University of Stavanger

Faculty of Science and Technology

MASTER'S THESIS

Study program/ Specialization: **Environmental Technology** **Offshore Environmental Engineering**	Spring semester, 2011 Open / Restricted access
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Titel of thesis: **Aerobic biological treatment of produced water from oil production.**	
Credits (ECTS):**30**	
Key words: **Produced Water** **Discharges** **Environmental Effects** **Aerobic biological treatment**	Pages: 128 + enclosure: 4 Stavanger, 14.06.2011 Date/year

Frontpage for master thesis
Faculty of Science and Technology
Decision made by the Dean October 30th 2009

Acknowledgements

I would like to thank my supervisor Professor Torleiv Bilstad for guidance and advice.
And I would like to especially thank Professor Leif Ydstebø for all the help and support during the period I worked with this thesis.

Finally I want to thank my family for their continuous support and encouragement during the period of completing this thesis.

Trine

Abstract

Produced water is the largest waste stream generated from the oil and gas industry. Water of varying quantities is always produced along with oil and has to be separated from the oil. The amount of produced water generated generally increases as the oil field gets older, because more water has to be injected into the reservoir in order to force the oil out.
The produced water can either be injected back into the reservoirs or be treated, typically by floatation units or hydrocyclones, and eventually be discharged to sea. The produced water still contains traces of oil, chemicals and a variety of dissolved compounds after this treatment. Experience has shown that the major contributors to environmental impact factor (EIF) are dispersed oil, volatile aromatics, heavy aromatics, alkylated phenols and different process chemicals.

The requirements set by the authorities, regarding produced water treatment, does not involve removal of dissolved organic compounds from produced water. But, recently the focus has been withdrawn from environmental effects of suspended oil, and a further reduction of the 30 mg/l oil in water level is not considered. However, the focus is now on water soluble, heavy (non-volatile) aromatics and phenols since the long-term environmental effects of which is not fully understood. Research is ongoing in many oil and gas companies, in cooperation with Klif (klima og forurensingsdirektoratet). Recent research has detected negative effects on fish in open sea area caused by exposure to produced water.

This thesis is a literature study on aerobic biological treatment technologies, for offshore use, for the removal of dissolved organic compounds and oil in water content from produced water. The aerobic treatment technologies assessed in this thesis was activated sludge (AS), biofilm (BF), membrane bioreactor (MBR) and aerated membrane biofilm reactor (MABR). The main focus, in the evaluation of the most beneficial biological treatment technology for produced water treatment, was put on required reactor volume due to the space limitations on offshore installations.

A model for the produced water composition was defined for the calculations carried out in this thesis. The reactor volumes, sludge production and oxygen demand was calculated for the

different biological systems based on the assumptions made for the model produced water characteristics and values for the kinetic coefficients found from literature.

The calculations clearly identified the relationship between the active biomass concentration and required reactor volume. A biological treatment system with a high active biomass concentration and high rate oxygen supply would be an advantage as it was found that the volume of the biological reactor decreased as the active biomass concentration of the system was increased. The formation of biofilm allow for a compact biomass formation compared with activated sludge systems. And therefore the required reactor volume for biofilm systems is typically smaller than for the activated sludge systems due to the high biomass concentration. The biomass concentration in biofilm systems largely depends on the specific surface area available for biomass growth, this was confirmed by the calculations carried out in this thesis.

The calculations carried out also proved that the overall performance of the biological treatment systems largely depended on the temperature within the system. From the literature, a typical temperature for produced water was found to be 75 ºC, but for the calculations it was assumed that the temperature of the produced water was reduced to 30 ºC and 20 ºC during the pre-treatment. The results from the calculations in this thesis showed that the minimum sludge retention time (SRT_{min}) nearly doubled as the temperature was reduced from 30 to 20 ºC, from 0.33 days to 0.67 days. The SRT in turn, was found to largely affect the biological treatment processes in terms of required reactor volume. The effect of the SRT, at 20 times SRT_{min}, was seen as an increase in reactor volume of 73.5 % as the temperature was decreased from 20 to 30 ºC. For SRT of 8.1 times SRT_{min} the increase in reactor volume was calculated to be 83.6 % larger for systems operating at 20º compared with systems operating at 30 ºC. Last, at 2 times SRT_{min} the reactor volume was calculated to increase with 93.8 % as the temperature was decreased from 20 ºC to 30 ºC.

The calculations in this thesis also showed that the volume of the biological reactor also depends on the active biomass concentration of the system, $X_{A,}$ which applies with literature. The relationship between biomass concentration and required reactor volume applies to all the biological treatment technologies, activated sludge as well as biofilms, therefore the relationship between active biomass concentration and reactor volume was calculated for X_A concentrations up to 50,000 mg/l where the lower range represents the X_A concentrations

found in AS systems and the higher range represents the possible active biomass concentrations of MABRs. For MBRs it was found that the active biomass concentration could get as high as 14400 mg/l.
If the wastewater-loading rate is high, oxygen supply could limit the removal of organic substrate in biofilms. From literature it was found that MABRs outperformed both conventional biofilm reactors and activated sludge systems under conditions of high organic loading due to the fact that MABRs could contain an active biomass concentration higher than any other system because of the oxygen supply through the membrane. This technology would be able to provide the most compact biological reactor system of all the technologies assessed in this thesis. Further development of both MBRs and MABRs revolves around increasing the biomass concentration and, hence, reduce the reactor volume. But, the biomass concentration will eventually reach a limit due to physical constraints and/or substrate/oxygen transport limitations.

The sludge production was found to depend on the MLSS concentration, reactor volume and SRT. The sludge production was lower for the system operating at 20ºC due to the increased SRT. The oxygen demand was found to be slightly lower at 30ºC due to the difference in reactor volume reaction rates for the two temperatures. It was calculated that the sludge production decreased with increased SRT and the oxygen demand was found to increase as the SRT was increased.

It was concluded that that MABRs should be further investigated if biological treatment were to be used for produced water treatment on offshore installations.

Because of uncertainties related to the produced water composition and other assumptions made in the calculations, it was recommended to carry out pilot testing of the actual water to be treated in order to provide the necessary design criteria.

Contents

Figure list

Table list

1. Introduction.

Produced water is the larges waste stream generated from the oil and gas industry. High amounts of dissolved compounds are discharged into the sea with the produced water.
Some of the dissolved organic compounds in produced water can cause harmful effect to the marine environment, and therefore technologies for removal of dissolved organic compounds in produced water should be assessed in order to develop technologies for the removal of dissolved organic compounds. Today there exist no performance standards for the removal of dissolved compounds from produced water, however, the overall goal for the oil and gas industry and the government is to reach the goal of "zero harmful discharge", a policy initiated by the Norwegian authorities.
This thesis is a literature study on aerobic biological treatment technologies for the removal of dissolved organic compounds and oil in water content from produced water.
The aerobic treatment technologies assessed in this thesis was activated sludge (AS), biofilm (BF), membrane bioreactor (MBR) and aerated membrane biofilm reactor (MABR).
The main focus, in the evaluation of the most beneficial technology for produced water treatment, was put on required reactor volume due to the space limitations on offshore installations.

2. Politics and environmental concerns regarding produced water discharges.

2.1 Discharges to sea.

Globally, the production of produced water is over thee times the production of oil [1]. The water-cut has increased the last decade and continues to do so because the fraction of oil in the reservoir decreases and it is more difficult to get the oil out from an old field. It therefore requires more sea water to be injected in order to force the oil out; hence more produced water is generated.
In 2009, 134 million m^3 of produced water was discharged on the Norwegian Shelf [2]. This is a reduction of about 10 per cent compared with 2008. This is due to reduced production on the Norwegian Shelf. In 2009 about 30 million m^3 was injected back into the reservoir which represents about 19 per cent of the total produced water production.

Today all offshore installations on the Norwegian Shelf have installed hydrocyclones, centrifuges or flotation units in order to meet with the dispersed oil regulations, of maximum 30 mg oil per liter produced water, set by the authorities. Deoiling hydrocyclones are very efficient and have the ability to remove 75-80 per cent of the dispersed oil in the produced water. Various manufacturers and models of hydrocyclones exists and the most efficient ones have the ability to remove oil droplets down to approximately 7-10 µm size, i.e. very often well below the 30 mg/l discharge limit [3].

The Environmental Report carried out by OLF in 2010 states that in 2009, the average oil concentration in produced water was 11 milligrams per liter (analysed by the ISO 9377-2 modified method) which is far below the regulatory requirement of maximum 30 milligrams per liter. The concentration of dispersed oil from 2003 to 2009 is shown in Figure X. A total of 1487 tonnes of dispersed oil was discharged to sea in 2009 compared with 2008 this is a reduction of nearly 6 per cent.

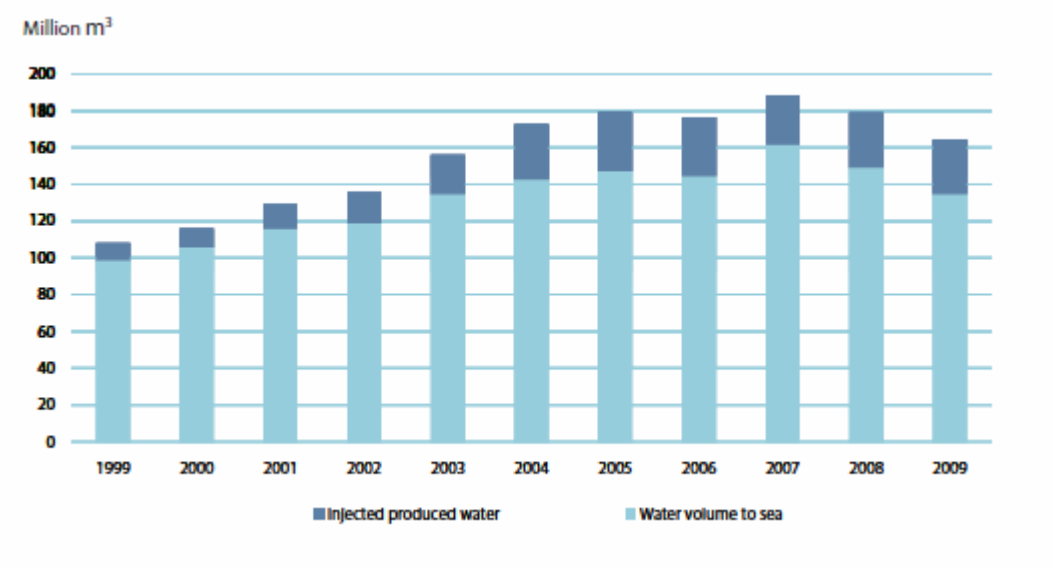

Figure 1: Amount of produced water discharged and injected on the Norwegian shelf [2].

This shows that in later years better management methods has helped reducing the quantity of produced water. But overall it is estimated that the volume of produced water will continue to increase because of production from old fields as well as new fields [1].

2.2 ”Zero discharge”

The goal of zero environmentally harmful discharges to the sea was in Norway introduced in Report no 58 (1996-97) to the Storting (The Norwegian Parliament) on environmental policy for sustainable development [4].
This objective of "zero discharge" is often misunderstood. It means that discharge of environmentally harmful substances are to be reduced and minimised down to an amount where the discharge is not causing any harm to the environment surrounding, not eliminated completely.
In later years more stringent regulations have been applied in the Norwegian Sea of the Lofoten islands and in the Barents Sea. The authorities have determined that the zero discharge goal is to be reached within acceptable limits for the environment, safety and economics which have been underlined by several subsequent reports to the Storting.
This objective involves the following restrictions on chemical usage[4]:

- no discharges of toxic or environmentally harmful chemicals
- no discharges of other chemicals that could cause environmental impact.
- no or minimum discharges of substances which rank as pollutants in chemicals.

The restrictions are also imposed on discharges of hydrocarbons and other natural substances produced together with oil and gas [4]:

- no or minimum discharges of environmental toxins.
- no discharges of other substances that could cause environmental harm.

Special regulations applied in the Lofoten/Barents Sea areas include zero discharges of produced water from normal operation. In order to comply with possible stricter discharge limits in the future and the policy of "Zero harmful discharge", research should be performed on current technologies focusing on the combination of physico-chemical and/or biological treatment of produced water.

2.3 Produced water treatment

The produced water discharged from offshore platforms is typically treated by use of compact chemical and physical systems because of space constraints on the platforms. These conventional technologies, however, does not remove the small suspended oil particles and dissolved compounds (see chapter 3 for detailed characteristics of produced water). Some chemical treatment technologies also produce hazardous sludge and the cost of running the

process can be significant. Biological treatment of oily wastewater can be a cost-effective and environmental friendly method, but could be a problem on offshore installation due to the space limitations on the installations. A study carried out by OLF in 1992 [3] investigated more than 30 possible processes for removal of organic components from produced water. The most interesting processes were evaluated, among them were biological oxidation [3] utilizing a High Compact Reactor (HCR).
Biological treatment of produced water may also have to include some kind of physical treatment technology in order to refine the final effluent, because produced water has high salinity and also contains various compounds that seriously could influent the turbidity of the effluent. Membrane technology is one physiological treatment technology that could be used for physical treatment of the produced water.

2.4 Produced water discharges

2.4.1 Produced water discharges and environmental concerns.

Produced water is discharged into the sea and this can cause harm to the surrounding environment. The effects of the produced water components on the environment can be listed as follows [1]:

- Dispersed and soluble oil: Volatile and/or toxic compounds can evaporate from dispersed oil and oil droplets that has risen to the water surface and it will also increase the BOD value of the effected water. Nonpolar organics of various sources in produced water are consistently toxic.
- Treating chemicals: When comparing water and oil soluble production chemicals at equal concentrations it has been shown that the water soluble chemical does not have toxic effects in the aquatic phase, but oil soluble chemicals does. Some production chemicals can increase the partitioning of oil compounds in the aqueous phase. Precipitation and accumulation of production chemical may also occur in marine sediments.
- Heavy metals: In produced water the concentration of heavy metals are usually higher than in seawater. The toxicity of heavy metals are considered lower than the nonpolar

organic compounds because dilution of meta concentration happens very rapid, and the heavy metals does not have an adverse effect on the marine environment.

- Radionuclides: Depending on the fields geological formation there can be radionuclides present in the produced water, but risks connected to discharge of radionucleides containing produced water to surrounding environment are small.

2.4.2 Environmental impact factor

Environmental impact factor (EIF) is a value used to assess the environmental risk of a discharge in the North Sea and for ranking measures (i.e. new treatment technologies, substitution of chemicals, produced water reinjection (PWRI)) in effort to reach the goal of "zero harmful discharge"[5]. For the EIF calculations it is necessary to have data on the composition and flow of produced water. The EIF-model simulates the spreading of the discharge and calculates the risk of harmful effect in the recipient by comparing predicted environmental concentration (PEC) with the predicted no effect concentration (PNEC).
The model was developed in order to obtain a basis for defining treatment targets and assessment of technologies. The calculations have been employed to estimate the concentration levels of naturally occurring components in produced water that would give a discharge with no harmful effect to the environment. An EIF (PEC/PNEC) of 1 or lower represents discharges defined as "zero harmful discharge"[5].
The next figure shows the framework of the risk assessment process:

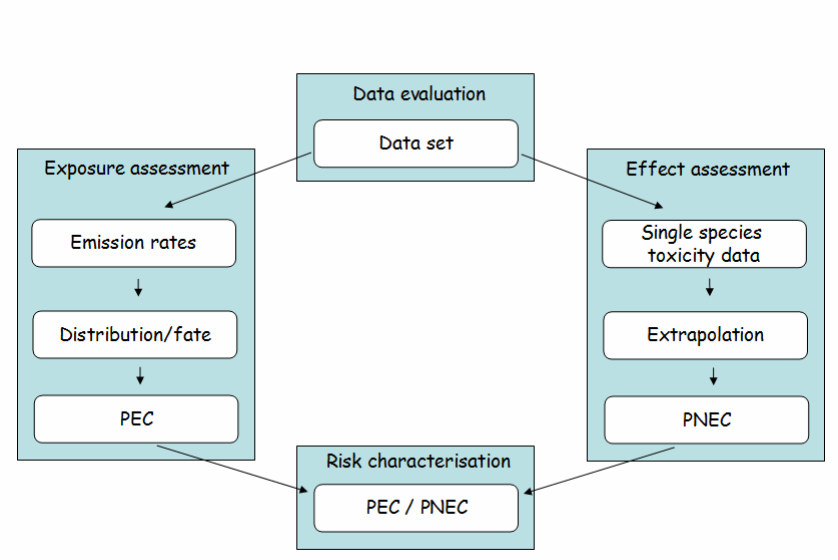

Figure 2: Environmental risk assessment framework [6].

The table below [5] presents the different concentrations of discharges resulting in an EIF=1 for each component discharged separately and for discharges containing all components.

Table 1: Concentrations of discharges resulting in an EIF=1 for each component discharged separately and for discharges containing all components.

Compound (mg/l)	3000 m3/d individual	3000m3/d sum of compounds	8000 m3/d individual	8000m3/d sum of compounds	30000 m3/d individual	30000m3/d sum of compounds
Dispersed oil	28.4820	4.615	10.3020	1.6232	2.7876	0.46150
BTEX	16.2010	2.838	6.5280	1.03	1.7	0.28380
Napthalenes	2.0013	0.3506	0.8064	0.128	0.21	0.03506
PAH 2-3 rings	0.1430	0.025	0.0576	0.0091	0.015	0.0025
PAH 4-6 rings	0.0353	0.0055	0.0128	0.002	0.00345	0.00055
Phenols C0-C3	9.5300	1.6694	3.8400	0.6088	1	0.16694
Phenols C4-C5	0.3431	0.0601	0.1382	0.0219	0.036	0.00601
Phenols C6+	0.0282	0.0046	0.0102	0.0016	0.00276	0.00046
Zinc (Zn)	0.4384	0.0768	0.1766	0.028	0.046	0.00768
Copper (Cu)	0.0191	0.0033	0.0077	0.0012	0.002	0.00033
Nickel (Ni)	1.1627	0.2037	0.4685	0.0743	0.122	0.02037
Cadmium (Cd)	0.0267	0.0047	0.0108	0.0017	0.0028	0.00047
Lead (Pb)	0.1734	0.0304	0.0699	0.011	0.0182	0.00304
Mercury (Hg)	0.0076	0.0013	0.0031	0.00049	0.0008	0.00013

These calculations are used to obtain a basis for defining treatment targets and assessing technologies for produced water treatment.

The following table presents a comparison of concentrations found for the discharges containing all the components with the average values reported for the Norwegian Continental Shelf (NCS).

Bold font represents the values found by EIF calculation to be lower than the reported NCS average. Values highlighted with yellow background represent the values in the table where the NCS averages were higher than all EIF results. These results states that in order to improve the produced water treatment, with respect to the naturally occurring compounds in produced water, the focus should be put on dispersed oil, BTEX, napthalenes and most water-soluble PAHs and phenols.

Table 2: Comparison of the average values reported for the NCS with the concentrations found for the discharge containing all components [5].

Compounds (mg/l)	OLF, average 05-07	3000 m3/d sum of compounds	8000 m3/d sum of compounds	30000 m3/d sum of compounds
Aliphatics	17.5	**4.615**	**1.6232**	**0.46150**
BTEX	10.9	**2.838**	**1.03**	**0.28380**
Napthalenes	0.98	**0.3506**	**0.128**	**0.030506**
PAH 2-3 rings	0.13	**0.025**	**0.0091**	**0.0025**
PAH 4-6 rings	0.002	0.0055	0.002	**0.00055**
Phenols C0-C3	3.3	**1.6694**	**0.6088**	**0.16694**
Phenols C4-C5	0.09	**0.0601**	**0.0219**	**0.00601**
Phenols C6+	0.001	0.0046	0.0016	**0.00046**
Copper (Cu)	0.02	0.0768	0.028	**0.00768**
Zinc (Zn)	0.04	**0.0033**	**0.0012**	**0.00033**
Nickel (Ni)	0.005	0.2037	0.0743	0.02037
Lead (Pb)	0.005	**0.0047**	**0.0017**	**0.00047**
Cadmium (Cd)	0.00015	0.0304	0.011	0.00304
Mercury (Hg)	0.00005	0.0013	0.00049	0.00013

2.5 Produced water and public policy.

To protect the marine environment of the North-East-Atlantic, which includes the North Sea, there is an international cooperation carried out through the OSPAR Convention. The work under this convention is managed by the OSPAR Commission which consists of representatives of the Governments of 15 Contracting Parties and the European Commission, all representing the European Community. The firs Ministerial Meeting of the OSPAR Commission took place in 1998, in Portugal, where the Contracting parties committed themselves ”to the application of the precautionary principle and the polluter-pays-principle” and “to prevent pollution of the maritime area by continuously reducing discharges, emissions and losses of hazardous substances (that is, substances which are toxic, persistent and liable to bioaccumulate or which give rise to an equivalent level of concern), with the ultimate aim of

achieving concentrations in the environment near background values for naturally occurring substances and close to zero for man-made synthetic substances" and making "every endeavour to move towards the target of cessation of discharges , emissions and losses of hazardous substances by the year 2020" [7]. The OSPAR commission recommended that all production installations in the OSPAR area should not surpass 30 mg/l dispersed oil in water in the discharged produced water by the end of 2006.
The main public policy issues regards the potential of the produced water substances to cause harm to the marine environment, environmental impacts due to actions taken and last, the cost of these actions with regard to industry and society.
In order to assess the risks caused by produced water discharges one has to investigate a number of areas [7]:

- Assessment of the properties of the substances in produced water, to gauge the extent to which they are likely to be intrinsically hazardous.
- Testing of the substances, on animals or otherwise, to assess the concentrations at which they cause harm.
- Theoretical modelling of produced water discharges, to assess the extent to which these concentrations are reached.
- Experiments with fish or other biota at the sites of produced water discharges, exposing them to higher than normal doses of produced water, to assess whether this causes harm.
- Scientific monitoring of actual produced water discharges and their environmental impacts to assess the actual evidence of harm.

2.6. Oilfield waste.

2.6.1 Management of oilfield waste

Management of oilfield waste such as produced water should include a system for pollution prevention. This means that one should always utilize the best available technologies to minimize the generation of produced water. For instance reuse and recycling of produced water should always have priority, and disposal of the water should be the last option.
New technologies have made it possible to manage the produced water by: reinjecting the produced water into the formation that it was produced from, treatment of the produced water

in order to meet with the authorities discharge regulations and then discharge the produced water to the sea, reuse in oil and gas operation.

2.6.2 Produced water treatment technologies.

Next follows an overview over conventional and possible future technologies for treatment of produced water [3]:

Table 3: Conventional and possible future technologies for treatment of produced water [3].

	Components to remove:	Commonly used today:	Limited used today:	Possible future technology:
Degasser vessel	Free gas	X		
Plate separators	Suspended oil	X		
Flotation units		X		
Static hydrocyclones		X		
Rotating hydrocyclones			X	
Centrifuges			X	
Media filters			X	X
EPCON			X	X
Activated carbon	Oil + dissolved components			X
Membranes (MF, NF)			X	X
Ctour			X	X
Ione exhange filter	Heavy metals			X
Air/stream stripping	Dissolved components		X	X
Wet air oxidation				X
Biological treatment*				X

*Main object in this thesis

2.6.3 Effects, goals and future requirements regarding produced water discharges.

The Norwegian climate and pollution control directorate published in April 2010 a report assessing how far the petroleum industry have come in order to meet with the authorities zero discharge goal (Petroleumsvirksomhetens arbeid med nullutslipp 2010[4]), the report also provided further recommendations for the petroleum industry to assess.
One of the main conclusions carried out from this work states that there is reason to continue to focus on the discharge of produced water and set stricter requirements for produced water discharge and also to work towards a further reduction of produced water discharge, because the reduction of oil and naturally occurring substances discharged to sea have been less than expected and the amount of produced water will increase in the years to come [4]. OLF also claim that there is a lack of knowledge in relation to environmental effects long term caused by produced water discharge [4]. Other conclusions and recommendations for further work evaluated in the report published by The Norwegian climate and pollution control directorate published in April 2010[4], states that the climate challenges and major air emissions from the Norwegian continental shelf should be evaluated when the new zero discharge measures are considered, and the report recommend a general requirement of produced water injection on the Norwegian shelf .
The goal of "zero discharge of hazardous chemical additives" is considered to be achieved, but a comprehensive review of disposal of drill cuttings was recommended.
As stated earlier, the reduction of oil and natural occurring substances in produced water such as PAHs have been less than what was expected from reports in 2003[4]. Meanwhile, the quantities of produced water is assumed to increase in future years and therefore the discharges will continue to increase if no new measures are made.
The institute of marine research (Havforsknings Instituttet) published an article the 26th of May 2011, stating that fish, in the area near oil installations in the North Sea, have been affected negatively by the oil components found in produced water. Negative effects on the liver was detected and several biomarkers in the fish showed that the fish in areas with high oil-production was affected the most [7]. It was concluded that fish, living in areas with large produced water discharges, had a poorer health status than those not living in these surroundings [7]. Researcher Jarle Klungsøyr says that it is most remarkable to obtain biomarker responses in natural fish populations in the open sea that are similar to the biomarker responses found in fish from highly polluted areas close to a point source.

3. Produced water characteristics

3.1 Produced water definition

Produced water is a by-product in the production of oil and gas hydrocarbons from underground reservoirs that consist of formation water which is water that is naturally present in the reservoir, and in the case of gas production, condensed water and seawater that has been injected in order to maintain reservoir pressure during production and occasionally some smaller streams like displacement water from oil storage facilities, process and drainage water [5].

3.2. Produced water composition

3.2.1 Produced water content

Produced water is a mixture of formation water, condensate and injected seawater. The produced water follows the production stream of oil and gas and contains compounds that originate from contact with other compounds like oil, minerals and salt.
Although there currently does not exist a performance standard for removal of *dissolved* components from produced water the Norwegian authorities have, as discussed in chapter 2, initiated the "zero harmful discharge" policy, and the regulations on the Norwegian Continental Shelf (NCS) are getting stricter with regard to the quality of the produced water that are discharged into the sea.

Produced water is the largest waste stream generated in the oil and gas industries [1], and it is a mixture of (reference number 5 is used for all bullets below):

- Inorganic components: Depending on the fields geology and production process, the salinity of produced water can vary from saturated to nearly fresh. The concentration of total dissolved salts in the North Sea produced water can vary from 3 g/l to far above the average concentration in sea water of 35 g/l. The produced water changes during production time, formation water has similar properties to seawater, but in

general the formation water has higher salinity and lower pH than sea water. Metals are the main inorganic constituent considered to be of environmental concern. Most frequent studied metals are: iron, cadmium, chromium, copper, lead, mercury, nickel, arsenic and zinc. A gas field usually generates higher values of heavy metals.

- Organic constituents: Commonly divided into two categories: dispersed oil and dissolved organic compounds. For instance some compounds such as the aliphatic hydrocarbons are found primarily in the dispersed phase because of their solubility properties, while for example carboxylic acids are found in the water phase normally. Aromatic compounds are found in both phases depending on molecular weight and structural complexity.

Low molecular weight aromatics like benzene, toluene, ethylbenzene and xylene (referred to as BTEX) and naphthalene are fairly soluble in water. Polycyclic aromatic hydrocarbons (PAHs) are fused aromatic rings that have no hetero-atoms and do not have any substituents, and they remain in the dispersed oil phase primarily.
The highest concentration among all organic compounds in produced water is carboxylic acids which are not considered to be environmentally harmful, but it increases the BOD value. Phenols are the second largest group of dissolved organic compounds and the solubility of the alkylphenols decreases with increasing molecular weight. Studies on C4-C9 phenols indicate endocrine disruption in cod exposed to alkylated phenols and the compounds are also believed to bioaccumulate.
Aromatic compounds are divided into the three groups based on their potential of causing environmental effects: BTEX, NDP and PAH.
Among aromatic compounds in produced water, BTEX are found in the highest concentration. BTEX compounds are somewhat soluble in seawater, they are highly volatile, and are rapidly biodegraded. BTEX are not accumulated by marine organisms.
Naphtalene is the most abundant compound in the NPD group (naphtalene, phenanthrene and dibenzothiophene, including their C1-C3 alkyl homologues), but because of the low bioaccumulation potential and rapid biodegradability, naphtalenes are considered a relatively low environmental risk.
PAHs (polycyclic aromatic hydrocarbons) range widely in structures and properties. The potential for bioaccumulation in marine organisms increases and the solubility decreases as the molecular weight of the compound increases. The PAHs are found

mainly in the oil droplets or particulate matter. They represent a small fraction of the aromatic compounds, but are of high environmental concern because of their possible mutagenic, carcinogenic or teratogenic effects on marine organisms. Also exposure to some PAHs can cause endocrine disruptions in marine organisms. PAHs can be biodegraded at a slow rate, but there is a risk of producing intermediate metabolic products that are even more toxic than the initial compound. The higher the molecular weight of the PAHs the more toxic the compound is to the environment.

- Production and processing chemicals: Are used in oil and gas production to enhance production and reduce operating problems. To enhance the recovery and production rate there are chemical available to inhibit corrosion, inhibit scaling, increase separation of oil, gas and water among others. Some of the chemicals are more soluble in oil than the produced water and will therefore remain in the oil phase but other chemicals are water-soluble and will therefore remain in the produced water and get disposed with the produced water.

- Other substances and properties: such as total suspended solids (TSS) that are not considered an environmental concern in the North Sea.
  And other parameters like COD (chemical oxygen demand and BOD (biological oxygen demand) of the produced water are not commonly measured because they are normally not an issue in offshore discharge of produced water.

3.2.2 Characteristics of some of the components in produced water

The next table lists some of the components in produced water along with some important characteristics of the different components.

