University of Stavanger

FACULTY OF SCIENCE AND TECHNOLOGY

MASTER'S THESIS

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Titel of thesis: Possible inhibitory effect of selected detergents used in food industry on wastewater treatment and especially on Grødaland wwtp.	
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Key words: Activated Sludge Detergents Inhibition Oxygen Uptake Rate Respirometry	Pages: 68…… + enclosure: …… Stavanger, 15.06.20012

Abstract

Grødaland waste water treatment plant (wwtp) is treating industrial waste water coming from food industry. As food industry consumes large amounts of detergents for food processing equipment cleaning, the wwtp receives wastewater contains large amount of chemicals.

The presence of high detergents concentration in biological wwtp may interact with active biomass resulting in lower treatment efficiency.

The goal of this project was to look at the possible effects of detergents used in upstream facilities on Grødaland wwtp.

Based on industrial chemical consumption, a model was created in order to calculate the maximum concentration of each detergent in the reactor. Respirometric inhibition test were performed according to the model results.

The maximum concentration of the various detergents varies between 0.5 and 143 ml/m^3. As the range was wide, different testing ranges were defined.

The inhibition experiments on the 17 chemicals results in constant inhibition with increasing concentration on 2 decades. Only one chemical shows high inhibition at the highest concentration but as this concentration was almost 10 times higher than the maximum concentration, it has been status that under normal conditions or under more of concentrated ones, the presence of chemical should not impact the waste water treatment process.

Acknowledge

I would like to say thank you to my friend for their help and their advices,

My supervisor Roald Kommedal for his guidance and his help during all my master degree,

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List of Abbreviations

SBR	Sequenced Batch Reactor
HRT	Hydraulic Retention Time
COD	Chemical Oxygen Demand
BOD	Biological Oxygen Demand
ECx	Effect concentration of x%
NOEC	Non Effect Concentration
OUR	Oxygen Uptake Rate
Av	Average
Std ded	Standard Deviation
VSS	Volatile Suspended solids
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
WWTP	Waste water treatment plant

1. INTRODUCTION

Food industry is an industry consuming very large amount of various detergents for food processing equipment cleaning and disinfection. When those chemicals are used, they normally drain into the sewer system where they follow waste water stream to a waste water treatment plant. Grødaland is a biological wwtp treating waste water coming from mainly food industry in the Varhaug and Nærbø region. As this water may contain high concentration of detergents, the waste water treatment process may be disturbed due to the interaction with microorganisms resulting in lower treatment efficiency.

Possible effects of chemicals on active biomass is an important subject of study in order to find if they have an impact on the treatment. In case some effects are identified, measures can be applied in order to balance those effects.

In the case of Grødaland wwtp, we know the detergents used and their amount. From theses information, the concentration in the wwtp can be model and some inhibition test can be performed.

2. BACKGROUND/THEORY

2.1 Respirometry and Static respirometry

Respirometry is a common way to measure biomass activity. It consists in measuring the oxygen consumption rate under aerobic condition. The presence of toxic compound lowers the biomass activity resulting in reduced oxygen uptake rate (OUR).

In order to analyze toxicity of a certain compound, OURs in presence of various doses of toxicant are compared to OURs in non inhibitory conditions. One of the result of respirometric test is the EC50 value that show the inhibitory compound concentration needed to have an OUR 50% lower than in non inhibited conditions.

BOD measurement using static respirometry is based on barometric measurement of oxygen partial pressure inside a closed batch test system. During measurement, microorganisms consume oxygen and release carbon dioxide which is absorbed by a NaOH solution in the system headspace. Oxygen consumption results in a pressure drop inside the bottle, and by measuring the pressure drop in real time BOD time series of degradation can be presented. By simultaneously monitoring of temperature, initial air pressure, liquid and total system volumes, liquid phase oxygen consumption in mg/l (equation 1 [1]) may be estimated. This method is usually used for biodegradation test with OECD method 301f [2].

$$BOD = \frac{M(O_2)}{R * T_m} * \left(\frac{V_t - V_l}{V_l} + \alpha \frac{T_m}{T_0}\right) * \Delta p(O_2) \qquad (1)$$

$M(O_2)$	Molecular weight (32000 mg/mol)
R	Gas constant (83,144 l.mbar/mol.K)
T_0	Reference temperature (273,15K)
T_m	Measuring temperature in K
V_t	Bottle volume (nominal volume in ml)
V_l	Sample volume in ml
α	Bunsen absorption coefficient (0,03103)
$\Delta p(O_2)$	Difference of oxygen partial pressure (mbar)

2.2 Inhibition definition

Inhibition and toxicity are two concepts based on the effects of physical or chemical agents on cells. Inhibition is defined as the decrease in the enzymatic activity of the cell or the direct damage to the cell structure. When the inhibited reaction is vital for the cell then this compound is defined as toxic. When a cell is inhibited, results are lower growth rate due to higher difficulty to take up nutrients[3].

The toxicity of a medium is a continuum: it varies from medium with very degradable compounds to medium in which the cell activity ceases after very short contact. Toxicity is also linked to the concentration of the toxicant, from a concentration for which there is no or extremely low effect (NOEC) to a concentration at which the cell die.

This concentration also depends on previous exposure of the cell to the same compound: as the cell stay in contact especially for long time and at low concentrations, it may become more tolerant to the chemical to a level where the inhibitory compound may be used as substrate.

This possibility of adaptation is used to acclimatize the biomass to toxic compounds in order to lower their impact on the waste water treatment. The effect of toxic compound on wastewater treatment plant biomass are lower treatment efficiency, possibility of lower separation efficiency due to flocs division resulting in lower effluent quality and a higher impact on the receiving environment [3].

2.3 Classes of inhibition

There are different classes of inhibition based on how the inhibitory compound interacts with cells and especially with the enzymatic system.

The normal function of an enzyme consists in the attachment with a substrate leading to the release one product and the original enzyme.

$E + S \leftrightarrow S^* \rightarrow P + E$

E, S and P represent enzyme, substrate and product respectively while S* represents the enzyme-substrate complex. The last step is considered as the slower step defined by k_2 and the substrate/enzyme attachment is considered as equilibrium with k1 defining the forward reaction while k-1 the reverse one.

This mechanism gives the michaelis-Menten kinetics expression:

$$r_s = \frac{r_{s,max} * S}{k_s + S}$$

With $k_s = \frac{k_{-1}+k_2}{k_1}$

r_s the specific degradation rate
k_x the rate coefficient
S substrate concentration
I the inhibitor concentration

The presence of a substance may interfere at one stage of the reaction. Three types of interaction exist: either with the same active site of the enzyme (competitive inhibition), with a different site (non- competitive inhibition) or with the active complex himself (un-competitive inhibition). In all cases, the product is not formed after the interaction with the inhibitor [3].

