 45 minutes of permeation phase and 15 minutes of relaxation phase. For permeation a peristaltic pump (Minipuls 2, Gilson) was used. The reactor was fed quasi-continuously by a membrane pump (Prominent Electronic, CfG) to maintain a constant volume of 3 litres. The TMP was measured with an analogue precision manometer (WIKA, display accuracy ±0.1%, scaling 0.01). It was adjusted not to exceed 400mbar.

The Table 5-11 shows the operating parameters of the 3 L lab-scale reactor, operated in Morocco and treating greywater from shower effluent.

Table 5-11: Operating parameters of the lab-scale MBR

Operating Parameters	Average	Maximum	Minimum
HRT, h	13	18	9
Membrane area, cm^2	400	-	-
Pore size, µm	0.1	-	-
Transmembrane pressure, mbar	249	402	73
Flux, $L(m^2h)^{-1}$	8	11	7
Aeration flow rate, $Nm^3(h)^{-1}$	0.32		
MLSS, gL^{-1}	1.30	0.42	1.85
MLVSS, gL^{-1}	0.94	0.26	1.32
L_{org}, kg_{COD} $(m^3d)^{-1}$	0.16	0.21	0.09
Feed/Biomass, mg_{COD} $(d\ g_{VSS})^{-1}$	256	390	118

The raw greywater was filtered with a 1cm x 1cm and a 1mm x 1mm screen successively, before it was pumped into the vessel. To achieve oxygen saturation and complete mixing in the reactor, compressed air was continuously supplied at a flow rate of 0.32 m^3h^{-1}. It was partly introduced from the bottom of the membrane to enhance membrane cleaning, and partly from a pipe, placed on the bottom around the reactor perimeter to prevent bacteria from adhering to the reactor wall and settling in its edges. During the reported period the reactor temperature increased from 9 to 20°C. The pH was in the range of 7.6±0.4.

Influent and effluent characteristics as well as overall removal performance are summarised in Table 5-12. The shower effluent shows an average COD concentration of 109 mgL^{-1} and daily peak loads not exceeding 170 mgL^{-1}. Hence, it can be said that this greywater is highly diluted. Similar values are reported for a shower effluent of a students residence in Tunisia where a mean COD of 102 mgL^{-1} and a mean BOD_5 of 56 mgL^{-1} are found (Lamine et al., 2007). Remarkably, the ratio COD/BOD_5 is low with values between 1.1 and 2.0, which indicates high biodegradability. In literature values up to 4 are reported (Scheumann and Kraume, 2009).

The treatment of greywater with the MBR reduced the COD load on average by 85%. A mean effluent concentration of 15 mgL^{-1} was obtained (Figure 5-36). The COD/BOD_5 ratio in the permeate reached values up to 25 indicating that BOD_5 was almost completely removed. Temperature and biomass concentration did not have a marked influence on removal performance, because on day 40, the COD removal reached 86% at 11°C with a TS concentration of 0.4 $g_{VSS}L^{-1}$, whereas at day 137, the COD removal was 88% at 20°C with a biomass concentration of $1.4g_{VSS}L^{-1}$.

Table 5-12: GW characteristics, incl. standard derivation, and removal performance of the 3 L MBR

Parameter	Influent	Permeate	removal
pH	7.6±0.4	7.9±0.4	-
EC, µScm^{-1}	645±67	711±130	-
DO, mgL^{-1}	0.4±0.2	8.4±0.3	-
Turbidity, NTU	29±11	0.5±0.3	98
COD, mgL^{-1}	109±33	15±11	85
BOD_5, mgL^{-1}	59±13	4±1.2	94
TKN, mgL^{-1}	15.2±4.5	5.7±1.9	63
NH_4^+, mgL^{-1}	11.8±4.2	3.3±2.9	72
NO_3^-, mgL^{-1}	0.0±0.0	2.1±2.5	-
Total phosphor, mgL^{-1}	1.6±0.5	1.3±0.4	19
PO_4^{3-}, mgL^{-1}	1.0±0.4	0.9±0.2	4
Surfactants (LAS), µgL^{-1}	299±233	10±5	97
Faecal Coliforms, 100 mL^{-1}	1.4*10^5±1.1*10^5	68±120	99

EC: electrical conductivity; DO: dissolved oxygen; TKN: Total Kjeldahl Nitrogen

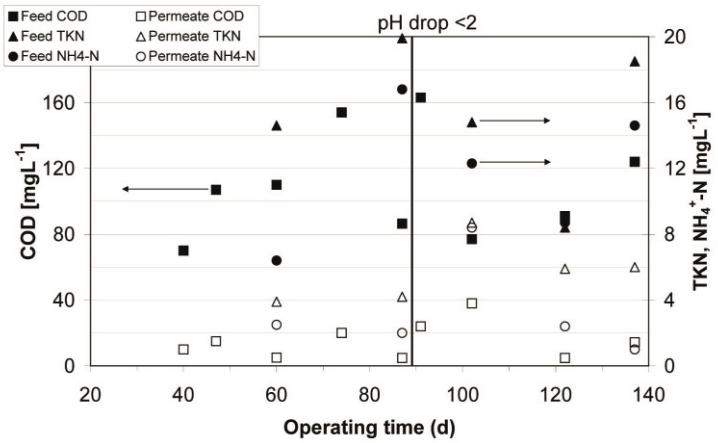

Figure 5-36: Evaluation of COD and nutrient concentrations in the 3L- MBR

In the permeate nitrate accounted for the difference between TKN and ammonium. Remarkably, in spite of the oxygen saturation and the high HRT, no complete nitrification was achieved in the MBR. The high ammonium percentage in the permeate on day 102 is explained by an accidental pH-shock (overnight drop to pH 2) on day 89. Apparently, it had a lasting effect on the nitrifying population so that even 13 days afterwards no nitrification could be observed and practically all nitrogen (97%) in the permeate was present as ammonium.

Anionic surfactant concentration was reduced by 97% to a concentration of 13 µgL^{-1} in the

permeate. Suspended and colloidal matter were retained by the membrane and permeate dissolved oxygen concentration (near saturation) indicated that bacterial activity in the permeate was very low. Thus the effluent was very clear (turbidity <1NTU) and completely free from odours.

Bacteriological Contamination

The membrane pore size of ZeeWeed membranes was approximately 0.1 µm, so that most bacteria and particularly faecal coliforms should be retained. However, in the first analysis after 60 days of operation, a concentration of 2log units per 100 mL was detected as shown in Table 5-13. Visibly, a biofilm (algae, bacteria) had developed inside the suction pipe of the permeate pump. The biofilm was removed by disinfection of the permeate pipe and the membrane (3h with chlorinated water and 3h with water; every 10 min, the membrane was backflushed). Afterwards, no bacteria were detected for 37 days, indicting and confirming membrane tightness for bacteria. The contamination came most probably from the outlet of the permeate pipe (bacterial re-growth). Nevertheless, analysis revealed the presence of bacteria after 122 days of operation, but no faecal coliforms were detected. Further evolution and experimental test should be made closely in order to assess the possible appearance of faecal coliforms. Still, when zero faecal coliform levels have to be guaranteed at all times, disinfection will be necessary. (Lazarova et al., 2003)

The presence of bacteria in the permeate could be explained by protein migration which may facilitate the transport of faecal coliforms through the membrane and their subsequent re-growth in the distribution system as cited in (Jefferson et al., 1999). The permeate characteristics in this study met commonly adopted standards regarding recycling for toilet flushing or other household uses, which do not require potable water quality (Table 5-13).

Table 5-13: Water quality standards for domestic wastewater reuse (from Surendran et al. (1998))

	Total coliforms $(100mL)^{-1}$	**Faecal coliforms $(100mL)^{-1}$**	**BOD_5 (mgL^{-1})**	**Turbidity (NTU)**	**pH**
US EPA		non detectable	10	2	6-9
EC bathing water directive	10000^{m}	2000^{m}			6-9
Germany	500^{g}	100^{g}	20^{g}	$1\text{-}2^{m}$	6-9

m = mandatory, g = guideline

Biomass development

The reactor was not inoculated with return sludge from an ASP, as usually done to fasten the start-up period. A specific sludge environment was expected to develop by itself, adapted to the greywater. Over the first 80 days at a mean temperature of 13°C the bacteria showed a fairly constant growth rate of 19 mg $(L\ d)^{-1}$ (cf. Figure 5-37), which equals to a specific growth rate of 0.016 d^{-1}. This is near the growth rate from the studies with synthetic greywater

carried out with set-up B and set-up C. There, values between 19 and 25 mg $(L\ d)^{-1}$ were found at a mean average temperature of 15°C, although the specific growth rate for set-up C and B is lower by a factor of 10 and is calculated to 0.002 d^{-1} and 0.004, respectively.

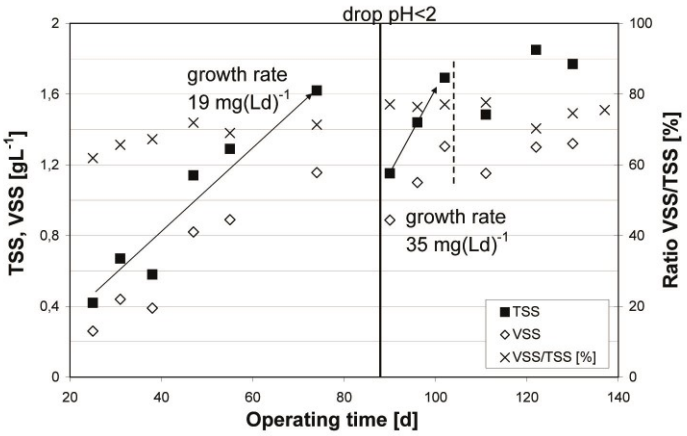

Figure 5-37: Evolution of total and volatile suspended solids in the MBR

After a pH-shock in the lab-scale MBR, which destroyed nearly 25% of the biomass, a quick recovery with a growth rate of 35 mg $(L\ d)^{-1}$, which equals to a specific growth rate of 0.023 d^{-1}, was observed. One reason for the quicker development could be the higher average temperature (18°C) in the reactor at that time, because all other conditions stayed constant. Another hypothesis could be that due to the death of the slow growing nitrifiers a selection advantage for faster growing organisms was given.