Table 4: Environmental effects of components in produced water discharges[3]:

	Toxicity	**Biodegradability**	**Bioacc. potential**
Aliphatics	Low	High	None
Aromatics and phenols	Medium/high	Variable	Variable
Production chemicals	Variable	Variable	Variable
Carboxylic acids	Low	High	None
Heavy metals	Variable	----------	Variable

Brief explanations (further defined in chapter 4):

- Toxicity is a term used to describe a components ability to damage a living organism if it is exposed to the toxic component.
- Biodegradability is used to explain the degree of which microorganisms can break down a certain organic component biologically.
- The bioaccumulation potential referrers to the ability for a toxic compound to be accumulated within living organisms at a higher rate than at which the substance is lost.

3.2.3 Typical composition of produced water from oil and gas fields

The produced water composition varies from one field to another, within the field and during its life span. Gas and condensate producing fields usually only produce condensed water during their early production years. Condensed water is a fluid that contains few salts and inorganic particles, but it may contain high concentrations of dissolved light hydrocarbons. When significant quantities of reservoir water are being produced the productivity of gas wells decrease very rapidly, therefore the quantity of produced water from gas production is typically low, but the composition of the water evolves distinctly.

Next follows a detailed overview over the concentrations of all the different components in produced water from a major oil field and a major gas field [3]. The calculations made in chapter 6 are based on the values found in this table.

Table 5: Detailed overview over the concentrations of all the different components in produced water from a major oil field and a major gas field [3].

Component		Major Oil Field	Major Gas Field
Water production	m^3/d	30,000	160
Temperature	°C	75	75
Suspended oil *	mg/l	30 (15-40)	40 (15-100)
Aliphatics <C5	mg/l	1 (0-6)	1 (0-6)
Aliphatics ≥ C5	mg/l	5 (0-30)	10 (0-60)
BTX (Benzene, Toluene, Xylene)	mg/l	8 (0-20)	25 (0-50)
Naphtalenes	mg/l	1.5 (0-4)	1.5 (0-4)
Fatty acids (carboxylic acids)	mg/l	300 (30-800)	150 (0-500)
Phenols	mg/l	5 (1-11)	5 (0-22)
Salinity	%	3.5 (1-8)	0.5 (0.01-3)
Sulphate	mg/l	500	50
Barium	mg/l	30	10
Strontium	mg/l	40	20
Calcium	mg/l	450	400
Suspended solids	mg/l	<2 (1-20) *	<2 (1-20) *
Residual production chemicals:	mg/l		
Corrosion inhibitor		4 (2-10)	4 (2-10)
Scale inhibitor		10 (4-30)	0
Emulsion breaker		1 (0.1-2)	0
Coagulant		2 (0-10)	0
Biocide		0 (0-200)	0
Methanol		0	2,000 (1,000 - 15,000)
Glycol		0	1,000 (500 – 2,000)
Heavy metals:	µg/l		
Cadmium (Cd)		50 (0-100)	50 (0-100)
Chromium (Cr)		100 (0-390)	100 (0-400)
Copper (Cu)		800 (0-1500)	800 (0-1500)
Lead (Pb)		500 (0-1500)	500 (0-1500)
Mercury (Hg)		3 (0-10)	3 (0-10)
Nickel (Ni)		900 (0-1700)	900 (0-1700)
Silver (Ag)		80 (0-150)	80 (0-150)
Zinc (Zn)		1000 (0-5000)	1000 (0-5000)

* After treatment. Before treatment the content of suspended oil is typically 200-100 mg/l.

The amount and composition of the soluble organic compounds that may be present in the produced water stream will vary depending on several factors [5]:

- Type of oil.
- Volume of water production.
- Artificial lift technique.
- Age of production.

And, according to the components chemical characteristics, the dissolved organic compounds are divided into the following classes as described above [5]:

- Aliphatic hydrocarbons.

- Phenols.
- Carboxylic acids.
- Low molecular weight aromatic compounds.

3.2.4 Dissolved organic compounds in produced water

Usually, the amount of dissolved compounds in produced water is provided by the non-hydrocarbon organic compounds. Next follows an overview over the contribution from specific organic compound groups in produced water, carried out by OLF in 2007.

Table 6: Contribution from specific dissolved organic compound groups [5]:

Organic compound group:	Amount of total contribution %
Carboxylic acids	93.6 %
BTEX	4.8 %
Phenols	0.5 %
Environmental protection agency (EPA) PAHs	0.13%
Alkylphenols (C1-C3)	0.89 %
Alkylphenols (C4-C9)	0.03 %

3.2.5 Amounts of organic compounds discharged with produced water

The next table contains information about the amount of selected groups of organic compounds discharged on the Norwegian Continental Shelf with produced water in kg (OLF, 2010).

Table 7: Discharge in kg of selected groups of organic compounds in produced water [2]

Organic group (Kg)	2002	2003	2004	2005	2006	2007	2008	2009
Other	17412	273449	8025465	8131449	7519086	7959150	8838787	7814585
BTEX	1089889	861160	1485212	1479637	1644661	1826674	1803998	1902925
Alkylphenols C1-C3	196465	281116	278173	257668	335937	341254	324626	310191
Alkylphenols C4-C5	7935	10104	12809	13273	15571	12513	12473	12949
Alkylphenols C6-C9	266	401	225	302	132	173	198	184
Phenols	243552	184168	206962	170118	179405	212822	207560	185041
Oil in water		1698382	2075894	2097498	1057837	1178851	947549	1156501
Organic acids	29055706	33576880	32754134	34711299	34838267	35818064	31263700	27204909
Total EPA-PAH	47204	45176	61860	44392	66968	52567	48312	51512
PAH	100856	99465	110511	121454	89899	73776	81157	101664

As stated earlier in this chapter, the composition of the produced water varies from field to field depending on several factors. The next table presents the different concentrations of some organic compounds in produced water, from seven different fields on the Norwegian Continental Shelf.

Table 8: Concentrations of organic components in produced water in mg/l (2002) [8]:

Field (horizontal): Component/Group (vertical):	**Åsgard A**	**Åsgård B**	**Heidrun**	**Draugen**	**Njord**	**Kristin**	**Ormen lange**
BTEX	37.8	166	7.09	3.96	21.72	30.43	3.48
Napthalenes	3.38	6.43	1.56	0.076	0.228	2.62	0.482
2-3 rings PAH	0.274	0.098	0.38	0.112	0.0172	0.35	0.007
4+ rings PAH	0.004	0.0002	0.008	0.0012	0.0022	0.0046	0.0001
Phenol C0-C3	15.5	12.5	2.68	1.838	6.14	10.68	15
Phenol C4-C5	0.061	0.231	0.0096	0.0044	11.27	0.12	0.06
Phenol 6+	0.001	0.0002	0.00622	0.00004	0.1716	0.032	0.001
Dispersed oil	23.3	30.6	63.8	23.6	12.66	36.9	4.3

4. Characteristics and distribution of organic compounds discharged with produced water.

4.1 Organic compounds

Most compounds that contain carbon are referred to as organic compounds with the exception of a few simple molecules such as CO_2 and CO. The carbon atoms have the ability to form stable bonds with other carbon atoms as well as stable bonds with hydrogen, oxygen and nitrogen atoms, and are therefore capable of forming a large diversity of complex organic compounds. The organic compounds behaviour is depending on the compounds molecular structure, molecular size, molecular shape and possible functional groups which is also important in the determination of metabolic fate and toxicity of the organic compound.
Hydrocarbons are composed only of the elements carbon and hydrogen. Most hydrocarbons are liquid or solid at normal temperature and pressure except for some low molecular weight hydrocarbons like methane and ethane which exists as gases.
The majority of hydrocarbons is of low polarity and has therefore low water solubility, but is highly soluble in oil and most organic solvents.

From chapter three it is found that the constituents of produced water can be classified into the following four groups:

- Inorganic compounds
- Organic components
- Production and processing chemicals
- Other substances and properties

In this chapter only the organic compounds in produced water are assessed.
The organic constituents in produced water can be divided in two groups:

- Dispersed oil
- Dissolved organic compounds

Oil can be present in the produced water as dispersed droplets and/or in the dissolved phase.

The dissolved organic compounds that may be present in the produced water include aliphatic hydrocarbons, carboxylic acids, phenols and low molecular weight aromatics. As mentioned earlier the concentration and nature of soluble organics depends on type of oil and technological factors like production stage.

4.2 Produced water and persistent organic pollutants (POPs)

During 2002, the United Nations affiliated Inter-Organization Program for the Sound Management of Chemicals (IOMC), and issued a report that identified POPs as chemicals that [10]:

- are extremely stable and persistent in the environment.
- bio-accumulate in organisms and food chains.
- are toxic to humans and animals and have chronic effects such as disruption of reproductive, immune and endocrine systems, as well as being carcinogenic.
- are transported in the environment over long distances to places far from the points of release.

The regulations set by the authorities regarding produced water discharges has, as mentioned, for a long time focused only of the concentration of non-polar oil in water (OIW) concentrations, and paid little notice to the dissolved organics. But, at present day there is a wide agreement within governments, oil production industry and scientists that the focus should be put on the dissolved organic compounds as well as heavy metals and production chemicals in produced water.
Field specific environmental impact factor (EIF) calculations have shown that the most significant contributor to environmental risk are, commonly, the water-soluble fraction; essentially alkylated phenols and polycyclic aromatic hydrocarbons (PAHs) and in some cases specific production chemicals [11].

Carboxylic acids represent the largest group among all organic compounds in PW and are not considered to be environmentally harmful.
The phenols represent another large group of dissolved organics in produced water. Phenol is the most abundant compound in this group and studies on C4-C9 phenols have indicated negative effect on hormone balance and reproduction abilities in exposed cod, and these compounds are also believed to bioaccumulate [11].

The aromatic compounds are divided into the following groups based on their differences in possible negative effect on the environment and the wide range of concentrations in produced water [11]:

- BTEX: Benzene, Toluene, Ethylbenzene and Xylenes (ortho, meta and para isomers of monocyclic aromatic compounds). BTEX are relatively soluble in water, highly volatile, rapidly biodegraded in the water environment and toxicity increases with increased molecular weight.
- NPD: Naphthalene, Phenanthrene, Dibenzothiophene as well as their C1-C3 alkyl homologues- 2-3 ring aromatic compounds. NPDs have a lower potential for bioaccumulation and are rapidly biodegraded, but dibenzothiophenes are moderately toxic.
- PAH: Polycyclic Aromatic Hydrocarbons. The least water soluble fraction of aromatic compounds resulting in higher bioaccumulation potential. PAHs can be biodegraded at relatively low rates but during the microbial degradation even more toxic intermediate metabolic compounds are often produced. Higher molecular weight PAHs are thought to be more toxic than lower molecular weight aromatics to marine organisms. PAHs represents a small fraction of the aromatic compounds, but are still of environmental concern due to possible mutagenic, carcinogenic or teratogenic effects, and some PAHs may cause endocrine disruptions as well.

4.3 The OSPAR PLONOR list

In the Norwegian regulations colouring code for offshore chemicals (black, red, green and yellow) is used to classify the different chemicals, and to environmentally monitor the petroleum activities on the Norwegian Continental Shelf.
The different offshore chemicals are classified as follows [11]:

- Black: Chemicals that cannot be discharged. Permits are only given in special cases.
- Red: Chemicals that pose an environmental hazard and should for this reason be replaced. Permits are given on the condition that special priority is given to identify substitutes for these substances.
- Yellow: Chemicals in use but not included in any of the other categories. Permitted, normally, without specific conditions.

- Green: Chemicals on the list from the OSPAR PLONOR list (defined below), permitted without specific conditions.

The OSPAR PLONOR lists the chemicals used in offshore processes that are considered to pose little or no risk to the environment (PLONOR) including [11]:

- Inorganic salts that are naturally occurring constituents of seawater (excluding salts of heavy metals).
- Minerals which are not soluble in water.
- Organic substances that meet the following criteria: no CRM (carcinogen, mutagen, reproductive toxicity) properties and LC_{50} or EC_{50} >100 mg/l and $LogK_{OW}$ <3 or BCF(bioaccumulation factor)<100 or MW>1,000, and readily biodegradable according to the seawater biodegradation test, OECD 360 (further explained later in this chapter).
- Other organic substances that are non-water soluble (e.g., nutshells and fibers).

Discharge of produced water is, in Norway, under the restriction authority of the Pollution Act that gives permits for discharge to the environment. Internationally, OSPAR is the most important international agreement regulating discharges to the sea, and in addition to that OSPAR is also an important convention for the protection of the marine environment of the north-east Atlantic.

4.4 Ecotoxicity tests recognized by the OSPAR

In order to classify the different chemicals present in produced water, different ecotoxicity tests are recognized by the OSPAR and the Norwegian Pollution authorities [11]:

- Algae test (ISO/DIS 10253): Inhibition of algae growth is measured and the concentration of which the chemical is inhibiting algae growth by 50 %, EC50 (EC50 definition: effect concentration at which a predetermined level of effect occurs to 50% of the sample population), is determined. The test is carried out for all chemicals and the phytoplankton skeletonema costatum is used for all chemicals.
- Marine biodegradation test (OECD 306): Regular seawater (supplied with essential nutrients in excess) is used as source for biodegradation of the chemical being tested

to a concentration of 2 mg chemical per liter seawater. The test is carried out in an air-tight BOD bottle for 5-28 days at 20°C. The oxygen consumption is measured as the difference between dissolved oxygen (DO) in seawater with and without chemicals. The biodegradation potential is determined as % of a theoretical oxygen demand for the chemical.

- Bioaccumulation test: Is a chemical test used to determine the distribution of a chemical between two immiscible phases (the partitioning coefficient); octanol and water (defined later). Bioconcentration is defined as net result of uptake, distribution and elimination of a compound in an organism due to exposure of the chemical via water. The bioconcentration factor (BCF) expresses the ratio between the concentration in organisms and the aqueous concentration. Therefore the concentration of which 50 % of the exposed sample organisms are killed are referred to as LC50 (LC: lethal concentration) depends on the BCF.

4.5 Distribution of organic components from produced water in the surrounding environment.

The movement of chemicals within water and air and their movement across interphases are determined by physical processes. Movement depends on the properties of the chemicals themselves and the environmental compartments properties. These properties are important in order to determine the environmental fate of for instance persistent organic pollutants discharged with produced water.

Chemical properties.

- Polarity and water solubility[12]: Water is a polar liquid, meaning that the oxygen atom attracts electrons away from the two hydrogen atoms in the water molecule resulting in a partial negative charge on the oxygen atom and the hydrogens develop a partial positive charge. The molecule is said to be polar because the charges are separated within the molecule. On the contrary there is hardly any charge separation in nonpolar compounds as for instance nonaromatic hydrocarbons. Opposite charges attract each other and the solubility depends on the strength of charge on the solute. Among organic compounds will the presence of for example oxygen or nitrogen,

which are polarizing atoms in molecules, tend to increase charge separation and therefore it will affect the water solubility [12].

- Partition Coefficient, K_{OW}: Nonpolar liquids like for instance octanol and hexane are immiscible with water. If mixed with water, two phases will be formed, with the less dense liquid on the top. Solutes will partition between the two phases and as equilibrium is reached, the ratio of the concentrations in the two phases is given by the partitioning coefficient [12]. The relationship in the case of octanol and water partitioning coefficient (K_{OW}) is given as[12]:
  K_{OW} = Concentration in octanol/Concentration in water.
  This coefficient is commonly used to predict the environmental distribution and bioconcentration (recognized by the OSPAR and the Norwegian Pollution authorities as stated earlier in this chapter) of environmentally harmful chemicals because it provides an index of hydrofobicity.

- Vapour pressure: The tendency for a liquid or solid to volatilize is expressed by its vapour pressure which is defined as the pressure exerted by the vapour of a substance on its own solid or liquid surface at equilibrium [12]. Vapour pressure will increase with rising temperature because the kinetic energy in surface molecules will increase. The boiling point is reached as the vapour pressure of the liquid reached atmospheric pressure.

- Partitioning between different compartments of the environment: Chemicals partition not only between immiscible liquids but also between compartments of the environment, such as partition between air and water, air and soil etc. The distribution between the different phases is also here described by partitioning coefficient, but they are usually referred to with other terms. Henry´s constant, for instance, relates to the distribution of a volatile chemical between air and water. Models of environmental fate can be constructed based on the concept of fungacity (the escaping tendency that drives the movement of substances from one compartment to another) by utilizing the distribution coefficients[12].

- Molecular stability: The length of time that a certain chemical will be present in the environment and consequently the distance it can travel is all dependent on the

components molecular stability. Environmental chemicals are broken down by chemical and biochemical processes [12]. Some common chemical transformations are transformation by hydrolysis and by oxidation and photodegradation [12]. The rate at which chemical degradation occurs is not only a result of the stability of the chemical itself, but it is also influenced by environmental factors such as temperature, level of solar radiation, nature of adsorbing surface and pH.

Many organic pollutants are readily biotransformed, but there is a large difference between groups and species, and compounds that are readily metabolized by one species can be very persistent in other species. And even though high degradability is considered as a desirable characteristic it is necessary to strike a cautionary note because some transformations can lead to compounds with increased toxicity[12].

The figure below illustrates the ecotoxicology of produced water discharge offshore.

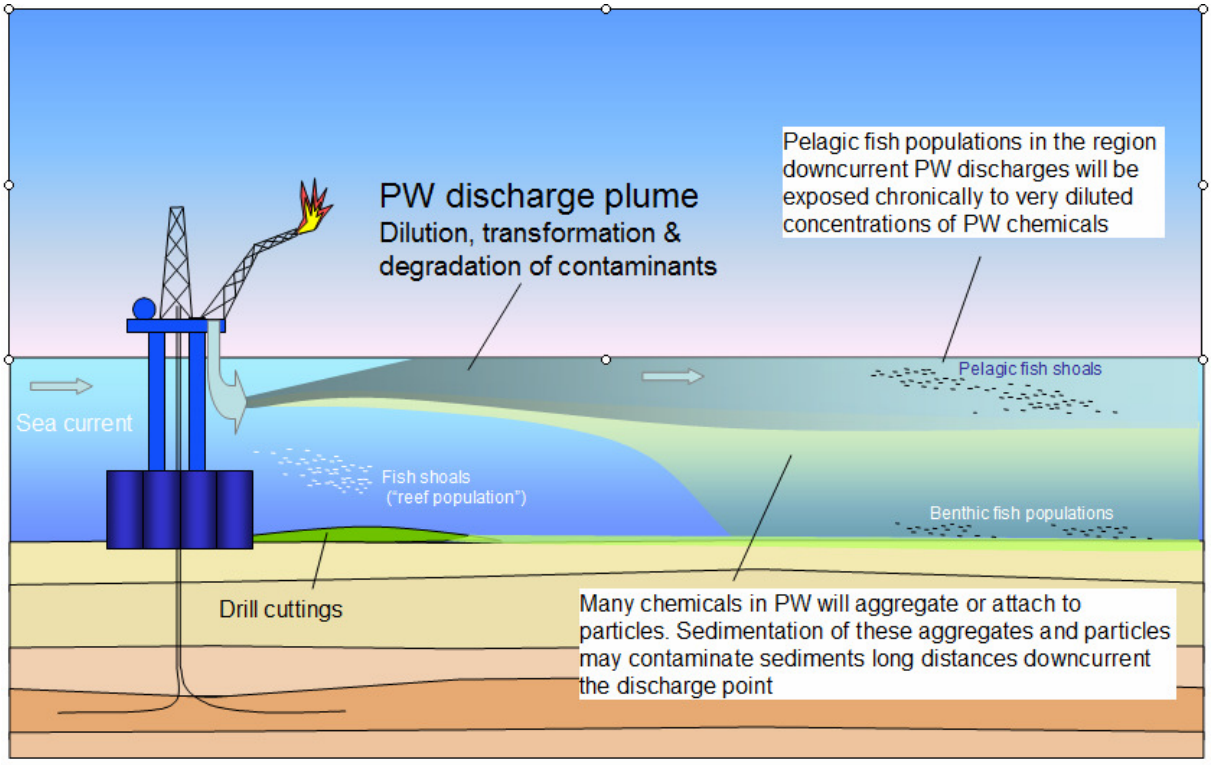

Figure 3: Ecotoxicology of produced water discharge [6].

4.6 Environmental monitoring

The oil and gas industry conducts extensive environmental monitoring to investigate potential negative effects of its discharges to sea. The regional monitoring is based on requirements

from the authorities, and individual companies also carry out their own more detailed studies and surveys. Environmental monitoring is a systematic collection of samples using verifiable methods and procedures [2]. The purpose of the environmental monitoring is to document the environmental state and its development over time and determine if the changes are due to human influence or natural changes. The main goal is to develop monitoring methodology, and to obtain a better understanding of what possible impact discharges from the oil and gas industry may have on the marine environment. Klif (klima og forurensingsdirektoratet) evaluates the results of the environmental monitoring and decides what measures to make. Monitoring of the water column consists of the following two elements: Condition monitoring and Effect monitoring. There are many challenges in proving pollution in the water column due to dilution, water currents and stratification of the water column.
Environmental risk tools have also been developed, such as dose response assessments through DREAM (Dose Related Risk and Effect Assessment Model. The effect monitoring shall include fish and mussels, cod and mussels have been used as test organisms. The conclusions of the Effect monitoring, published by OLF (Oljeindustriens Landsforening) [2], was that it was possible to prove that cod and mussels a few hundred metres from the discharge point, had been exposed to produced water because of response in some of the biomarkers defined. But, new research (More details in chapter 3) has documented that negative effects on fish due to produced water discharges have been detected in open sea areas [8].

5 Biological wastewater treatment

5.1 Introduction

Biological wastewater treatment is a process based on the natural role of bacteria to close the elemental cycles of for instance carbon, nitrogen and phosphorous on earth. In a wastewater treatment plant, naturally occurring bacteria is utilized. Natural limitations for bioconversion such as limited aeration or limited amount of biomass is possible to overcome by pooper engineering of the system. The design of the biological system should be based on the creation and exploration of ecological niches that select for microorganisms best adapted to reproduce under such environmental conditions [13]. Some conditions that are important to take into consideration when designing a biological treatment plant are [13]:

- Availability of electron donor (most often organic matter).
- Electron acceptor (for instance oxygen or nitrate).
- Nutrients demand.
- pH.
- Temperature.
- Hydrodynamic (Washing out non-attached microorganisms).

5.2 Microbiology

5.2.1 Classification of organisms

There are two types of organisms, prokaryotes and eukaryotes (see figure 4).

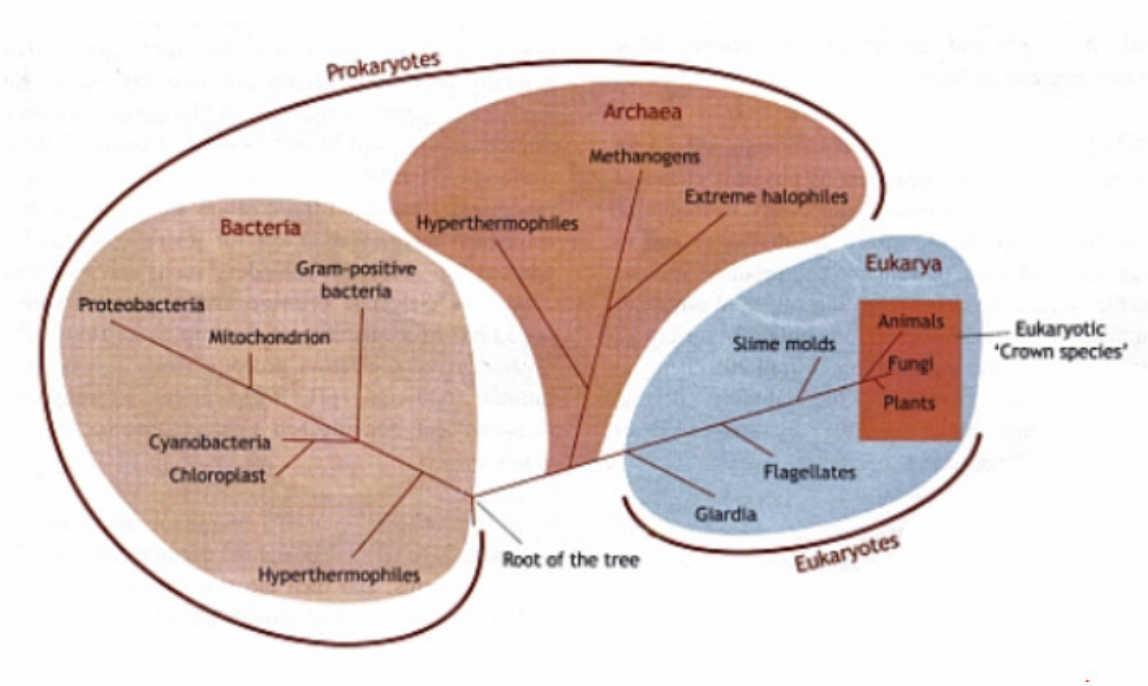

Figure 4: The phylogenetic tree of life [13].

Procaryotes include bacteria, cyanobacteria and archaea and eukaryotes include the unicellular organisms like protozoa, algae and fungi and the multicellular organisms like fungi, plants and animals.

5.2.2 The microorganisms role in biological wastewater treatment

The organisms found in wastewater treatment plants include mainly the microorganisms: viruses, bacteria and protozoa, and some higher organisms like algae, plants or animals [13]. The microorganisms role in biological wastewater treatment is to remove dissolved and carbonaceous BOD (defined later in this chapter) found in the wastewater. Mainly bacteria are used for this purpose, and the microorganisms oxidize the dissolved and carbonaceous organic matter into simple end products and biomass growth. The following equation (1) represents the aerobic biological oxidation of organic matter [14]:

$$organic\ material + O_2 + NH_3 + PO_4^{3-} \xrightarrow{\textbf{\textit{Microorganisms}}} new\ cells + CO_2 + H_2O \quad (1)$$

In this equation the oxygen, ammonia and phosphate represents the needed nutrients for the conversion of the organic matter to its end products to take place. The word *microorganisms* over the arrow show that the microorganisms are needed for the oxidation process to take place.
Hence, the microorganisms role in the biological treatment process is to:

- Act as a catalyst for biotransformation.
- Produce bioaggregates (for instance flocks and films) that can adsorb and sediment.
- Consume dissolved components by generating new biomass (growth).

5.2.3 Microbial growth and bioenergetics

For growth to take place, it is a necessity that the bacteria are able to replicate their genetic material and carry-out the necessary chemical transformations that allow the synthesis to take place. The chemical transformations are catalyzed by specialized proteins, enzymes.
Energy needed for the metabolism of bacteria comes from chemical oxidation reduction reactions. There are two main pathways of energy generation: The glycol sis and the tricarboxylic acid cycle (TCA, also referred to as citric acid cycle or Krebs cycle). Short told the two pathways generate energy by degradation of the sugar glucose into pyruvate and acetylCoA which then feeds into the TCA cycle see figure 5.
Chemical energy is transferred to ATP (adenosine triphosphate) which is an energy-rich compound, and electrons are then transferred to NAD^+ (oxidized form of coenzyme

nicotinamide dinucleotide) which is then reduced to NADH. When an electron acceptor, such as oxygen, is presence the NADH can transfer the electrons via the electron transport chain to the electron acceptor. in this process, protons are transported across the cell membrane to the outside of the cell, producing ATP.

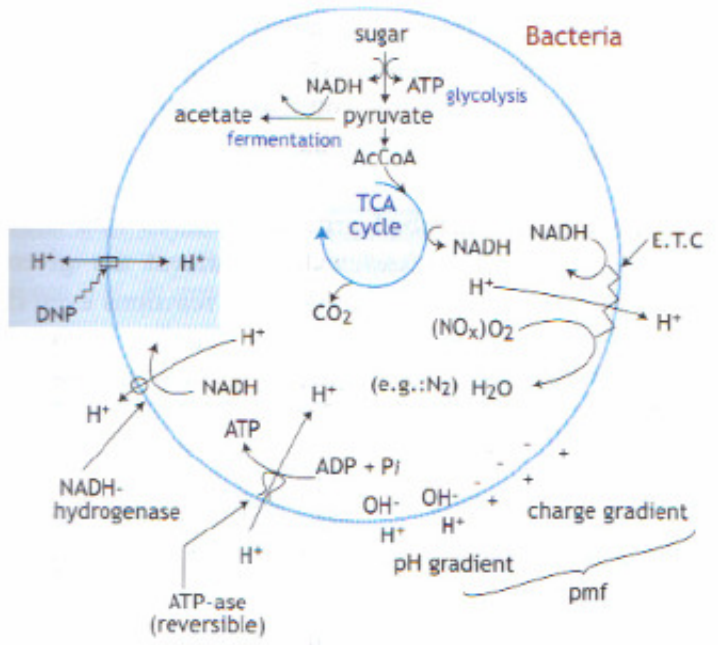

Figure 5: Overview of the bacterial bioenergetics [13]:

5.2.4 Nutritional requirements for microbial growth.

For microorganisms to synthesize cellular components they require energy and sources of carbon and certain inorganic compounds. The bacteria found in wastewater treatment plants are composed of 78-80 % water and 20-25 % dry matter, typically [13].
The dry matter can be determined from a liquid sample of known volume by retaining the biomass on a glass fiber filter with nominal pore sizes of 1.2 micron and then dry the filter at 105°C to evaporate the water. After cooling the filter containing the dry mass, the filter is weight, and the filter weight is subtracted and the result is divided by the known volume used in the analysis and the result is expressed as total suspended solids (TSS) in g/m^3. By combusting the filter with the dry mass at 550 °C in a muffle oven, the organic matter in the sample is burned of, and the remaining ash is weight after drying. This weight divided by the sample volume is termed the fixed suspended solids or inert suspended solids (FSS or ISS).

The organic matter, volatile suspended solids (VSS), is calculated by subtracting the FSS value from the TSS value.

The following table presents the typical composition of the dry matter (TSS) of bacteria.