2.3.1 Competitive inhibition

E + S ⟷ S* → P + E
E + I ⟷ I*

In this case, the inhibitor is taking the same site than the substrate. As the 2 compounds are using the same site, the affinity of the substrate toward the enzyme is modified.

$$r_s = \frac{r_{s,max} * S}{k_s(1+\frac{I}{k_i}) + S}$$

ki represents the affinity of the inhibitor and is inversely proportional to the inhibition power. Inhibition= $\alpha\frac{1}{k_i}$

2.3.2 Non-Competitive inhibition

The substrate and the inhibitor are not using the same site. So 3 reactions are possible the normal one leading to the product, and 2 more where the enzyme react with the inhibitor or the substrate leading to the formation of one complex himself reacting with the complementary compound.

E + S ⟷ S* → P + E
E + S ⟷ S* + I → SI*
E + I ⟷ I* + S → IS*

The kinetic equation of these reactions can be described by:

$$r_s = \frac{r_{max} * S}{(k_s + S)(1+\frac{I}{k_i})}$$

One case of non-competitive inhibition is the product inhibition.

$$r_s = \frac{r_{max} * S}{(k_s + S)(1+\frac{P}{k_p})}$$

2.3.3 Un-Competitive inhibition

In the case of un-competitive inhibition, the inhibitor attached to the enzyme-substrate complex blocking the product formation.

E + S ⟷ S* → P + E
E + S ⟷ S* + I → SI*

$$r_s = \frac{r_{max} * S}{k_s + S(1 + \frac{I}{k_i})}$$

One special form of un-competitive exists. It's the case when substrate can react with the enzyme but also with the enzyme/substrate complex resulting in the absence of product formation.

E + S ⟷ S* → P + E
E + S ⟷ S* + S → SS*

In this particular case, the kinetic model becomes:

$$r_s = \frac{r_{max} * S}{k_s + S + \frac{S^2}{k_i}}$$

This equation have a maximum rate for a substrate concentration of $s_{crit} = (k_s k_i)^{1/2}$.

2.3.4 Mixed case inhibition

This case consist inhibitor with competitive and un-competitive properties.

$$r_s = \frac{r_{max} * S}{k_s(1 + \frac{I}{k_i}) + S(1 + \frac{I}{k'_i})}$$

2.4 Previous works on inhibitions

The effect of inhibitory compounds on activated sludge has been studied in many articles. But from those the major part talks about heavy metals.

In 2007, Bodik et al. studied the effect of various disinfectants on activated sludge. Their test concentrations were fixed between 0.1 and 1 ml/l. Their results shown that disinfectant based on sodium hypochlorite were highly inhibiting activated sludge from low concentration (0,1 or 0,2 depending on the disinfectant) while disinfectant based on other active compounds had low effect or even no effect on activated sludge at the same concentrations.

Figure 1 show the inhibition in presence of 0,3ml/l of various compounds based on NaOCl. [4]

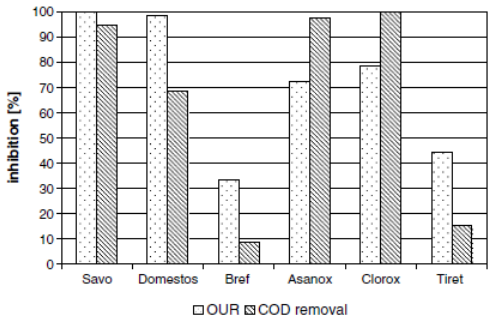


Figure 1: Comparison of NaOCl based disinfectant at the concentration of 0,3ml/l

Inhibition is an effect that varies with the concentration. Figure 2 show a typical inhibition curve (in this case 3,5 dichlorophenol from OECD 209 method). We can observe that the inhibition is a continuum consisting in 3 phases: one with no inhibition then an increase until reaching a value close to 90-100% then a last stable phase.

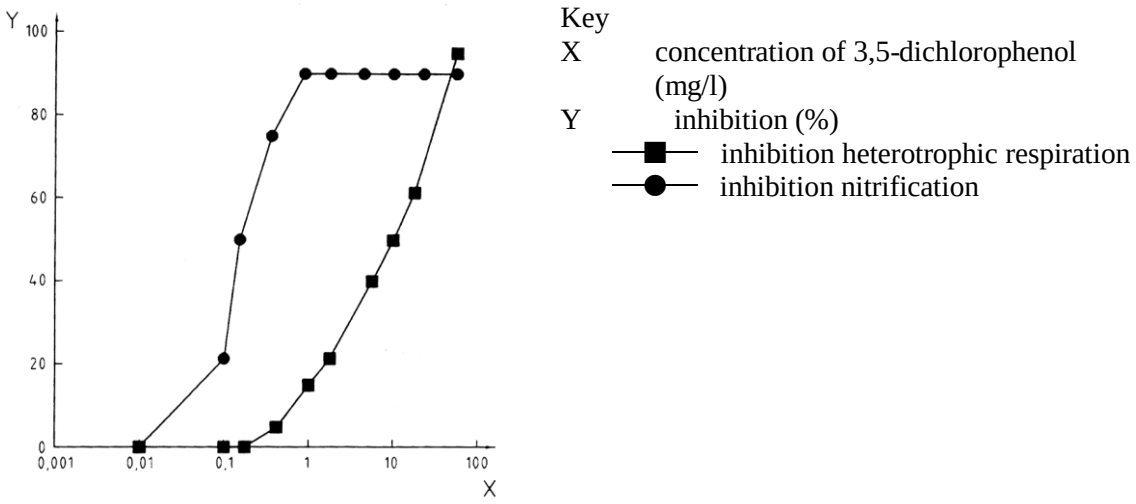


Figure 2: typical inhibition curve

2.5 Different type of chemicals

Detergents are chemical solutions containing some active components. The inhibitory properties of detergents are then linked to its constituents.

This chapter is looking at the tested detergents, their active compounds and how they interact with microorganisms.

Table 1 is summarizing the detergents data sheets information on the chemical composition.