Above 1.3 $g_{VSS}L^{-1}$ biomass stayed nearly constant. This indicates that at an average F/M ratio of 0.12 $g_{COD}(g_{VSS}\ d)^{-1}$ substrate was almost exclusively consumed by endogenous respiration. Average F/M-ratios for MBR treating municipal wastewater can be even below 0.12 $g_{COD}(g_{VSS}\ d)^{-1}$ for systems with a low sludge yield. This is advantageous with respect to waste generation and can be seen as one of the key advantages of MBR (Judd, 2006).

During the time of operation the suspended organic solids (VSS) increased due to biomass development, but their relative contribution to the total suspended solids (TSS) stayed almost constant. After a slight initial increase the VSS/TSS-ratio stabilised at 76% indicating that about one fourth of the TSS in the reactor was particulate inorganic as shown in Figure 5-37. No accumulation of external inorganic matter took place in the system, because the augmentation was due to particulate inorganics arising from biomass decay.

Summary

This study demonstrated that MBR technology can be used to treat greywater with a low COD concentration and a low absolute nutrient content. With a ratio of 100:14:1.5 COD:NH_3:P the relative nutrient content was high in comparison to that observed by other authors cited earlier in the text (cf. chapter 5.1). The permeate characteristics met commonly adopted standards for recycling of treated wastewater. It could be used for toilet flushing or other household uses, which do not require potable water quality. To guarantee zero faecal coliform levels at all times, disinfection of the permeate should be necessary. The permeate was of excellent aesthetic quality and free from odours, a fact that is very important in view of public acceptance of treated water recycling.

5.5.2 600L Pilot MBR

As already said, three 600 L pilot scale MBR were operated at the Zer0-M partner institutes. They are similar to set-up B, but with only a working volume of 600 L and also operated in a sequential batch mode. They were manufactured by the BUSSE GmbH, and included a submerged PF module made out of a polyelelectrolyte complex (PEC) by Kubota with a nominal pore size of 0.4 µm, and total membrane area of 5 m². The building of filtration cake layers on the membrane surface were controlled by a mixture of fine and course bubble air scouring. The TMP was set by gravity flow through the water head above the membrane (TMP ~ 0.12 bar). The flux of the systems during operation was measured between 26 and 36 L $(m^2h)^{-1}$. Air was automatically controlled via time sequences stored in the system's PLC, for permeation and setting the anoxic-aerobic conditions. (Atasoy et al., 2007)

The 600L SM-SBR in Turkey was fed with real GW from 28 apartments, including kitchen wastewater at low share. The COD of the received greywater varied in the range of 120 - 449 mgL^{-1}. The GW was stored in a buffer tank serving as a homogenising unit before it was pumped into the MBR. Coarse and fine particles were removed with a 6 mm² and a 3 mm² mesh screen, placed in the buffer tank.

The biomass concentrations increased gradually throughout the operation and reached a level of near $10gL^{-1}$ after almost 300 days of operation. The specific growth rate was calculated to 0.005 d^{-1}, little above the value for set-up C. The settling characteristics as well as the permeability of the activated sludge decreased with increasing MLSS concentration, as shown in Figure 5-38. During the operation period, the initial average permeability dropped from 280 $L(m^2hbar)^{-1}$, as achieved in the first 50 days, down to 80 $L(m^2hbar)^{-1}$ at day 160. A cleaning of the membrane with pressurised water improved the permeability only slightly. A rise in temperature and an initial 96h continuous aeration resulted in an increase of permeability from day 250 by a factor of 3. The increasing biomass concentration had no effect on the low permeability.

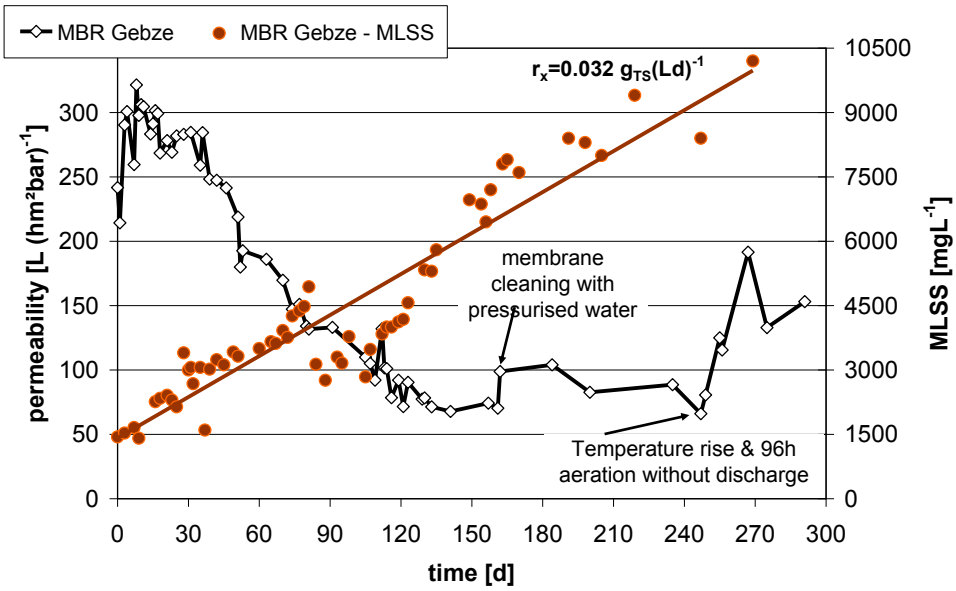

Figure 5-38: Permeability and biomass development of the 600L SM-SBR in Turkey

The 600L SM-SBR in Morocco was also fed with real GW from showers of a sports and leisure club near by. The COD of the received greywater varied in the range of 98 - 152 mgL^{-1}. The GW was stored in a buffer tank serving as a homogenising unit before it was pumped into the MBR. Coarse and fine particles were removed with two 3 mm² mesh screen, one placed at the collection tank near the club and the other in the buffer tank near the MBR.

Although the greywater quality was very different in both systems, the removal performance was comparable. In terms of COD removal, the SM-SBR in Turkey achieved a higher removal of ~96% than the SM-SBR in set-up C operated with synthetic greywater, which could only remove ~90% of the COD (compare Figure 5-12). The SM-SBR in Morocco could only remove 84% of the incoming COD. These differences may be explained by the different greywater and its resulting inlet concentrations. These varied from as low as ~120mgL^{-1} (Morocco) up to ~300mgL^{-1} (Turkey), compared to the effluent quality, which was for all set-ups in average between 13-21mgL^{-1}. The greywater treatment plant fed with the highest COD concentration showed therefore the highest removal performance.

The ammonia degradation of the 600 L SM-SBR in Turkey was lower compared to the SM-SBR from set-up A, B, and C in this study. This might be an indicator for optimisation potential in terms of setting properly the times for each phase. The biological reaction time after feeding raw greywater into the tank was set to 33 min before the permeate withdrawal starts (Atasoy et al., 2007). This might be not enough for complete ammonia removal.

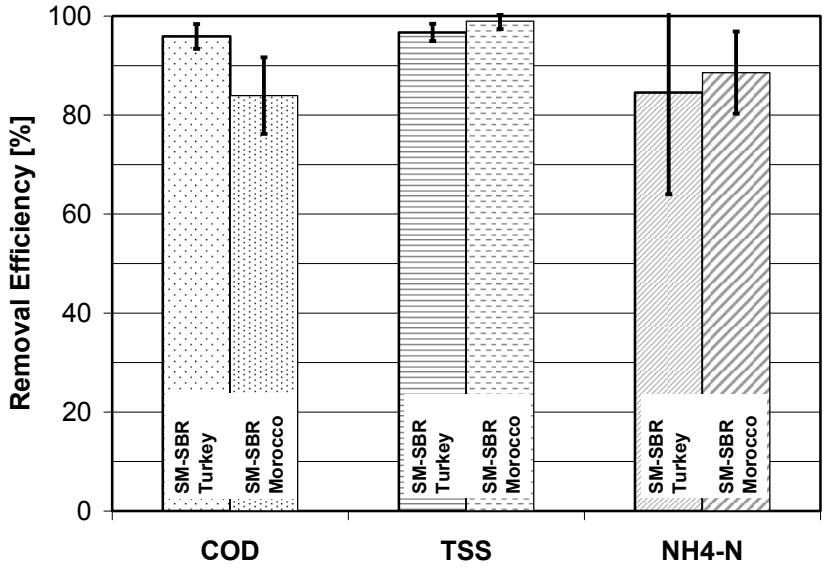

Figure 5-39: Removal efficiency of the pilot plants treating real greywater with its standard derivation

The MBR performance data reported generally refer to domestic wastewater treatment. There are very few studies with detailed results of greywater treatment with an MBR. A pilot scale study carried out by Lesjean and Gnirrs (2006) showed >85% COD, >80% TKN, and 99% TSS removal performance for grey water generated from bathrooms and kitchens. It was reported by Merz *et al.* (2007), that 85% COD, 63% TKN, and 94% BOD removal were achieved by laboratory-scale MBR treatment of grey water generated form sport club showers. The results from the above mentioned studies carried out by the Zer0-M project team proved the technical feasibility of greywater treatment with membrane technology. Yet, an important drawback remains: each treatment system has to be judged separately due to the variations in greywater composition. If flux cannot be maintained at a high level, the required membrane area must be increased and the associated costs will be high. However, in cases of space limitation like e.g. in hotels or leisure clubs, the small footprint of the MBR can compensate these inconveniences.