Table 9: Typical composition of bacteria [13]:

Constituent/Element	**% TSS**	**Empirical formula for cells $C_5H_7O_2N$**
Major cellular constituents		
Protein	55.0	
Polysaccharides	5.0	
Lipid	9.1	
DNA	3.1	
RNA	20.5	
Other (sugars, amino acids)	6.3	
Inorganic ions	1.0	
As cell elements		% VSS
Organic (VSS)	93.0	
Carbon	50.0	53.1
Oxygen	22.0	28.3
Nitrogen	12.0	12.4
Hydrogen	9.0	6.2
Inorganic (FSS)	7.0	
Phosphorous	2.0	
Sulphur	1.0	
Potassium	1.0	
Sodium	1.0	
Calcium	0.5	
Magnesium	0.5	
Chlorine	0.5	
Iron	0.2	
Other trace elements	0.3	

From the table it is shown that the organic content of bacteria is 93 % and the inorganic content is therefore 7 %. The macro nutrients like nitrogen and phosphorous need to be present for cells to grow, along with other essential micro nutrients. Lack of essential

nutrients will limit the microbial growth and synthesis. The most important inorganic nutrients a microorganism need is N, S, P, K, Mg, Ca, Fe, Na and Cl, and the nutrients that is required in a smaller amount is Zn, Mn, Mo, Se, Co, Cu and Ni [13].
Organic nutrients are growth factors that an organism need as a precursor or as a part of the organic cell material that can not be synthesized from other carbon sources. Different types of microorganisms require different growth factors that can be divided into three major classes: amino acids, nitrogen bases and vitamins. In domestic wastewater these nutrients are rarely missing, but they are most likely missing in industrial effluents such as produced water. Therefore sufficient amount of nutrients have to be added to ensure microbial growth in the biological reactor in the system.

5.2.5 Effects related to pH and temperature on the microorganisms.

Microorganisms are affected by the pH in the surrounding environment, and have optimum growth at a pH value between 6.5 and 7.5 [14]. The majority of all bacteria will not survive pH levels below 4 or above 9.5 [14]. During the growth process certain bacteria will produce CO_2 which will decrease the pH because CO_2 is a weak acid. With proper aeration of the reactor, the CO_2 will be stripped out and therefore have low effects on the pH value in the reactor. During the endogenous (will be discussed later in this chapter) phase, cell material from dead cells be oxidised aerobically and produce carbon dioxide, water and ammonia.
The plot below show the results of a laboratory scale test of an aerobic biological reactor. It illustrates how the pH changes over time [15].

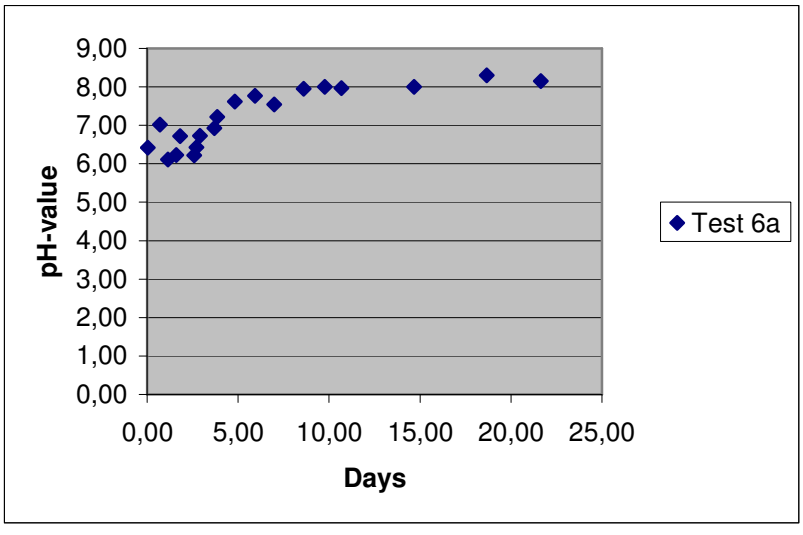

Figure 6: Change in pH over time [15].

Biological processes are also affected by the temperature in the system, generally the higher the temperature the higher the microbial activity, continuing until the temperature reaches its optimum. If the temperature is increased above the optimum temperature, the microbial activity will decrease. The higher the microbial activity, the higher the rate of substrate removal. The hydraulic retention time in the system is also a function of the temperature, because the retention time gets higher as the temperature decreases from the optimum temperature.
The equation below shows how the hydraulic retention time is related with the microorganisms growth rate, μ[14] (defined later in this chapter).

$t_h = 1/\mu$ (2)

μ = growth rate (1/d)
t_h = Hydraulic retention time (d).

The microorganisms can be divided into different groups according to its temperature range as shown in table 10.

Table 10: Typical temperature ranges for microorganisms [14]:

	Temperature ^{0}C	Temperature ^{0}C
Type of microorganism	**Range**	**Optimum temperature**
Psychrophile /cryophile	**- 10 – 30**	**12 – 18**
Mesophile	**20 – 50**	**25 – 40**
Termophile	**35 – 75**	**55 – 65**

Figure 7 also illustrates how significant the temperature affects the microorganisms. It is also shown that those microorganisms that operate at a higher temperature range have a higher maximum growth rate than those operating at a lower range.
Therefore, the type of microorganisms found in a biological treatment plant is dependent on the temperature of the water.

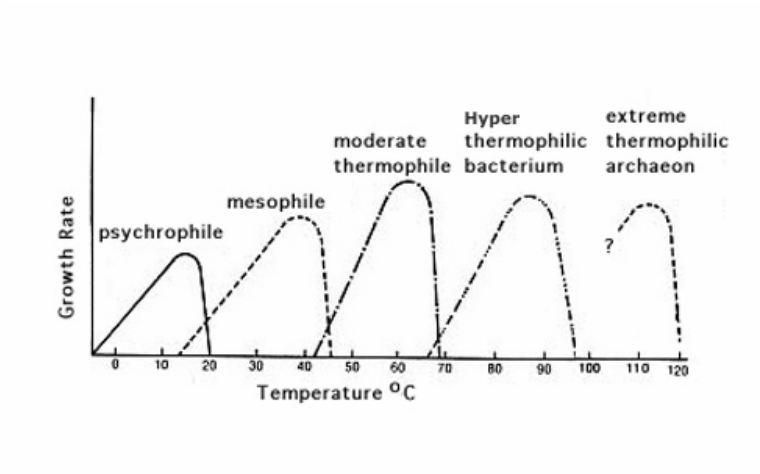

Figure 7: Effect of temperature on microbial growth rate [13]:

The effect of temperature on reaction rates can be expresses by the following relationships:

Effect on growth rate: $\mu_{max}(T) = \mu_{max}(20ºC)\theta^{(T-20)}$ θ : 1.07 [14] (3)

Effect on decay rate: $k_d(T) = k_d(20ºC)\theta^{(T-20)}$ θ : 1.04 [14] (4)

Where:

μ_{max}: maximum growth rate.

k_d: decay rate

θ: temperature-activity coefficient

T: temperature

5.2.6 Osmotic pressure and sensitivity for molecular oxygen

In addition to pH and temperature conditions the osmotic pressure, which depends on the concentration of salts, and amount of oxygen available must also be appropriate.
As shown in table 11, the sensitivity for molecular oxygen varies widely among microorganisms. The aerobes use oxygen and may need it (obligate), function without it (facultative) or require the oxygen in low levels (microaerophilic). Anaerobes do not utilize oxygen in its metabolism, they can either tolerate the oxygen (aerotolerant) or not (obligate anaerobe). In the aerobe microorganisms the enzymes needed for the reduction of oxygen, meaning that the oxygen is functioning as an electron acceptor, is always induced [13].

Table 11: Oxygen demand/tolerance and microorganisms [13]:

Group	Relationship to oxygen	Type of metabolism
Aerobes		
Obligate	Required (e.g. 20 %)	Aerobic respiration.
Facultative	Better if present, not essential	Aerobic or nitrate respiration, fermentation.
Microaerophilic	Requires low levels (e.g. 1%)	Aerobic respiration.
Anaerobes		
Aerotolerant	Not required and not affected by its presence.	Fermentation or sulphate reduction.
Obligate	Oxygen harmful or lethal.	Fermentation of anaerobic fermentation.

5.3 Stoichiometry and energetics.

Organic material in waste water is usually quantified as oxygen demand. By oxidizing the organic material the oxygen demand can be determined chemically or biologically. Biological oxygen demand (BOD) is a measure of how much oxygen aerobic microorganisms use in order to oxidize organic material in waste water. Therefore, the BOD value is also related to the biodegradability of the organic matter. For anaerobic treatment a standardized anaerobic biodegradability test is carried out in stead of the conventional aerobic BOD test. The BOD value will always be less than the chemical oxygen demand (COD) value since not all the organic material in waste water can be biologically degraded [14].
COD is usually determined at a laboratory as the organic compound is oxidized in the presence of an acidic dichromate solution heated at 150 °C for 2 hours and then the number of electrons donated by dichromate in the test is expressed as oxygen equivalents in gO_2/m^3[13]. By knowing that 1 mole of O_2 weighs 32 g and contains 4 electron equivalents (two electrons per atom in the molecule), the electron equivalents of oxygen can be determined. Hence, 1 electron equivalent (eeq) corresponds to 8 g of COD[13]. Defining O_2 as the electron acceptor and the organic material as the electron donor, then O_2 represents a negative COD value, 1g O_2 equals -1 gCOD [13]. The theoretical chemical oxygen demand (thCOD) for a certain organic substrate is found from a balanced equation over the process in which O_2 is added and the compound is mineralized to end products with ammonia remaining in its NH_3 (III)

oxidation state. If the compound is not reacting in the COD test then the theoretical COD value will deviate from the measured COD. Next is a generalized equation derived for the calculation of thCOD for an organic compound containing C, H, N and O [13].

$$C_nH_aO_bN_c + 0.5\,(2n + 0.5a - 1.5c - b)\,O_2 \rightarrow nCO_2 + cNH_3 + (a-3c)*0.5)\,H_2O \quad (5)$$

From equation (5) the thCOD can be calculated by the following equation[13]:

$$thCOD/weight\ (2n + 0.5a - 1.5c - b)16/\ 12n + a + 16b + 14c \quad (6)$$

For substrates the thCOD/VSS ratio varies greatly depending on the degree of reduction of the organic substrate. For instance the ratio may vary from 0.35 for formate to 4.0 g COD/g methane.

5.4 Energy demand and microbial metabolism.

The microorganisms microbial metabolism requires energy in order to synthesise cell growth. The electron acceptor and the electron donor couples and the energy produced decides the amount electrons available for the biomass synthesis, and this information can further be used to estimate the biomass yield of a reaction. With help from bioenergetics tools it is possible to quantify the amount of energy available from various biological reactions. The energy produced from the catabolism is depending on the oxidation and reduction of compounds available to the microorganisms. In the biological system, the electron donor (ED), which is considered to be the substrate or "food" in the reaction, is oxidized and the electron acceptor (EA), an oxidized form of for example oxygen, is reduced. The change in Gibbs energy is a thermodynamic property that is useful in order to characterize the maximum amount of energy obtainable for a given reaction.
If an empirically balanced stoichiometric equation can be obtained for biomass synthesis from a given wastewater (e.g. produced water), then the biomass yield can be calculated.

5.5 The processes in the biological reactor.

5.5.1 Biomass growth and biomass decay

(The equations in this chapter are taken from Metcalf & Eddy [14] and lecture notes from *Renseteknikk* [18] except where noted).

When speaking of the major processes that take place in the biological reactor, one is primarily referring to the processes of biomass growth and biomass decay.

There are four phases used to describe the cell growth in a batch test. During these different phases the substrate and biomass concentrations changes as shown in figure 8.

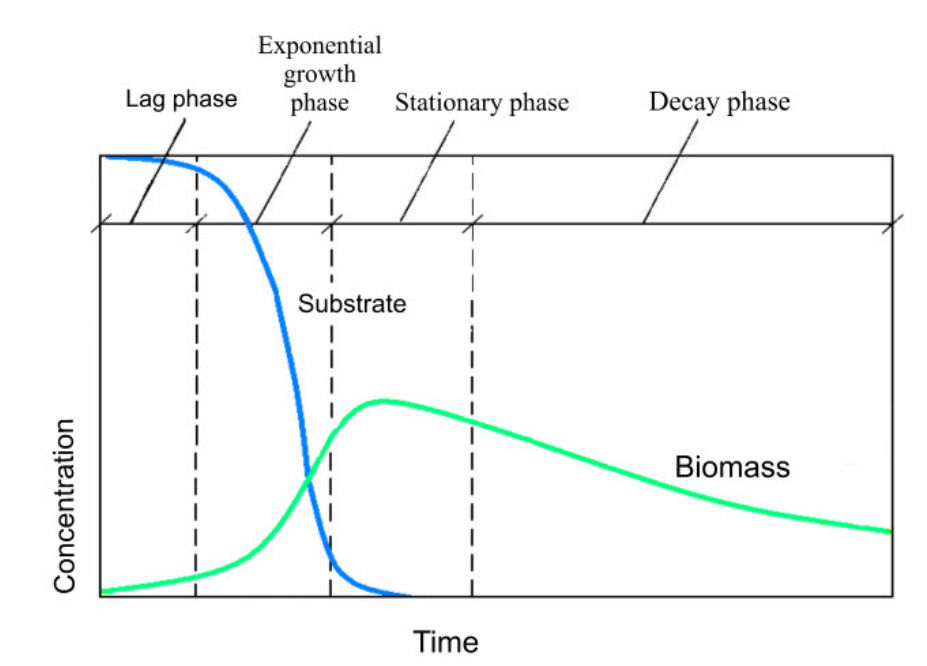

Figure 8: Biomass growth in batch mode [14].

The four phases are [13]:

- The lag phase: During this phase there is little increase in biomass as well as little substrate consumed as the cells acclimate to the new conditions.
- The exponential growth phase: Follows the lag phase, and is the phase where the biomass growth is at its maximum rate and the substrate available is readily consumed.

- Stationary phase: Is the next phase, and now there is little external substrate available and therefore the biomass concentration is relatively stable.
- Decay phase: Is the final phase in association with cell growth in which internal carbon and energy reserves are consumed to provide for the cells maintenance needs, and because of predation and lysis.

The process of biomass growth therefore involves increased biomass concentration (X_A), substrate utilization (C) and oxygen demand (O_2), whereas the decay process involves loss of biomass (X_A), oxygen demand for endogenous respiration and accumulation of inert residue (X_E) (typical fraction, f_d : 0.1 – 0.2).

5.5.2 Sludge production and oxygen demand

From the processes in the biological reactor, sludge is produced and oxygen is consumed. The sludge production and associated oxygen demand comes from:

- Sludge production: biomass growth – biomass decay + inert residue.
- Oxygen demand: biomass growth + endogenous respiration.

5.6 Microorganism kinetics.

5.6.1 Substrate utilization rate.

The rate of which substrate is utilized by microorganisms depends on several factors such as maximum substrate utilization rate and half saturation and inhibition constants [13].
The substrate utilisation rate depends on the microorganisms maximum substrate utilization rate, amount of biomass present and substrate concentration used for growth. The substrate utilisation rate can be written as follows [13]:

$$r_s = k \; M_s \; X \qquad (7)$$

Where:

r_s : Substrate utilization rate (gCOD/m^3.h).

k: maximum specific substrate utilisation rate (gCOD/gVSS.h)

M_s: Saturation function for soluble substrate, C_S, (gCOD/gCOD).

X: Biomass concentration (gVSS/m^3).

The saturation function, M_s, is affected by the substrate concentration according to equation (8) [13]:

$$M_s = C / (K_s + C) \quad (8)$$

where:
C: substrate concentration (gCOD/m^3).
K_s: substrate half saturation constant (gCOD/m^3).

Figure 9 illustrates an example of the effect of substrate concentration on the saturation function and kinetic of substrate utilization.

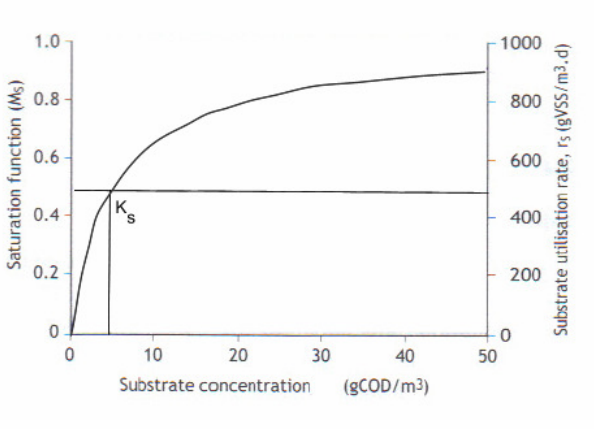

Figure 9: Effect of substrate concentration on the saturation function and kinetic of substrate utilization. Constants used in the figure: K_s = 5 gCOD/m^3 , k = 4 gCOD/gVSS.d and X = 250 gVSS/m^3.[13].

By multiplying with the various saturation functions (switching functions) such as the saturation function for oxygen (M_{SO2}), ammonia (M_{SNH3}) and phosphate (M_{SPO4}) these limiting effects can also be considered when calculating the substrate utilization rate [13]:

$$r_s = k \; M_s \; M_{SO2} \; M_{SNH3} \; M_{SPO4} \; X \quad (9)$$

But, according to Liebig`s law of minimum, the microorganism growth is limited by only one nutrient. Therefore, a more suitable formulation would be to consider only the minimum of

the different saturation functions in equation 9. Giving an adjusted equation with the MIN operator as follows [13]:

$$r_s = k \cdot MIN\ (M_s\ M_{SO2}\ M_{SNH3}\ M_{SPO4}\ ) \cdot X \qquad (10)$$

If an inhibitory compound is present, then a saturation function can be used to slow down the substrate utilisation rate according to the equation below [13]:

$$r_s = k \cdot I_I \cdot X \qquad (11)$$

where:

I_I : is the inhibition function for the inhibitory compound (g/g).

A commonly used inhibition function has the form [13]:

$$I_I = K_I / (K_I + C_I) \qquad (12)$$

where:

K_I : Is the half saturation constant of the inhibitory compound (g/ m^3).

C_I : Is the concentration of the inhibitory compound (g/ m^3).

5.6.2 Biomass growth rate

The growth rate of the microorganisms is at its maximum, μ_{max}, when the substrate utilisation rate is at its maximum. And theoretically, μ_{max} is a function of true yield, Y, multiplied with k, and is written as follows [13]:

$$\mu_{max} = Y\ k \qquad (13)$$

where:

μ_{max} : is maximum growth rate of biomass (gVSS/gVSS.d)

The growth rate of biomass is depending on its substrate utilisation rate for cell synthesis and its rate of decay which is proportional to the concentration of the present biomass. And can be written as follows [13]:

$$r_g = Y\ r_s - k_d\ X \qquad (14i)$$

or [14]

$$r_g = -Y\ r_{su} - k_d\ X \qquad (14ii)$$

where:

r_g : is biomass growth rate (gVSS/ m^3.d).

k_d : is specific biomass decay rate (gVSS/gVSS.d)

r_{su}: rate of substrate concentration change due to utilization (g/ m^3.d).

By substituting equations presented in this chapter one is able to get the following equations:

$$r_g = Y\ k\ M_s\ X - k_d\ X \qquad (15)$$

$$r_g = \mu_{max}\ M_s\ X - k_d\ X \qquad (16)$$

$$r_g = \mu_{max}\ (C / (K_s + C))\ X - k_d\ X \qquad (17)$$

By dividing the growth rate by the biomass concentration, the specific growth rate is obtained [13]:

$$\mu = r_g / X \qquad (18)$$

where:

μ : is specific growth rate (gVSS/gVSS.d)

or

$$\mu = \mu_{max}\ (C / (K_s + C)) - k_d \qquad (19)$$

or

$$\mu = Y\ k\ (C/ (K_s + C)) - k_d \qquad (20)$$

Figure 10 illustrates the effect of substrate concentration on the specific growth rate calculated from the equation above.

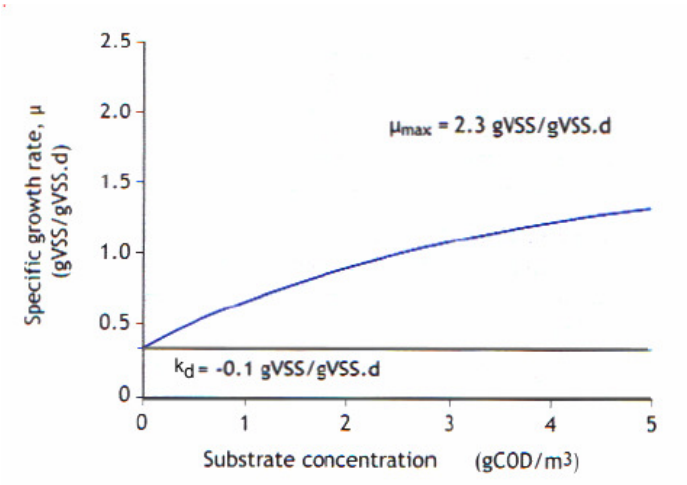

Figure 10: Effect of substrate concentration on biomass growth rate. Where: k_d = 0.1 g VSS/gVSS.d, k = 4 VSS/gVSS.d, K_S = 5 gCOD/m^3 , Y = 0.6 gVSS/gCOD [13].

From figure 10 it is shown that the maximum specific growth rate is obtained at a high substrate concentration where $M_s = C/ (K_s + C) = 1$,and hence, $\mu_{max} = Y\ k - k_d$ [13] . The substrate concentration required to which the biomass growth equals the decay rate is found at the point where the specific growth rate is zero [13]. When the substrate concentration is zero, then the specific growth rate becomes negative, and is equal to the decay rate, $\mu = - k_d$ [13].

5.7 Mathematical modelling of wastewater treatment systems

Symbol explanations for the entire chapter 5.7:

X : Concentration of particulate solids (mgSS/l).

X_A : Concentration of biomass in the reactor (mgVSS/l).

X_{Ain} : Biomass concentration in the influent (mg VSS/l).

X_{Aout} : Biomass concentration in the effluent (mg VSS/l).

X_{Ie} : Concentration of inert residue in the effluent (mg VSS/l).

X_W : Concentration in the waste sludge (mgSS/l).

X_R : concentration of biomass in return line from clarifier (g VSS/m^3)

X_r : concentration of biomass in sludge drain (g VSS/m^3)

X_E : Concentration of endogenous residue from cell decay (mg VSS/l).

X_{Ii} : Inert concentration from the inlet (mg VSS/l).

C : Concentration of biological degradable COD in the reactor(mg COD/l)

C_{out}: effluent soluble substrate concentration (bsCOD g/m^3)

C_{in} : Concentration of biological degradable COD in the inlet (mg COD/l)

C_w : Concentration of biological degradable COD in the waste flow (mg COD/l)

K_s : Half saturation constant (substrate concentration at μ_{max} /2) (mg COD/l)

μ : Specific growth rate (mg X_A/ (mg X_A*d))(1/d)

μ_{max} : maximum specific growth rate (1/d)

k_d : rate of decay (endogenous respiration) (mg X_A/ (mg X_A*d))(1/d)

f_d : inert residue fraction, typical f_d : 0.1 – 0.2).

f_{cv} : COD/VSS ratio (typical: 1.42 gCOD/gVSS)

Y_H : Maximum yield factor (mg VSS/ mg COD)

Y : Yield factor mg VSS/ mg COD)

V : Volume of the biological reactor (l).

SRT : sludge age (d)

Q : flow rate of influent (m^3/d)

Q_W: waste sludge flow rate (m^3/d)

Q_r : flow rate in return line from clarifier (m^3/d)

r_g : net rate of biomass production (gVSS/ m^3.d)

5.7.1 Steady models and dynamic simulation models

For mathematical modelling of wastewater treatment systems there are two models commonly used; steady state models and dynamic simulation models. The principle of steady state models is that the system has constant flows and loads which make the system relatively simple and this simplicity makes the model very useful for design. The models do not require complete description of all the parameters in the system, but instead the models are derived in order to determine the important system parameters from performance criteria [13]. The dynamic models are much more complex models, and have varying flows and loads in and out of the system. Therefore time is also an included parameter in the dynamic models. Because of this, the dynamic models are useful in predicting time dependent system response in the system.

All biological treatment system designs are based on applying mass balances across a defined volume for each specific constituent of interest like biomass, substrate etc. The mass balances includes the flow rates for the mass of the constituent entering and/or leaving the system as well as suitable reaction rate terms for the reduction or production of the constituent in the system.

5.7.2 Biomass massbalance

The mass balance for the mass of microorganisms in a complete-mix reactor is written as follows [14]:

Accumulation rate of microorg. within the system boundary	= Rate of flow of microorganisms into the system boundary	- Rate of flow of microorganisms. out of the system boundary	+ Net growth of microorganisms within the system boundary

Figure 11 shows a schematic diagram of an activated sludge process (defined later) with system boundary and model nomenclature.

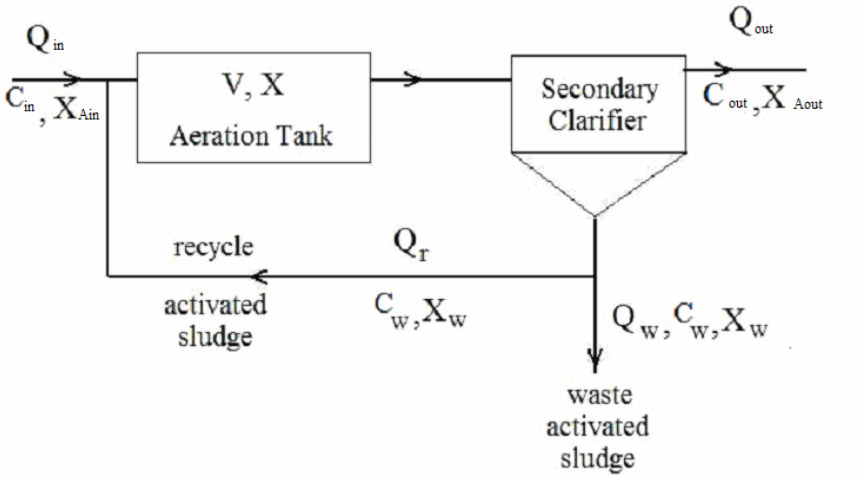

Figure 11: Activated sludge process with model nomenclature [14].

The symbolic presentation of biomass mass balance is then [14]:

$$dX/dt\ V = QX_{Ain} - [(Q - Q_W)\ X_{Aout} - Q_W\ X_R\ ] + r_g\ V \qquad (18)$$

If steady state conditions prevail (dX/dt= 0) and the concentration of microorganisms in the influent is neglected then the equation above can be simplified yielding the following equation [14]:

$$(Q- Q_W)\, X_{Aout} + Q_W\, X_R = r_g\, V \qquad (19)$$

By combining this equation with equation (14ii), the resulting equation can be written as follows [14]:

$$((Q- Q_W)\, X_{Aout} + Q_W\, X_R)/ VX = -Y (r_{su} / X)\, k_d \qquad (20)$$

5.7.3 Solid retention time

The term sludge age is also referred to as the sludge retention time (SRT), and is defined as the relationship between the amount of sludge in the system and amount of sludge wasted from the system as shown in the following equation:

$$SRT = \frac{V \cdot X}{Qw \cdot Xw} \qquad (21)$$

The massbalance for biomass growth relates the sludge age with biomass growth:

$$V\frac{dX_A}{dt} = QX_{Ain} - QX_{out} + \mu X_A V - k_d X_A V - Q_W X_{AW} \qquad (22)$$

Assuming steady state ($dX_A/dt = 0$) and $X_{Ain} = X_{Aout} = 0$, the following equation can be obtained:

$$0 = \mu X_A V - k_d X_A V - Q_W X_{AW} \qquad (23)$$

Total growth is defined as the inverse of the SRT:

$$\mu - kd = \frac{1}{SRT} = \frac{Qw \cdot Xw}{V \cdot X} \quad (24)$$

The solid retention time is an important parameter in design and operation for the activated sludge system. SRT is the average time the activated sludge solids are in the system.

The solid retention time, SRT, can be written as follows:

$$SRT = VX/(Q_W X_W) \quad (25)$$

In this equation the nominator represents the total mass of solids in the aeration tank and the denominator corresponds to the amount of solids lost per day via the effluent and sludge wasting (Q_W).

5.7.4 Mass balances over a continuous stirred tank reactor (CSTR).

Specific biomass growth rate, μ, according to Monod`s equation can be written as follows:

$$\mu = \mu_{MAX} \frac{C}{K + C} \quad (26)$$

From Monod`s equation it is found that total biomass growth over time is a function of biomass production and specific biomass growth rate as shown in the equation below:

$$\frac{dX_A}{dt} = \mu \cdot X_A = \mu_{MAX} \frac{C}{K + C} X_A \quad (27)$$

According to 1. order kinetics in a batch reactor it is assumed that the death of microorganisms can be found from the following equation:

$$\left[\frac{dX_A}{dt} \right]_d = -k_d \cdot X_A \quad (28)$$

When a cell/microorganism die it is assumed that a part of the organism is oxidized to CO_2 by the living organisms (according to the oxygen utilization rate, OUR), and the portion of the biomass that is not oxidized is accumulated as inert residue, X_E. The accumulation of the inert residue is written as follows:

$$\frac{dX_E}{dt} = f_d \cdot k_d \cdot X_A \qquad (29)$$

By combining equation (28) and (29), total biomass growth can be determined:

$$\frac{dX_A}{dt} = \mu \cdot X_A - k_d \cdot X_A \qquad (30)$$

5.7.5 Oxygen demand

The portion of substrate not used for biomass growth is oxidized to CO_2 and is proportional to the oxygen used. In the biological reactor oxygen is used for the oxidation of substrate, OUR_{exo}, and endogenous respiration, $OUR_{endo.}$
Oxygen demand for biomass growth:

$$\frac{dO}{dt} = (1-Y)\frac{dC}{dt} = (1-Y)\frac{\mu \cdot X_A}{Y} \qquad (31)$$

Endogenous respiration:

$$\frac{dO}{dt} = (1-f_d)\left[\frac{dX_A}{dt}\right]_d = (1-f_d)k_d \cdot X_A \qquad (32)$$

For a given system the total oxygen demand can be determined with a simplified equation for oxygen demand as follows [18]:

$$\text{Oxygen demand} = (1-Y\cdot f_{cv})\cdot(C_{in}-C_{out})\cdot Q + k_d\cdot X_A(1-f_d)\cdot V\ (kg/d)\cdot f_{cv} \qquad (32)$$

5.7.6 Substrate removal.

The total amount of substrate consumption is the sum of substrate used for growth and substrate used for energy production.
The change in biomass concentration divided by the change in biodegradable COD concentration in the biological reactor is the definition of the biomass yield, Y, in the system ($Y = \Delta X/\Delta C$). Substrate removal over time can be written as follows:

$$\frac{dC}{dt} = \frac{dX_A/dt}{Y} = \frac{\mu \cdot X_A}{Y} \qquad (33)$$

5.7.7 Sludge production and reactor volume

The maximum yield factor, Y_H, indicates the theoretical maximum percentage of substrate used for biomass growth. The rest ($1- Y_H$) is used for energy production via respiration, and is proportional with the oxygen consumed.