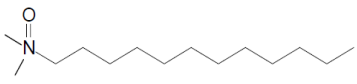
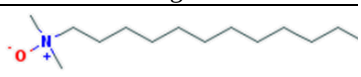
Table 1 : List of detergents and their chemical composition

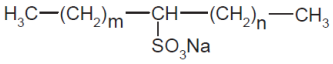
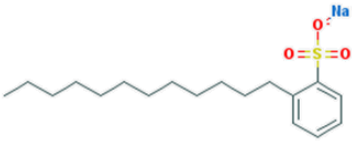
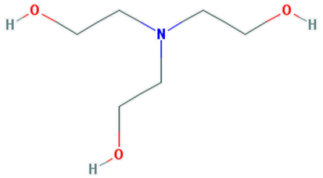
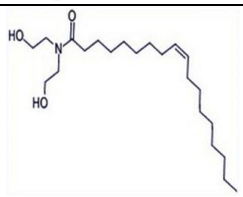
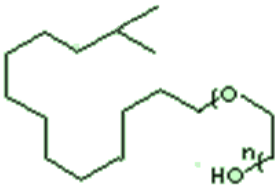
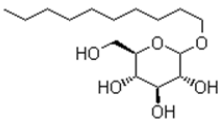
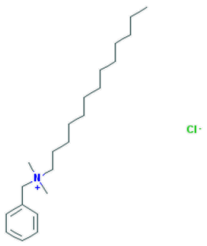
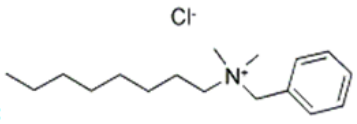
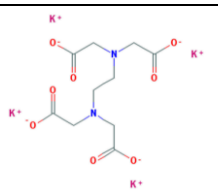
Detergents	Constituents
Addi SU 935 [5]	5-10% Dodecylbenzenesulfonic Acid; 5-10% Glycolic acid; 10-30% Citric acid deshidrated;
Addiquat SU 321 [6]	5-10% benzyl-C12-16-alkyldimethyl; 5-10% iso tridecanol ethoxylate; 1-5% Coconut diethanolamide; 5-10% EDTA-Na4;
Titan Hypo [7]	5-15% Sodium hypochlorite; <2% Sodium hydroxide;
Titan 951 [8]	5-15% benzyl-C12-16-alkyldimethyl; 5-15% Fettalkohol alkoksilat ; >30% water;
Climax TK [9]	<5% Sodium hypochlorite; 10-30% Potassium silicate;
Alka des [10]	15-24 % benzylcoco alkyldimethyl, chlorides;
Addi SU 932 [11]	5-10% Sodium hydroxide; 1-5% Sodium hypochlorite; 1-5% Lauryl dimethylamine oxide;
Titan Kassevask XL [12]	>30% Potassium hydroxide; 5-15% EDTA 4K-salt;
Mip Ea [13]	25-30% Potassium hydroxide; 5-10% EDTA; 2-5% Sodium hydroxide; 0.25-0.5% Fettalkoholalkoksilat;
Basol M [14]	1-5% Potassium phosphate; 1-5% Potassium hydroxide;
ACO hygene skum Alkaklor [15]	1-5% Potassium hydroxide; 1-5% Sodium hydroxide; 1-5% Sodium hypochlorite;
TP 66 [16]	2.5-5% Sodium hypochlorite; 2-5% Sodium hydroxide; 1-5% C12-16-alkyldimethyl;
Ecofoam CL [17]	2-5% Sodium hydroxide; 2-5% Sodium hypochlorite; 2-5% Alkyl (c10-16) dimethyl amine oxide;
Top Active des [18]	5-10% Hydrogen peroxide; 5-10% Acetic acid; 2-5% C12-16-alkyldimethyl; 1-2% perAcetic acid;
TP 36 [19]	25-30% Sodium hydroxide; 5-10% decyl glycosides; 2-5% Potassium hydroxide;
CIP ACID [20]	5-15% Sulfamic acid; <5% Formic acid; <5% Sulfuric acid;
Addi SU 931 [21]	<5% triethanolamine; 5-10% Alkane sulfonate; <5% EDTA-Na4;

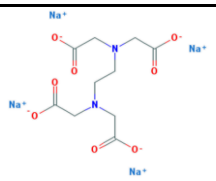
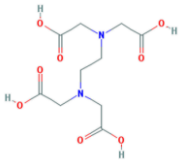
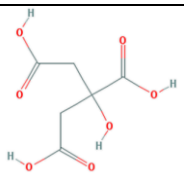
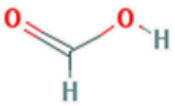
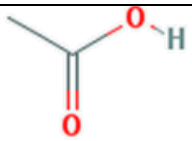
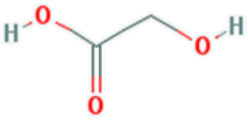
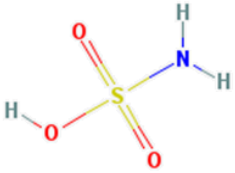
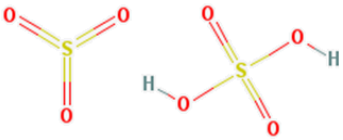
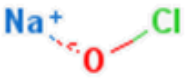
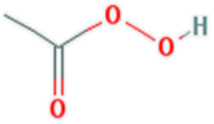
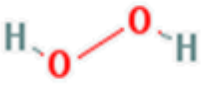
From table 1 information, researches have been done in order to get active conpounds chemicals properties.

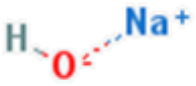
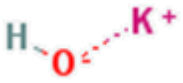
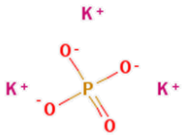
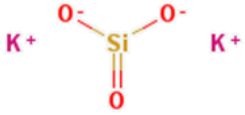
Table 2 shows chemical formula, structure and family of components constituting the tested chemicals.

Table 2 : List of chemical components used in the tested detergents

family	name	Cas nbr	Chemical formula	Chemical structure
Anionic surfactant	Amines, C12-16-alkyldimethyl, N-oxides [22] [23]	85408-49-7	$C_{14\text{-}18}H_{31\text{-}39}NO$	
Anionic surfactant	Amine oxides, cocoalkyldimethyl	61788-90-7		Same type of chemical structure as above with different tail length
Anionic surfactant	LAURYL DIMETHYLAMINE OXIDE	70592-80-2	$C_{15}H_{33}NO$	

family	name	Cas nbr	Chemical formula	Chemical structure
Anionic surfactant	Alkane sulfonate [24]	85711-69-9		
Anionic surfactant	Dodecylbenzenesulfonic Acid [25] [26]	27176-87-0	$C_{18}H_{30}O_3S$	
nonionic surfactant	triethanolamine	102-71-6	$C_6H_{15}NO_3$	
nonionic surfactant	Coconut diethanolamide	68603-42-9	$C_{22}H_{43}NO_3$	
nonionic surfactant	iso tridecanol ethoxylate [27] [28] [29]	69011-36-5	$C_{14}H_{29}(OCH_2CH_2)_nOH$	
nonionic surfactant	decyl glycosides	68515-73-1	$C_{16}H_{32}O_6$	
Quaternary ammonium compounds	benzylcoco alkyldimethyl, chlorides	61789-71-7	$C_{22}H_{40}ClN$	
Quaternary ammonium compounds	benzyl-C12-16-alkyldimethyl	68424-85-1	$C_{17}H_{30}ClN$	
	EDTA 4K-salt	5964-35-2	$C_{10}H_{12}N_2O_8K_4$	