6 Process Description with a Mathematical Model

The increasingly stricter nitrogen and phosphorus limits on wastewater discharges have stimulated studies on both:

- understanding and modelling of the behaviour of activated sludge process, and
- developing and improving the single sludge biological nutrient removal process configurations.

With its intrinsic flexibility the modern SBR enjoys a gradually widening application, and is subject to extensive research for a better comprehension and exploitation of the offered advantages. Nevertheless, the influence of variable operation conditions or variable influent concentrations should not affect the desired effluent quality. Therefore, a model can help to understand, define and manipulate a performance evaluation as well as a prediction of the desired design.

There are two main approaches to develop process models. The first one is based on empirical data, and the second is based on the underlying physics and chemistry governing the behaviour of the process. With the empirical models, such as lab scale or pilot scale reactors, enough data can be collected from the process, but usually these data are site specific. Even if a correlation structure between variables can be gained and maximised with the help of a numerical technique, much depends on the availability of representative data for model building. It is difficult to find parameters for the structure among the data and to validate them against an artificial data set. Maybe many trial and error approaches need to be adopted, before achieving a more general conclusion.

The development of mechanistic models uses fundamental knowledge of the interactions between process variables to define the model structure. Different experiments need to be performed to determine the parameters of the model independently, which can be very time consuming. Numerical techniques can be applied to parameterise the model. In this case, although the structure has been determined from process knowledge, the modelling procedure becomes an empirical one. The numerical techniques in use are very different from those usually encountered in purely empirical modelling. They tend to be iterative and more complex. In general the mechanistic models can provide a more realistic prediction of the process. Thus, while mechanistic models are used to design processes, empirical models are frequently used as the basis for process controllers. The point is that model based controllers only require the models to represent the trends in process behaviour with less accuracy. Conservative tuning, together with the feedback mechanism are usually sufficient enough to overcome any inaccuracies.

Another comparison can be made between the two modelling approaches when the focus is on costs. Due to the complexity of many processes, mechanistic modelling is indeed very expensive in terms of human effort and expertise. As the mechanistic modelling approach forces a detailed examination of fundamental process behaviour, some of the cost can be

recovered in terms of increased 'deep' knowledge of process behaviour. On the other hand, empirical models can be expensive as well, because they require large amounts of 'representative' data. The advantage with empirical modelling lies in the fact that empirical modelling will deliver a form of working model in a much shorter time. The consequence is that the question: "What is the purpose/ the usage of the model?" must be answered before handed. If it is to design control algorithms, then an empirical model will serve, but if there is a need to design a new process; or to trouble-shoot a process that is behaving poorly; or to point towards fundamental improvements in process operability, then it is best to develop a mechanistic model.

To describe the activated sludge process for biological treatment of wastewater, the first mechanistic models were proposed in the sixties of the last century by McKinney, 1962 and Jenkins and Garrison, 1968. The breakthrough came with the work of G. v. R. Marais, G. A. Ekama and P. L. Dold. They described the activated sludge process in steady state (Marais and Ekama, 1976), investigated the dynamic behaviour (Ekama and Marais, 1979) and came up with the first general model, while identifying different COD fractions (Dold et al., 1980). The work by the IAWPRC (later IAWQ and now IWA) task group on mathematical modelling for design and operation of biological wastewater treatment processes, which started in 1983, improved the model and lead over the years to the different activated sludge models ASM1, ASM2, ASM2d and ASM3 (Henze et al., 2000).

Biological wastewater treatment involves a wide spectrum of biochemical reactions adopted in different appropriate sequences of anaerobic, anoxic and aerobic conditions. The number of processes during operation of the SM-SBR, the specific hydraulic behaviour of an SBR and the number of compounds in the synthetic greywater make it mandatory to use a modelling tool to predict the effluent quality and to specify accurate design criteria. This chapter aims to develop and propose a simplified mechanistic model for nutrient removal in greywater treatment with a membrane coupled SBR, based on the ASM 3 and relying on the relevant principles of process stoichiometry and modelling.

6.1 Description of the Mathematical Model

As described earlier, the backbone of the activated sludge model is a matrix, which reflects the stoichiometric relationship and which corresponds to the involved processes and compounds. With increasing complexity of interactions and with a deeper understanding of the biochemical process, the process rate equations become more and more difficult.

In the derived model the kinetic expressions are based on hyperbolic terms, Monod based equations, and Michaelis-Menten based equations. They are called switching functions for mathematical convenience: all biological processes are stopped when the educt concentration reaches zero. Inhibition is modelled as $1-S/(K_m+S) = K_m/(K_m+S)$.

The activated sludge model No. 3 (ASM 3, (Henze et al., 2000)) is selected as basis for the derivation of an own mathematical model and therefore simplified, but also extended with a

two-step nitrification, as done by Manser *et al.* (2006), to enable separate modelling of ammonia and nitrite oxidation. Denitrification is a single step process ($NO_x \rightarrow N_2$), neglecting the possible intermediate of nitrite, whereas the nitrification is simulated as a two step process ($NH_4 \rightarrow NO_2 \rightarrow NO_3$). Ammonia is oxidised to nitrite as the first step, and further nitrite is oxidised to nitrate in a second step. This approach is made necessary to predict possible nitrite accumulation (Brouwer et al., 1998; Nowak et al., 1995). The loss of activity associated with the loss of bacteria is modelled as a single process (endogenous respiration), but individually for each group of bacteria, as well as separately for the anoxic and aerated phase.

The model includes seven soluble compounds (dissolved oxygen, ammonia, nitrite, nitrate, organic nitrogen, rbCOD, and stored soluble COD) and three particulate compounds (heterotrophic biomass, autotrophic biomass, and sbCOD). Concentration of soluble compounds are characterised by "S", and particulate compounds by "X". The soluble fraction can only be transported by water and carry ionic charge. The particulate fraction can be assumed to be the activated sludge, capable of sedimentation in the clarifier or retained by the membrane in the process. The stoichiometric and kinetic parameter values are given in the known ASM matrix v_{ji} in the Table 6-1 to display the process in the SM-SBR.

Cell internal or external storage products are not identified separately in batch tests, although they play an important role in this model, because growth of heterotrophic bacteria is based on the stored substrate only. Therefore, the amount of storage products comes from the hydrolysis and from the storage of readily biodegradable compounds (S_S). Hydrolysis is the necessary step for uptake of slowly biodegradable compounds (X_S) into the cells.

The following soluble compounds are identified and used in the model.

- dissolved oxygen S_{DO}, which can be directly measured in the reactor
- readily biodegradable organic substrates S_S, which is directly stored and which can be determinate with the help of respiration tests
- stored substrate S_{STO}, which comes from hydrolysis of X_S and from storage of S_S and is directly available for consumption by the heterotrophic organisms
- ammonia nitrogen S_{NH4}, which is assumed to be NH_4^+ for the balance of the ionic charges and is equivalent to the observed concentrations in the reactor and in the effluent
- nitrate S_{NO3} and nitrite S_{NO2}, as single compounds, because nitrification cycle analysis show the production of nitrite
- organic nitrogen S_{orgN} (mainly urea of the synthetic wastewater), which is transformed into ammonia during the anoxic phase

The following particulate compounds are identified and used in the model.

- slowly biodegradable substrate X_S, which is substrate of high molecular weight and which must undergo an external cell hydrolysis before degradation
- heterotrophic organism X_{BH}, which is the quantitatively biggest group of organism in the activated sludge and capable of growth under aerobic and anoxic conditions as

well as metabolism of all degradable organic substrate

- nitrifying organism X_{BA}, which are obligate aerobic and chemo-litho-autotrophic and responsible for oxidation of ammonia directly to nitrate

Growth and decay processes are described as suggested in the ASM 3. Substrate, such as S_{NH} and S_{STO}, is utilised by the microorganism. Since not all of the stored COD is needed for growth, but also for maintenance purposes, a factor (=x4) is introduced into the matrix.

Table 6-1: Matrix v_{ji} of the used model based on the ASM 3

j	Process	Component *i*									
		1	2	3	4	5	6	7	8	9	10
		X_{BH}	X_{BA}	S_{STO}	S_S	X_S	S_{orgN}	S_{NH}	S_{NO3}	S_{NO2}	S_{DO}
0_{AX}	switch AE → AX										-1
0_{AE}	switch AX → AE										1
1	hydrolysis and storage of X_S			x1		-1					
Heterotrophic organism, aerobic and denitrifying activity											
2	aerobic storage of S_S			x2	-1						
3	anoxic storage of S_S			x3	-1						
4	aerobic growth of X_{BH} (substrate degradation)	x4		$-\frac{1}{Y_H}$				- y4			$-\frac{Y_H}{1-Y_H}$
5	anoxic growth of X_{BH} (denitrification)	1		$-\frac{1}{Y_H}$				- y5	-x5		
6	Ammonification (hydrolysis of urea)						-1	1			
7	aerobic endogenous respiration	-1						y7			- x7
8	anoxic endogenous respiration	-1						y8	-x8		
Autotrophic organism, nitrifying activity											
9	aerobic growth of X_{BA}		1					$-\frac{1}{Y_A}$		x9	$-\frac{Y_A}{1-Y_A}$
10	transformation nitrite to nitrate								1	-1	
11	aerobic endogenous respiration		-1					y11			- x11
12	anoxic endogenous respiration		-1					y12	-x12		

All empty elements of v_{ij} indicate values of zero. All values of x_j and y_j can be calculated using equation (6-1).

$$r_i = \sum_j v_{ij} \cdot p_j \qquad \textbf{(6-1)}$$

where:

r_i: observation conversation rate;
v_{ij}: stoichiometric matrix;
p_j: process rate

Furthermore it is known that the biochemical energy yield in form of ATP of the anoxic respiration is smaller than in aerobic respiration. The following energy relationship can be applied, assuming η_{anoxic} = 0.60 - 0.70 of the aerobic energy yield:

$$\frac{1 - Y_{H,O_2}}{Y_{H,O_2}} = \eta_{anoxic} \cdot \frac{1 - Y_{H,NO_x}}{Y_{H,NO_x}} \qquad \textbf{(6-2)}$$

The model includes only microbiological transformation processes. The 12 different processes and their kinetic rates are shown in Table 6-2. The process number 0 serves only as a switch to simulate the aeration when changing from anoxic to the aerated phase and back to the anoxic. The heterotrophic organisms grow on the available stored substrate under aerobic conditions as well as under anoxic condition, where the respiration is based on denitrification. According to the ASM3, the anoxic reduction factor in this model is set to η_{NOX} = 0.6 to meet the fact that only a fraction of the heterotrophic biomass in the activated sludge is capable of denitrification. Endogenous respiration describes all forms of biomass loss and energy requirements not associated with growth, like decay, lysis, predation, death and so on. The process takes place under aerobic conditions as well as under anoxic conditions and must be referred to both groups of organisms: autotrophic and heterotrophic.