Amount of substrate used for biomass growth:

$$\Delta X_A = \Delta C \cdot Y_H \qquad (34)$$

Amount of substrate used for respiration and energy production:

$$\Delta O = \Delta C \cdot (1 - Y_H) \qquad (35)$$

Hence, biomass growth and oxygen consumption are proportional to each other, but this relationship will not be observed as biomass decay will cause sludge loss, which further results in a lowered Y_H value called observed yield, Y_{obs}.
At the same time, dead biomass will be oxidized by the remaining microorganisms causing the oxygen demand to get higher. The endogenous residue is accumulated in the sludge along with particulate particles from the reactor inlet.
The organic fracton of the sludge, volatile suspended solids (VSS), therefore consists of :

- Avtive biomass (X_A).
- Endogenous residue (X_E).
- Inert matter from the inlet (X_{Ii}).

The sludge production from a biological treatment system is the sum of biomass growth minus biomass death plus the accumulated inert fraction.

In an ideal CSTR system it is assumed that the condition of steady state prevails, that all the biological transformations take place in the biological reactor and that $X_{in} = X_{out} = 0$
From the massbalances for substrate in the reactor it is possible to relate sludge age to the biomass concentration, and from there it is possible to calculate the remaining sludge fractions in the system.

Substrate massbalance in a CSTR system is written as follows:

$$V\frac{dC}{dt} = Q(Cin - Cout)\frac{V \cdot \mu \cdot X_A}{Y_H} \qquad (36)$$

From equation (24) it is found that: $\mu - kd = \frac{1}{SRT}$

This relationship can be used for the calculation of amount of biomass in the reactor, as shown in the next equation:

$$X_A = \frac{Q \cdot (C_{in} - Cout)Yh \cdot SRT}{V(1 + k_d \cdot SRT)} \qquad (37)$$

In this thesis this relationship is used to calculate the reactor volume required for different X_A concentrations and SRT values as shown in the equation below:

$$V = (Q \cdot (C_{in} - C_{out}) \cdot Y \cdot SRT) / (X_A \cdot (1 + k_d \cdot SRT)) \qquad (38)$$

Massbalance for the endogenous residue in the sludge:

$$V\frac{dX_E}{dt} = f_d k_d X_A - Q_W X_{EW} \qquad (39)$$

The concentration of the endogenous residue can be determined from the following equation:

$$X_E = k_d \cdot X_A \cdot f_d \cdot SRT \qquad (SRT = V/Q_W) \qquad (40)$$

Massbalance for the particulate inert COD in the sludge from the inlet:

$$V\frac{dX_{Ii}}{dt} = Q \cdot X_{Ii} - X_{IR} \cdot Q_W \qquad (41)$$

$$0 = Q \cdot X_{Ii} - X_{IR} \cdot \frac{V}{SRT} \quad (Q_W = V/SRT) \qquad (42)$$

From this, the concentration of inert residue can be determined:

$$X_{IR} = \frac{Q \cdot X_{Ii} \cdot SRT}{V} = \frac{X_{Ii} \cdot SRT}{t_h} \qquad (t_h = V/Q) \qquad (43)$$

The total amount of sludge can be determined by adding the results from equation : 41, 42 and 43.

The sludge production may also be calculated in a simpler manner if the MLSS concentration is known as shown below:

$$\text{Sludge production} = \frac{V(m^3) \cdot MLSS(g/m^3)}{SRT\ (d)} \qquad (44)$$

5.7.7 Methods for determination of k_d, Y_H and $\mu_{max.}$

The rate of biomass decay, k_d, can be estimated by performing OUR and VSS measurements on a sludge sample where the added substrate has been completely utilized and therefore the available carbon source is dead biomass. Then the change in OUR and VSS in the sample can only be caused by endogenous respiration.

From equation (28) biomass change over time can be determined, and the endogenous residue is found from equation (29).

The biologically degradable part of the dead biomass ($1-f_d$) is oxidized and represented as oxygen demand according to equation ():

$$\frac{dO}{dt} = (1 - f_d)\left[\frac{dX_A}{dt}\right]_d = (1 - f_d)k_d \cdot X_A \qquad (45)$$

At the start of the OUR measurement, time (t) equals zero:

t = 0: $OUR_0 = (1 - f)\, K_d \cdot X_A = OUR$ (46)

t =1: $OUR_1 = (1 - f)\, Kd \cdot X_{A1} = OUR_0 \cdot e^{-k_{d1}}$ (47)

$$OUR_1 = OUR_0 \cdot e^{-kd1}$$

$$ln\ OUR_t = ln\ OUR_0 - k_d * t$$

The decay rate is found graphically, by plotting the results from equation (47) k_d is given as the negative value of the slope of the graph.

When k_d is a known factor, then the maximum yield can be estimated.

Yield factor: $Y = \frac{\Delta Xa}{\Delta TOC}$ (48)

Where:

ΔXa : Is change in active biomass concentration.

ΔTOC : Is change in total organic carbon.

Equation (1) illustrates the stoichiometric relationship between substrate removal, oxygen demand and observed biomass yield.

Microorganisms will reach its maximum growth rate when all substrates are in excess and the growth rate is limited by the microorganisms themselves. Therefore, μ_{max} is a parameter that indicates how fast a microorganism can take up and degrade the substrate. Experimentally μ_{max} can be determined in several ways, but what all the methods have in common is that the measurements must take place when the microorganism in the system are in the exponential growth phase with excess nutrients and substrate available. When these conditions are met, then it is reasonable to assume that $\mu_{max} = \mu$:

$$\mu = \mu_{max} \cdot \frac{C}{K + C} \quad \text{if C>>K} \Rightarrow \mu = \frac{\mu_{max} \cdot C}{K + C} = \mu_{max} \tag{49}$$

The easiest way to estimate μ_{max} is to base the calculations on OUR measurements according to the equation below:

$$\mu_{max} = \frac{Y_H \cdot OUR}{X_A (1 - Y_H)} \qquad (\text{if } \mu \approx \mu_{max}) \tag{50}$$

5.8 Different biological treatment systems

5.8.1 Introduction to different biological treatment systems

Removal of dissolved organic compounds can be achieved in both aerobic and anaerobic bioreactors, but only aerobic biodegradation of the organic compounds in produced water will be assessed in this thesis. The biological treatment is divided in two processes: suspended growth (activated sludge) and attached growth (biofilm).
For the treatment of aromatic compounds in produced water such as BTEX, different reactor configurations have been used. The most common technologies are fluidized bed reactors (FBR), moving bed biological reactors (MBBR), submerged fixed film reactors (SFFR) and fixed film activated sludge (FAS)[5]. All these systems are based on fixed film technology, which can retain larger concentration of biomass and therefore increase the microbial degradation when operated as a continuous process [5].
In this thesis the following four methods for aerobic biological waste water treatment was assessed:

- Activated sludge system.
- Biofilm.
- Membrane bioreactors.
- Membrane aerated biofilm reactors.

The major focus, when designing a biological treatment plant offshore, is the obvious space limitations on the offshore installations as well as design and operating cost. Therefore, space requirements for the different biological treatment technologies will be the major focus. As of

this date the Norwegian authorities do not require removal of the dissolved compounds from the produced water, but by utilizing biological treatment for this purpose, it may be possible to remove the dissolved organic compounds from the produced water and meet with the possible stricter discharge requirements in the future. As described in chapter 3, produced water contains a high amount of organic acids that would pose the largest burden on the biological process in terms of oxygen and nutrients requirements, since the organic acids are present at a much higher concentration than the aromatics.

5.8.2 The activated sludge system.

In all biological treatment systems it is necessary to characterize the waste water (in this case the produced water) both physically and biologically [13]:

- Physical characterisations: soluble or non-settleable (colloidal or suspended), settleable (organic or inorganic).
- Biological characterisations: biodegradable or unbiodegradable.

Physical and chemical transformations of the organic and inorganic components take place in the biological reactor. These transformations are important in order to achieve the required effluent quality. In the biological reactor, the biodegradable organics are all transformed to ordinary heterotrophic organisms (OHOs, X_{BH}), that becomes part of the organic volatile suspended solids (VSS) in the reactor. The death of these microorganisms leaves behind endogenous residue (X_{EH}) that is not-soluble, unbiodegradable particulate organics. The endogenous residue also becomes part of the VSS mass in the reactor. The unbiodegradable suspended and settleable organics (X_I) from the influent follows the OHOs and endogenous residue masses. Together these three groups form the organic part of the settleable solids that will accumulate in the biological reactor (VSS, X_A). The inorganic component of the settleable solid mass (ISS) consists of the inorganic settleable and suspended constituents and the precipitable soluble organics.

An activated sludge system is based on the principal of suspended growth, meaning that the microorganisms responsible for the biological treatment are kept in a suspension with help of an appropriate mixing technology. There are many suspended growth applications, both

aerobic and anaerobic, but the aerobic activated sludge system is the most common suspended growth application used for biological treatment of waste water.
The activated sludge system was developed in 1913, and the process got its name because it involved the production of an activated mass of microorganisms that were capable of stabilizing a waste under aerobic conditions. Figure 12 illustrates an activated sludge system.

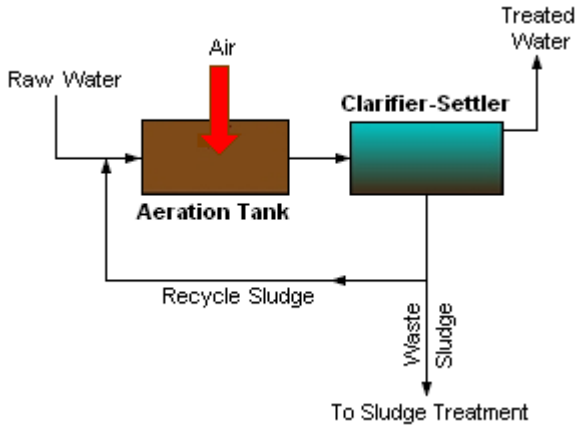

Figure 12: Activated sludge process [16].

In the aeration tank, contact time is provided when mixing and aerating the influent waste water with the microbial suspension, refers to as mixed liquor suspended solids (MLSS) or mixed liquor volatile suspended solids (MLVSS). To ensure mixing and oxygen supply into the system, mechanical equipment is used. The mixed liquor flows from the aeration tank to a clarifier where the microbial suspension will settle and thicken. The settled biomass is described as *activated sludge* because there are active microorganisms living in the sludge. Part of the sludge is returned back into the aeration tank to continue the biodegradation of the influent biodegradable material, the rest of the sludge is removed from the process. The possible formation of flocculent particles can affect the clarifier design and performance.

5.8.3 Biofilm system

(The equations defined in this chapter are taken from lecture notes presented by Professor Leif Ydstebø and Professor Roald Kommedal [18] except where noted)

5.8.3.1 Introduction to biofilm system

In attached growth treatment processes so called carriers are utilized on which the microorganisms establish a biofilm consisting of microorganisms, particulate material and extracellular polymers that covers and support the package material (can be plastic, rock or other materials). For attached growth processes, substrate is consumed within the biofilm, by diffusion across a stagnant liquid layer to the biofilm. The biofilm thickness may vary from 100 µm - 10 mm depending on the growth conditions and hydrodynamics of the system [14]. The microorganisms in biofilms are immobilized in the dense layer growing attached to the solid surface; therefore a settler is not necessary in order to maintain active biomass in the biofilm. The bacteria are protected from washout and they can grow in locations where their food remains abundant. The washout rate of suspended biomass (SRT) determines weather or not a biofilm will develop in a system, because if the rate of washout is larger than the growth rate of a certain group of microorganisms, then these microorganisms will preferentially grow as biofilm [13].

A stagnant liquid layer, called the diffusion layer, is separating the biofilm from the liquid flowing over the biofilm, called the bulk liquid. Figure 13 illustrates the cross section of a biofilm [14]:

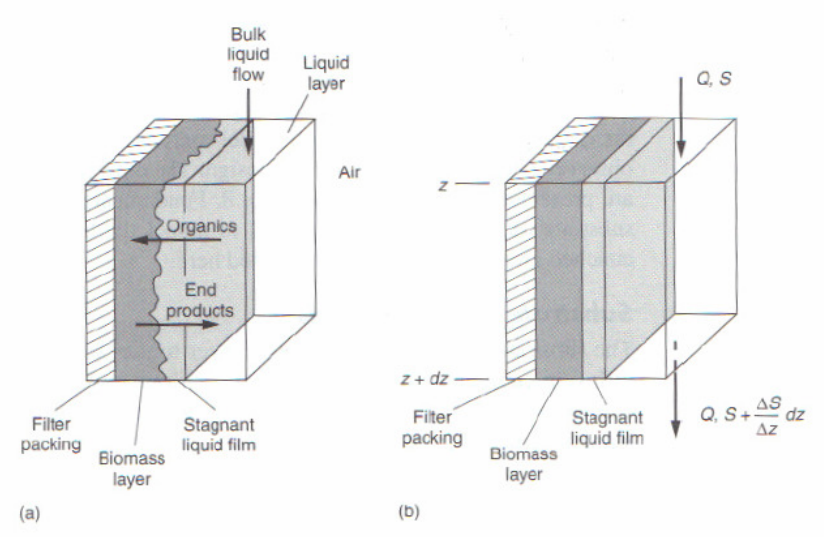

Figure 13: Schematic representation of the cross section of a biological slime in a trickling filter: (a): pictorial, (b): idealized [14]:

The amount of substrate, S, used per unit of biofilm cross-sectional area has to diffuse across the stagnant layer and this rate of mass transfer is referred to as the surface flux and is expressed as mass per unit area per unit time ($g/m^2 \cdot d$).
The biofilm layer is not a planar surface as the idealized biofilm in figure 12 (b), but rather a very complex nonuniform structure with uneven protrusions and possibly vertical and horizontal pores through which the liquid flow. The concentration of VSS may vary from 40 to 100 g/l, and the growth across the support packing is not uniform due to periodic sloughing and hydrodynamics and media configurations [14].

The next figure illustrates the different phases in biofilmformation:

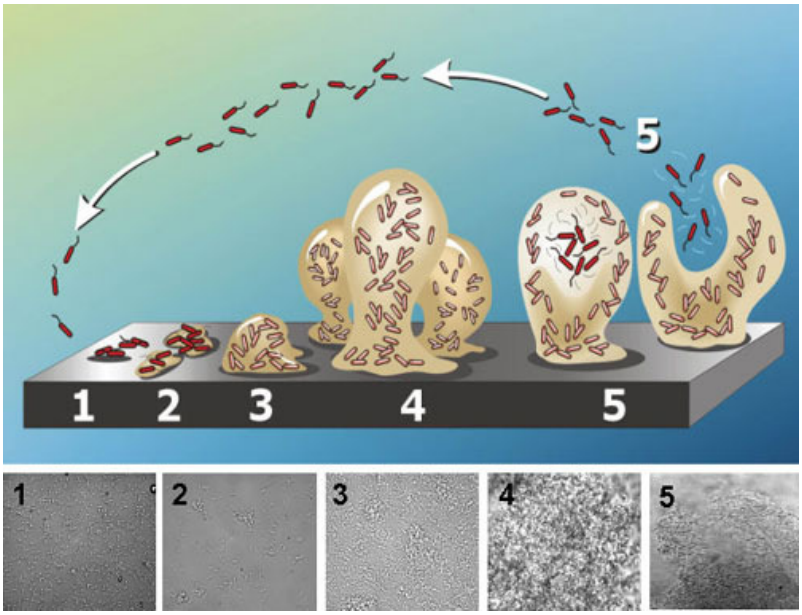

Figure 14: Biofilm formation [17].

where:

1. Initial attachment on a substratum (surface where biofilm is adhered) by adsorption, accumulation or concentration of cells on a substratum or interphase, or adhesion, which is connective interaction between a microbial cell and substratum by an *adhesin* (pili, flagella, surface proteins).
2. Irreversible attachment: the microorganisms are synthesizing the formation of extracellular polymeric substances (EPS) which are attached to the cell surfaces to form a polymer matrix in the inter spatial voids between the cells.

3. Maturation 1: by further attachment of solids by (cells or particles) adhesion to the biofilm matrix from the bulk phase.
4. Maturation 2.
5. Dispersal/detachment: By solid (cells and particles) desorption (the reverse of adsorption from the substratum back into solution) and movement from the biofilm matrix to the bulk phase.

The next figure shows a schematic over the different biofilm compartments.

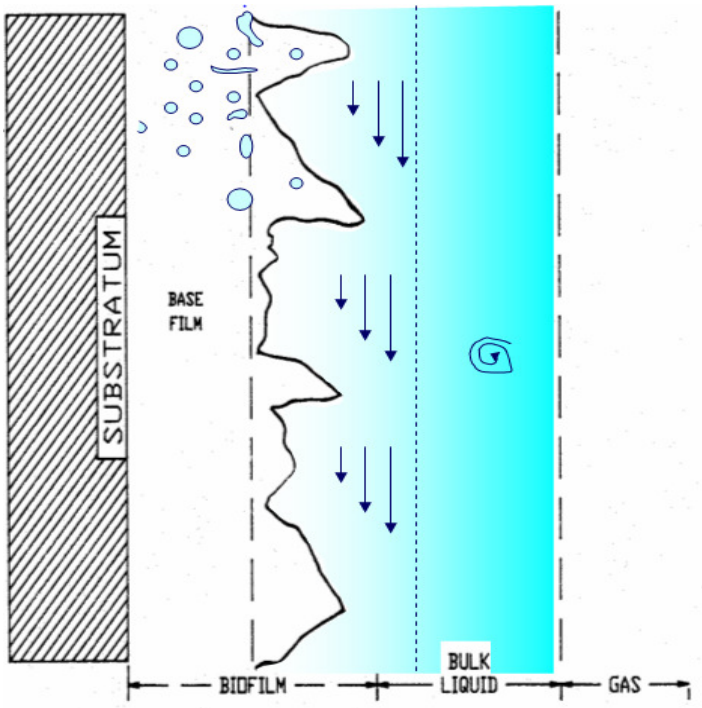

Figure 15: Different compartments of a biofilm [18].

where:

- The biofilm matrix is defined as all cellular and molecular parts (including particles) physically connected to the biofilm cells or it's EPS matrix.
- The bulk phase is defined as the fluid compartment outside the biofilm surface and its nearby liquid boundary layer.
- Liquid Boundary Layer is the liquid layer outside the biofilm surface of laminar fluid transport parallel to the substratum (laminar bulk flow) or biofilm surface (turbulent bulk flow). The transport to and from the biofilm surface is obtained by diffusion.
- The pore volumes illustrated by the blue "bubles" (pores) within the biofilm are void spaces inside the biofilm.

5.8.3.2 Biofilm models

Symbol explanations for the entire biofilm chapter:
S: Bulk phase limiting substrate concentration (g/m^3)
S_f: Local limiting substrate concentration in biofilm (g/m^3)
A: Biofilm surface area (m^2)
a_c : Specific area (m^2/m^3)
x: Biofilm depth (perpendicular to substratum) coordinate (m)
N: Flux rate limiting substrate ($g/m^2 \cdot d$)
r_f: Reaction rate per biofilm volume unit ($g/m^3 \cdot d$)
r_A: Total substrate removal rate ($g/m^3 \cdot d$)
D: Molecular diffusion coefficient limiting substrate (m^2/d)
k_{1f}: First order reaction rate coefficient (1/d)
k_{0f}: Zero order reaction rate coefficient ($gCOD/m^3_{BF} \cdot d$)
$k_{1/2f}$: Half order reaction rate coefficient ($g1/2/m^3/2 \cdot d$)
X_{BF} : biomass concentration within the biofilm ($gVSS/m^3_{BF}$)
V_{Bf}: Biofilm volume (m^3)
L_f: Biofilm thickness (m)

Many mechanistic models have been developed to describe the mass transfer and biological substrate utilization kinetic in biofilms, and these models are useful tools when evaluating the biofilm processes. But, because of the complexity of biofilm reactors and the inability to define the physical and model coefficients accurately, empirical relationship, based on observed performance, are used for design of the biofilm system.
The fundamental concepts of mass transfer and substrate utilization can be used in order to model the behaviour of substrate removal in biofilm processes as illustrated in the figure below.

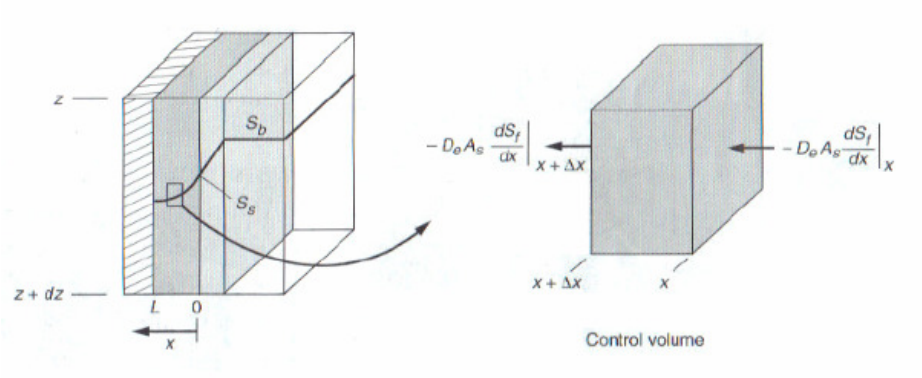

Figure 16: Definition sketch for the analysis of substrate concentration in the biofilm[14].

The figure above, figure 16, is a definition sketch of the analysis of substrate concentration in biofilms. Substrate mass balance around the differential element (dx) in the figure is [14]:

Rate of substrate accumulation within = differential element	Rate of substrate flow into differential - element.	Rate of substrate flow out of differential + element.	Rate of substrate utilization in differential element.

There have been developed several mathematical biofilm models that vary in terms of the processes considered within the biofilm, the information predicted by the model, and the effort required for solving the model ranging from simple analytical to complex multidimensional numerical models [13]. Therefore, it is important to clearly define the modelling objective before deciding on a particular model. The following objectives are relevant in order to predict the performance of biofilm reactors [13]:

- *Substrate flux as function of bulk phase substrate concentration:* Influence of mass transport and microbial kinetics inside the biofilms on substrate conversion rates, influence of mass transport limitations in the mass transfer boundary layer on the availability of substrate within the biofilm. The model should provide the flux of substrate into the biofilm as a function of substrate concentration in the bulk phase.
- *Multi-component diffusion:* The model should predict the penetration of multiple substrates into the biofilm in order to determine the limiting substrate.
- *Distribution of microorganisms:* The model should predict biomass distributions and corresponding substrate removal in order to explain how the substrate availability influences the distribution of microorganisms and how the distribution of microorganisms influence the removal of substrate.

- *Overall reactor performance:* The model should integrate the local substrate fluxes in order to best predict the biofilm reactor performance.

There exists several numerical solvers for complex biofilm models and analytical solutions for biofilms are available for one dimensional biofilms with a homogeneous organism distribution over thickness of the biofilm with simple first or zero order rate expressions (further described later in this chapter).

5.8.3.3 Loading factors and specific area

Established biofilm systems have showed that typical loading factors for 85 – 90 % COD removal are:

- Area loading: $L_A = 10 – 20$ gCOD/m^2·d ($Q \cdot C_{in}/A$).
- Volume loading: $L_V = 0.1 – 2$ kgCOD/m^3·d ($Q \cdot C_{in}/V$)

The variations in the loading factors are due to the effect of temperature, level of treatment, possible nitrogen removal and wastewater composition.

The available area for biofilm growth per unit volume reactor is defined as specific area, a_c:

$$a_c = A/V \ (m^2/m^3) \qquad (51)$$

Typical values of a_c for different biofilm configurations can be seen in table 12.

5.8.3.4 Steady state biofilm model

As discussed earlier, in biofilm systems the microorganisms grow attached to surfaces in the bioreactor, causing the biomass in the bioreactor to possibly become very high, further resulting in a high rate and low volume requirements which are important when designing for offshore installations because of the space limitations. The biomass in a biofilm reactor is a function of available area for microorganisms to grow on, substrate loading and shear forces. The available area for biofilm growth is the most important criteria when designing the biofilm reactor.

The biological processes are the same as for the activated sludge system, meaning that the two systems apply the same stoichiometric and kinetic parameters for biomass growth and biomass decay.
The main difference, though, between biofilm and activated sludge is the availability of substrate. The activated sludge flocks are surrounded by nutrients and substrate in the liquid, providing a short distance from substrate to microorganisms (~ 0 – 100 μm). As for biofilms the film on the surface (variable thickness, may be several millimetres) have relatively long distance from substrate to the majority of microorganisms except for those on the surface (~ 0 – 1000 μm).
When a biofilm system reaches steady state the major factor influencing the system is organic loading which causes biomass growth, attachment of particles, decay of biomass and shear forces acting on the biofilm surface due to turbulence in the liquid.

The increase in biomass can be seen as :

1. Growth: Function of substrate loading, specific growth rate and yield.
2. Adsorption: Immobilisation of cells and substrates on the substratum.
3. Attachment: Immobilisation of cells and substrates to the biofilm.

Decrease in biomass is a function of:

1. Biomass decay: This is a function of biofilm age and substrate availability.
2. Desorption: Loss of cells and compounds from the substratum.
3. Detachment: Loss of compounds from the biofilm by:
    - Sloughing: A rapid massive loss of biofilm.
    - Erosion: A continuous loss of small biofilm portions.

During establishment of a biofilm the processes increasing biomass dominates, resulting in an increase in biofilm thickness (L_f). The biofilm has reached steady state at the point where the mechanisms causing biomass loss is significant, causing a biomass loss corresponding to the biomass increase. One general way to describe biofilm thickness is by evaluating the active fraction of the biofilm. The active fraction of a biofilm referrers to the fraction that is penetrated by substrates.
Substrate in the bulk liquid is transported to the biomass in the biofilm by the following three transport processes:

1. Convective transport: Transport of substrates to the boundary layer.

2. Diffusive transport in liquid: Transport of substrates across the boundary layer to the biofilm surface.
3. Diffusive transport in biofilm: Transport of substrates into the biofilm.

5.8.3.5 Design criteria for a steady state biofilm model

Transport of substrate in the biofilm and reaction rate of substrate in the biofilm is important factors in when determining design criteria for different biofilm configurations.

The transport of substrate from the bulk phase and into the biofilm takes place in two ways:

1. Substrate transfer from the liquid phase into the biofilm surface by convection
2. Substrate transfer into the biofilm by diffusion

If convection >> Diffusion
Then the diffusion controls the transport rate.

Diffusion is driven by a concentration gradient (dS) over a distance (dx), and depends on the characteristics of the diffusing compound, diffusivity (D).

Fick's 1st law: $$J = -D\frac{dS}{dx} \quad (51)$$

The linear concentration gradient (dS/dx) means that only diffusion occurs (in the boundary layer).

Fick´s law describes mass transfer within a biofilm by relateing the diffusive flux (J) to the concentration, with the assumption that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient

Fick's 2nd law: $$J = -D\frac{d^2S}{dx^2}$$

Yields a non-linear concentration gradient meaning that both diffusion and reaction takes place, which is the case for biofilms.

For steady state models one-dimensional ideal biofilms is assumed meaning a homogenous distribution of biomass, smooth surface and constant thickness as shown in figure 17 below.

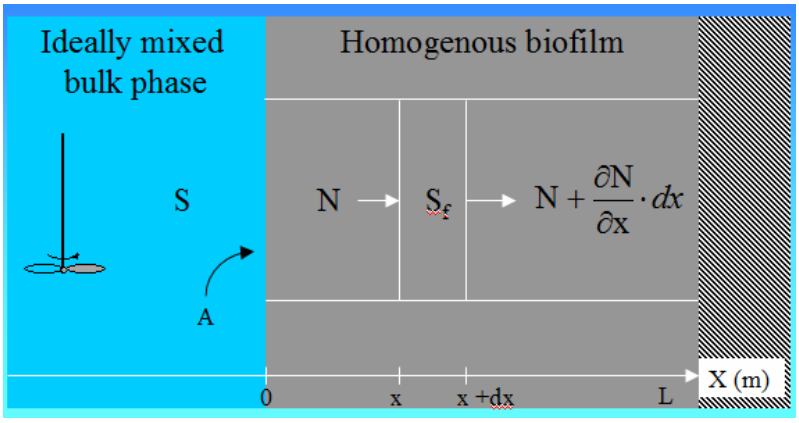

Figure 17: simple biofilm model [18].

Where the following assumptions are made:

- Homogenous distributed biomass.
- No biomass growth only conversion.
- Transport into the biofilm by molecular diffusion.
- No boundary.
- Diffusion limitations.
- Limiting substrate, S.