	EDTA 4Na-salt	64-02-8	$C_{10}H_{12}N_2O_8Na_4$	
	EDTA	64-02-8	$C_{10}H_{16}N_2O_8$	
Organic acid	Citric acid deshidrated [30]	77-92-9	$C_6H_8O_7$	
Organic acid	Formic acid	64-18-6	CH_2O_2	
Organic acid	Acetic acid	64-19-7	$C_2H_4O_2$	
Organic acid	Glycolic acid	79-14-1	$C_2H_4O_3$	
Inorganic acid	Sulfamic acid	5329-14-6	H_3NSO_3	
Inorganic acid	Sulfuric acid	8014-95-7	$H_2S_2O_7$	
Halogen realizing agent	Sodium hypochlorite	7681-52-9	NaOCl	
peroxygens	perAcetic acid	79-21-0	$C_2H_4O_3$	
peroxygens	Hydrogen peroxide [31]	7722-84-1	H_2O_2	

family	name	Cas nbr	Chemical formula	Chemical structure
Strong base	Sodium hydroxide	1310-73-2	NaOH	
Strong base	Potassium hydroxide	1310-58-3	KOH	
	Potassium phosphate	7778-53-2	K_3O_4P	
	Potassium silicate	10006-28-7	K_2SiO_3	

As table 1 and 2 were looking at the chemical properties of the chemical components, Table 3 is showing the mechanisms of action and targets of various types of chemical.

Table 3 : targets and mechanism of action of the different type of chemical used as biocide

Target	Antiseptic or disinfectant	Mechanism of action
Cell envelope (cell wall, outer membrane)	Glutaraldehyde	Cross-linking of proteins
	EDTA, other permeabilizers	Gram-negative bacteria: removal of Mg2_, release of some LPS, Metal ion chelation
Cytoplasmic (inner) membrane	QACs	Generalized membrane damage involving phospholipid bilayers
	Chlorhexidine	Low concentrations affect membrane integrity, high concentrations cause congealing of cytoplasm
	Diamines	Induction of leakage of amino acids
	PHMB, alexidine	Phase separation and domain formation of membrane lipids
	Phenols	Leakage; some cause uncoupling
	Anionic surfactants	Membrane-protein solubilization
	Organic acid, Ester	proton motive force disruption and transport processes inhibition
Cross-linking of macromolecules	Formaldehyde	Cross-linking of proteins, RNA, and DNA
	Glutaraldehyde	Cross-linking of proteins in cell envelope and elsewhere in the cell
DNA intercalation	Acridines	Intercalation of an acridine molecule between two layers of base pairs in DNA
Interaction with thiol groups	Silver compounds	Membrane-bound enzymes (interaction with thiol groups)
Effects on DNA	Halogens	Inhibition of DNA synthesis

Target	Antiseptic or disinfectant	Mechanism of action
	Hydrogen peroxide, silver ions	DNA strand breakage
Oxidizing agents	Halogens	Oxidation of thiol groups to disulfides, sulfoxides, or disulfoxides
	Peroxygens	Oxydationand disruption of thiol groups in proteins and enzymes

The table 3 has been adapted from [32] and completed from [33] and [34].

Tables 1 and 2 show that tested detergents contains mainly surfactant, organic acids, peroxygen and halogen. So according to this information and the table 3, the principal targets of the detergents are inner and outer membranes, DNA and oxidizing agents.

2.6 Substrate effect on inhibition

The type of substrate may affect the response of microorganisms toward an inhibitory compound. Indeed as substrate affects the biochemical reactions and the enzymes involved, the inhibitory compound will continue to react to the same enzyme but this one will have less impact as the reactive substrate is not present.

In order to test the effects of substrate on inhibition, cokgor et all conducted inhibition experiment on Nickel with different substrates: *glucose*, a starch acetic acid mixture, an easily biodegradable substrate, and a peptone-meat extract (five-components) mixture. [35]

Table 4 show the EC50 value of nickel in presence of these 4 substrates

Table 4 : effect of substrate on nickel EC50 value

Substrate type	Ec50 (mg/L)
Peptone-meat extract mixture (ISO substrate)	33
Glucose	180
Readily biodegradable synthetic substrate mixture	182
Starch-acetic acid	145

2.7 Effect of acclimation

Acclimation is the process also called adaptation that occurs when microorganisms change their metabolism due to an external stress caused by some changes in the surrounding environment. As biological adaptation take place organisms become more resistant to the inhibitory compound.

Acclimatized biomass has been observed to have lower growth rate than unacclimatized one [36]. One phenomenon to explain this lowering in the μ value is a change in the microbial community toward a more specialized one with lower growth rate. [37]

As acclimation consists in having more resistant bacteria, the resulting EC50 becomes higher after acclimation[36].

2.8 Effect of sludge age

EC_{50} of 2-chlorophenol and of 2,4-dichlorophenol have been found to increase with longer sludge age.[38]

Two reasons may explain this increase: on one hand, as the solid retention time increase, the MLSS increase resulting in more active biomass concentration, on the other hand, as we saw in the acclimation part, acclimation may consists in the increase of more specialized biomass with lower growth rate, in this case a longer SRT can allow them to multiply easily.

2.9 Objective

The objective of this thesis is to look for the possible inhibitory effect of selected detergents used in food industry on wastewater treatment and especially on Grødaland wwtp. Based on the detergents list and doses, dilution model was made and static respirometric tests were performed.

3. MATERIAL AND METHOD

This section presents how inhibition analysis has been conducted. It is divided in two subparts the modelisation section and the inhibition testing.

3.1 Dilution modelisation

Modelisation of the sewer system was the first step of the experimental work. The main idea was to create a model that provides the chemical concentration in the waste water treatment plant based on known parameters Ci=f(mass, hydraulic loading, volumes,…).

The program AQUASIM was designed for the identification and simulation of aquatic systems. It consists in 4 subsections: variables, process, compartments and links.

As we are looking at a dilution, no process will be taken in account.

3.1.1 Known informations.

Grødaland WWTP consists in one flotation unit, one equilibration tank and three sequenced batch reactors (SBR). Volumes, cycle duration and hydraulic loading values are in table 5.

Table 5 : Grødaland wwtp design informations

parameters	value	unit
Flotation unit volume	430	m^3
Equilibration tank volume	1000	m^3
SBR maximum volume	700	m^3
SBR cycle duration	4	h
Hydraulic loading Qin min/av/max	2500/3500/7000	m^3/d

3.1.2 Define the sbr cycle.

In order to model the reactors, we had to define which in type they consist. Flotation and equilibration tanks were defined as mixed reactor with constant volumes while SBRs was defined as mixed reactor with variable volume. SBR cycle was defined to last 4 hours and 3 SBRs are working in parallel starting one after the other. So every 1,33h one new reactor starts his cycle and during this time the water coming from the equilibration tank is flowing to this reactor. When the reactor is filled up, the volume remains constant until it starts to diminish to end up at the initial one.