Table 6-2: Kinetic rate expression ρ of the used model

j	Process	Process Rate ρ
0_{AX}	switch AE → AX	$k_{DO} \cdot \left(\frac{S_{DO}}{K_{DO} + S_{DO}} \right)$
0_{AE}	switch AX → AE	$k_L a \cdot \left(S_{DO}^{saturation} - S_{DO} \right)$ with k_La of sludge
1	hydrolysis and storage of X_S	$k_h \cdot \left(\frac{\frac{X_S}{X_{BH}}}{K_h + \frac{X_S}{X_{BH}}} \right) \cdot X_{BH}$

Table 6-2: Kinetic rate expression ρ of the used model (cont.)

j	Process	Process Rate ρ
Heterotrophic organism, aerobic and denitrifying activity		
2	aerobic storage of S_S	$k_{sto} \cdot \left(\frac{S_{DO}}{K_{DO} + S_{DO}} \right) \cdot \left(\frac{S_s}{K_s + S_s} \right) \cdot X_{BH}$
3	anoxic storage of S_S	$k_{sto} \cdot \eta_{AX} \cdot \left(\frac{K_{DO}}{K_{DO} + S_{DO}} \right) \cdot \left(\frac{S_s}{K_s + S_s} \right) \cdot \left(\frac{S_{NOx}}{K_{NOx} + S_{NOx}} \right) \cdot X_{BH}$
4	aerobic growth of X_{BH} (substrate degradation)	$\mu_H \cdot \left(\frac{S_{DO}}{K_{DO} + S_{DO}} \right) \cdot \left(\frac{\frac{S_{STO}}{X_{BH}}}{K_{STO} + \frac{S_{STO}}{X_{BH}}} \right) \cdot \left(\frac{S_{NH}}{K_{NH} + S_{NH}} \right) \cdot X_{BH}$
5	anoxic growth of X_{BH} (denitrification)	$\mu_H \cdot \eta_{AX} \cdot \left(\frac{K_{DO}}{K_{DO} + S_{DO}} \right) \cdot \left(\frac{\frac{S_{STO}}{X_{BH}}}{K_{STO} + \frac{S_{STO}}{X_{BH}}} \right) \cdot \left(\frac{S_{NH}}{K_{NH} + S_{NH}} \right) \cdot \left(\frac{S_{NOx}}{K_{NOx} + S_{NOx}} \right) \cdot X_{BH}$
6	Ammonification (hydrolysis of urea)	$k_{orgN} \left(\frac{S_{orgN}}{K_{orgN} + S_{orgN}} \right) \cdot X_{BH}$
7	aerobic endogenous respiration	$k_{d,H(DO)} \cdot \left(\frac{S_{DO}}{K_{DO} + S_{DO}} \right) \cdot X_{BH}$
8	anoxic endogenous respiration	$k_{d,H(NOx)} \cdot \left(\frac{K_{DO}}{K_{DO} + S_{DO}} \right) \cdot \left(\frac{S_{NOx}}{K_{NOx} + S_{NOx}} \right) \cdot X_{BH}$
Autotrophic organism, nitrifying activity		
9	aerobic growth of X_{BA}	$\mu_A \cdot \left(\frac{S_{DO}}{K_{A,DO} + S_{DO}} \right) \cdot \left(\frac{S_{NH}}{K_{A,NH} + S_{NH}} \right) \cdot X_{BA}$
10	transformation nitrite to nitrate	$k_{A,NOx} \cdot \left(\frac{S_{DO}}{K_{A,DO} + S_{DO}} \right) \cdot \left(\frac{S_{NOx}}{K_{A,NOx} + S_{NOx}} \right) \cdot X_{BA}$
11	aerobic endogenous respiration	$k_{d,A(DO)} \cdot \left(\frac{S_{DO}}{K_{A,DO} + S_{DO}} \right) \cdot X_{BA}$
12	anoxic endogenous respiration	$k_{d,A(NOx)} \cdot \left(\frac{K_{A,DO}}{K_{A,DO} + S_{DO}} \right) \cdot \left(\frac{S_{NOx}}{K_{A,NOx} + S_{NOx}} \right) \cdot X_{BA}$

Based on the matrix v_{ij} and on the process rates ρ_j, the following mass balances during the anoxic phase (cf. Table 6-3) and during the aerated phase (cf. Table 6-4) for each compound can be identified.

Table 6-3: Mass balance equations during the anoxic phase

Component *i*	Mass Balance Equations for the Anoxic Phase
S_{DO}	$V\frac{dS_{DO}}{dt} = -\rho_{0,AX}V$
X_S	$V\frac{dX_S}{dt} = \dot{Q}_{in}X_S^{in} - \dot{Q}_{out,AX}X_S^{out,AX} - \rho_1 V$
S_S	$V\frac{dS_S}{dt} = \dot{Q}_{in}S_S^{in} - \dot{Q}_{out,AX}S_S^{out,AX} - x3\cdot\rho_3 V$
S_{STO}	$V\frac{dS_S}{dt} = \dot{Q}_{in}S_S^{in} - \dot{Q}_{out,AX}S_S^{out,AX} + x1\cdot\rho_1 V + x3\cdot\rho_3 V - \frac{1}{Y_H}\rho_5 V$
X_{BH}	$V\frac{dX_{BH}}{dt} = \dot{Q}_{in}X_{BH}^{in} - \dot{Q}_{out,AX}X_{BH}^{out,AX} + \rho_5 V - \rho_8 V$
X_{BA}	$V\frac{dX_{BA}}{dt} = \dot{Q}_{in}X_{BA}^{in} - \dot{Q}_{out,AX}X_{BA}^{out,AX} - \rho_{12} V$
S_{orgN}	$V\frac{dS_{orgN}}{dt} = \dot{Q}_{in}S_{orgN}^{in} - \dot{Q}_{out,AX}S_{orgN}^{out,AX} - \rho_6 V$
S_{NH}	$V\frac{dS_{NH}}{dt} = \dot{Q}_{in}S_{NH}^{in} - \dot{Q}_{out,AX}S_{NH}^{out,AX} + \rho_6 V - y5\cdot\rho_5 V + y8\cdot\rho_8 V + y12\cdot\rho_{12} V$
S_{NO2}	$V\frac{dS_{NO2}}{dt} = \dot{Q}_{in}S_{NO2}^{in} - \dot{Q}_{out,AX}S_{NO2}^{out,AX}$
S_{NO3}	$V\frac{dS_{NO3}}{dt} = \dot{Q}_{in}S_{NO3}^{in} - \dot{Q}_{out,AX}S_{NO3}^{out,AX} - x5\cdot\rho_5 V - x8\cdot\rho_8 V - x12\cdot\rho_{12} V$

Table 6-4: Mass balance equations during the aerated phase

Component *i*	Mass Balance Equations for the Aerated Phase
S_{DO}	$V\frac{dS_{DO}}{dt} = \rho_{0,AE}V - \frac{Y_H}{1-Y_H}\cdot\rho_4 - x7\cdot\rho_7 V - \frac{Y_A}{1-Y_A}\cdot\rho_9 - x11\cdot\rho_{11} V$
X_S	$V\frac{dX_S}{dt} = \dot{Q}_{out,AX}X_S^{out,AX} - \dot{Q}_{out}X_S^{out} - \rho_1 V$
S_S	$V\frac{dS_S}{dt} = \dot{Q}_{out,AX}S_S^{out,AX} - \dot{Q}_{out}S_S^{out} - \rho_2 V$
S_{STO}	$V\frac{dS_S}{dt} = \dot{Q}_{in}S_S^{in} - \dot{Q}_{out,AX}S_S^{out,AX} + x1\cdot\rho_1 V + x2\cdot\rho_2 V - \frac{1}{Y_H}\rho_4 V$
X_{BH}	$V\frac{dX_{BH}}{dt} = \dot{Q}_{out,AX}X_{BH}^{out,AX} - \dot{Q}_{out}X_{BH}^{out} + x4\cdot\rho_4 V - \rho_7 V$
X_{BA}	$V\frac{dX_{BA}}{dt} = \dot{Q}_{out,AX}X_{BA}^{out,AX} - \dot{Q}_{out}X_{BA}^{out} + \rho_9 V - \rho_{11} V$
S_{orgN}	$V\frac{dS_{orgN}}{dt} = \dot{Q}_{out,AX}S_{orgN}^{out,AX} - \dot{Q}_{out}S_{orgN}^{out}$
S_{NH}	$V\frac{dS_{NH}}{dt} = \dot{Q}_{out,AX}S_{NH}^{out,AX} - \dot{Q}_{out}S_{NH}^{out} - y4\cdot\rho_4 V + y7\cdot\rho_7 V - \frac{1}{Y_A}\cdot\rho_9 V + y11\cdot\rho_{11} V$
S_{NO2}	$V\frac{dS_{NO2}}{dt} = \dot{Q}_{out,AX}S_{NO2}^{out,AX} - \dot{Q}_{out}S_{NO2}^{out} + x9\cdot\rho_9 V - \rho_{10} V$
S_{NO3}	$V\frac{dS_{NO3}}{dt} = \dot{Q}_{out,AX}S_{NO3}^{out,AX} - \dot{Q}_{out}S_{NO3}^{out} + \rho_{10} V$

A set of ordinary differential equations (ODE) was established with the above acquired mass balance equations and solved numerically with the program MatLab® and its 'ode45' solver. The codec of the program can be found in the annex.