5.8.3.6 Biofilm kinetics

The specific growth rate for the microorganisms in a biofilm is according to Monod, similar to activated sludge.

$$\mu = \frac{\mu_{max} \cdot S}{K_S + S}$$

The equation below is used for the determination of the systems reaction rate:

$$r_f = \frac{\mu \cdot X_{BF}}{Y} \left(g\ S / m^3_{Bf} \cdot d \right) \qquad (52)$$

The biofilm volume, V_{Bf}, in a biofilm biological reactor can be calculated as follows:

$V_{Bf} = A \cdot L_f$ (53)

Assumptions made when defining the different reactions rates:

If $K_S >> S \quad \Rightarrow \quad \mu = \frac{\mu_{max} \cdot S}{K_S}$

Then: 1. order reaction is assumed (area highlighted with light green in figure 18).

If $K_S << S \quad \Rightarrow \quad \mu = \frac{\mu_{max} \cdot S}{S} = \mu_{max}$

Then: 0. order reaction is assumed (area highlighted with dark green in figure 18).

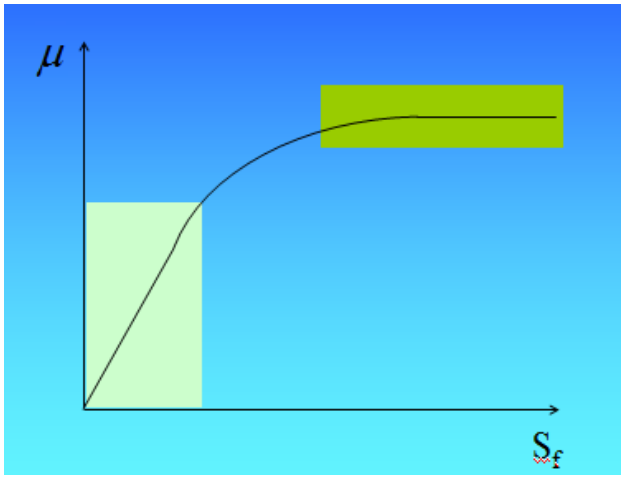

Figure 18: Illustrates the relationship between μ and S_f [18].

Reaction rates:

1. order rate: $r_f = \frac{\mu_{max} \cdot X_{BF}}{K_S \cdot Y} \cdot S = k_{1f} \cdot S \qquad k_{1f} = \frac{\mu_{max} \cdot X_{BF}}{K_S \cdot Y}$ (54)

0. Order rate: $r_f = \frac{\mu_{max} \cdot X_{BF}}{Y} = k_{0f} \qquad k_{0f} = \frac{\mu_{max} \cdot X_{BF}}{Y}$ (55)

5.8.3.7 Limitations by transport or diffusion.

In order to decide if a biofilm is limited by the reaction or the substrate transport, it is necessary to study the substrate penetration in the biofilm.

- If full penetration takes place, then the whole biofilm is active and is therefore operating at near maximum rate. Thin biofilms are because of this reaction rate limited.
- If only partly penetration takes place, then a fraction of the biofilm is active, while the interior receives no substrate and is therefore inactive.
  This is true for thick biofilms and they are therefore diffusion (transport) limited.

5.8.3.8 Mass balance in biofilms at steady state.

In order to use the equation for the steady state expression it is necessary to model the flux to get a value for the system flux to use in the equation.
Flux can be defined as conversion in the biofilm and from massbalance analysis it may be shown that flux is equal to $r_{A,}$ where here r_A is the total substrate removal rate inside the biofilm. This removal rate is related to the local substrate removal rate, depending on the bulk phase concentration and the biofilm thickness.

The transport of substrate is equal with the reaction rate of substrate:

$$D\frac{d^2S}{dx^2} = r_f \qquad (56)$$

The solution to the equation above depends on the reaction order of the system. Harremöes (1978) showed that the total removal rate relates to the bulk phase concentrations as follows:

1. *0rder rate:* $r_{1A} = k_{1A}\cdot S = k_{1f}\cdot L_f\cdot\varepsilon\cdot S$

$$\varepsilon = \frac{\tanh(\alpha)}{\alpha}$$

$$\alpha = \sqrt{\frac{k_{1f}\cdot L_f^2}{D}}$$

ε: Efficiency factor (57)

If $\varepsilon \geq 1$; 100 % efficient biofilm, full penetration of substrates

If $\varepsilon < 1$; less than 100 % efficient biofilm partial penetration of substrates

0. order rate:

Penetration ratio (dimensionless): $\beta = \sqrt{\frac{2 \cdot D \cdot S}{k_0 \cdot L_f^2}}$

Fully penetrated: $\beta \geq 1$: $r_A = k_{0A} = k_{0f} \cdot L_f$

Partly penetrated: $\beta < 1$: $r_A = (2 \cdot D \cdot k_{0f})^{1/2} \cdot S^{1/2} = k_{1/2A} \cdot S^{1/2}$ (58)

5.8.3.9 Biofilm analysis – determination of the limiting substrate in a biofilm.

The limiting substrate is the compound that penetrates less into the biofilm meaning that this compound has the lowest penetration ratio.

- If all substrates penetrate more than 100 % then the biofilm is reaction rate limited and therefore it is not necessary to consider which substrate that penetrates less.
- The overall reaction rate and reactor design is done with respect to the limiting substrate.

For aerobic COD degradation one has to consider the penetration of oxygen (O_2) and COD into the biofilm. In this regard one must take into account the differences in the characteristics for the compounds involved, like:

- Diffusion characteristics (D): Small molecules diffuse more rapid than larger molecules (oxygen diffuses faster than COD).
- Half-saturation coefficient (K_S, K_{O2}): Indicates the affinity of a compound to the microorganisms (large value indicates lower affinity).

5.8.3.10 Biofilm configurations.

Since the sludge in biofilms is physically retained, the SRT is totally independent of the hydraulic retention time. The sludge retention time varies typically from 15-60 days and the hydraulic retention time can be as low as 10 minutes [14]. This means that the biofilm reactor produce less sludge because of the high SRT and the sludge that is produced by biofilm detachment has good separation qualities. In contrast to activated sludge, the biofilm process is often diffusion limited. Since the substrate removal and electron donor utilization occur within the depth of the attached growth biofilm, the overall removal rate is a function of diffusion rate and electron donor and electron acceptor concentrations at various locations within the biofilm. The process kinetics are, by comparison, generally characterized by the bulk liquid concentrations.
Attached growth processes can be divided into the following three groups [14]:

1. Nonsubmerged attached growth process (trickling filter: a nonsubmerged fixed-film made of rock or plastic over which wastewater is distributed continuously): that have the following advantages over the activated-sludge process:
    - require less energy.
    - simpler process operation due to no issues of mixed liquor inventory control and sludge wasting.
    - no problems of bulking sludge in secondary clarifiers.
    - better sludge thickening properties.
    - less equipment needed for maintenance.
    - better recovery from shock toxic loads.

2. Suspended growth process with fixed-film packing(synthetic packing material suspended in the activated sludge mixed liquor or fixed in the aeration tank): these activated sludge process enhancement have the following advantages over the conventional activated sludge process:
    - increased treatment capacity.
    - greater process stability.
    - less sludge production
    - enhanced sludge settleability.

- reduced solid loadings on the secondary clarifier.
- No increase in operation and maintenance cost.

3. Submerged attached growth aerobic process: that are upflow and downflow packed-bed reactors and fluidized-bed reactors that do not incorporate secondary clarification. Unique advantage for these processes:
   - small footprint with an area requirement that is a fraction of that needed (one-fifth to one-third) of that needed for the conventional activated sludge treatment.

The following table presents some applications for biofilm reactors from the different attached growth groups.

Table 12: Some conventional biofilm configurations:

Reactor type:	Characteristics:	Dimensioning:
Trickling filters	Non submerged fixed film biological reactor using rock or plastic packing over which the wastewater is distributed continuously. The treatment occurs as the liquid flows over the attached biofilm. Packing depth: 0.9-2.5 m. usually circular and waste water is distributed over the top of the bed by a rotary distributor. Aeration is necessary and is provided simultaneously. Easy to operate. Specific area, a_c: $a_{carrier} = \frac{A_{carrier}}{V_{carrier}}$ a_c for trickling filters: typically: 100-200m^2/m^3	*Low or standard rate:* - Rock packing. - organic loading: 0.07-0.22 kg BOD/ $m^3 \cdot d$. - hydraulic loading: 1-4 $m^3/m^2 \cdot d$. - depth: 1.8-2.4 m. 80-90 % BOD removal efficiency. *High rate:* - Plastic packing. - organic loading: 0.6-3.2 kg BOD/ $m^3 \cdot d$. - hydraulic loading: 10-75 $m^3/m^2 \cdot d$. - depth: 3- 12.2 m. 60-90 % BOD removal efficiency.
Rotating biological contactors (RBC)	Consists of a series of closely spaced circular discs of polystyrene or polyvinyl chloride that are partially submerged (typically 40 %) in wastewater and is rotating slowly through it (1.0-1.6 revolutions per minute). The cylindrical plastic disks are attached to a horizontal shaft and are provided at sizes of standard unit of 3.5 m in diameter and 7.5 m in length. The total surface area for standard units are 9300 m^2. Advantages: - Relatively good a_c. - Simultaneous aeration. - Compact system. Disadvantages:	BOD removal: - hydraulic loading: 0.08-0.16 $m^3/m^2 \cdot d$. - organic loading: 8-20 kg BOD/ $m^3 \cdot d$ (4-10 kg sBOD/ $m^3 \cdot d$). - maximum 1. stage organic loading: 24-30 kg BOD/ $m^3 \cdot d$ (12-15 kg sBOD/ $m^3 \cdot d$). - hydraulic retention time: 0.7-1.5 h. Effluent BOD: 15-30 mg/l.

	-Poor biofilm control	
Combined aerobic treatment processes: 1. group: trickling filter/ activated sludge (TF/AS), trickling filter/ solids contact (TF/SC), roughing filter /activated sludge (RF/AS) processes. 2. group. Activated biofilter (ABF), biofilter/activated sludge	Common for all combined aerobic treatment processes are the following advantages: - higher stability and resistance to shock loads of the attached growth process. - volumetric efficiency and low energy requirement for the attached growth process for partial BOD removal. - the attached growth works as pre-treatment and a biological selector to improve activated sludge settling characteristics. High quality effluent due to the activated sludge secondary treatment. The principal difference between TF/AS and TF/SC is the shorter aeration period (few minutes) in the latter process versus hours for the TF/AS process. The RF/AS system is the most common application for the TF/AS process. In this design the trickling filter is designed as roughing filter for 40-70 % BOD removal. All the processes above use a filter (trickling or roughing) followed by an activated sludge aeration tank and next a final clarifier. The return activated sludge from the secondary clarifier is fed directly to the AS aeration basin. The second group of combined processes is similar to the first but with the exception that the return activated sludge (RAS) is directly fed to the trickling filters.	TF/SC: For cross flow plastic packing: - trickling filter organic loading: 0.3-1.2 kg BOD/ $m^3 \cdot d$. activated sludge process: - hydraulic retention time: 10-60 min. - solids retention time: 0.3-2 days. - MLSS 1000-3000 mg/l. Clarifier peak overflow rate: 1.8-3.0 m/h. RF/AS: For cross flow plastic packing: - trickling filter organic loading: 1.2-4.8 kg BOD/ $m^3 \cdot d$. activated sludge process: - hydraulic retention time: 10-60 min. - solids retention time: 2.0-7 days. - MLSS 2500-4000 mg/l. Clarifier peak overflow rate: 2.0-3.5 m/h. ABF - trickling filter organic loading: 0.36-1.2 kg BOD/ $m^3 \cdot d$. activated sludge process: - No hydraulic retention time. - solids retention time: 0.5-2.0 days. - MLSS 1500-4000 mg/l. Clarifier peak overflow rate: 1.8-3.0 m/h. BF/AS: - trickling filter organic loading: 1.2-4.8 kg BOD/ $m^3 \cdot d$. activated sludge process: - hydraulic retention time: 2-4 hours. - solids retention time: 2.0-7 days. - MLSS 1500-4000 mg/l. Clarifier peak overflow rate: 2.0-3.5 m/h.
Moving-bed biofilm reactor (MBBR). Kaldnes©	An activated sludge with fixed-film packing process where small cylindrical shaped polyethylene carrier elements (with specific density of 0.96 g/ml and 10 mm in diameter and 7 mm in height with a cross inside the cylinder and longitudinal fins on the outside) are added to an aerated or non-aerated basin to support biofilm growth. a_c of about 500 m^2/m^3 (Kaldnes©). No return activated sludge flow or backwashing. Final clarifier to settle sloughed solids. By upgrading a plant with MBBR, the solid loadings on the clarifier reduces.	Typical parameters for a MBBR: -Aerobic detention time: 3.5-4.5 h. - Biofilm area: 200-250 m^2/m^3 . - BOD loading: 1.0 - 1.4 kg BOD/ $m^3 \cdot d$. - secondary clarifier hydraulic application rate: 0.5-0.8 m/h.

Fluidized bed biofilm reactors (FBBR)	Is an application of the submerged attached growth process where the process consist of the following three phases: a packing, biofilm, and liquid. The BOD removed from the liquid as it passed the biofilm is oxidized. Oxygen is supplied by diffused aeration into the packing or by being predissolved into the influent wastewater. In FBBR wastewater is fed upward to a bed of 0.4-0.5 mm sand or activated carbon providing an a_c of 1000 m^2/m^3 of reactor volume. Main advantage for the FBBR: - long SRT for degradation of xenobiotic and toxic compounds. -shock loads or nonbiodegradable toxic compounds can be absorbed onto the activated carbon. -high-quality effluent with low TSS and COD values. - the pre oxygenation prevents stripping and emission of toxic organic compounds to the atmosphere. - simple and reliable system operation.	- Specific surface area: 1000 m^2/m^3. hydraulic retentiontime: 5-20 minutes. Upflow velocity: 30-36 m/h.

5.8.3.11 Biofilm versus activated sludge

Both the biofilm process and the activated sludge process are capable of treating the wastewater equally, but with different operational characteristics. The activated sludge process achieve the high biomass concentration in the reactor by recycling parts of the sludge produced, while in the biofilm process, the sludge is physically retained on the substratum due to the formation of biofilm.

The next table compares the suspended growth process to the attached growth process by listing the different characteristics of the two processes:

Table 13: Biofilm versus suspended culture (CSTR) [24]:

Biofilm	Activated sludge
• Heterogeneous • Substrate gradients • $\theta_C >> T_H$ • High local cell density • High resistance to toxins • High genetic exchange rate • Low average growth rates Where: θ_C = sludge retention time (SRT). T_H = Hydraulic retention time.	• Homogenous • No gradients (ideally) • $\theta_C \sim T_H$ • Low local cell density • Low toxin tolerance • Higher average growth rates

5.8.4 Membrane biological reactors.

5.8.4.1 MBR introduction

A membrane bioreactor (MBR) is the combination of a membrane process like microfiltration (pore sizes: 0.1-0.4 µm) or ultrafiltration (pore sizes: 0.01-0.1 µm) with a suspended growth bioreactor [14].

The most important advantages for the MBR process over the conventional activated sludge process are [13]:

- The process produces a high quality, clarified and largely disinfected permeate product in a single stage.
- Absolute and dependent control of SRT and HRT which are coupled in a conventional activated sludge plant.
- The process can operate with a much higher MLSS concentration which reduces the reactor volume needed.

- By operating at a longer SRT, the opportunity to select for slow-growing bacteria to enhance the treatment, is possible. These bacteria can be used to degrade organic micro-pollutant.
- The amount of sludge produced is reduced.

5.8.4.2 Process and membrane configurations.

Figure 19 illustrates the two main MBR process configurations which are:

1) Submerged/immersed membrane bioreactors (A in figure 19).
2) sidestream membrane bioreactors (B in figure 19)

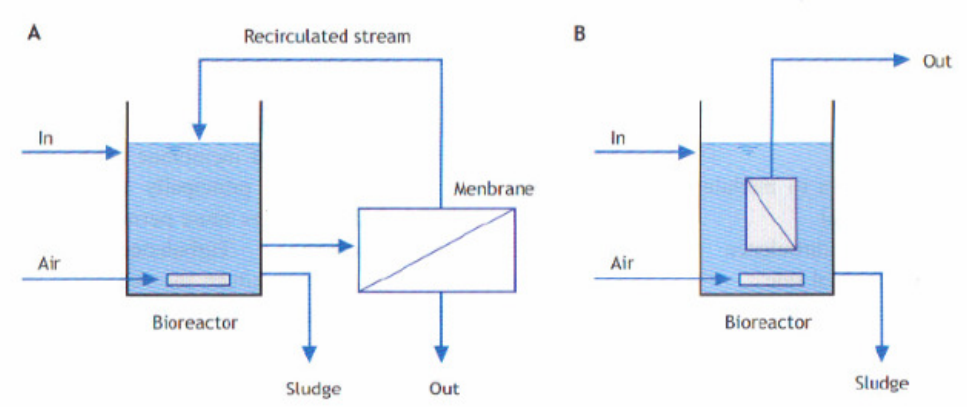

Figure 19: MBR process configurations A: sidestream MBR (sMBR) and B: submerged/immersed MBR (iMBR)[13].

The most commercial geometries of membranes are flat sheet (FS), hollow fibre (HF) and multi tube (MT) membranes [13].
The submerged MBRs are generally less energy demanding than the sidestream MBRs, since employing membrane modules in a pumped sidestream crossflow to scour the membrane require energy because of the high pressures and volumetric flows imposed. Therefore the flowpath has to be as long as possible (typically in excess of 20 m) to make use of the latent energy to ensure that as much as possible of the liquid flowing at high pressure is used for permeation [13]. By comparison, for immersed MBR scouring of the membrane is achieved by aeration, which in turn leads to lower energy demand for operation. But, for sidestream MBR there is the trade-off between pumping energy demand and flux. To reach the maximum flux for the system a high trans membrane pressure (TMP) along with high crossflow velocity

(CFV or retentate velocity U_R) is required. The energy demand is directly proportional to retentate flow multiplied with pressure drop; $Q_R\Delta P$, therefore it is of interest to reduce these parameter values as much as possible, but since Q_R determines U_R (because: $U_R = Q_R/A_t$ where A_t is the tube cross-sectional area) and ΔP relates to TMP, a reduced value for $Q_R\Delta P$ further results in reduced flux for the system. And if Q_R is reduced (by reducing A_t) then the pressure drop along the length of the module is increased.

The ideal membrane configuration in a MBR should have the following characteristics [13]:

- High membrane area to module bulk volume ratio (high packing density).
- High degree of turbulence to promote mass transfer on the feed side.
- Low energy demand per unit water volume produced.
- Low cost per unit membrane area.
- A design that facilitates proper membrane cleaning.
- A design that permits modularization.

5.8.4.3 Membrane fouling

The dimensions for different MBR processes are in practice largely limited by membrane fouling (deposition of solid material onto the membrane surface and within the membrane structure) and clogging (filling of membrane channels with solids due to poor hydrodynamic performance). Figure 20 illustrates the inter-relationships between MBR parameters and fouling.

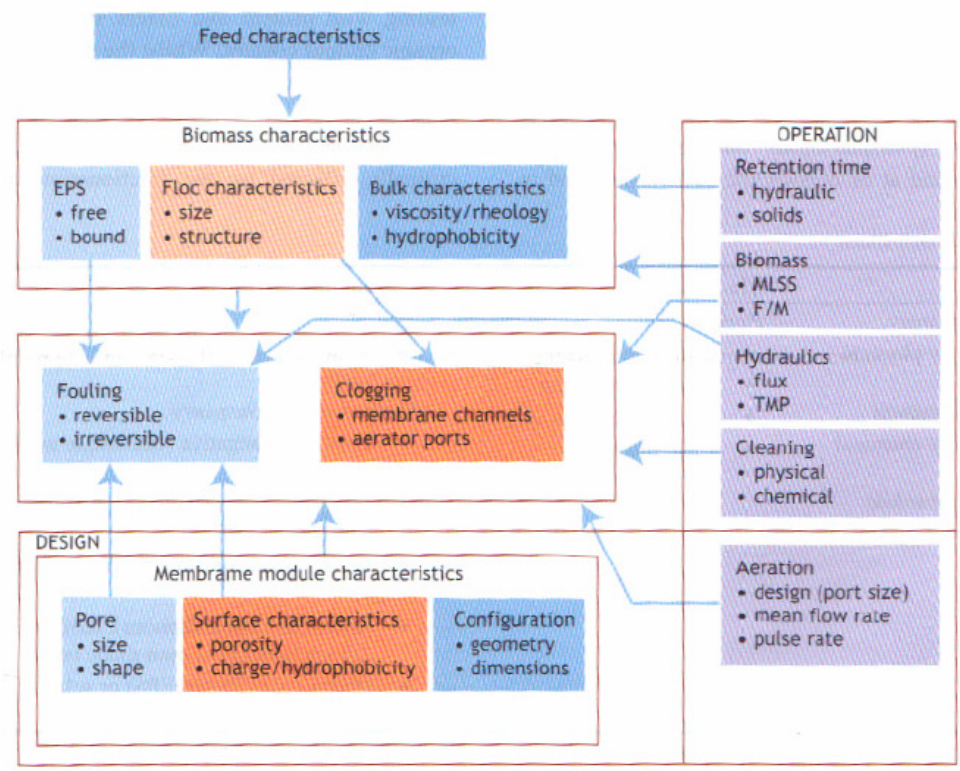

Figure 20: Inter-relationships between MBR parameters and fouling [13].

The foulants in a system can be defined:

- *mechanistically*: based on fouling mechanism such as cake filtration, intermediate blocking, standard blocking and complete blocking.
- *practically:* Based on permeability recovery divided in the following groups reversible/temporary(removed by physical cleaning), irreversible/permanent (removed by chemical cleaning) and irrecovereable/absolute (fouling that are not possible to remove by any cleaning method).
- *material type*: based on the chemical or physical nature of the compound such as size, surface charge/chemistry, chemical type (inorganic or organic, carbohydrate or protein etc) and the origin of the compound like microbial, terrestrial or man-made compounds or extracted EPS (products directly associated with the cell wall) or soluble microbial products (SMP) .

The filtration and fouling mechanisms have to be derived in order to interpret flux or pressure transients and the inter-relationship between the two parameters. For immersed MBRs aeration is considered to be the most important parameter along with flux and TMP in relation

to MBR operation. The aeration is of critical importance because it is required both for bioreactor maintenance and membrane permeation.

5.8.4.4 Immersed MBRs

Since immersed MBRs have a lower energy demand than the sidestream MBRs, the immersed MBRs are the most economically viable configurations for large-scale applications and are therefore most widely used.

The key elements for iMBR process design and operation are [13]:

- The membrane design and sustaining of permeability by cleaning.
- Feedwater characteristics and pre-treatment.
- Aeration of membrane and bulk biomass.
- Sludge withdrawal and residence time (i.e. SRT).
- Nature of biomass and bioactivity.

These elements are largely inter-related as shown in the figure below.

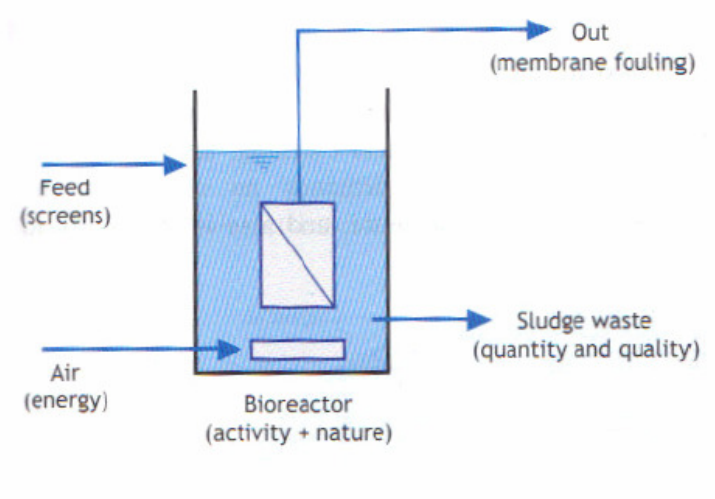

Figure 21: Elements of an MBR [13].

The sludge retentiontime time is controlled by the rate at which sludge is withdrawn which further determines the concentration of the mixed liquor suspended solids (MLSS). The MLSS concentration impacts the biological properties and the physical properties such as the viscosity and oxygen transfer rate. The largest impact on MBR operation is caused by the

feedwater chemistry which largely determines the possibility/degree of fouling of the membrane.

Figure 22 illustrates the biomass inter-relationships.

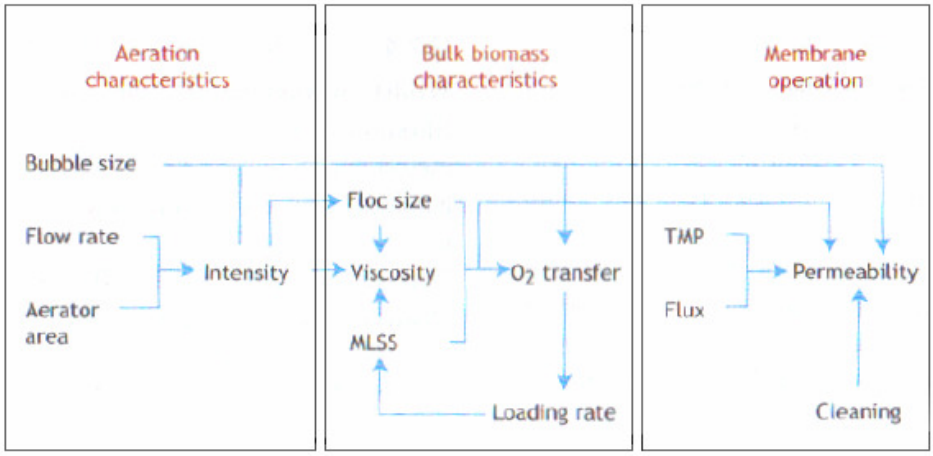

Figure 22: Biomass inter-relationships [13].

5.8.4.5 MBR plant design.

Main elements in MBR plant design:

- Liquid pumping: transfer of sludge between tanks and permeate withdrawal.
- Membrane maintenance: Cleaning the membrane by aeration (iMBRs), physical and chemical cleaning.
- Aeration:

  - *aerobic treatment demand*: the demand of the mixed liquor for air required for agitation of the solids and dissolved oxygen for the maintenance of viable microorganisms for the biological treatment.

  - *membrane aeration demand*: is based on previous experience and can be expressed in terms of specific aeration demand with respect to membrane area (SAD_m) or permeate or permeate volume (SAD_p) [13]:

$$SAD_m = Q_A/A \quad (59)$$

$$SAD_p = Q_A/JA \quad (60)$$

where:

SAD_m: specific aeration demand with respect to membrane area (Nm^3/m^2h).

SAD_p: specific aeration demand with respect to permeate volume (Nm^3/m^3).

Q_A: airflow (Nm^3/h).

J : Flux (m/h).

A: Area (m^2).

The treatment capacity of a MBR process is evaluated in terms of BOD, TSS, coliform, and nitrogen removal (not necessary for produced water, but important in domestic waste water treatment) based on laboratorie, full-scale and pilot-plant studies. The following table summarizes the reported operating performance characteristics for MBR systems. $kg/m^3 \cdot d$

Table 14: Typical operational and performance data for a membrane bioreactor [14]:

Parameter	Unit	Range
Operational data		
COD loading	$kg/m^3 \cdot d$	1.2-3.2
MLSS	mg/l	5000 - 20,000
MLVSS	mg/l	4000 - 16,000
F/M	g COD/gMLVSS·d	0.1-0.4
SRT	D	5-20
HRT	H	4-6
Flux	$L/m^2 \cdot d$	600-1100
Applied vacuum	kPa	4-35
DO	mg/l	0.5-1.0
Performance data		
Effluent BOD	mg/l	<5
Effluent COD	mg/l	<30
Effluent NH3	mg/l	<1
Effluent total nitrogen (TN)	mg/l	<10
Effluent turbidity	NTU	<1

Next follows a table with some examples of commercially available MBR systems.

Table 15: Commercially available MBR systems [13]:

Membrane configuration	Process configuration	
	Immersed (iMBR)	Sidestream (sMBR)
Flat sheet (FS)	A3	Novasep-Orelis
	Colloide	
	Brightwater	
	Huber (rotating membrane)	
	Kubota	
	Microdyn-Nadir	
	Toray	
Hollow fibre (HF)	Aashi Kasei	Polymem
	Han-S Environmental	Ultraflo
	ITT	
	Koch-Puron	
	Kolon	
	Korea Membrane Separation	
	Mitsubishi Rayon	
	Motimo	
	Siemens-Memcor	
	Zenon	
Multi Tube (MT)		Berghof
		Milleniumpore
		Norit X-flow

5.8.5 Membrane biofilm.

In this thesis membrane aerated biofilm reactors will be assessed for the purpose of biological degradation of organic compounds in produced water.

5.8.5.1 Membrane aerated biofilm reactors (MABRs)

Membrane aerated biofilm reactors (MABRs) represent a technology for aerobic wastewater treatment where oxygen diffuses through a gas permeable membrane into a biofilm where oxidation of organic compounds takes place. The waste water is supplied on the biofilm side of the membrane as shown in figure 23 below.

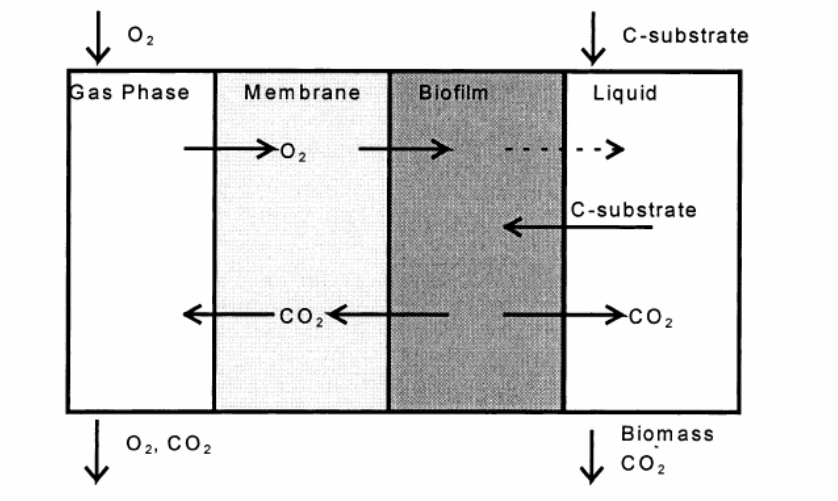

Figure 23: Schematic of a membrane aerated biofilm reactor (MABR) [27].