The duration of the stationary phase depend on the outflow. Higher is the outflow shorter the emptying phase last. As the emptying of the reactor don´t influence the concentration, the outflow has been assumed to be equal to the inflow. So the cycle is divided in 3 equal phases of 1,33h each.

Now that the cycle has been defined, the minimum volume should be calculated based on the inflow. $\Delta V = Qin * 1{,}33$ with Qin in m³/h

In the model the hydraulic loading was fixed to 100 m³/h (approx dry weather conditions) because lower is the flow rate lower is the dilution. So the minimum volume of the reactor is defined as 567 m³.

One extra compartment has been created to be used as outlet.

In order to simplify the model only one SBR has been model. When this reactor is at maximum volume, the water flow is directed to the outlet.

3.1.3 Define the variables.

In order to model the dilution, 7 variables have been defined. Table 6 shows these variables and in which type they consists.

Table 6 : Variables and their types

variables	Type of variable
Concentration Ci	State variable
Inlet concentration Ci_inlet	Real list variable
Water loading Qin	Formula variable
Reactor inlet flow Qr	Real list variable
Reactor outlet flow Q_out	Real list variable
Time t	Program variable
Reactor volume Vr	Probe variable

Based on the previous statements, one of these variables cannot be defined: indeed in order to create the inlet concentration one parameter should be define. This parameter is the application duration (flushing time Ft) and it shows how broad and concentrated will be the plugflow arriving at the wastewater treatment plant. So C_inlet consist in three phases: one period with a concentration of 0, one of duration Ft and of concentration C_inlet, and one last period with a concentration of 0.

3.1.4 Define the links.

Two links should be created for the model: one from flotation to the equilibration tank and one from the equilibration to the outlet with a bifurcation of water flow Qr to the SBR (table 7).

Table 7 : list of links

links	From/to	bifurquation	Waterflow of biffurquation
Link1	Flotation/equilibration	no	
Link 2	Equilibration/outlet	To the SBR	Qr

The main sewer arriving at the wwtp (plugflow reactor) was not model outlets of industries have been assumed to be directly linked to the flotation unit. This assumption result in a slightly increase of the chemical concentration in the WWTP due to the absence of the plugflow dispersion.

3.2 Inhibition analysis

OECD 209 is the standard method for inhibition analysis on activated sludge. [39]

This standard method has been modified in order to respond to OUR needs. The following chapter explains how inhibition experiments were performed.

3.2.1 Static respirometry system.

Static respirometric test has been performed using Oxitop-C head from WTW. The utilization of this equipment has some consequences. As the system is closed, the maximum oxygen available is fixed defining a range of measurement. This range is related to the volume of the bottle and the liquid content. The liquid volume was set to 100ml in order to get a range that can allow the inhibitory experiments. For a liquid volume of 100ml in 510 ml bottles, the BOD range was 850mg/l.

3.2.2 Inoculums and substrate.

Activated sludge from Vik wwtp was used during 4 set of experiments then activated sludge from Grødaland wwtp was used due to the closing up of Vik wwtp.

Typical Activated sludge MLVSS is 3000mgVSS/l with a typical food to mass ration of 0,33 mgBOD/mg MLVSS.

The amount of sludge was set to 20ml per bottle resulting in a mass of volatiles suspended solids in the bottle is 60mgVSS. In order to keep the same food to mass ratio, the initial BOD content in the bottle should be 20 mgBOD. As the BOD content is approximately 2 time lower than the COD then the amount of COD needed in the bottle is 40mgCOD. We want a COD concentration in the liquid phase of CCOD=40mg/0,1l= 400mg/l

The synthetic sewage composition is known (see table 8), and the ThOD of the synthetic sewage correspond to the COD of peptone and yeast extract. The COD value for yeast extract is 1,5gCOD/$g_{extract}$ and for peptone 1,3gCOD/$g_{peptone}$. The synthetic sewage COD is then 1,5*11+10*1,3= 29,5gCOD/l. Based on the COD content of synthetic sewage, we decided to use 1ml of synthetic sewage per bottle.

The initial easily biodegradable COD in the bottle is 295 mgCOD/l.

The total COD concentration in the bottle is composed of the easily biodegradable COD due to synthetic sewage and slowly biodegradable COD due to VSS .

The initial slowly biodegradable COD can be calculated from the MLVSS:

Xvss=3000mgVSS/l

The particulate COD X_{COD}=Xvss*1,42gCOD/gVSS =4.26 gCOD/l

As the volume of sludge in the bottle has been set to 20 ml, the slowly biodegradable COD per bottle is $4.26*20*10^{-3}$=0.0852 gCOD or 852mgCOD/l as the liquid volume in the bottle is 100ml. On this total particulate COD, the slowly biodegradable COD fraction is around 50%.

The total biodegradable COD in the bottle is then equal to 295+426= 721 mgCOD/l .

The total biodegradable COD is in the measurement range so the experiments can be performed.

3.2.3 Abiotic

The abiotic control is one of the sample that have been the most modified from the method. Indeed, instead of sterilize the sample, some chemical (1g NaN3) was added in order to kill all micro organisms present. No reactions between sodium azid and detergents have been observed.

3.2.4 Solution preparation

Chemical solutions and synthetic sewage were the two types of solutions prepared during experiments.

Tested chemical concentrations were defined to vary between 0,1 and 1000 g/m3 (or ml/m3) with a liquid volume of 100ml (table 13). Dilutions were performed for each needed concentration and the volume of the final solution introduce in the bottle was fixed to 2ml. The concentration of the final solution became 5-50000 mg/l or µl/l. In order to prepare these diluted solutions, 1 or 2 dilutions were needed (table 8).

Table 8 : Synthetic sewage constituents and their concentrations

Final concentration in mg/l or µl/l	First dilution by	Second dilution by
5	100	2000
50	100	200
500	100	20
5000	200	/
50000	20	/

For the synthetic sewage, 100ml of solution were prepared the days of experiments in order to avoid change in composition. Table 9 shows the synthetic sewage composition.

Table 9 : Synthetic sewage constituents and their concentrations

Synthetic sewage constituents	Concentration in g/L
Peptone	10
Yeast extract	11
Urea	3
Sodium chloride (NaCl)	0,7
Calcium chloride dehydrate (CaCl2, 2H2O)	0,4
Magnesium sulphate monohydrated (MgSO4, H2O)	0,1
anhydrous potassium monohdydrogen phosphate (K2HPO4)	2,8

For the solutions preparation, 100ml volumetric flasks were used as recipient. The liquid volume were sampled using precision pipette according to the volume and solids using Mettler Toledo xp205 scale. Pipette biohit m5000 was used for 1000 to 5000 µl samples, thermoscientific finnpipette 200-1000 for 500 µl samples and biohit m100 for 50µl samples.