6.2 Parameter Determination

As a first step it was necessary to calculate the needed half saturation concentrations and the specific rate constants. Therefore, the established set of ODE was solved numerically with a parameter fitting procedure. The simulated curves were fitted with the experimental data sets from cycle analysis with the least square method to minimise the sum of squared residuals. Starting values for the iteration were taken from the ASM 3 (Henze et al., 2000), if not determined by own respirometric measurements in separated batches, like $\mu_{max,H}$ or $k_{d,H}$.

The x and y vectors from the matrix v_{ji} (Table 6-1) were let constant and the values were set to one or to 0.1 (assumed to be involved at 10%) as described in Table 6-5. The resulting constant can be seen in Table 6-6 and Table 6-7.

Table 6-5: x- and y-vector for parameter fitting of the half saturation constants and specific rates

process *j*	x - vector	y - vector
1	1	/
2	1	/
3	1	/
4	1	0.1
5	$1/Y_H$	0.1
6	/	/
7	1	0.1
8	1	0.1
9	$1/Y_A$	/
10	/	/
11	1	0.1
12	1	0.1

Table 6-6: Values for the half saturation constants, either from MatLab® fitting, batch tests or literature

[mgL^{-1}]	mean value	ASM 3 (Henze et al., 2000)	Brenner (2000)	(Ni and Yu, 2007)
K_{DO}	0.19 ± 0.082	0.2	1.35	0.2
$K_{A,DO}$	0.55 ± 0.232	0.5	0.60	0.5
K_{NH}	0.10 ± 0.040	0.01	1.15	0.01
$K_{A,NH}$	21.2 ± 10.42	1	/	1
K_{NOx}	21.5 ± 13.57	0.5	0.70	0.5
$K_{A,NOx}$	0.21 ± 0.183	/	/	/
K_{STO}	1*	1	/	1
K_{orgN}	67.8 ± 26.13	/	/	/
K_h	1*	1	/	/
K_S	689**	2	40	15.9

*taken from ASM 3 **batch tests

Table 6-7: Values for the specific rates, either from MatLab® fitting, batch tests or literature

[d^{-1}]	mean value	ASM 3 (Henze et al., 2000)	Brenner (2000)	(Ni and Yu, 2007)
k_{orgN}	12.0 ± 6.85 (set-up C)	/	/	/
	1 (set-up A and B)	/	/	/
$k_{d,H}$	0.42 ± 0.14**	0.2	0.40	0.38
$k_{d,A}$	0.15*	0.15	0.13	0.15
k_h	1.07**	3	8	/
k_{STO}	689***	5	/	5.04

*taken from ASM 3 ** batch tests ***fixed manually

Attention should be paid to the high value for $K_{A,NH}$ compared with the value given in the ASM 3. The other saturation concentration of K_{orgN} and K_{NOx} are high as well, but all three parameters correspond with the high μ_{max} rate calculated from the batches. The reason for the high specific storage rate is the high K_S value, determined during batch experiments. A high storage rate k_{STO} represents the COD removal measured in the cycle analysis, because a low k_{STO} would mean that COD degradation is only due to hydrolysis of X_S. This would mean that an uptake of S_S could not be accomplished.

In a second step, the mean values for the constants and rates are used to fit the x- and y-sectors. The results are presented in Table 6-8 and compared among example values taken from the ASM 3 (Henze et al., 2000).

Table 6-8: x- and y-vector for parameter fitting of the half saturation constants and specific rates

process *j*	x - vector		y - vector	
	own study	ASM 3	own study	ASM 3
1	1.30 ± 0.259	/	/	/
2	1.18 ± 0.117	0.85	/	/
3	1.16 ± 0.189	0.80	/	/
4	0.53 ± 0.026	1	0.08 ± 0.012	0.07
5	7.04 ± 1.851	0.30	0.09 ± 0.021	0.07
6	/	/	/	/
7	0.90 ± 0.071	0.80	0.07 ± 0.002	0.066
8	0.34 ± 0.046	0.28	0.05 ± 0.026	0.066
9	4.26 ± 0.397	$1/Y_A$	/	/
10	/	/	/	/
11	0.93 ± 0.122	0.80	0.07 ± 0.006	0.066
12	0.25 ± 0.138	0.28	0.06 ± 0.021	0.066

6.3 Model Validation and Simulation of a Series of Cycles

Interpretation of simulation results is only useful when the significant microbial mechanisms are supported by the relevant mass balance relationship among the involved compounds. Therefore, with the evaluated set of constants, the experimental data from the cycle analyses are compared with the simulated results as shown exemplarily from Figure 6-1 to Figure 6-4.

The modelled profiles for the nitrogen compounds fit well with the experimental data. As long as oxygen is dissolved in the reactor no denitrification takes place. Ammonia increases due to ammonification (mainly degradation of urea), because of the composition of the synthetic feed with a high concentration of urea and because of the direct mixing of greywater concentrate with drinking water in the biological reactor (set-up C_{direct}). With a storage tank (most of the transformation of organic nitrogen to ammonia takes place in that tank) k_{orgN} is set to 1 and almost no ammonification takes place (cf. Figure 6-2). Nitrate is converted into gaseous nitrogen.

Corresponding to the denitrification process, the vector x5 has a value of 7.04, which is 23 times higher than the given ASM 3 data. Along with the high rate x5 for the process goes a high saturation concentration for K_{NOx}. The value here is 21.5 mgL^{-1}, which is around 40 times higher than the ASM 3 data. During aeration, the rate for nitrification is lower by a factor of 1.6 compared to the denitrification rate x5, but still in the same range (x9 = 4.26). The same can be stated for the saturation concentration $K_{A,NH}$, which is as high as K_{NOx} with a value of 21.2 mgL^{-1}. The data correspond well to the high μ_{max} and the high K_S.

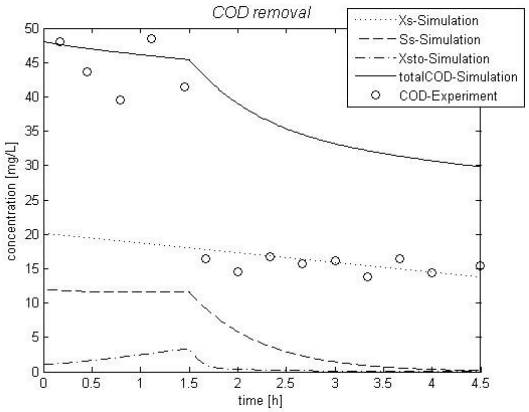

Figure 6-1: MatLab® plot for the validation of substrate simulation with COD results from 08.03.2004 (set-up A)

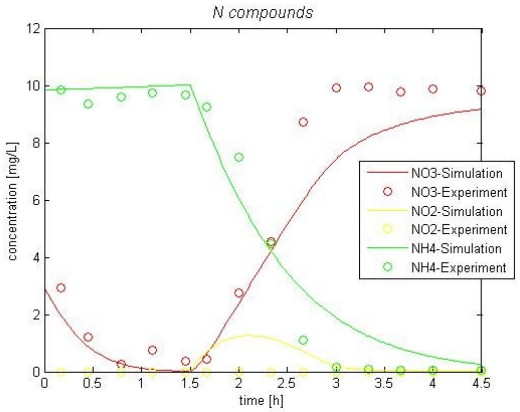

Figure 6-2: MatLab® plot for the validation of simulating nitrogen compounds with experimental results from 08.03.2004 (set-up A)

The experimental data points of the COD in Figure 6-1 only fit the simulated curve in the anoxic phase. During aeration, the samples are taken from the permeate, indicating a COD removal effect of the cake layer of the membrane when compared to COD analysis from the sludge tank as shown in Figure 6-3. This behaviour is not incorporated into the biological

process model equations, and can be seen as an outlook for further work.

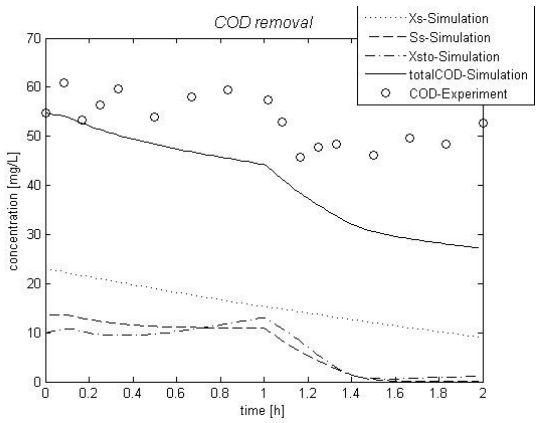

Figure 6-3: MatLab® plot for the validation of substrate simulation with COD results from 18.02.2008 (set-up C)

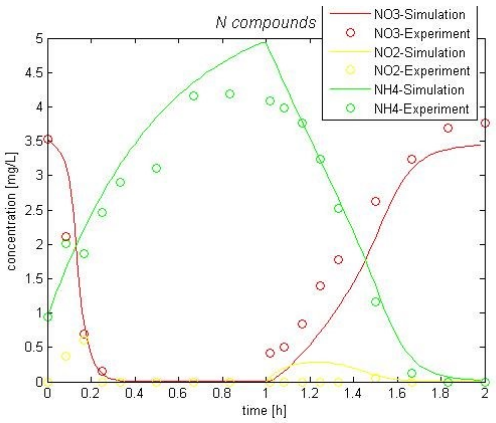

Figure 6-4: MatLab® plot for the validation of simulating nitrogen compounds with experimental results from 18.02.2008 (set-up C)

Next to the description of the single cycle of the SM-SBR, it is of need to simulate the biological behaviour of the SM-SBR for several cycles. This was done with the following boundary conditions:

- V_R = 500L, VER = 0.25, HRT = 8h, t_{AX} = 1h, t_{AE} = 1h
- inlet concentrations: COD = 200 mgL^{-1} (fraction S_S: 0.25, X_S: 0.42, X_i: 0.33)
- inlet concentrations [mgL^{-1}]: TN = 18, NH_4-N = 15, NO_3-N = 0.75
- oTS = 12 gL^{-1} (= 17.04 $g_{COD}\,L^{-1}$) with X_{BH} = 0.6*oTS, X_{BA} = 0.4*oTS
- The change of concentrations during permeate withdrawal is neglected.