One of the main differences between a MABR and a conventional biofilm reactor is the difference in active layers within the biofilm and the location of the active layers. The immobilisation of biofilm on permeable membranes for the biodegradation of organic compounds is becoming more and more interesting for applications where conventional biological treatment technologies are unsuitable.

5.8.5.2 High rate organic removal in MABRs

The concept of active layers is important in the understanding of the performance of MABRs. In conventional biofilms, the active layer is generally an oxic layer (typically 50-200 µm) which corresponds to the depth of oxygen penetration into the biofilm. If the overall biofilm thickness is greater than the oxygen penetration depth, then an anoxic layer, adjacent to the biofilm support, occurs. But in MABRs there are typically more than one active layer.

It is because the conventional biofilms in wastewater treatment systems are relatively thick that it results in only partial penetration of oxygen to a depth of between 50 and 200 µm. Therefore, if the wastewater-loading rate is high oxygen supply limits the removal of

pollutants. In conventional biofilm systems, a high fraction of the oxygen supplied is lost to the atmosphere, but by using a MABR with high intramembrane oxygen pressure, complete oxygen penetration can be achieved. This technology ensures that, for situations with high organic loading rate, the entire biofilm thickness is utilised for biodegradation of organic compounds in the waste water.

Research has shown that MABRs outperformed both conventional biofilm reactors and activated sludge systems under conditions of high organic loading due to the fact that MABRs can contain an active biomass concentration higher than any other system because of the oxygen supply through the membrane. MABRs have the additional advantage of operation with very high oxygen conversion due to the use of sealed ended membranes. Oxygen conversion efficiencies of 100% have been demonstrated and, simultaneously, very high organic carbon removal rates have been achieved [27].

Because of the low solubility of oxygen in water, the maximum oxygen diffusion rate in conventionally aerated biofilms is typically about 10 $g/m^2 \cdot d$ which is low enough to cause oxygen limitation in many biological wastewater processes [27]. For MABRs a maximum value of 20 g $oxygen/m^2 \cdot d \cdot bar$ have been reported, and for fully optimised conditions, modelling has predicted that values as high as 30 g $oxygen/m^2 \cdot d \cdot bar$ should be achievable [27].

5.8.5.3 Configurations and design

The required membrane area, A, for the biological treatment in MABR depends on the flux, J ($g/ m^2 \cdot d$) according to the equation below [28]:

$$A = Q(C_{in} - C_{out})/J \qquad (60)$$

Where:

Q : the volumetric flow rate (m3/day)

C_{in} : influent concentration (g/m^3)

C_{out}: effluent concentration (g/m^3)

The specific surface area, $A_{c,}$ of the membranes (in m^2/m^3) should be high, as long as

it does not compromise the performance of the system. The membrane surface area is the product of the specific surface area and the volume (in m^3). From this it is clear that by making the specific surface area large it allows for a smaller and less expensive reactor volume for a given membrane area required. The specific surface area is maximized by utilizing small diameter fibers and by providing a high packing density of the membrane fibers. These strategies must be balanced against the increased risk that of plugging the void space around the fibers and fiber clumping, both of which would cause unfortunate flow distribution in the membrane.

The membranes in MABRs can be either tubular or flat and may be of the hydrophobic porous type such as polypropylene, or of the dense film type such as silicone, or of the composite type [27]. Studies on MABRs show that a wide variety of pollutants have been successfully treated using various system configurations and various types of membranes. For the instance removal of BTEX and phenol from waste water has been successfully tested using a silicone membrane in a tubular coil configuration [27].

6 Calculations and results:

Dimensioning of the biological reactor for different biological treatment systems based on a produced water *model*.

6.1 Produced water model

6.1.1 Composition and physical/chemical properties

In order to calculate the reactor volume for the different biological systems for produced water treatment, the COD value for produced water model was determined. Based on the two tables from chapter three, table 5 and 6, the model produced water composition and related COD values for the biodegradable organics were calculated. Since the carboxylic acids contribution was 93.6 percent and BTEX contribution was 4.8 percent of the total dissolved organic compounds in produced water, the model water used in the calculations in this thesis was based on these two dissolved organic compound groups and the oil in water content.
The different types of carboxylic acids found in produced water are: Acetic acid, formic acid, propionic acid, butyric acid, pentanoic acid and napthhenic acid. Table 16 shows an overview over the average concentrations of the different carboxylic acids in produced water discharged in the Norwegian sector.

Table 16: Average carboxylic acid concentrations in mg/l discharged with PW in the Norwegian sector:

Type of carboxylic acid	2007	% of total carboxylic acid concentration.
Formic acid	2.7	1.2
Acetic acid	187.4	84.8
Propionic acid	22.2	10.0
Butyric acid	4.8	2.2
Bentanoic acid	2.3	1.0
Napthhenic acid	1.7	0.8

Since the acetic acid and propionic acid contributions is nearly 95 % of the total carboxylic acid content, these two acids will represent the carboxylic acids when calculating the COD value for the model produced water.

Table 17: Physical properties of propionic and acetic acids [19] [20]:

Physical properties	**Propionic acid**	**Acetic acid**
Molecular formula	$C_3H_6O_2$	$C_2H_4O_2$
Molar mass	74.08 g/mol	60.05 g mol/mol
Appearance	colourless liquid	Colourless liquid
Density	0.99 g/cm³	1.049 g/cm^3 (l) 1.266 g/cm^3 (s)
Melting point	−21 °C	16.5 °C
Boiling point	141 °C	118.1 °C
Solubility in water	Miscible	miscible
Acidity (pK_a)	4.87	4.76
Viscosity	10 mPa·s	1.22 mPa·s at

The organic compound group BTEX is, as stated earlier, the second largest contributor of dissolved organic compounds in produced water and the table below shows an overview over the average BTEX concentrations in mg/l discharged with PW in the Norwegian sector.

Table 18: average BTEX concentrations in mg/l discharged with PW in the Norwegian sector [5].

BTEX compound	2007	% of total BTEX concentration.
Benzene	5.3	47.7
Ethylbenzene	0.2	1.8
Toluene	4.1	36.9
Xylenes	1.5	13.5

In order to predict the environmental and biological consequences of toxins such as BTEX exposure, their log K_{OW} values should be assessed. As shown in the following table, table 18, the log K_{OW} values for BTEX are less than 3.5 which indicates a moderate affinity for partitioning into tissue lipids, and a low potential for bioaccumulation [21].

Table 19: physical properties of BTEo-X [21][5]:

Compound	**Benzene**	**Toluene**	**Ethyl benzene**	**o-Xylene**
Structure	**C_6H_6**	**C_7H_8**	**C_8H_{10}**	**C_8H_{10}**
Molecular weight (g/mol)	78.1	92.1	106.2	106.2
Density (kg/m^3)	0.879	0.867	0.867	0.879
Log K_{OW}	2.13	2.65	3.13	3.13
Water solubility at 25° C (ppm)	1791	535	161	*146-175
Seawater solubility (mg/l)	1398	389	114	133
Henry`s constant (c/c)	0.224	0.224	0.404	0.294

*variation in water solubility for o, m and p-Xylene.

It has been observed that BTEX compounds can be utilized as carbon and energy source by a number of pure and mixed cultures of microorganisms, normally bacterial consortia from domestic or industrial sludge, oil contaminated soil and polluted groundwater [5].

6.1.2 COD calculations for the dissolved organic compounds in the model water

With the exception of energy production a general stoichiometric description of aerobic biodegradation can be written as follows [22]:

- Autocatalytic:
  $$\text{Substrate} + a\,O_2 + bNO_3^- + cHPO_4^{2-} \rightarrow \text{dbiomass} + eCO_2 + fH_2O + gH^+ \quad (61)$$
- Non-autocatalytic:
  $$\text{Substrate} + a\,O_2 \rightarrow bCO_2 + cH_2O \quad (62)$$

Propionic acid: Mw: 74.08 g/mol

$C_3H_6O_2 + aO_2 \rightarrow bCO_2 + cH_2O$

a:3.5

b:3

c:3

COD Calculations: COD= 3.5 * 32g/mole = 112 g/mole.

COD/propionic acid = 112/74.08 = 1.512 gCOD/g propionic acid.

Acetic acid: Mw 60.05 g/mole

$C_2H_4O_2$+ $aO_2 \rightarrow bCO_2 + cH_2O$

a:2

b:2

c:2

COD Calculations: COD= 2* 32g/mole = 64 g/mole.

COD/acetic acid = 64/60.05 = 1.066 gCOD/g acetic acid.

Benzene: Mw 78.1 g/mole

C_6H_6 + a $O_2 \rightarrow bCO_2 + cH_2O$

a:7.5

b:6

c:3

COD Calculations: COD= 7.5* 32g/mole = 240 g/mole.

COD/benzene = 240/78.1 = 3.073 gCOD/g benzene.

Toluene: Mw 92.1g/mole

C_7H_8 + a $O_2 \rightarrow bCO_2 + cH_2O$

a:9

b:7

c:4

COD Calculations: COD= 9* 32g/mole = 288 g/mole.

COD/toluene = 288/92,1 = 3.127 gCOD/g toluene.

Ethyl benzene: Mw 106.2 g/mole

C_8H_{10} + a $O_2 \rightarrow bCO_2 + cH_2O$

a:10.5

b:8

c:5

COD Calculations: COD= 10.5* 32g/mole = 336 g/mole.

COD/ ethyl benzene = 336/106.2 = 3.164 gCOD/g ethyl benzene.

o-Xylene: Mw 106.2 g/mole

$C_8H_{10} + a\ O_2 \rightarrow bCO_2 + cH_2O$

a:10.5

b:8

c:5

COD Calculations: COD= 10.5* 32g/mole = 336 g/mole.

COD/ o-Xylene = 336/106.2 = 3.164 gCOD/g o-Xylene.

o-Xylene represents the entire Xylene group.

6.1.3 COD contribution from the oil in water content

In the pre-treatment of produced water most of the dispersed oil droplets are separated from the water by for instance hydrocyclones, but the authorities have allowed 30 mg oil to be discharged per liter produced water. The hydrocarbon composition in the dispersed phase/droplets is the same as for the raw oil produced; normal alkanes (n-alkanes) (dominating), alkylated aromatics and cyclo-alkanes, which are all of the type: CnH(2n+2). COD for the dispersed oil can be calculated by alkane distribution, but in this thesis the alkane hexane is assumed to represent the average in the dispersed fraction and the COD contribution from the dispersed oil is calculated based on hexane alone.

The physical and chemical properties of n-hexane are listed in the table below.

Table 20: Physical and chemical properties of n-hexane [23]:

Physical and chemical properties of n-hexane	
Molecular formula	C_6H_{14}
Molar mass	86.18 g/mol
Appearance	Colorless liquid
Density	0.6548 g/ml
Melting point	–95 °C
Boiling point	69 °C
Solubility in water	13 mg/L at 20°C
Viscosity	0.294 cP

Recent research [24] has shown that a bacterium, EH831, isolated from an enriched hexane-degrading consortium, was able to biologically degrade hexane and various other hydrocarbons under aerobic conditions. Because of the low solubility of hexane, surfactants were added to the aqueous phase to improve the degradation of hexane in this study [24], but there exists several microorganisms that produce natural surfactants, in which case surfactant supply might not be necessary.

The maximum hexane degradation rate (V_{max}) of EH831 was found to be 290μmol g dry cell/weight ·h at 30°C, and the saturation constant (K_s) was found to be15 mM. Using 14C-hexane, EH831 was confirmed to mineralize approximately 49% of the hexane into CO2 and, converted approximately, 46% into biomass; the rest (1.7%) remained as extracellular metabolites in the liquid phase. So, Rhodococcus sp. EH831, isolated from oil contaminated soil, has been shown to degrade a wide range of hydrocarbons and completely metabolize hexane. Therefore, EH831 may be useful for the bioremediation of sites contaminated with various hydrocarbons or for the treatment of industrial discharge.

The maximum degradation rates of BTEX were also examined in the same research [24], and the research showed that the BTEX compounds were relatively less biodegradable than hexane.

COD calculations for the oil in water content (hexane) in the model produced water:

Hexane: Mw 86.18 g/mole

$C_6H_{14} + a\ O_2 \rightarrow bCO_2 + cH_2O$

a:8.5

b:6

c:7

COD Calculations: COD= 8.5* 32g/mole = 272 g/mole.

COD/hexane = 272/86.18 = 3.156 gCOD/g hexane.

6.1.4 Total COD content in the produced water model

The table below shows an overview over the composition and COD contribution for all the organic compounds in the model produced water.

Table 21: COD calculations for the model water:

Organic compound/ substrate:	ThOD: mgCOD/mg substrate	Average amount discharged with PW in mg/l.	mgCOD/l
Acetic acid	1.066	187.4	199.8
Propionic acid	1.512	22.2	33.57
Benzene	3.073	5.3	16.29
Toluene	3.127	0.2	0.63
Ethyl benzene:	3.164	4.1	12.97
o-Xylene	3.164	1.5	4.75
Hexane	3.156	30*	94.7

*Not the average amount discharged, but maximum oil in water discharge limit.

Total COD contribution per liter from the dissolved organic compounds in the model produced water:

199.8+33.57+16.29+0.63+12.97+4.75mg COD/l= 268.01 mg COD/l

To account for the dissolved organic compounds not included in this model, a safety factor of 5 % was included:

Total COD contribution from the dissolved organic compounds: 268.01 *1.05 mg COD/l = 281.4 mg COD/l.

Total COD value for dissolved and suspended organic compounds in model produced water:

281.4 + 94.7 mg COD/l model PW = **376.1 mg COD/l model PW**.

6.1.5 Kinetic coefficients for the different compounds in the model produced water.

Table 22: Typical kinetic coefficients for the activated sludge process for the removal of organic matter from domestic waste water at 20°C [14]:

		Value	
Coefficient	**Unit**	**Range**	**Typical**
k	g bsCOD/gVSS·d	2-10	5
K_s	mg/l BOD	25-100	60
	Mg/l bsCOD	10-60	40
Y	mgVSS/mgBOD	0.4-0.8	0.6
	mgVSS/mg bsCOD	0.3-0.6	0.4
k_d	gVSS/gVSS·d	0.06-0.15	0.10

k: maximum specific substrate utilization rate.

Y: true yield coefficient.

k_d: endogenous decay rate.

K_s: half-velocity constant.

Table 23: Activated sludge kinetic coefficients for heterotrophic bacteria at 20°C [14]:

Coefficient	Unit	Range	Typical
μ_{max}	gVSS/gVSS·d	3.0-13.2	6.0
K_S	gbCOD/m3	5.0-40.0	20.0
Y	gVSS/g bCOD	0.30-0.50	0.40*
k_d	gVSS/gVSS·d	0.06-0.20	0.12

*Typical bacteria synthesis yield coefficient for the aerobic (oxygen as electron acceptor) biological degradation of organic compounds (electron donor) is 0.40 gVSS/gCOD [14].

Carboxylic acids are readily biodegraded by microorganisms in an aerobic bioreactor. In this thesis it is assumed that the degradation rates of acetic acid are equal to the rates of degradation of propionic acid. Research has found that by utilizing a mixed bacterial culture, enriched over a period of several weeks, in a continuous stirred tank reactor (CSTR) periodically fed with synthetic waste water (known amounts of organic compounds of known concentrations added to clean water), steady state readings could be noted to further determine the kinetic constants according to Monod`s kinetics [25]. In order to obtain values for μ_{max} and K_S for the acetic acid, the mixed culture was grown in synthetic waste water containing only acetic acid. The kinetic constants found from this research are listed in the table below.

Table 24: Kinetic constants for cell growth based on experimental data [25]:

Type of carboxylic acid	Concentration mg/l	ThCOD mg/l	K_S mg/l	μ_{max} 1/h
Acetic acid	3280	3500	3240	0.35

The kinetic coefficients for the BTEX compounds are taken from an article, published in 2008, from the department of chemical engineering at Queens University in Kingston, Canada, [26]. In this article a model was developed to describe the biodegradation of benzene, toluene, ethylbenzene and o-xylene and associated biomass growth from a series of aerobic batch degradation experiments. Parameter estimates were reported for both conventional Monod parameters obtained from single substrate degradation experiments and interaction parameters obtained from dual substrate experiments. It was found that o-xylene was not metabolized by the consortium when being the only carbon source present, but it was shown that the compound was cometaboliced in the presence of toluene and/or benzene and this interaction was described by a mathematical model. Experiments also showed that when a combination of BTEX components was present, relative to single substrate degradation, several interactions could be identified including enhancement, inhibition and cometabolism. A sum kinetics with interaction parameters (SKIP) model was combined with cometabolism models in order to predict BTEX degradation and biomass production from a consortium. Results from this research are presented in the table below.

Table 25: Parameter estimates for single substrate experiments at 30°C [26]:

Compound	μ_{max} (1/h)	μ_{max} Likelihood interval	K_S (mg/l)	K_S Likelihood interval	$Y_{X/S}$ (mg/mg)	$Y_{X/S}$ - R^2
Benzene	0.44	0.39-0.50	27.57	19.51-38.58	1.35	0.991
Toluene	0.60	0.52-0.68	34.12	25.04-46.24	1.25	0.981
Ethylbenzene	0.13	0.11-0.16	0.36	0.11-2.12	0.85	0.879

Several studies have investigated the degradation of combination of BTEX components. A summary of some of these findings, along with kinetic parameter estimates and inhibition constants or interaction parameters are listed in the following table.

Table 26: Kinetic parameters obtained from the degradation of BTEX components [26].

Compounds	Model type	Parameters	Microorganism
Benzene	Monod	K_s = 0.12 ±0.02 mg/l	P.Putida F1
		μ_{max}= 0.73 ±0.03 1/h	
		$Y_{X/S}$ =1.20±0.05g/g	
Toluene	Monod	K_s = 13.8 ±0.9 mg/l	P.Putida F1
		μ_{max}= 0.86 ±0.01 1/h	
		$Y_{X/S}$ =1.28±0.01g/g	
Toluene	Monod	K_s = 13.8 ±0.9 mg/l	Consortium
		μ_{max}= 0.86 ±0.01 1/h	
		$Y_{X/S}$ =1.28 ±0.01g/g	
BT	SKIP	$I_{T,B}$ =5±0.3	P.Putida F1
		$I_{B,T}$ =0.01±0.003	
BTEX	Competitive inhibition	$K_{s,B}$=0.08 ±0.003 mg/l	Consortium
		$K_{s,T}$=0.20 ±0.14 mg/l	
		$K_{s,E}$=0.21 ±0.13 mg/l	
		$K_{s,X}$=0.18 ±0.18 mg/l	
BT	Competitive inhibition	$\mu_{max,B}$= 0.34 ±0.0004 1/h	Pseudomonas fragi
		$K_{s,B}$ = 3.17 ±0.82 mg/l	
		$Y_{X/S,B}$ =1.04±0.09g/g	
		$\mu_{max,T}$= 0.54 ±0.0004 1/h	
		$K_{s,T}$ = 1.96±0.91 mg/l	
		$Y_{X/S,T}$ =1.22±0.1g/g	
		$K_{I,B}$ = 3.10 ±0.12 mg/l	
		$K_{I,T}$ = 1.71 mg/l	
Tp-X	Cometabolism of p-xylene	T_g^c - 0.45 mg/mg	Pseudomonas fragi
BTEo-X	SKIP, cometabolism	$\mu_{max,B}$= 0.44 1/h	
		$K_{s,B}$ = 27.57 mg/l	
		$Y_{X/S,B}$ =1.35g/g	
		$\mu_{max,T}$= 0.60 1/h	
		$K_{s,T}$ = 34.12 mg/l	
		$Y_{X/S,T}$ =1.25g/g	
		$\mu_{max,E}$= 0.13 1/h	
		$K_{s,E}$ = 0.36 mg/l	
		$Y_{X/S,E}$ =0.85g/g	
		$I_{T,B}$ = 2	
		$I_{B,T}$ = -0.4	
		$I_{E,B}$ = 4	
		$I_{X,B}$ = -0.7	
		T_g^c -0.5	

Where:

Nomenclature:

$I_{2,i}$: interaction parameter for effect of substrate 2 on substrate i.

K_s : Half saturation constant (mg/l).

K_I : Inhibition constant (mg/l).

S : Substrate concentration (mg/l).

T_g^c : growth substrate transformation capacity (mg_N/mg_G).

μ_{max} : maximum specific growth rate.

X: biomass concentration (mg/l).

$Y_{X/S}$: biomass yield (mg/mg).

Subscripts:

B: Benzene.

E: Ethylbenzene.

G: growth substrate.

i: species i, one of B, T, E or o-X components.

I: Interacting species for mixed substrate experiments.

N: non-growth substrate.

T: Toluene.

o-Xylene.

In this thesis the kinetic values from table 25 are used in the calculations carried out later in the thesis.
Since o-Xylene in the model produced water is present together with both benzene and toluene it is assumed that all BTEX compounds are biologically degraded in the aerobic bioreactor. It is also assumed that ethylbenzene is the most slowly degradable BTEX compound.

Maximum specific growth rate for hexane can be calculated from the maximum hexane degradation rate of 290µmol/g dry cell weight·h [24] as follows:

290 µmole/g dry cell weight·h * 86.18 µg/µmole = 25mg hexane/gTSS·h
= (25mg hexane/gTSS·h) · 3.156 gCOD/g hexane = (78.9 mgCOD/ gTSS·h)/1.3 gCOD/gTSS
= (60.7 $mgCOD_{substrate}$ /$gCOD_{biomass}$·h) ·24h/d = 1.456 $mgCOD_{substrate}$ /$gCOD_{biomass}$·d

Hence, μ_{max} for the degradation of hexane: <u>1.456 1/d at 30°C.</u>

Calculated μ_{max} for ethylbenzen based on maximum ethylbenzene degradation rate of 120 µmole/g dry cell weight·h [24] was found to be 0.60 1/d. This value for the specific growth

rate differs from that found in table 25, but ethylbenzene was assumed to be the compound most slowly biodegraded in the calculations carried out in this thesis according to table 25.

6.1.6 Produced water *model* characteristics

The table below lists the waste water characteristics (model produced water characteristics) used in this thesis.

Table 27: Model produced water characteristics.

Item	Unit	Value
Inlet flow	m^3/d	30,000
COD in	g/m^3	376.1
Temperature	°C	30

* Typical PW temperature: 75°C, assumed to be cooled down to 30°C during in the pre treatment process.

In the calculations carried out for the different biological treatment configurations, the specific growth rate for the compound most slowly biodegraded had to be used to ensure degradation of all the compounds. For the compounds in the model water the lowest μ_{max} value was found for the degradation of ethylbenzene of 0.13 1/h (table 23). It was assumed that the k_d value was 0.12 gVSS/gVSS·d at 30°C.

6.2 Calculations for the suspended growth systems.

6.2.1 Assumptions made

Assumptions made for the calculation of the volume of the biological in the suspended growth systems.

- k_d value of 0.12 gVSS/gVSS·d at 30°C.
- Excess nutrients available (such as macronutrients like N and P and other micronutrients).
- Sufficient dissolved oxygen present.
- Substrate concentration is the limiting factor for biomass growth in the systems.

- No substrate interactions in the model PW.
- μ_{max} for the slowest degraded compound in the model PW: 0.13 1/h at 30°C.
- 90 % removal efficiency, effluent COD concentration: 37.6 g COD/m3.
- The net yield factor is assumed to be 0.4 g biomass/g COD.
- COD/VSS ratio, f_{cv}: 1.42 g COD/gVSS

6.2.2 Calculation of sludge retention time

SRT is determined based on the relationship between SRT_{min} (minimum SRT value), μ_{max} and k_d :

$1/SRT_{min} = \mu_{max} - k_d$

Determination of sludge retentiontime (SRT) at 30°C:

1/SRT = (0.13 1/h * 24h/d) -0.12 gVSS/gVSS·d

SRT_{min}= 1/3 days

In order to ensure adequate treatment of the waste water, biological treatment processes are usually designed and operated with a design SRT value from 2 to 20 times SRT_{min} [14]. The ratio between the designed SRT to minimum SRT can be considered to be a process safety factor (SF) against system failure. In this thesis the design SRT are calculated at 2, 8.1 and 20 times SRT_{min}, resulting in design SRT values of:
Design SRT: 1/3 days*2 ≈ 0.67 days.
Design SRT: 1/3 days*20 ≈ 2.7 days.
Design SRT: 1/3 days*20 ≈ 6.7 days.

As discussed earlier in this thesis, the major issues when designing a biological treatment plant for offshore use are the space limitations on the installations. In this thesis different biological treatment systems have been assessed, and from the literature in chapter 5, the different reactor volumes needed for each system were calculated.

6.2.3 Theory behind the calculation of reactor volume

The volume of the biological reactor can be determined from the equation below (defined in chapter 5, repeated here for easy reference):

$V = Q \cdot (Cin-Cout) \cdot Y \cdot SRT/(Xa \cdot (1+k_d \cdot SRT))$

The MLSS in the aeration tank equals the total suspended solid concentration. The MLVSS concentration represents the organic matter which consists of biomass (X_A) and other organic suspended solids. It is reasonable to assume that the biomass fraction of the MLVSS is 80 % [18].

For the conventional AS system, the MLSS concentration ranges from 2000-5000 mg/l for a sequencing batch reactor (SBR) [14].

The MLVSS fraction of the MLSS concentration is assumed to be 90 %.

The relationship between biomass concentration and volume counts for both the suspended growth system and the attached growth system. Biofilm systems often achieve higher biomass concentrations therefore the volume of the biofilm systems are usually lower than for activated sludge systems. From the literature for MBRs it is found that the MLSS concentration in the system may reach 20 000 mg/l which corresponds to an active biomass, X_A, concentration of 14400 mg/l based on the assumptions above. The active biomass in MABRs can reach even higher concentrations than the MBRs due to the beneficial oxygen supply through the membrane. The objective of this thesis was to assess different biological treatment technologies for produced water treatment, therefore the different parameters were calculated for X_A concentrations up to 50,000 mg/l (which are concentrations that probably not would be reached, but the calculations are carried out in order to better display the relationship between biomass concentration and reactor volume) with that in mind that MABRs may operate at very high X_A concentrations.

6.2.4 Calculation of the reactor volume

Example:

- X_A: 4000 mg/l.
- Temperature: 30°C.
- SRT: 6.7 d

V= 30,000 m^3/d * (376.1 gCOD/m^3-18.8 gCOD/m^3) * 0.4 g BM/g COD*6.7 d/ (4000 g/m^3 * (1-0.12 1/d *6.7d)) = 3772 m^3

The table below lists the calculated reactor volumes at different X_A concentrations at SRT: 6.7 days. The results from the calculations carried out at SRT: 2.7 and 0.67 days are found in appendix 1.

Table 28: Calculated reactor volumes for different X_A concentrations, SRT: 6.7 days:

X_A	V	X_A	V
mg/l	m^3	mg/l	m^3
1000	15086	13000	1160
2000	7543	14000	1078
3000	5029	15000	1006
4000	3772	16000	943
5000	3017	17000	887
6000	2514	18000	838
7000	2155	19000	794
8000	1886	20000	754
9000	1676	21000	718
10000	1509	22000	686
11000	1371	40000	377
12000	1257	50000	302

The results show that the calculated reactor volume is affected by the change in SRT, but even more affected by the increase in X_A concentration. The relationship is graphically illustrated in the three figures below.

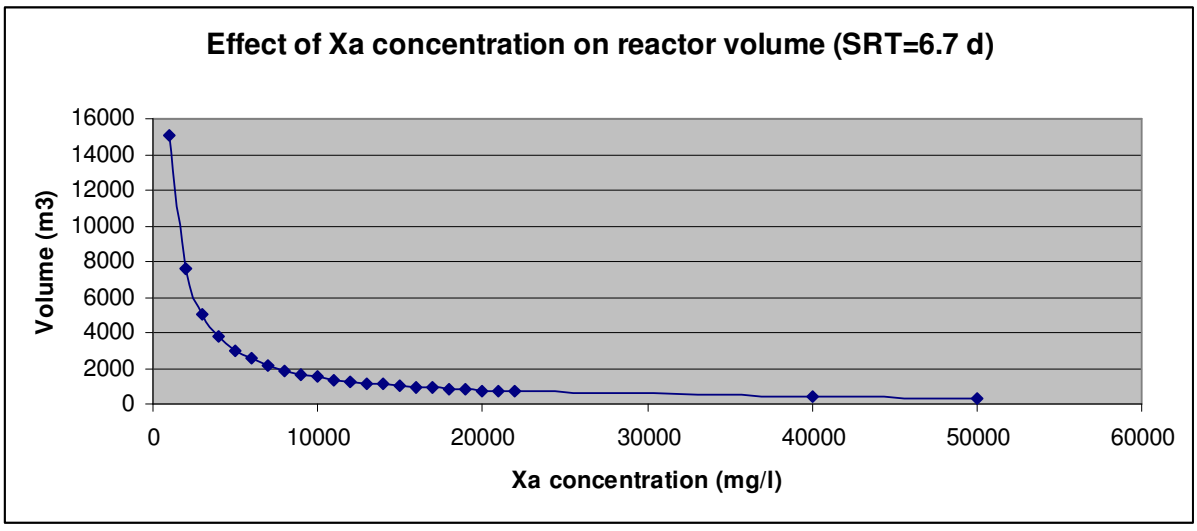

Figure 24: Relationship between X_A concentration and reactor volume, SRT: 2.7d.