3.2.5 Bottle preparation

Twelve bottles were prepared for each chemical. These bottles consist in 3 tested concentrations with 3 parallels each, 1 blank at the beginning then 2 and 2 abiotics replaced by 1. Changes in blanks and abiotics number of bottles were done due to the low variability of abiotics compare to blanks.

Table 9 shows the different components constituting the samples.

Table 10 : kinetic parameters value at 5-10 and 20°C

component	Volume (ml)	Absent in
Chemical solution	2	blank
Synthetic sewage	1	
sludge	20	abiotic
Sodium azid NaN3	1g	All except abiotic
Tap water	Complement up to 100ml	

During the bottle preparation, sludge was shacked prior sampling in order to get homogenous concentration and sampled using 20ml syringe.

Chemical solution and synthetic sewage were sampled using pipette biohit m5000 and the filling of bottles with water was done using Sartorius LE6202P.

Sodium azid was measured using Mettler Toledo xp205 scale and added after water filling.

Then bottles were closed, started and put in cooled chamber at 10°C under magnetic mixing for 7days.

4. RESULT

This section presents the different results obtained during the modeling and the static respirometric tests. The first part shows the result on the concentration modeling in the wwtp and the definition of the tested concentrations while the second one shows the results on chemical inhibition.

4.1 Dilution model

The first step of our research project was to find out the maximum concentration of the different chemicals in the wastewater treatment plant.

The following chapter shows the results of this dilution modeling between upstream food processing industries and the Grødaland treatment plant reactors.

Daily consumption information has been given by identified industrial facilities upstram. Table 11 shows the different chemicals used and their daily consumption. As this table shows the total consumption between from all facilities, the utilization of these amounts assumes that the chemicals are used in the different industries at the same time. This assumption can be justified because all these detergents are used for cleaning at the end of the working day.

Table 11 : daily total consumption of detergents

Produktnavn	total consumption per day	
CIP ACID	3,5	l
Addi SU 931	5,2	kg
Addi SU 932	62,0	kg
Addi SU 935	6,5	kg
Addiquat SU 321	4,7	kg
Titan Hypo	3,3	kg
Titan Kassevask XL	19,2	kg
Titan 951	1,1	kg
Climax TK	2,2	l
Alka des	0,9	l
Ecofoam CL	66,0	kg
Mip Ea	2,0	kg
Top Active des	58,0	kg
TP 36, Ecolab	13,2	kg
ACO hygene skum Alkaklor	16,5	l
TP 66*	300,0	l
Basol M	1,1	l

*TP66 is used only once a week

Using the volume or the mass of chemical (from table 11) in addition to the typical flow rate of 2500 m^3/d and different flushing durations (time for which the chemical is totally removed and enter the sewer system), potential inlet concentration is calculated as follow:

$$Cinlet = \frac{Vc}{(\frac{Qin}{24 * 60} * Ft)}$$

Cinlet, the concentration at the entrance of the wwtp in ml/m3 or g/m3
Vc, the volume or the mass of detergent used daily upstream industrial facilities in ml or g
Ft, the flushing time in minutes
Qin, the hydraulic loading in m^3/d
The inlet concentration is defined by the dilution of the amount of chemical in one plug flow section of duration Ft. The volume of this section is calculated by Qin*Ft.

Based on the obtained inlet values, the model calculate the concentration in the different compartments (figure 3).

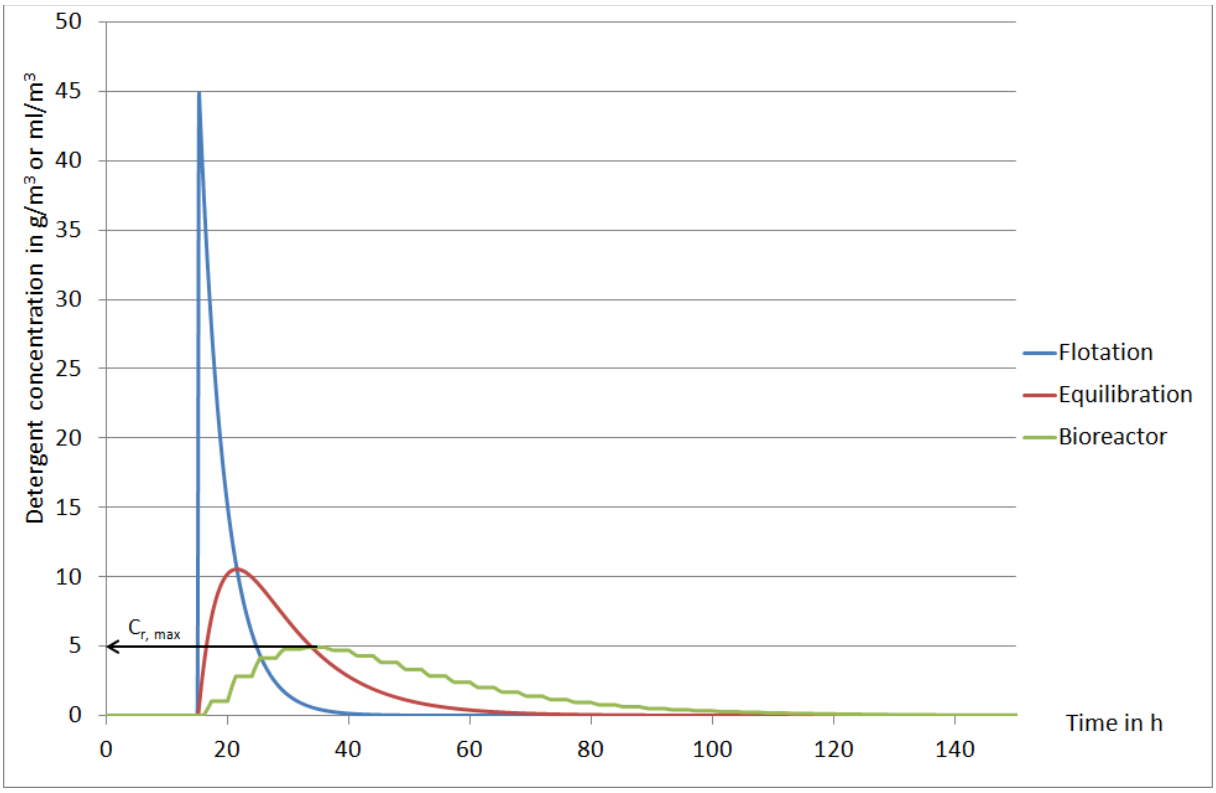


Figure 3: typical model dilution curve.