The calculated results can be seen in Figure 6-5 and Figure 6-6.

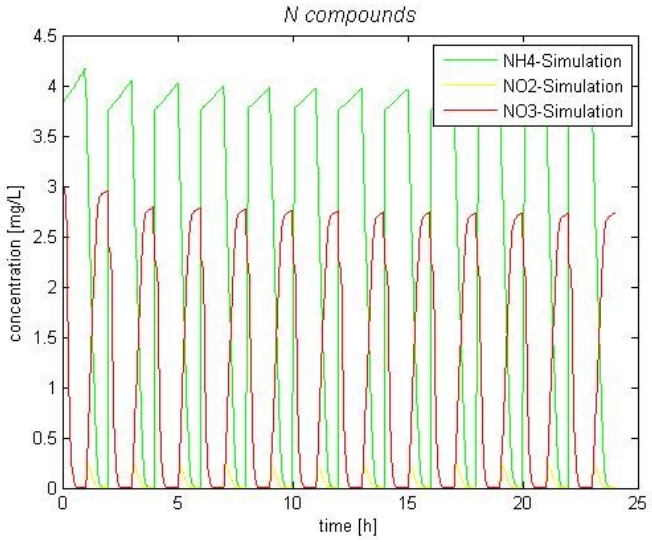

Figure 6-5: Evolution of N-compounds over one day, HRT = 8h, tc = 2h; simulated with MatLab®

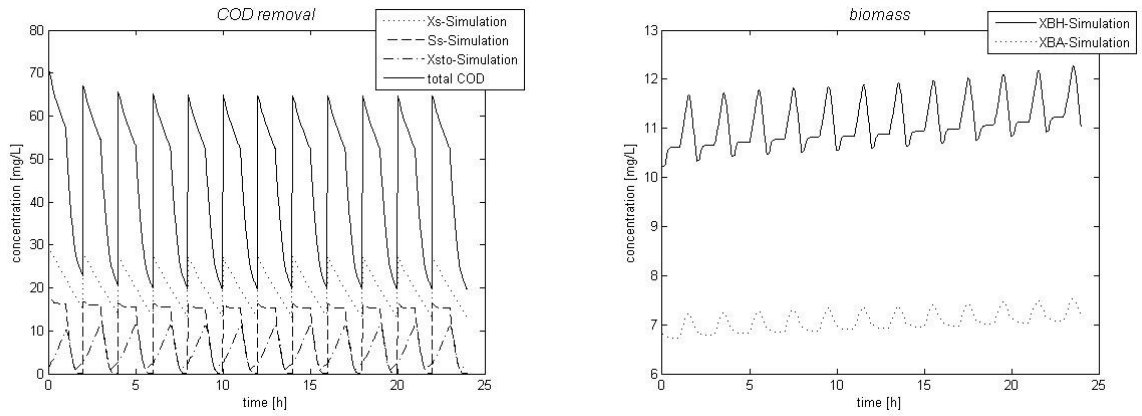

Figure 6-6:Evolution of substrate and biomass over one day, HRT = 8h, tc = 2h; simulated with MatLab®

The drop on the nitrate concentration at the beginning of each cycle is due to dilution with feed of a minor NO_3-concentration. After 2 cycles the denitrification/ nitrification stabilises. The COD removal is constant at all 12 cycles. The biomass undergoes a strong fluctuation during one cycle. Theoretical the concentration increases from a little over $10 g_{COD} L^{-1}$ up to near $12 g_{COD} L^{-1}$ as an attribute to the growth processes (denitrification and substrate degradation) and decreases after ammonia concentration reaches zero almost down to its starting point due to decay. The obtained net biomass yield of $0.81 g_{COD} L^{-1}$ is higher than the observed biomass yield, which was almost negligible in a single cycle. Different phenomena are likely to lead to a decrease in VSS (Heran et al., 2008; Jefferson et al., 2001):

- reflection of the fact that GW is nutrient limited in terms of macro and trace elements (not incorporated in the model)
- bacterial lysis phenomena, which are not in correlation with the decay coefficient k_d from the batch tests
- the action of predator microorganisms
- the uptake of storage products accumulated in the cells

The erected mathematical model on the basisof the ASM3 describes all the experimental profiles. However, it has to be taken into account that the estimation via curve fitting of the storage rates and saturation concentrations is the "Achilles' heel" of the procedure to determine the x and y vectors. Each phase is represented with a set of nine ODEs. In the first curve fitting procedure, seven parameters for the AX phase and five for the AE phase are adjusted. In the second curve fitting procedure, even eight and nine parameters are adjusted, respectively. The considerable storage of substrate in an SBR can be well predicted, although k_{STO} and K_{STO} are not identifiable. Simultaneous storage and growth on external substrate, as already developed in other works (van Loosdrecht and Heijnen, 2002), should be evaluated deeper in order to improve the mechanistic meaning of the estimated parameters.

7 Conclusions

Synthetic greywater was treated in an SM-SBR with anoxic and aerobic phases for denitrification and nitrification. Its composition is comparable to real greywater, but several authors stated that greywater showed strong variations – depending mainly on the user behaviour.

Cycle analyses gave an insight look into the biological behaviour. The results were in accordance with an overall good removal performance:

Table 7-1: Removal performance from the SM-SBR treating synthetic greywater

	Feed [mg L^{-1}]	Permeate [mg L^{-1}]	Removal efficiency
COD	203 ± 69	19.2 ± 6.1	91%
TN	18.4 ± 6.7	5.8 ± 4.0	72%
NH_4-N	9.4 ± 6.1	0.38 ± 0.70	97%

The reuse of the treated greywater was possible since the permeate quality was within the guidelines applicable for different reuse options (e.g. as irrigation water for green areas, or as a substitute for drinking water when flushing the toilet). The determination of NUR and AUR as reactor design values were comparable to literature data and showed that nitrogen removal is generally feasible in these systems. The TN removal efficiency achieved under the different HRT illustrated the optimisation success for cycle and phase time as operational parameters. In addition the change of feeding pattern could enhance the biological activity, e.g. the establishment of a higher storage-induced denitrification, while adding the feed during the aerobic instead of anoxic phase. Low loading rates resulted in low oTS concentration at the beginning. Due to the reduction of HRT, the loading rates increased and yielded higher oTS concentrations where a membrane coupled process, like the SM-SBR, was applicable. Nevertheless, the low growth rate must be taken into consideration when designing a technical application for greywater treatment.

The operational functionality of the membrane modules was crucial for the SM-SBR performance. Decreasing permeability resulted either in a decreasing idle phase (which even could led to an increase of the HRT when the permeate withdrawal became too long) or in increase of membrane cleaning frequency.

In a balance of design, operation and maintenance criteria, as shown in Table 7-2 and Table 7-3, the SM-SBR may be an attractive technology for remote areas, especially where a small footprint for the installation of the treatment system is needed.

Table 7-2: Summary of design criteria for an SM-SBR

design criteria	range	comment
reactor dimensions (d/H)	1/2 … 1/4	-
membrane area to reactor volume	15.6 m² / m³	The ratio shall be seen as a minimum value. More membrane area is good to achieve short withdrawal phases and operation under sustainable fluxes.
membrane type	plate & frame	-
aeration unit	coarse and fine	The fine bubbles are needed for a better oxygen transfer for the microorganism, whereas the coarse aeration is for the shear stress on the membrane surface to reduce fouling.

Table 7-3: Summary of operation and maintenance parameters for an SM-SBR

operation & maintenance parameters	range	comment
cycle time, h	2	-
order of phases	fill, anox, aerated, withdrawal	-
flux, L $(m^2h)^{-1}$	5 … 30	An optimum would be 10 to 15 L $(m^2h)^{-1}$ to achieve higher cleaning intervals.
HRT, h	8 … 33	The process of denitrification and nitrification is possible with a short HRT of 8 h.
TS concentration, g L^{-1}	2 … 10	The anticipated TS concentration should be between 8 and 10 gL-1, in order to use the advantage of the membrane and still have longer cleaning intervals.
SRT, d	> 360	The SM-SBR can be operated without excess sludge removal. This enhances the removal performance of substance done with slow growing bacteria.
cross flow velocity on membrane, m s^{-1}	1	comparable to MBR
anticipated effluent quality	to fulfil reuse guidelines	When humans are most likely to get in contact with treated greywater than a residual disinfection might be useful.
membrane cleaning interval, month	1 … 6	The membrane operation must be set to run stable with long cleaning intervals.
excess sludge removal	none	-

It was shown that physical greywater treatment with NF membranes may be a simple and efficient way to treat greywater, and therefore be an interesting alternative to conventional

MBR and advanced SM-SBR. The NF membranes Desal DK 25 by the company Osmonics were suitable for this purpose with a permeate quality around 5 $mg_{COD}L^{-1}$, significant lower than needed for reuse. In addition to a space-saving construction, the big advantage of the treatment of greywater with NF-membranes was its robustness of the process against fluctuations in feed composition and concentration, which can be a major problem for biological treatment.