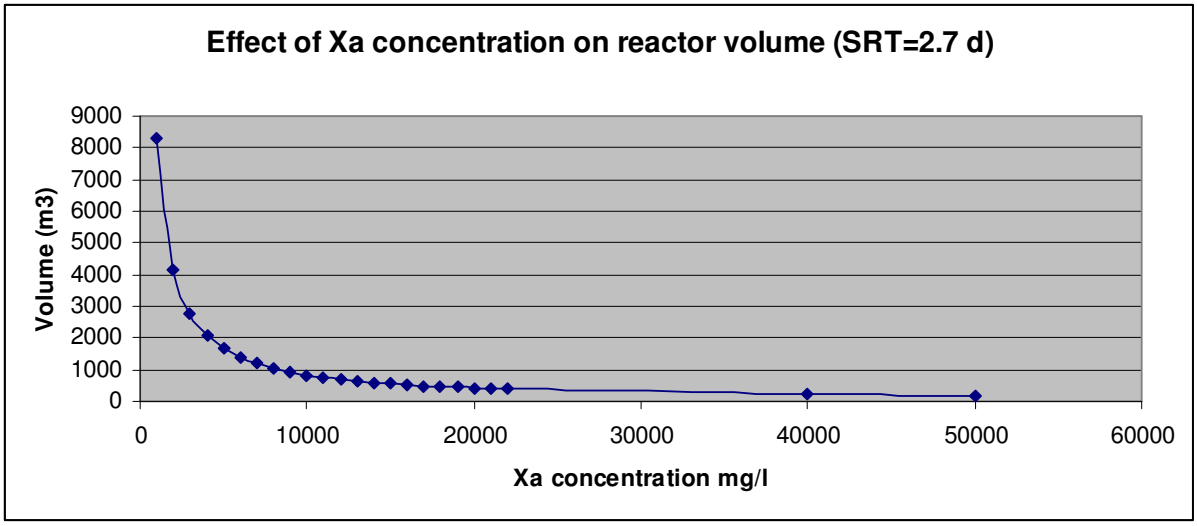

Figure 25: Relationship between X_A concentration and reactor volume, SRT: 2.7d.

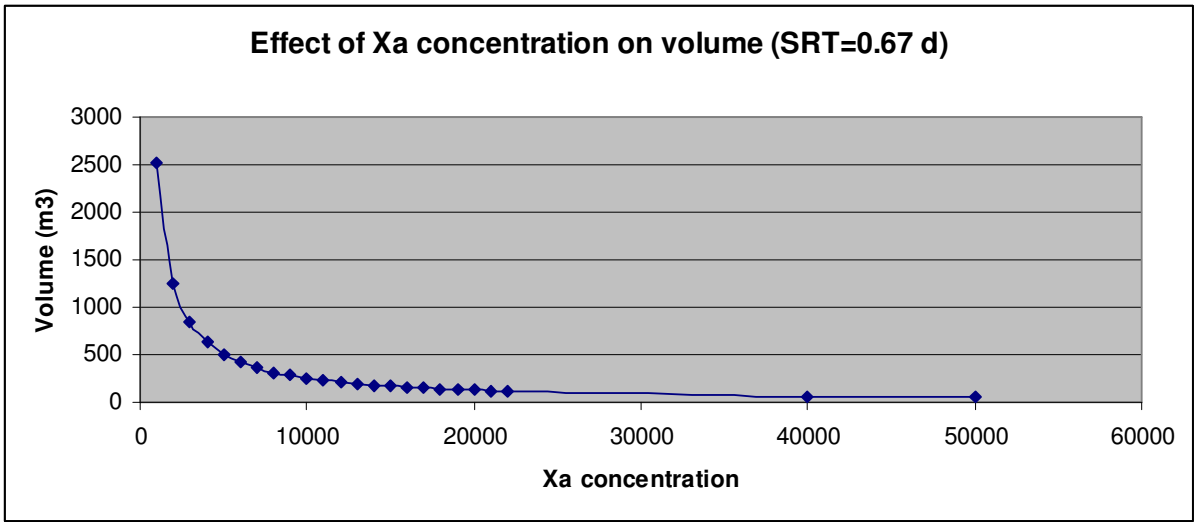

Figure 26: Relationship between X_A concentration and reactor volume, SRT: 0.67d.

The results from the three graphs above are all presented in the graph below in order to better display how the SRT affects the calculated reactor volume.

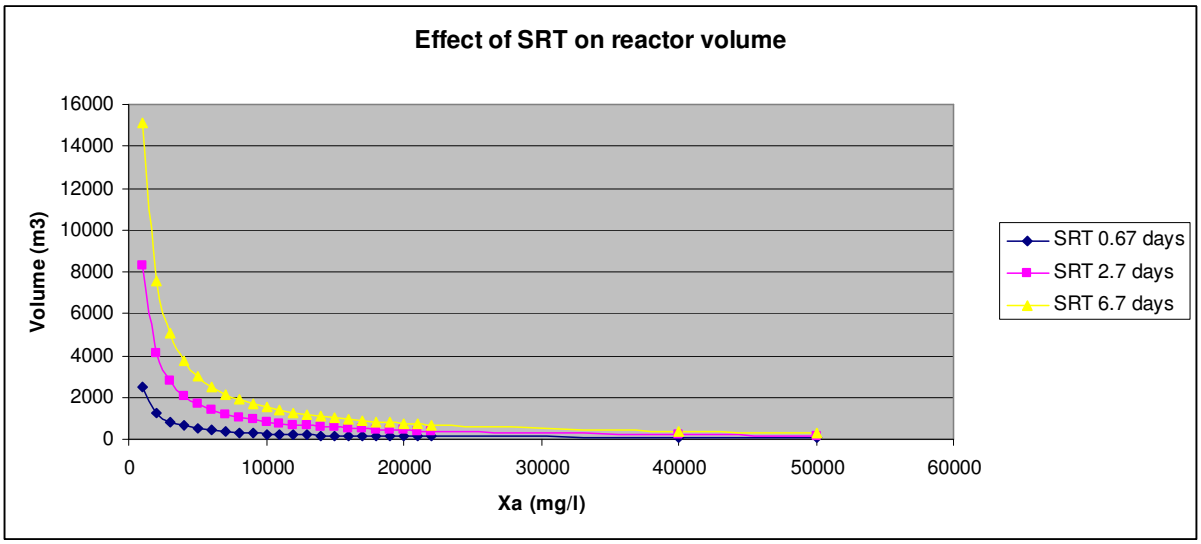

Figure 27: Effect of SRT on the calculated reactor volume at 30ºC.

6.3 Calculations for the attached growth systems.

6.3.1 Assumptions and characteristics

Model produced water characteristics:

Wastewater flow-rate: Q = 30,000 m^3/d

COD –concentration: C_{in} = 376.1 gCOD/ m^3

μ_{max} = 0.13 1/h = 3.12 1/d (for the compound most slowly degraded).

K_S = 0.36 g/ m^3 (for the compound most slowly degraded).

Assumptions:

- Removal efficiency: 90% COD removal ⇒ effluent COD, C = 37.6 gCOD/ m^3
- Biomass concentration within the biofilm, X_{BF} = 100 kgVSS/m^3_{Bf} (10% solids and 90% water is assumed. The maximum solids concentration within a biofilm is 20 % of the total volume and 80 %water, but this is practically impossible, therefore X_{BF} = 100 kgVSS/m^3_{Bf} is a reasonable assumption [Ydstebø, Leif 2011]).
- Y = 0.4 gVSS/gCOD.
- Specific surface area: a_c = 500 m^2/m^3.
- Biofilm thickness: L_f = 1 mm
- Steady state conditions.
- Excess macro and micro nutrients available.

- Molecular diffusion coefficient, D =$1 \cdot 10^{-4}$.
- Biofilm density 0.3kg/m^3.

6.3.2 Calculation of the reactor volume needed for the attached growth systems.

Determination of the reaction rate for the biofilm:

Since K_S << C ; 0.order reaction is assumed for the system.

From the biofilm literature defined in chapter 5, the following calculations were carried out in order to determine the required reactor volume for biofilm treatment of the model produced water.

Biofilm volume,V_{BF} = 500 m^2/m^3 $\cdot 1 \cdot 10^{-4}$ = 0.05 $m^3_{BF}/ m^3_{Reactor}$.

k_{0f} = (3.12 $\cdot$ 100 kg VSS/ m^3_{BF}) /0.4 kgVSS/kgCOD = 780 kg COD/ $m^3_{BF} \cdot d$

Calculating the β value in order to decide which equation to use for the calculation of r_A:

$\beta = \sqrt{((2 \cdot 1 \cdot 10^{-4} \cdot 37.6)/(780000 \cdot 0.0001^2))} = 0.98$

$\beta < 1$ gives:

Rate per area, $r_A = \sqrt{(2 \cdot 780000 \cdot 1 \cdot 10^{-4})} \cdot 37.6^{0.5} = 12.49 \cdot \sqrt{37.6} = 78.6$ g COD/ $m^2 \cdot d$

Rate per volume, r_V = 78.6 g COD/ $m^2 \cdot$ d 500 m^2/m^3 = 38.29 kg/ $m^3 \cdot$ d

Reactor volume:

$V = (Q \cdot C)/(r_A \cdot a_c)$

$V=(30\ 000\ m^3/d \cdot 376.1\ gCOD/\ m^3)/ (78.6\ g\ COD/\ m^2 \cdot d \cdot 500\ m^2/m^3)$

$\underline{V = 287\ m^3}$

The calculations were carried out for a range of different surface area values, the results are listed in the table below.

Table 29: Volume requirements for different surface area, a_c, values:

Surface area, $a_{c.}$ (m^2/m^3)	Corresponding reactor volume (m^3)
200	718
350	410
500	287
700	205
1000	143

The relationship between the surface area and reactor volume is shown in the figure below:

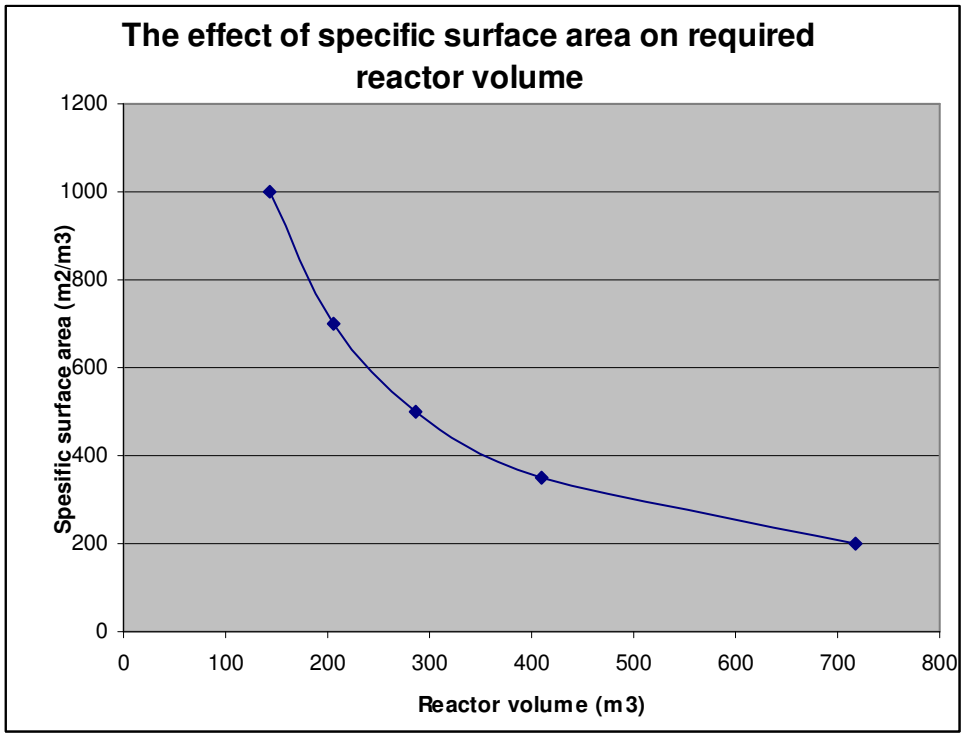

Figure 28: The effect of specific surface area on required reactor volume.

Calculation of required reactor volume for a conventional biofilm configuration with known loading rates:

For a biodisc configuration typical loading rate and specific area can be:

Area loading rate: L_A = 15 gCOD/m^2·d

Specific surface area: A_c = 200 m^2/m^3

Waste water characteristics:
Wastewater flow-rate: Q = 30,000 m^3/d
COD –concentration: C_{in} = 376.1 gCOD/m^3
Removal requirements: 90 % COD

Volume calculations:
Total area required = Total COD-removal/Area loading rate

A_T = (30,000 m^3/d ·376.1 gCOD/m^3)/15 gCOD/m^2·d = 742200m^2
V = A_T/A_c = 742200 m^2/200 m^2/m^3 = <u>3761 m^3</u>

6.4 Sludge production

Simplified equation for sludge production repeated here for easy reference:

(V·MLSS)/SRT = g/d

In table 26 the different volumes and X_A concentrations are calculated for a biological system at SRT= 6.7 days.
It is assumed that the biomass concentration, X_A, represents 80 % of the total MLVSS concentration and that the MLVSS represents 90 % of the MLSS. The MLSS concentrations are then calculated as follows:

MLSS = X_A/(0.80·0.90)

Example:
X_A : 1000 mg/l →MLSS = 1000/(0.80·0.90) mg/l=1389 mg/l.
Calculated V when X_A is 1000 mg/l = 15086 m^3

Calculating the sludge production:

(15086 m^3 ·1389 g/m^3) /(6.7 d·1000g/kg) = <u>3127 kg/d</u>

Table 30 lists the calculated MLSS values and corresponding sludge production for all the X_A values in table 28 (SRT:6.7 d).

Table 30: Calculated MLSS values and corresponding sludge production for all the X_A values in table 28 (SRT:6.7 d).

Xa	V	MLSS	Sludge production
mg/l	m3	mg/l	kg/d
1000	15086	1389	3127
2000	7543	2778	3127
3000	5029	4167	3127
4000	3772	5556	3127
5000	3017	6944	3127
6000	2514	8333	3127
7000	2155	9722	3127
8000	1886	11111	3127
9000	1676	12500	3127
10000	1509	13889	3127
11000	1371	15278	3127
12000	1257	16667	3127
13000	1160	18056	3127
14000	1078	19444	3127
15000	1006	20833	3127
16000	943	22222	3127
17000	887	23611	3127
18000	838	25000	3127
19000	794	26389	3127
20000	754	27778	3127
21000	718	29167	3127
22000	686	30556	3127
40000	377	55556	3127
50000	302	69444	3127

The table above illustrates that the sludge production is the same in all the calculations.
The sludge production was also calculated for the following sludge retention times of 2.7 and 0.67 days (see appendix 1). The results are found in the table below:

Table 31: Sludge production at different solid retention times.

SRT	Sludge production kg/d
0.67	5222
2.7	4261
6.7	3127

The calculations illustrates that the sludge production decrease with higher SRT. The relationship is presented graphically in the figure below:

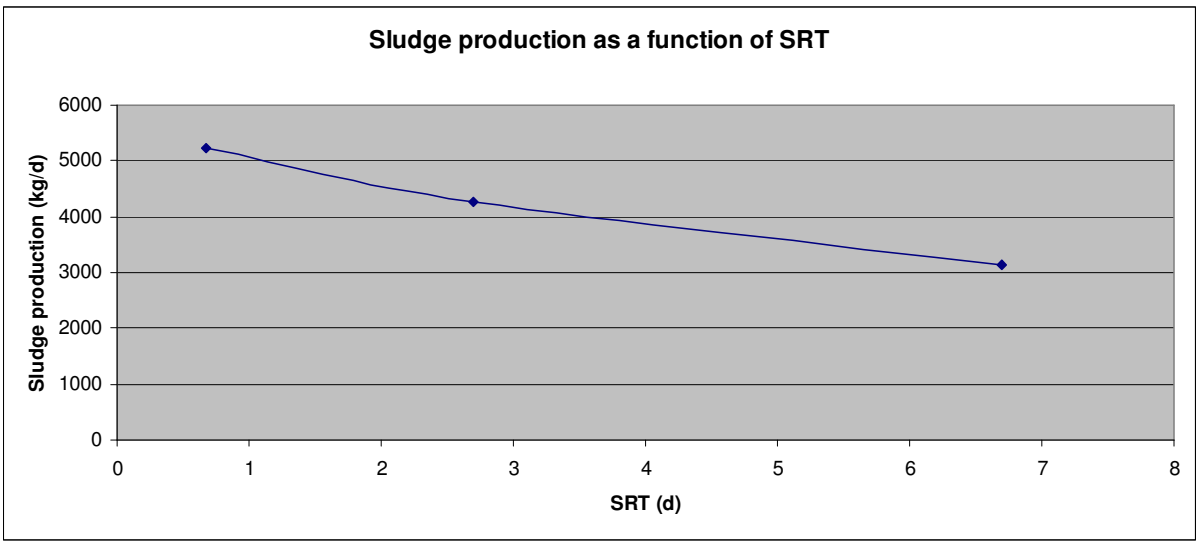

Figure 29: Sludge production as a function of SRT.

6.5 Oxygen demand

Model produced water characteristics at 30°C:

Wastewater flow-rate: Q = 30,000 m^3/d

COD –concentration: C_{in} = 376.1 gCOD/ m^3

Assumptions:

- Removal efficiency: 90% COD removal ⇒ effluent COD = 37.6 gCOD/ m^3
- Y = 0.4 gVSS/gCOD.
- f_d : 0.1
- 0.12 gVSS/gVSS·d
- f_{cv} : 1.42 gCOD/gVSS

Example:

X_A: 1000 mg/l

V: 15086 m^3 (for X_A: 1000 mg/l and SRT: 6.7 d)

The simplified equation for calculation of oxygen demand is repeated here for easy reference:

Oxygen demand = $(1\text{-}Y\cdot f_{cv})\cdot(C_{in}\text{-}C_{out})\cdot Q + k_d\cdot X_A(1\text{-}f_d)\cdot V\cdot f_{cv}$ (kg/d)

Oxygen demand = (1-0.4 gVSS/gCOD·1.42 gCOD/gVSS) ·(376.1-37.6 gCOD/ m^3)·30 000 m^3/d + 0.12 gVSS/gVSS·d·1000 g VSS/m^3 ·(1-0.1) ·15086 m^3·1.42 gCOD/gVSS =10966000 gVSS/d= <u>10966 kg/d</u>

The results from the calculations of oxygen demand for biological systems operating with different biomass concentrations and reactor volumes at a sludge retention time of 6.7 days are listed in the table below.

Table 32: Oxygen demand for systems operating with different biomass concentrations and reactor volumes and a sludge retention time of 6.7 days:

Xa	V	oxygen demand
mg/l	m3	kg/d
1000	15086	10966
2000	7543	10966
3000	5029	10966
4000	3772	10966
5000	3017	10966
6000	2514	10966
7000	2155	10966
8000	1886	10966
9000	1676	10966
10000	1509	10966
11000	1371	10966
12000	1257	10966
13000	1160	10966
14000	1078	10966
15000	1006	10966
16000	943	10966
17000	887	10966
18000	838	10966
19000	794	10966
20000	754	10966
21000	718	10966
22000	686	10966
40000	377	10966
50000	302	10966

It is clear that the oxygen demand is the same in all the calculations. The oxygen demand was also calculated for sludge retention times of 2.7 and 0.67 days. The results are listed in the table below.

Table 33: oxygen demand at different solid retention times.

SRT (d)	oxygen demand (kg/d)
0.67	9038
2.7	9922
6.7	10966

The calculations illustrates that the oxygen demand increase as the SRT increase. The relationship is presented graphically in the figure below:

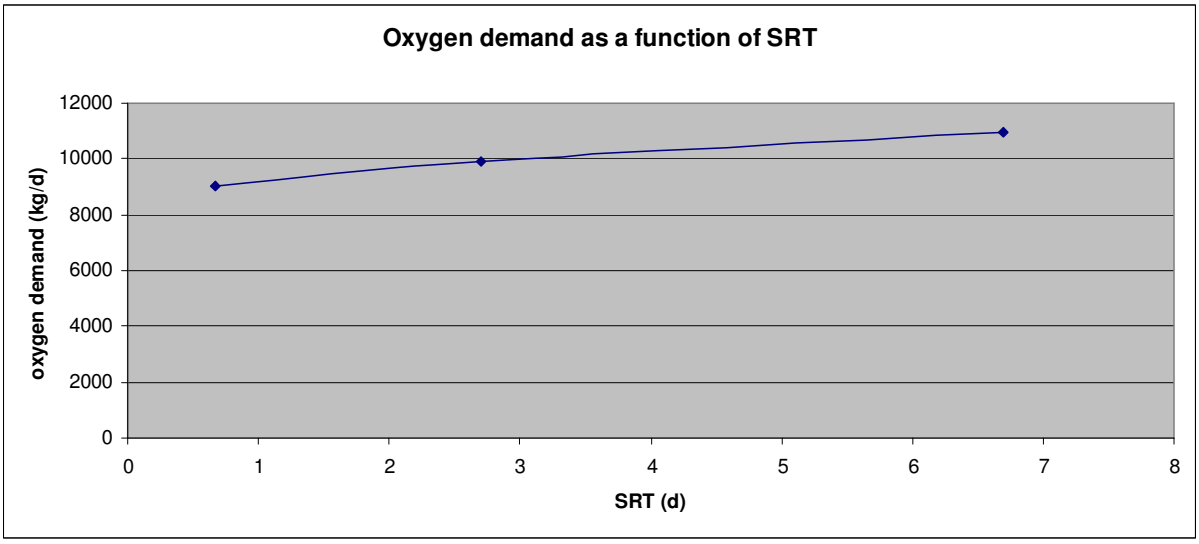

Figure 30: Oxygen demand as a function of SRT.

6.6 Effect of temperature

6.6.1 Results calculated for the model produced water at 20 ºC.

From the literature it is clear that the temperature of the water affects the microbial activity. The reaction rate constants are very important in assessing the overall efficiency.
The relationship between temperature and reaction rate are repeated here for easy reference:

Effect on growth rate: μ_{max} (T) = μ_{max} (20ºC) $\theta^{(T-20)}$ θ : 1.07 [14]
Effect on decay rate: k_d (T) = k_d (20ºC) $\theta^{(T-20)}$ θ : 1.04 [14]

Calculated μ_{max} and k_d at 20ºC:
μ_{max} 30ºC: 0.13 1/h (assumed slowest degraded compound)

k_d 30ºC: 0.12 1/d

Effect on growth rate: $0.13 = \mu_{max}$ (20ºC) $1.07^{(30-20)}$

μ_{max} (20ºC) = 0.066 1/h

Effect on decay rate: $0.12 = k_d$ (20ºC) $1.04^{(30-20)}$

k_d (20ºC) = 0.08 k_d (20ºC)

With these coefficients the following results was found for the treatment of the model produced water at 20ºC:

Sludge retentiontimes:

SRT_{min}= 0.66 d

$SRT_{min} \cdot 2$ =1.33 d

$SRT_{min} \cdot 8.1$ =5.346 d

$SRT_{min} \cdot 20$ =13.3 d

The table below lists all the calculated reactor volumes, sludge production and oxygen demand for different X_A concentrations at 20ºC when SRT is 13.3 days.

Table 34: calculated reactor volumes, sludge production and oxygen demand for different X_A concentrations at 20ºC and SRT: 13.3 days:

Xa	V	MLSS	Sludge production	Oxygen demand	Xa	V	MLSS	Sludge production	Oxygen demand
Mg/l	m3	mg/l	kg/d	kg/d	Mg/l	m3	mg/l	kg/d	kg/d
1000	26175	1389	2733	11328	16000	1636	22222	2733	11328
2000	13087	2778	2733	11328	17000	1540	23611	2733	11328
3000	8725	4167	2733	11328	18000	1454	25000	2733	11328
4000	6544	5556	2733	11328	19000	1378	26389	2733	11328
5000	5235	6944	2733	11328	20000	1309	27778	2733	11328
6000	4362	8333	2733	11328	21000	1246	29167	2733	11328
7000	3739	9722	2733	11328	22000	1190	30556	2733	11328
8000	3272	11111	2733	11328	40000	654	55556	2733	11328
9000	2908	12500	2733	11328	50000	523	69444	2733	11328
10000	2617	13889	2733	11328					
11000	2380	15278	2733	11328					
12000	2181	16667	2733	11328					
13000	2013	18056	2733	11328					
14000	1870	19444	2733	11328					
15000	1745	20833	2733	11328					

The calculated values for at the other calculated retentiontimes at both 20 and 30ºC can be found in appendix 1.

The relationship between the calculated reactor volumes and SRT is illustrated in the figure below.

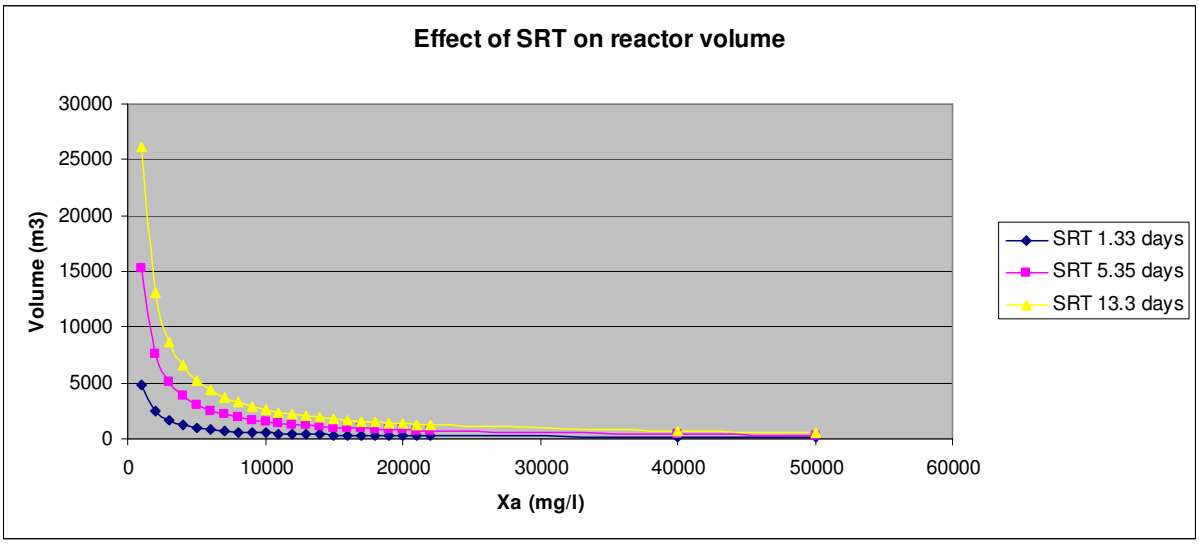

Figure 31: Effect of SRT on reactor volume at 20ºC.

6.6.2 Comparing the results obtained at 30ºC with those obtained at 20ºC

The figure below illustrates how the SRT values changes as the temperature is decreased to 20ºC.

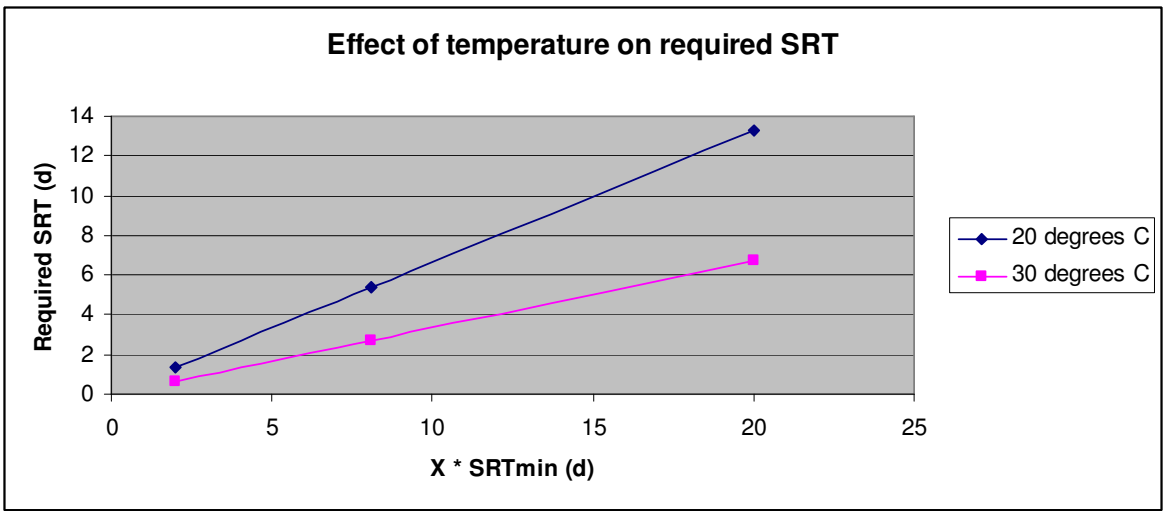

Figure 32: Effect of temperature on required SRT.

The figure below illustrates how the calculated reactor volume changes as the temperature is decreased to 20ºC.

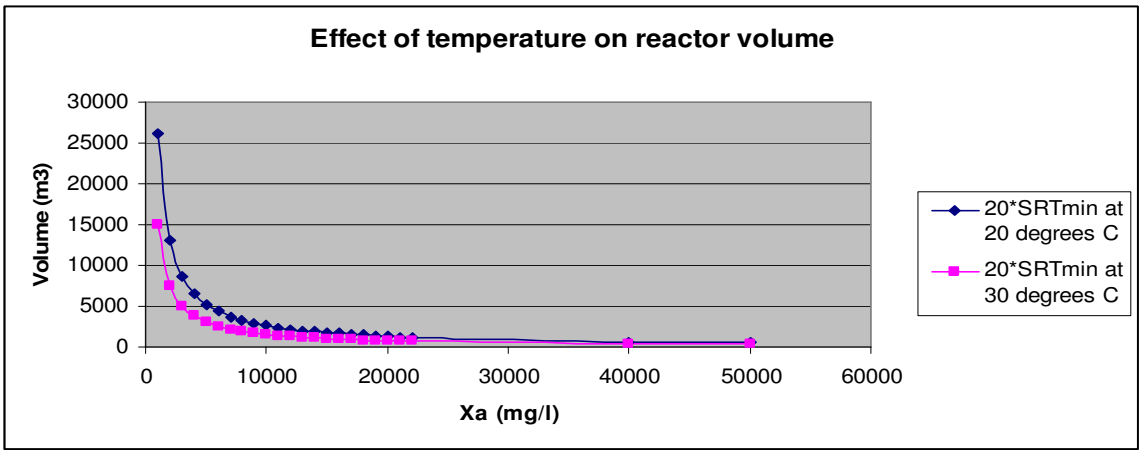

Figure 33: Effect of temperature on reactor volume.