Maximum reactor´s concentration ($C_{r,max}$) were estimated at various application time (flushing duration) for the tested detergents. Table 12 shows the obtained concentrations.

Table 12 : effect of flushing time on SBR concentration

	Cr max				
Application time	6 min	12 min	24 min	60 min	
CIP ACID	1,7	1,2	1	0,87	ml/m3
Addi SU 931	2,5	1,9	1,6	1,35	g/m3
Addi SU 932	30	22	18,4	16	g/m3
Addi SU 935	3,1	2,3	1,9	1,7	g/m3
Addiquat SU 321	2,2	1,7	1,4	1,2	g/m3
Titan Hypo	1,6	1,2	1	0,87	g/m3
Titan Kassevask XL	9,2	6,9	5,7	5	g/m3
Titan 951	0,5	0,4	0,3	0,27	g/m3
Climax TK	1	0,8	0,6	0,57	ml/m3
Alka des	0,4	0,3	0,25	0,22	ml/m3
Ecofoam CL	31,5	23,5	19,5	17	g/m3
Mip Ea	1	0,7	0,6	0,5	g/m3
Top Active des	27,5	21	17	15	g/m3
TP 36, Ecolab	6,3	4,7	3,9	3,4	g/m3
ACO hygene skum Alkaklor	7,8	5,9	4,9	4,3	ml/m3
TP 66	143	107	98,3	78	ml/m3
Basol M	0,5	0,4	0,3	0,27	ml/m3

From table 12 we can observe that the maximum concentration is divided by approximately 2 when the flushing time is multiplied by 10 (from 6 to 60 min). From this information, we decided to use the concentration for 6 minutes as approximate test concentration.

In order to define the 3 test concentrations, we decide to test the detergents on 3 decades.
In order to define C1 (the lowest concentration), 3 logical equations were applied:
If Ci max/5 <1 then 0,1
If Ci max/5 >10 then 10
Else 1

Table 13 shows these tested concentrations.

Table 13 : defined tested concentration for inhibitory test

	tested concentrations			
	C1	C2	C3	
CIP ACID	0,1	1	10	ml/m3
Addi SU 931	0,1	1	10	g/m3
Addi SU 932	1	10	100	g/m3
Addi SU 935	0,1	1	10	g/m3
Addiquat SU 321	0,1	1	10	g/m3

	tested concentrations			
	C1	C2	C3	
Titan Hypo	0,1	1	10	g/m3
Titan Kassevask XL	1	10	100	g/m3
Titan 951	0,1	1	10	g/m3
Climax TK	0,1	1	10	ml/m3
Alka des	0,1	1	10	ml/m3
Ecofoam CL	1	10	100	g/m3
Mip Ea	0,1	1	10	g/m3
Top Active des	1	10	100	g/m3
TP 36, Ecolab	1	10	100	g/m3
ACO hygene skum Alkaklor	1	10	100	ml/m3
TP 66	10	100	1000	ml/m3
Basol M	0,1	1	10	ml/m3

From this table we can observe that the majority of chemicals enter the lowest range of 0,1-10 while the rest except one were in the second one.

4.2 Results on inhibition.

Based on model results, inhibition test were processed. This section presents the results from inhibition test.

4.2.1 Abiotic control and temperature gradient correction.

Abiotic control is a sample normally used to check the presence of a competing chemical reaction.

Figure 4 shows the results on abiotic controls that were performed for various chemicals. We can see that curves consist in 2 phases: on massive OUR at the beginning that last for 300 minutes followed by a phase with without any variations in BOD.

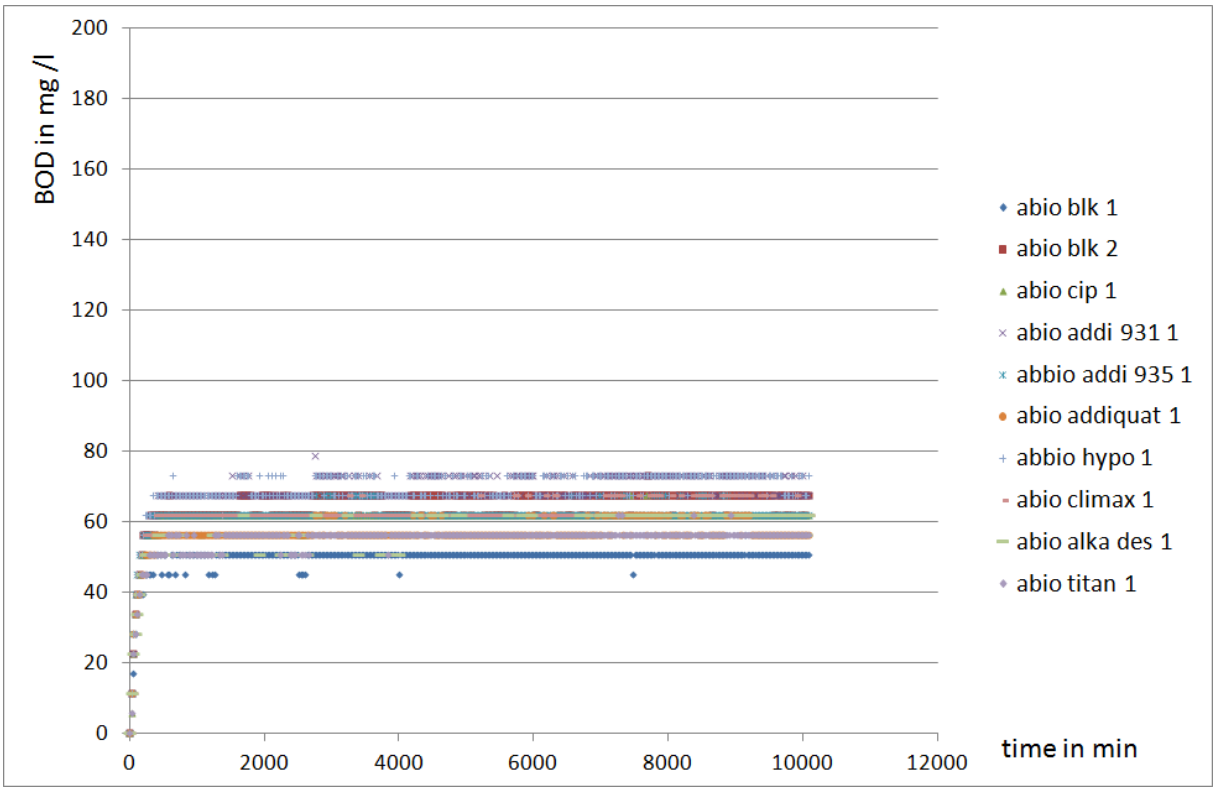


Figure 4: abiotic curves for various chemicals.