The kinetic studies in the batch tests were technically difficult, mainly because of foaming at high F:M ratio. Nevertheless, it was an informative tool to gain insight understanding of the biological behaviour of greywater sludge. The COD fractioning revealed that 25% belonged to the rbCOD, 42% to the sbCOD and the remaining 33% to the inert fraction of the COD. The share of soluble COD was low compared to the particulate one. OUR measurements were undertaken to determine the growth and decay rate of X_{BH}, as well as the hydrolysis rate. It could be shown that the evaluation of kinetic data for GW showed significant differences to municipal wastewater. Operation under substrate limitation due to long HRT led to a slow biomass growth, while the respirometer measurements resulted in a much higher maximum growth rate, regardless the low COD in GW. These results can be explained by the change of feast and hunger due to the batch operation mode in the SM-SBR. At the end, the kinetic studies helped to formulate a mathematical model, which pictured the sludge behaviour well. The adaptation of the ASM 3 was suitable. It was shown that some of the constants differ strongly from the proposed ASM values. Next to the high K_S concentration measured from batch tests, the saturation concentrations K_{NOx} and K_{NH} for nitrification and denitrification are very high as well.

The 3L lab scale MBR treating real greywater was operated for 137 days at an average organic loading rate of 0.16 $mg_{COD}(Ld)^{-1}$. Stable operation was achieved at a flux of 8 L $(m^2h)^{-1}$ resulting in a mean HRT of 13 h. A chemical membrane cleaning provided only a short term increase in flux while a more permanent decrease in the TMP was reached. Concluding, it can be stated that the low flux would have to be compensated by a big membrane area in order to treat large lowly polluted volumes with the MBR. Activated sludge concentration in the MBR under aerobic conditions reached $1.3gL^{-1}$, which was equivalent to a F/M-ratio of 120 $mg_{COD}(g_{VSS}d)^{-1}$. Specific growth rates were low with values around $0.03d^{-1}$, but higher than the specific growth rate of the sludge from the pilot scale SM-SBR with a value of $0.02d^{-1}$. The results from the pilot applications with 600L reactors operated from the Zer0-M project team in Turkey and Morocco proved the technical feasibility of greywater treatment with membrane technology as well, but an important drawback remains: The high investment costs for small remote applications.

The permeate of the SM-SBR satisfied the effluent quality requirements for reuse in toilet flushes or for other household uses, which do not require potable water quality. The treated greywater was of very high aesthetic quality. To minimise the biological re-growth within the distributing system, the BOD5 must be below 5 mgL^{-1} and an additional disinfection within the distributing system might be needed.

GW treatment with membrane coupled processes is therefore viable for the future with further optimisation potential of the membrane performance. MBR technology is preferable where little space is available, i.e. for example inside buildings or on ships to overcome the inconvenience of high investment cost.

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9 Appendices

MatLab® program codec

Cycles.m

```
clear all

%% Definition of variables
   global mueH kdH_NOx kdH_DO YH KS kh Kh ksto Ksto
   global kLaSludge kDO KDO KADO
   global KANH  kdA_NOx kdA_DO XBA KANOx
   global KNH KNOx KorgN korgN XBH
   global FAX YA mueA
   global x_vector y_vector


%given parameters
   %process parameter
   numbercycle = 12;
   tAX = 1; %[h]
   tAE = 1; %[h]
   VER = 0.25;
   Vr = 500; %[L]

   %fraction of feed (equals 100% of the inlet COD)
   FSs = 0.25;  %0.25
   FXs = 0.42;  %0.42
   FXi = 0.33;  %0.33

   %biomass [g/L]
   oTS = 12 * 1.42; %oTS as COD (1.42 gO2/ g cell tissue)
   XBH = 0.6*oTS; %fraction to be defined by user
   XBA = 0.4*oTS; %fraction to be defined by user

   %inlet concentrations in mg/L
   COD = 200;
      Ss = FSs*COD; %RBCOD
      Xs = FXs*COD; %SBCOD
      Xi = FXi*COD; %inertCOD
   TN = 18;
   NH4 = 15;
   NO3 = 0.75;
   DO = 7.95;
   orgN = TN - NH4 - NO3;

%oxygen transfer: kLa
   kDO = 50;
   KDO = 0.19;
   KADO = 0.55;
   kLaWasser = 14.196; %[1/h] from experiments in the reactor: 14.196

%biokinetic parameter from batch experiments
   mueH = 22.4;
   kdH_DO = 0.42;
   kdH_NOx = 0.21;
```

```
    YH = 0.53;
    KS = 689;
    kh = 1.07;
    Kh = 1; %ASM3

%biokinetic parameter from parameter fitting or literature as a vector
    %anoxic factor
    FAX = 0.6;

    %autotrophic bacteria with relation from ASM3
    YA = 0.24;
    mueA = 0.5*mueH;
    kdA_DO = 0.15;
    kdA_NOx = 0.05;
    KANOx = 0.21;
    KANH = 21.2;

    %heterotrophic bacteria
    ksto = 689;
    Ksto = 1;
    KNH = 0.1;
    KNOx = 21.5;
    KorgN = 67.8;
    korgN = 1;%12.0;

    %x vector
    x_vector(1) = 1.30; %Xsto: Hydrolysis
    x_vector(2) = 1.18; %Xsto: aerobic storage
    x_vector(3) = 1.16; %Xsto: anoxic storage
    x_vector(4) = 0.53; %XBH: aerobic growth
    x_vector(5) = 7.04; %SNO3 anoxic growth XBH
    x_vector(6) = 0; %not used
    x_vector(7) = 0.9; %SDO: aerobic endog. respiration (XBH)
    x_vector(8) = 0.34; %SNO3: anoxic endog. respiration (XBH)
    x_vector(9) = 4.26; %SNO2: aerobic growth XBA
    x_vector(10) = 0; %not used
    x_vector(11) = 0.93; %SDO: aerobic endog. respiration (XBA)
    x_vector(12) = 0.25; %SNO3: anoxic endog. respiration (XBA)

    %y vector for NH4
    y_vector(1) = 0; %not used
    y_vector(2) = 0; %not used
    y_vector(3) = 0; %not used
    y_vector(4) = 0.08; %aerobic growth of XBH
    y_vector(5) = 0.09; %anoxic growth of XBH
    y_vector(6) = 0; %not used
    y_vector(7) = 0.07; %aerobic endog. respiration (XBH)
    y_vector(8) = 0.05; %anoxic endog. respiration (XBH)
    y_vector(9) = 0; %not used
    y_vector(10) = 0; %not used
    y_vector(11) = 0.07; %aerobic endog. respiration (XBA)
    y_vector(12) = 0.06; %anoxic endog. respiration (XBA)


%% set time step
    step = 0.02;
    tcycle = tAX + tAE;

    tstepAX = step:step:tAX;
```

```
tstepAE = tAX+step:step:tcycle;


%% Solving ODE-System for the parameter DO COD NO3
  %start concentrations
  c0AX(1) = DO; %DO
  c0AX(2) = (Xs*VER*Vr + 28*FXs*(1-VER)*Vr)/Vr; %Xs
  c0AX(3) = (Ss*VER*Vr + 28*FSs*(1-VER)*Vr)/Vr; %Ss
  c0AX(4) = 1; %Xsto
  c0AX(5) = XBH;
  c0AX(6) = XBA;
  c0AX(7) = (orgN*VER*Vr + 3*(1-VER)*Vr)/Vr; %orgN
  c0AX(8) = (NH4*VER*Vr + 0.1*(1-VER)*Vr)/Vr; %NH4
  c0AX(9) = 3.0;%0.8*(NH4*VER*Vr + 0.5*(1-VER)*Vr)/Vr; %NO3

  laenge = 0;
  start = 1;
  j = 0;

  for runs = 1:numbercycle
    clear functions

    %oxygen transfer
    alpha = 1*exp(-0.081*1.12*((c0AX(5)+c0AX(6))/1.42)); %own experiments 0.5
    kLaSludge = alpha*kLaWasser;

    %anoxic phase
      [t,c_AX] = ode45(@DGL_AX,tstepAX,c0AX,[]);

    %aerated phase
    c0AE(1) = c_AX(end,1); %DO
    c0AE(2) = c_AX(end,2); %Xs
    c0AE(3) = c_AX(end,3); %Ss
    c0AE(4) = c_AX(end,4); %Xsto
    c0AE(5) = c_AX(end,5); %XBH
    c0AE(6) = c_AX(end,6); %XBA
    c0AE(7) = c_AX(end,8); %NH4
    c0AE(8) = 0; %NO2
    c0AE(9) = c_AX(end,9); %NO3

      [t,c_AE] = ode45(@DGL_AE,tstepAE,c0AE,[]);

    %combining vector of simulation AX and AE
    laenge = laenge + length(tstepAX) + length(tstepAE);
    %c_SIM = zeros(laenge,1);

    for i = start:laenge
      if i <= j + length(tstepAX)
        c_SIM(i,1) = c_AX(i-j,1); %DO
        c_SIM(i,2) = c_AX(i-j,2); %Xs
        c_SIM(i,3) = c_AX(i-j,3); %Ss
        c_SIM(i,4) = c_AX(i-j,4); %Xsto
        c_SIM(i,5) = c_AX(i-j,5); %XBH
        c_SIM(i,6) = c_AX(i-j,6); %XBA
        c_SIM(i,7) = c_AX(i-j,8); %NH4
        c_SIM(i,8) = 0; %NO2
        c_SIM(i,9) = c_AX(i-j,9); %NO3
        c_SIM(i,10) = c_AX(i-j,7); %orgN
        c_SIM(i,11) = (c_AX(i-j,2)+c_AX(i-j,3))/(1-FXi); %total COD
```

```
        else
            c_SIM(i,1) = c_AE(i-j-length(tstepAX),1); %DO
            c_SIM(i,2) = c_AE(i-j-length(tstepAX),2); %Xs
            c_SIM(i,3) = c_AE(i-j-length(tstepAX),3); %Ss
            c_SIM(i,4) = c_AE(i-j-length(tstepAX),4); %Xsto
            c_SIM(i,5) = c_AE(i-j-length(tstepAX),5); %XBH
            c_SIM(i,6) = c_AE(i-j-length(tstepAX),6); %XBA
            c_SIM(i,7) = c_AE(i-j-length(tstepAX),7); %NH4
            c_SIM(i,8) = c_AE(i-j-length(tstepAX),8); %NO2
            c_SIM(i,9) = c_AE(i-j-length(tstepAX),9); %NO3
            c_SIM(i,10) = c_AX(end,7); %orgN
            c_SIM(i,11) = (c_AE(i-j-length(tstepAX),2)+c_AE(i-j-length(tstepAX),3))/(1-FXi); %total COD
        end
    end

    j=i;
    start = laenge + 1;

    %set new start concentrations
    c0AX(1) = c_SIM(end,1); %DO
    c0AX(2) = (Xs*VER*Vr + c_SIM(end,11)*FXs*(1-VER)*Vr)/Vr; %Xs
    c0AX(3) = (Ss*VER*Vr + c_SIM(end,11)*FSs*(1-VER)*Vr)/Vr; %Ss
    c0AX(4) = c_SIM(end,4); %Xsto
    c0AX(5) = c_SIM(end,5); %XBH
    c0AX(6) = c_SIM(end,6); %XBA
    c0AX(7) = (orgN*VER*Vr + c_SIM(end,10)*(1-VER)*Vr)/Vr; %orgN
    c0AX(8) = (NH4*VER*Vr + c_SIM(end,7)*(1-VER)*Vr)/Vr; %NH4
    c0AX(9) = (NO3*VER*Vr + c_SIM(end,9)*(1-VER)*Vr)/Vr; %NO3
end


%% plotten
    tstep = 0:step:numbercycle*tcycle-step;

%plot DO profile
    figure(1)
    plot(tstep,c_SIM(:,1),'b');
    legend('DO-Simulation');
    title('\it{O2-profile}','Fontsize',12)
    xlabel('{time [h]}','Fontsize',10)
    ylabel('concentration [mg/L]','Fontsize',10)
    hold on

%plotten COD
    figure(2)
    plot(tstep,c_SIM(:,2),'k:',tstep,c_SIM(:,3),'k--',tstep,c_SIM(:,4),'k-.',tstep,c_SIM(:,11),'k-');
    legend('Xs-Simulation','Ss-Simulation','Xsto-Simulation','total COD');
    title('\it{COD removal}','Fontsize',12)
    xlabel('{time [h]}','Fontsize',10)
    ylabel('concentration [mg/L]','Fontsize',10)
    hold on

%plotten biomass
    figure(3)
    plot(tstep,c_SIM(:,5),'k',tstep,c_SIM(:,6),'k:');
    legend('XBH-Simulation','XBA-Simulation');
    title('\it{biomass}','Fontsize',12)
    xlabel('{time [h]}','Fontsize',10)
    ylabel('concentration [mg/L]','Fontsize',10)
```

```
    hold on

%plotten N compounds
    figure(4)
    plot(tstep,c_SIM(:,7),'g',tstep,c_SIM(:,8),'y',tstep,c_SIM(:,9),'r');
    legend('NH4-Simulation','NO2-Simulation','NO3-Simulation');
    title('\it{N compounds}','Fontsize',12)
    xlabel('{time [h]}','Fontsize',10)
    ylabel('concentration [mg/L]','Fontsize',10)
    hold on
```