The figure below shows how the temperature affects the sludge production.

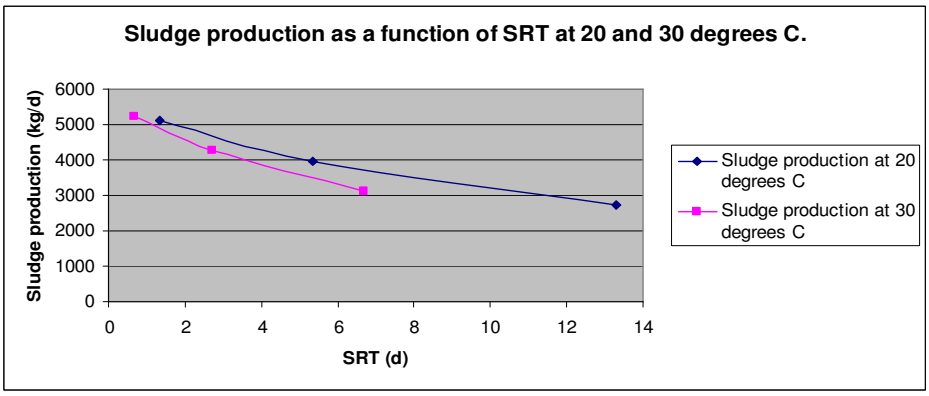

Figure 34: Sludge production as a function of SRT at different temperatures.

The figure below shows how the temperature affects the oxygen demand.

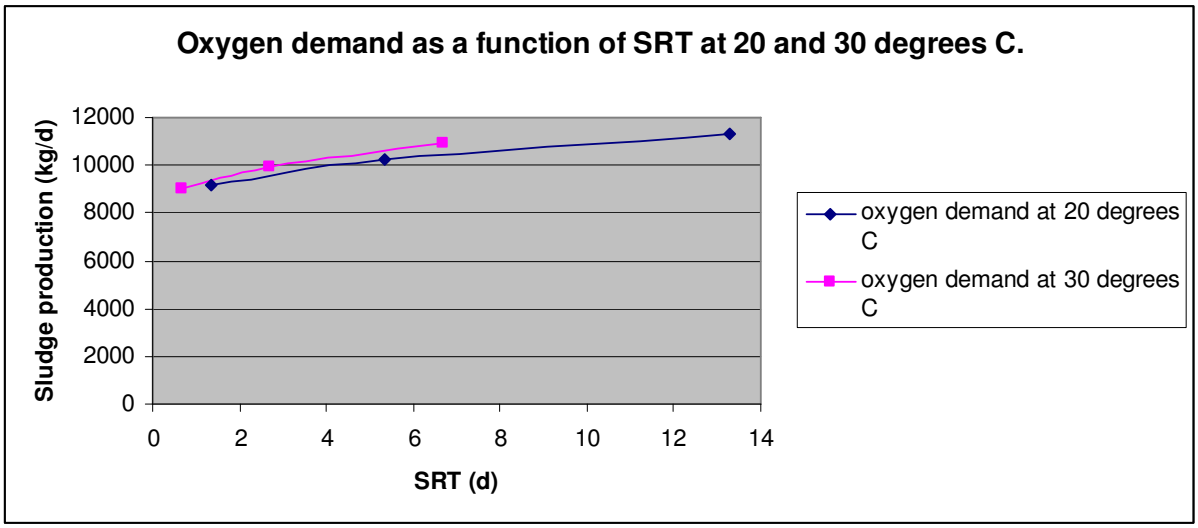

Figure 35: Oxygen demand as a function of SRT at different temperatures.

7. Discussion

The objective of this thesis was to assess different biological wastewater treatment technologies for the treatment of produced water, in order to meet with possible stricter treatment requirements in the future. The requirements set by the authorities does not involve removal of dissolved organic compounds from produced water, but there is joint agreement within the government and the oil and gas industry that the focus, regarding produced water discharges, should be on discharges of the dissolved organic compounds not the oil in water content. Recent research has detected negative effects on fish in open sea area caused by exposure to produced water.

This thesis is a literature study on aerobic biological treatment technologies for the removal of dissolved organic compounds and oil in water content from produced water.
The aerobic treatment technologies assessed in this thesis was activated sludge (AS), biofilm (BF), membrane bioreactor (MBR) and aerated membrane biofilm reactor (MABR).
The different technologies were assessed in the effort of finding the most beneficial system in terms of removal efficiency and space requirements on the offshore installation.
A biological treatment system with a high biomass concentration and high rate oxygen supply would be an advantage since the required volume of the biological reactor decreases with increasing biomass concentration.

In order to carry out the calculations for the required reactor volumes needed for the different technologies as well as sludge production and oxygen demand, it was necessary to characterize the waste water to be treated. The waste water in this thesis was produced water and the produced water characteristics for a typical oil field were used in the calculations. For the model produced water it was assumed that the dissolved organic compounds consisted of only carboxylic acids (assumed only acetic acid and propionic acid) and BTEX, since the contribution from these two dissolved organic compounds group was 98.4% of the total dissolved organic compounds contribution. In addition to the dissolved organic compounds it was assumed that the model produced water did contain 30 mg/l hexane representing the allowed oil in water discharge concentration.
The produced water flow rate was assumed to be 30,000 m^3/d in the calculations carried out in this thesis, but the produced water flow rate varies from field to field and during its lifespan,

therefore a change in produced water flow rate would affect all the parameters calculated in this thesis.
The total COD concentration for the produced water was then calculated with a safety factor. The assumptions made for the model produced water affects the calculated results and a change in the model produced water composition would be observed in the calculated results. The salinity of the produced water, and other factors not included in the model produced water, is likely to affect the microorganisms in the system. Therefore it would be an advantage to run tests on the produced water to be treated in order to fully identify which compounds the produced water consist of and at what concentrations the different compounds are present at. Since the produced water composition varies from one field to another, pilot tests would be highly recommended prior to any biological treatment system installations.

The calculations carried out depended on values found for the kinetic coefficients such as specific growth rate and decay rate. Different research results were assessed in order to determine the kinetic coefficients. The values for the kinetic coefficients may vary for different microorganisms, but it was assumed that ethylbenzene was the compound degraded at the slowest rate with the specific growth rate of 0.13 1/h and it was assumed that the decay rate was 0.12 1/d at 30ºC based on typical values found for activated sludge systems from well respected references (Metcalf & Eddy). It was assumed that surfactants was present (either added or produced by microorganisms) in order to increase the solubility of hexane and allow for biodegradation.
The calculations carried out proved that the overall performance of the biological treatment systems largely depended on the temperature in the system. From the literature, a typical temperature for produced water was found to be 75 ºC, but for the calculations it was assumed that the temperature of the produced water was reduced to 30 ºC and 20 ºC during the pre-treatment. The temperature of the produced water varies from one field to another. The results from the calculations in this thesis showed that the minimum sludge retention time (SRT_{min}) nearly doubled as the temperature was reduced from 30 to 20 ºC, from 0.33 days to 0.67 days. This is due to the reduced reaction rates caused by the temperature reduction. The SRT affects the biological treatment processes and biological systems are usually designed and operated with a design SRT value from 2 to 20 times SRT_{min} to provide a process safety factor against system failure. In this thesis the design SRT was calculated at 2, 8.1 and 20 times SRT_{min},

resulting in design SRT values of:

	SRT safety factor	SRT at 20 ºC	SRT at 30 ºC
2*SRTmin	2	1.33	0.67
8.1*SRTmin	8.10	5.346	2.7
20*SRTmin	20	13.3	6.7

The calculated reactor volume was in turn affected by the increased SRT caused by the temperature loss. The effect of the SRT, at 20 times SRT_{min}, was seen as an increase in reactor volume of 73.5 % as the temperature was decreased from 20 to 30 ºC. For SRT of 8.1 times SRT_{min} the increase in reactor volume was calculated to be 83.6 % larger for systems operating at 20º compared with systems operating at 30 ºC. Last, at 2 times SRT_{min} the reactor volume was calculated to increase with 93.8 % as the temperature was decreased from 20 ºC to 30 ºC. This illustrates how important the system temperature is with regard to required reactor volume.

The volume of the biological reactor also depends on the active biomass concentration in the system, X_A. The relationship between biomass concentration and required reactor volume applies to all the biological treatment technologies, activated sludge as well as biofilms, therefore the relationship between active biomass concentration and reactor volume was calculated for X_A concentrations up to 50,000 mg/l where the lower range represents the X_A concentrations found in AS systems and the higher range represents the possible active biomass concentrations of MABRs (though it is uncertain if the X_A concentration could get this high, but at least it clearly shows the relationship between the X_A concentration and required reactor volume). For the conventional AS system, the MLSS concentration ranges from 2000-5000 mg/l for a sequencing batch reactor (SBR). From the literature for MBRs it is found that the MLSS concentration in the system may reach up to 20 000 mg/l which corresponds to an active biomass, X_A, concentration of 14400 mg/l. Biofilm systems often achieve higher biomass concentrations than AS systems and therefore the volume of the biofilm systems are usually lower than for activated sludge systems. But, conventional biofilms in wastewater treatment systems can be relatively thick and therefore it could result in only partial penetration of oxygen into the biofilm, resulting in an anoxic layer of the biofilm unable to aerobically degrade organic substrate. If the wastewater-loading rate is high, oxygen supply could limit the removal of organic substrate in biofilms. In conventional biofilm systems, a high fraction of the oxygen supplied is lost to the atmosphere, but by using

a MABR with high intramembrane oxygen pressure, complete oxygen penetration could be achieved. MABRs are able to ensure that, for situations with high organic loading rate, the entire biofilm thickness is utilized for biodegradation of organic compounds.

The active biomass in MABRs is believed to reach even higher active biomass concentrations than AS systems, MBRs and biofilms due to beneficial oxygen supply system through the membrane.

The relationship between the required reactor volume as a function of active biomass is shown in the two figures below for different SRT at 20 and 30ºC.

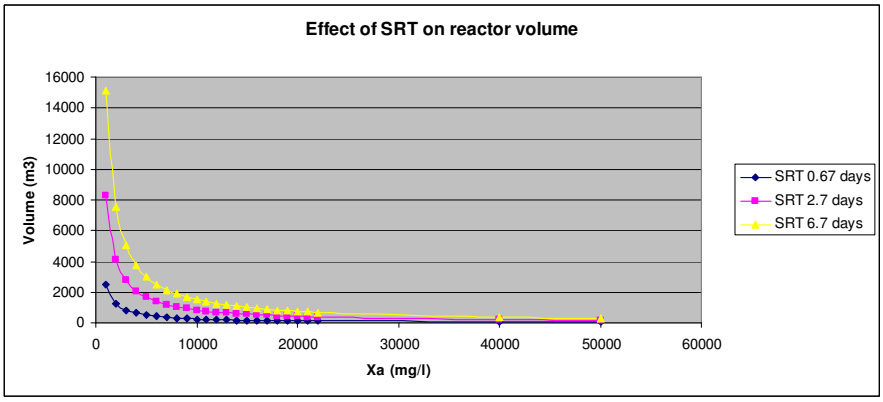

Figure 27: Effect of SRT on the calculated reactor volume at 30ºC.

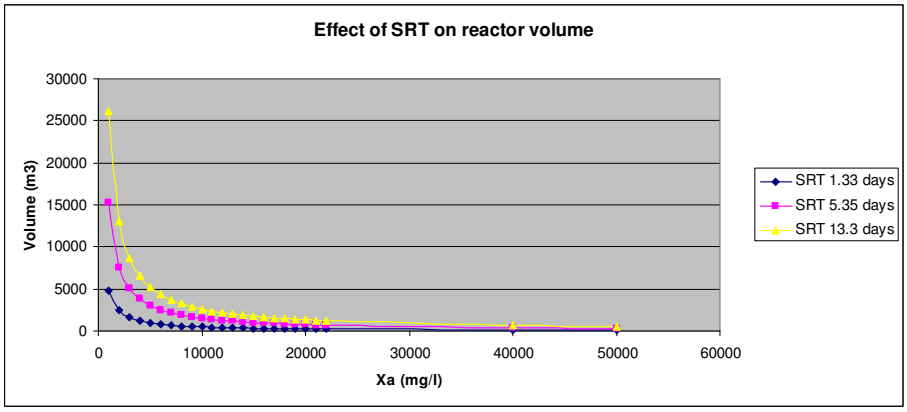

Figure 31: Effect of SRT on reactor volume at 20ºC.

The sludge production depends on MLSS concentration, reactor volume and SRT. The sludge production was lower for the system operating at 20ºC due to the increased SRT. The oxygen demand was found to be slightly lower at 30ºC due to the difference in reactor volume and k_d value for the two temperatures. The sludge production decreased with increased SRT and the oxygen demand increased as the SRT increased, which applies with the theory.

For biofilm systems, the required reactor volume was calculated for different specific surface area values. The relationship between the specific surface area, A_C, and the reactor volume is graphically displayed in the figure below. These calculations were based on assumed values for biofilm thickness, molecular diffusion coefficient, biofilm density and biomass concentration within the biofilm. The calculated reactor volume would be affected by a change in any of these parameters.

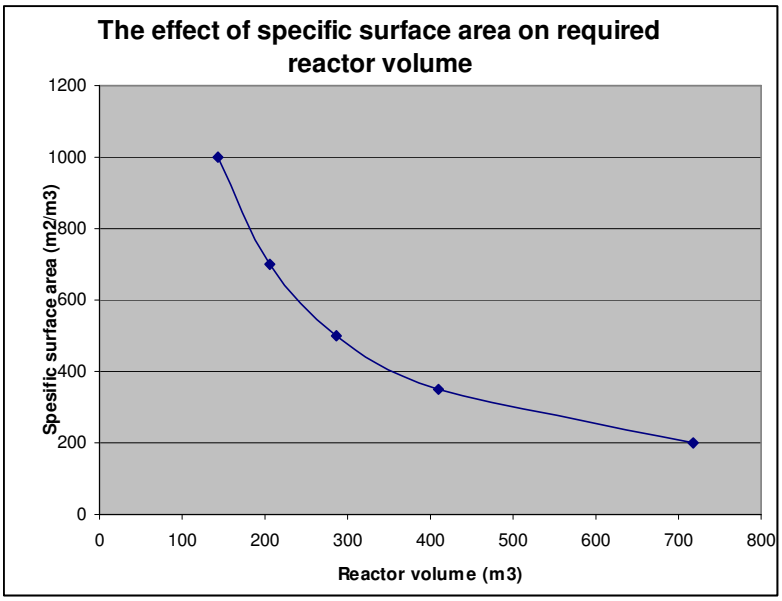

Figure 28: The effect of specific surface area on required reactor volume.

It is clear that the reactor volume decreases with increased specific surface area for the system. This is because the available area for microorganisms to grow on is related to the biomass concentration. These calculations do not incorporate any safety factor for the biofilm reactor volume, but a safety factor should always be included to provide a process safety factor against system failure.

The calculations carried out for a conventional a biodisc configuration with known loading rates and specific area of 200 m^2/m^3 resulted in a required reactor volume of 3761 m^3 compared with 718 m^3 calculated based on the assumptions above (biofilm thickness, molecular diffusion coefficient, biofilm density and biomass concentration within the biofilm). That is more than five times higher, this can be explained by the fact that loading rates for conventional biofilm systems does include a process safety factor and it takes into

account possible limitations due to insufficient oxygen supply. In addition, the biomass density in the biofilm was assumed to be 100 kg VSS/m^3_{BF} which is an important factor when calculating the reactor volume. A lower biomass density would result in a larger required reactor volume

Because of uncertainties related to the produced water composition and other assumptions made in the calculations, it is recommended that if one wants to treat produced water biologically, pilot testing of the actual water should be carried out, to provide the necessary design criteria.

8. Conclusion

Research has shown that dissolved organic components such as BTEX and carboxylic acids can be successfully removed by aerobic biological degradation. The technologies assessed in this thesis were activated sludge, biofilm, membrane bioreactor and aerated membrane biofilm reactors.

The calculations carried out in this thesis shows how the biomass concentration relates to the required reactor volume. For AS systems with a typical MLSS concentration of 4000 mg/l the calculated reactor volume was found to be 3772 m^3 compared with 754 m^3 for a MBR with a typical MLSS concentration of 20 000 mg/l (at 30ºC, SRT:6.7 d). The reactor volume was also calculated for MLSS values up to 50 000 mg/l to illustrate the relationship between biomass concentration and required reactor volume since conventional biofilms and, especially, MABFs have the potential to reach very high biomass concentrations. The calculated reactor volumes for MLSS concentrations of 40 000 and 50 000 mg/l were 377m^3 and 302 m^3, respectively (at 30ºC and SRT:6.7 d). The relationship between X_A and V was observed at both temperatures assessed and for all the different SRT values considered.
The calculations also showed that the temperature of the system also affects the reactor volume needed. By decreasing the temperature of the system by 10ºC (from 30 to 20ºC), the required reactor volume was calculated to be 73.5 % larger for the lower temperature system, at SRT= 20 times $SRT_{min.}$
It was also found, from the calculations, that the SRT value also has an influence on the required reactor volume. Higher SRTs results in higher reactor volumes, for instance when the MLSS concentration was 4000 mg/l the calculated reactor volume was 3772 m^3 at SRT of 6.7 days compared with 2071 m^3 at the same conditions at a SRT of 2.7 days (at 30ºC).

Research has shown that MABRs outperformed both conventional biofilm reactors and activated sludge systems under conditions of high organic loading due to the fact that MABRs can contain an active biomass concentration higher than any other system because of the oxygen supply through the membrane. This technology would be able to provide the most compact biological reactor system of all the technologies assessed in this thesis. Since the main focus was put on the required reactor volume, it is concluded that MABRs should be further investigated if biological treatment was to be used for produced water treatment on offshore installations.

9. References

[1]: Fakrhu`l Razi Ahmadun,Alireza Pendashteh, Luqman Chuah Abdullah, Dyang Radiah Awang Biak, Sayed Siavash Madaeni, Zurina Zainal Abidin *Review of technologies for oil and gas produced water treatment*. Journal of Hazardous Materials, 2009, 170: p. 530-551

[2]: Oljeindustriens Landsforening (OLF), Environmental Report 2010,
Available from:
http://www.olf.no/PageFiles/672/OLF%20milj%c3%b8rapport%202010.pdf

[3]: Grov, A., *MOT 200 Separation Technology,* University of Stavanger, 2009.

[4]: Klima og forurensings-direktoratet, *Petroleumvirksomhetens arbeid med nullutslipp*, 2010.
Available from:
http://www.klif.no/publikasjoner/2637/ta2637.pdf

[5]: Ciprian, T.S., *Treatment of produced water: targeting dissolved compounds to meet a zero harmful discharge in oil and gas production,* PhD 2009.

[6]: Beyer, J., *Ecotoxicology of drilling and produced water discharges*. Lecture notes, Offshoreindustrien og ytre miljø, 2010.

[7]: Ekins, P.,Vanner, R., Firebrace, J. *Zero emissions of oil in water from offshore oil and gas installations: economic and environmental implications*, Journal of Cleaner Production, 2009, 15: p.1302-1315

[8]: Havforskningsinstituttet, *Biomarkers in natural fish populations indicate adverse biological effects of offshore oil production*, 2011.
Available from:
http://www.plosone.org/article/info%3Adoi%2F10.1371%2Fjournal.pone.0019735

[9] SFT rapport TA 2366/2008, Akvaplan-niva AS Rapport: 4065, *Effekter i Norskehavet av petroleumsvirksomhet utenfor Norskehavet*, 2008

[10]: Dow AgroSciences
Available from:
http://www.dowagro.com/chlorp/eu/rpa/pop.htm

[11] : Zangaeva, E. *Produced water challenges. Influence of production chemicals on flocculation,* Master Thesis, University of Stavanger, 2010

[12] C.H. Walker, C. H., *Principles of ecotoxicology*, 2006

[13]: Henze, M., van Loosdrecht, M.C.M., Ekama, G.M., Brdjanovic, D., *Biological waste water treatment- principles, modelling and design,* IWA Publishing, 2008

[14]: Metcalf & Eddy, *Wastewater Engineering*, McGraw Hill, Fourth Edition, 2003

[15] Knutse, T., Solli, T.M., *Effekten av næringssalter på biologisk behandling av avløpsvann,* Bachelor Thesis, University of Stavanger, 2007

[16] Activated sludge figure.
Available from:
http://www.google.no/imgres?imgurl=http://www.websters-online-dictionary.org/images/wiki/wikipedia/commons/3/35/Activated_Sludge_1.png&imgrefurl=http://www.websters-online-dictionary.org/Ac/Activated_Sludge.html&usg=___8yGR6u5B19gmR-5pRe8DzooEkE=&h=229&w=300&sz=6&hl=no&start=0&zoom=1&tbnid=GIpu2N_V1t5-WM:&tbnh=159&tbnw=208&ei=Riy5TbrPBIOp8APd-dAm&prev=/search%3Fq%3Dactivated%2Bsludge%26hl%3Dno%26sa%3DX%26rlz%3D1T4GGLL_noNO403NO403%26biw%3D1366%26bih%3D644%26tbm%3Disch%26prmd%3Divnsb&itbs=1&iact=hc&vpx=1083&vpy=93&dur=6438&hovh=183&hovw=240&tx=60&ty=30&page=1&ndsp=15&ved=1t:429,r:4,s:0

[17] Biofilm figure.
Available from:
http://mathbio.colorado.edu/mediawiki/images/Biofilm.jpg

[18]: Kommedal, R., Ydstebø, L.,*Biological waste water treatment.* Lecture notes, Renseteknikk, 2006.

[19]: Properties of acetic acid.
Available from:
http://en.wikipedia.org/wiki/Acetic_acid

[20]: Properties of propionic acid.
Available from:
http://en.wikipedia.org/wiki/Propanoic_acid

[21]: Wold, Anders., *Anaerob behandling av avfallsvann med innhold av etylenglykoler,* Master Thesis, University of Stavanger, 2009

[22]: Lloyd, R.A., *Pressure effects on marine biodegradation of low molecular weight aromatics,* Master Thesis, University of Stavanger, 2005

[23]: Properties of n-hexane.
Available from:

http://www.inchem.org/documents/icsc/icsc/eics0279.htm

[24]: Lee, E.H., Kim, J., Cho , K.S., Ahn, Y.G., Hwang, G.S., *Degradation of hexane and other recalcitrant hydrocarbons by a novel isolate, Rhodococcus sp. EH831* Environ Sci Pollut Res, 2009, 17: p. 64–77

[25]: Chidambara Raj, C.B., Ramkumar, N., Haja Jahabarb Siraj, A., Chidambaram, Sp., *Biodegradation of acetic, benzoic, isophalic, toluic and terephthalic acids using a mixed culture: Effluents of PTA Profuction,* Institution of Chemical Engineers , 1997, p:245-256

[26]: Littlejohns, J.V., Daugulis, A.J., *Kinetics and interactions of BTEX compounds during degradation by a bacterial consortium,* Process Biochemistry, 2008, 43 p. 1068–1076

[26] Casey, E.,Glennon, B., Hamer, G., *Review of membrane aerated biofilm reactors*, Conservation and Recycling, 1999, 27 p. 203–215

[27] Rittmann, B.R., *The membrane biofilm reactor is a versatile platform for water and wastewater treatment*, Environ. Eng. Res. Vol. 12, No. 4, 2007, p.157-175

Appendix 1:

At 30ºC:

At 30 degrees celcius

SRT 6,7 d

X_A	V	MLSS	Sludge production	oxygen demand
mg/l	m^3	mg/l	kg/d	kg/d
1000	15086	1389	3127	10966
2000	7543	2778	3127	10966
3000	5029	4167	3127	10966
4000	3772	5556	3127	10966
5000	3017	6944	3127	10966
6000	2514	8333	3127	10966
7000	2155	9722	3127	10966
8000	1886	11111	3127	10966
9000	1676	12500	3127	10966
10000	1509	13889	3127	10966
11000	1371	15278	3127	10966
12000	1257	16667	3127	10966
13000	1160	18056	3127	10966
14000	1078	19444	3127	10966
15000	1006	20833	3127	10966
16000	943	22222	3127	10966
17000	887	23611	3127	10966
18000	838	25000	3127	10966
19000	794	26389	3127	10966
20000	754	27778	3127	10966
21000	718	29167	3127	10966
22000	686	30556	3127	10966
40000	377	55556	3127	10966
50000	302	69444	3127	10966

SRT 2.7 d

X_A	V	MLSS	Sludge production	oxygen demand
mg/l	m^3	mg/l	kg/d	kg/d
1000	8284	1389	4261	9922
2000	4142	2778	4261	9922
3000	2761	4167	4261	9922
4000	2071	5556	4261	9922
5000	1657	6944	4261	9922
6000	1381	8333	4261	9922
7000	1183	9722	4261	9922
8000	1035	11111	4261	9922
9000	920	12500	4261	9922
10000	828	13889	4261	9922
11000	753	15278	4261	9922
12000	690	16667	4261	9922
13000	637	18056	4261	9922
14000	592	19444	4261	9922
15000	552	20833	4261	9922
16000	518	22222	4261	9922
17000	487	23611	4261	9922
18000	460	25000	4261	9922

19000	436	26389	4261	9922
20000	414	27778	4261	9922
21000	394	29167	4261	9922
22000	377	30556	4261	9922
40000	207	55556	4261	9922
50000	166	69444	4261	9922

SRT 0.67 d

X_A	V	MLSS	Sludge production	oxygen demand
mg/l	m^3	mg/l	kg/d	kg/d
1000	2519	1389	5222	9038
2000	1260	2778	5222	9038
3000	840	4167	5222	9038
4000	630	5556	5222	9038
5000	504	6944	5222	9038
6000	420	8333	5222	9038
7000	360	9722	5222	9038
8000	315	11111	5222	9038
9000	280	12500	5222	9038
10000	252	13889	5222	9038
11000	229	15278	5222	9038
12000	210	16667	5222	9038
13000	194	18056	5222	9038
14000	180	19444	5222	9038
15000	168	20833	5222	9038
16000	157	22222	5222	9038
17000	148	23611	5222	9038
18000	140	25000	5222	9038
19000	133	26389	5222	9038
20000	126	27778	5222	9038
21000	120	29167	5222	9038
22000	115	30556	5222	9038
40000	63	55556	5222	9038
50000	50	69444	5222	9038

At 20ºC:

SRT 13.3

X_A	V	MLSS	Sludge production	oxygen demand
mg/l	m^3	mg/l	kg/d	kg/d
1000	26175	1389	2733	11328
2000	13087	2778	2733	11328
3000	8725	4167	2733	11328
4000	6544	5556	2733	11328
5000	5235	6944	2733	11328
6000	4362	8333	2733	11328
7000	3739	9722	2733	11328
8000	3272	11111	2733	11328
9000	2908	12500	2733	11328
10000	2617	13889	2733	11328
11000	2380	15278	2733	11328
12000	2181	16667	2733	11328
13000	2013	18056	2733	11328

14000	1870	19444	2733	11328
15000	1745	20833	2733	11328
16000	1636	22222	2733	11328
17000	1540	23611	2733	11328
18000	1454	25000	2733	11328
19000	1378	26389	2733	11328
20000	1309	27778	2733	11328
21000	1246	29167	2733	11328
22000	1190	30556	2733	11328
40000	654	55556	2733	11328
50000	523	69444	2733	11328

SRT 5.346

X_A	V	MLSS	Sludge production	oxygen demand
mg/l	m^3	mg/l	kg/d	kg/d
1000	15210	1389	3952	10207
2000	7605	2778	3952	10207
3000	5070	4167	3952	10207
4000	3803	5556	3952	10207
5000	3042	6944	3952	10207
6000	2535	8333	3952	10207
7000	2173	9722	3952	10207
8000	1901	11111	3952	10207
9000	1690	12500	3952	10207
10000	1521	13889	3952	10207
11000	1383	15278	3952	10207
12000	1268	16667	3952	10207
13000	1170	18056	3952	10207
14000	1086	19444	3952	10207
15000	1014	20833	3952	10207
16000	951	22222	3952	10207
17000	895	23611	3952	10207
18000	845	25000	3952	10207
19000	801	26389	3952	10207
20000	761	27778	3952	10207
21000	724	29167	3952	10207
22000	691	30556	3952	10207
40000	380	55556	3952	10207
50000	304	69444	3952	10207

SRT 1.33

X_A	V	MLSS	Sludge production	oxygen demand
mg/l	m^3	mg/l	kg/d	kg/d
1000	4883	1389	5099	9151
2000	2441	2778	5099	9151
3000	1628	4167	5099	9151
4000	1221	5556	5099	9151
5000	977	6944	5099	9151
6000	814	8333	5099	9151
7000	698	9722	5099	9151
8000	610	11111	5099	9151
9000	543	12500	5099	9151

10000	488	13889	5099	9151
11000	444	15278	5099	9151
12000	407	16667	5099	9151
13000	376	18056	5099	9151
14000	349	19444	5099	9151
15000	326	20833	5099	9151
16000	305	22222	5099	9151
17000	287	23611	5099	9151
18000	271	25000	5099	9151
19000	257	26389	5099	9151
20000	244	27778	5099	9151
21000	233	29167	5099	9151
22000	222	30556	5099	9151
40000	122	55556	5099	9151
50000	98	69444	5099	9151