DGL_AX.m

```
function dcdt = DGL_AX(t,c)
    global mueH kdH_NOx YH KS kh Kh ksto Ksto
    global kDO KDO KADO
    global KANOx kdA_NOx XBA
    global KNH KNOx KorgN korgN XBH
    global FAX
    global x_vector y_vector

    %x vector
    x1 = x_vector(1);
    x3 = x_vector(3);
    x5 = x_vector(5);
    x8 = x_vector(8);
    x12 = x_vector(12);

    %y vector
    y5 = y_vector(5);
    y8 = y_vector(8);
    y12 = y_vector(12);


    dcdt(1) = - kDO*c(1)/(KDO+c(1)); %cDO(t)
    dcdt(2) = - kh*(c(2)/XBH)/(Kh+c(2)/XBH)*XBH; %cXs(t)
    dcdt(3) = - FAX*ksto*KDO/(KDO+c(1))*c(3)/(KS+c(3))*c(9)/(KNOx+c(9))*XBH; %cSs(t)
    dcdt(4) = x1*kh*c(2)/XBH/(Kh+c(2)/XBH)*XBH +
x3*FAX*ksto*KDO/(KDO+c(1))*c(3)/(KS+c(3))*c(9)/(KNOx+c(9))*XBH -
(1/YH)*mueH*FAX*KDO/(KDO+c(1))*c(4)/(Ksto+c(4))*c(8)/(KNH+c(8))*c(9)/(KNOx+c(9))*XBH;
%cXsto(t)
    dcdt(5) =
mueH*FAX*KDO/(KDO+c(1))*(c(4)/XBH)/(Ksto+c(4)/XBH)*c(8)/(KNH+c(8))*c(9)/(KNOx+c(9))*XBH -
kdH_NOx*KDO/(KDO+c(1))*c(9)/(KNOx+c(9))*XBH; %cXBH(t)
    dcdt(6) = - kdA_NOx*KADO/(KADO+c(1))*c(9)/(KANOx+c(9))*XBA; %cXBA(t)
    dcdt(7) = - korgN*c(7)/(KorgN+c(7))*XBH; %corgN(t)
    dcdt(8) = korgN*c(7)/(KorgN+c(7))*XBH -
y5*mueH*FAX*KDO/(KDO+c(1))*(c(4)/XBH)/(Ksto+c(4)/XBH)*c(8)/(KNH+c(8))*c(9)/(KNOx+c(9))*XBH
+ y8*kdH_NOx*KDO/(KDO+c(1))*c(9)/(KNOx+c(9))*XBH +
y12*kdA_NOx*KADO/(KADO+c(1))*c(9)/(KANOx+c(9))*XBA; %cNH(t)
    dcdt(9) = -
x5*mueH*FAX*KDO/(KDO+c(1))*(c(4)/XBH)/(Ksto+c(4)/XBH)*c(8)/(KNH+c(8))*c(9)/(KNOx+c(9))*XBH
- x8*kdH_NOx*KDO/(KDO+c(1))*c(9)/(KNOx+c(9))*XBH -
x12*kdA_NOx*KADO/(KADO+c(1))*c(9)/(KANOx+c(9))*XBA; %cNO3(t)

    dcdt = [dcdt(1);dcdt(2);dcdt(3);dcdt(4);dcdt(5);dcdt(6);dcdt(7);dcdt(8);dcdt(9)];
```

DGL_AE.m

```
function dcdt = DGL_AE(t,c)
   global mueH kdH_DO YH KS kh Kh ksto Ksto
   global kLaSludge KDO KADO KANOx
   global KANH kdA_DO XBA
   global KNH XBH
   global YA mueA
   global x_vector y_vector

   %x vector
   x1 = x_vector(1);
   x2 = x_vector(2);
   x4 = x_vector(4);
   x7 = x_vector(7);
   x9 = x_vector(9);
   x11 = x_vector(11);

   %y vector
   y4 = y_vector(4);
   y7 = y_vector(7);
   y11 = y_vector(11);


   dcdt(1) = kLaSludge*(9.08-c(1)) - YH/(1-
YH)*mueH*c(1)/(KDO+c(1))*(c(4)/XBH)/(Ksto+c(4)/XBH)*c(7)/(KNH+c(7))*XBH -
x7*kdH_DO*c(1)/(KDO+c(1))*XBH - YA/(1-YA)*mueA*c(1)/(KADO+c(1))*c(7)/(KANH+c(7))*XBA -
x11*kdA_DO*c(1)/(KADO+c(1))*XBA; %cDO(t)
   dcdt(2) = - kh*(c(2)/XBH)/(Kh+c(2)/XBH)*XBH; %cXs(t)
   dcdt(3) = - ksto*c(1)/(KDO+c(1))*c(3)/(KS+c(3))*XBH; %cSs(t)
   dcdt(4) = x1*kh*(c(2)/XBH)/(Kh+c(2)/XBH)*XBH + x2*ksto*c(1)/(KDO+c(1))*c(3)/(KS+c(3))*XBH -
(1/YH)*mueH*c(1)/(KDO+c(1))*(c(4)/XBH)/(Ksto+c(4)/XBH)*c(7)/(KNH+c(7))*XBH; %cXsto(t)
   dcdt(5) = x4*mueH*c(1)/(KDO+c(1))*(c(4)/XBH)/(Ksto+c(4))*c(7)/(KNH+c(7))*XBH -
kdH_DO*c(1)/(KDO+c(1))*XBH; %cXBH(t)
   dcdt(6) = mueA*c(1)/(KADO+c(1))*c(7)/(KANH+c(7))*XBA - kdA_DO*c(1)/(KADO+c(1))*XBA;
%cXBA(t)
   dcdt(7) = - y4*mueH*c(1)/(KDO+c(1))*(c(4)/XBH)/(Ksto+c(4)/XBH)*c(7)/(KNH+c(7))*XBH +
y7*kdH_DO*c(1)/(KDO+c(1))*XBH - (1/YA)*mueA*c(1)/(KADO+c(1))*c(7)/(KANH+c(7))*XBA +
y11*kdA_DO*c(1)/(KADO+c(1))*XBA; %cNH(t)
   dcdt(8) = x9*mueA*c(1)/(KADO+c(1))*c(7)/(KANH+c(7))*XBA -
mueA*c(1)/(KADO+c(1))*c(8)/(KANOx+c(8))*XBA; %cNO2(t)
   dcdt(9) = mueA*c(1)/(KADO+c(1))*c(8)/(KANOx+c(8))*XBA; %cNO3(t)

   dcdt = [dcdt(1);dcdt(2);dcdt(3);dcdt(4);dcdt(5);dcdt(6);dcdt(7);dcdt(8);dcdt(9)];
```