All samples plot on this graph have been tested together so the initial pressure was the same for all bottles. As the massive OUR is present for all the bottles, this phenomenon was probably due to one common parameter. During tests, the bottles have been closed before cooling from ambient temperature to 10°C the increase in BOD is due to the pressure drop caused by the cooling. The abiotic control has been subtracted to all BOD results in order to suppress the pressure variation.

4.2.2 OUR values

4.2.2.1 Analysis of Addi 935 results.

From static respirometry, we get the BOD in function of time with a step size of 26 min.

The first job in order to analyze the effect of a detergent dose was to plot the BOD in function of time after subtracting the abiotic. One graph was plotted per detergent concentration. Each graph contains the 3 parallels and the blanks in order to observe easily how the curves vary from the blank with the concentrations.

Figure 5 shows these curves for Addi935

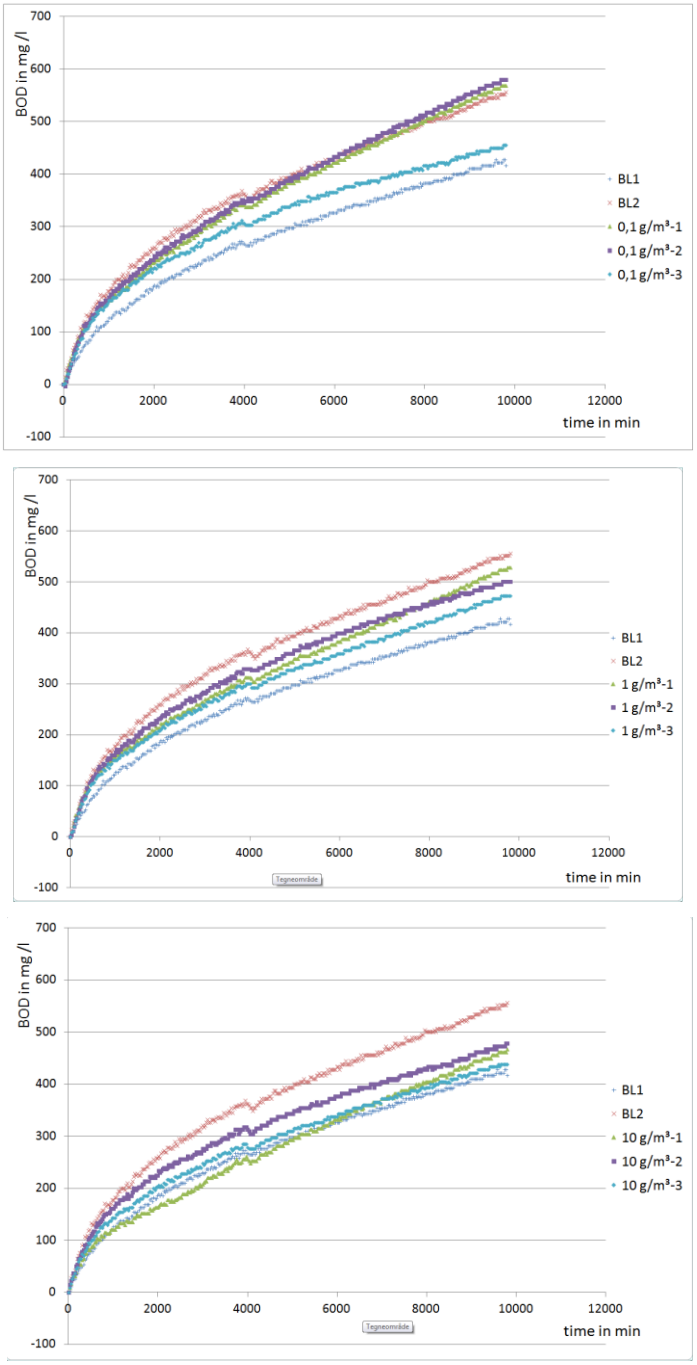


Figure 5: respirometric curve for Addi935.

Curves can be divide in 2 parts: the first one with a fast increase in the BOD that last for approximately 1000min corresponding to growth and a 2nd one with a slower one corresponding to maintenance.

As we are looking for inhibition, the OUR is giving us more information on the possible inhibition. Indeed it is during the growth that the inhibition shows mainly its effects, this due to the higher activity of the biomass. And as the growth period last 1000 min (16h40min), no biodegradation of detergents have time to take place.

The OUR is calculated as $OUR = \frac{BOD_{1008}}{1008/60}$ with BOD_{1008} the BOD value after 1008 minutes 1008/60 the duration in h resulting in an OUR in $mgO_2/l/h$

After calculating the OURs values, the average on the 3 parallels, standard deviation and standard error are calculated (see table 14)

Table 14 : OUR and inhibition analysis in presence of Addi 935

solution		blank (0)	0,1	1	10
	1	8,30	11,42	11,22	8,67
	2	12,55	11,42	11,48	11,25
	3		10,77	10,53	10,02
average		10,42	11,20	11,08	9,98
std dev		3,01	0,38	0,49	1,29
std error		2,13	0,22	0,28	0,74
inhibition based			-37,62	-35,21	-4,51
on BL1			-37,66	-38,35	-35,53
			-29,74	-26,91	-20,71
average			-35,01	-33,49	-20,25
inhibition based			9,00	10,59	30,90
on BL2			8,98	8,52	10,38
			14,21	16,08	20,19
average			10,73	11,73	20,49

After OUR calculations, the inhibition is calculated for all samples compare to each blank and average inhibition is calculated.

All BOD results have been analyzed the same way. All curves can be found in the appendix.

The variation of average inhibition in function of concentration will be observed in the next part.

From table 14, we can see that the 2 blanks are very different resulting in a large difference in the inhibitory values. As addi 935, addiquat su 321 and titan hypo have been tested together, this blank problem appears also for them.

Ph of 7.5 was measured at a concentration of 10g/m^3. Final BOD decreased with increasing concentration from 570 at 0.1, 500 at 1 and 470mgO_2/l at 10g/m^3

4.2.2.2 Addiquat su 321 results.

Table 15 : OUR and inhibition analysis in presence of Addiquat su 321

solution		0	0,1	1	10
	1	8,20	9,81	9,41	8,73
	2	12,45	10,01	10,39	8,33
	3		7,77	8,26	6,53
average		10,33	9,20	9,35	7,86
std dev		3,01	1,24	1,07	1,17
std error		2,13	0,72	0,62	0,68
inhibition based			-19,59	-14,74	-6,40
on BL1			-22,06	-26,69	-1,56
			5,30	-0,67	20,41
average			-12,12	-14,04	4,15
inhibition based			21,24	24,43	29,93
on BL2			19,61	16,56	33,12
			37,63	33,70	47,58
average			26,16	24,90	36,87

Table 15 and figure 10 show how the microorganisms reacts in presence of 0,1 to 10 g/m^3 of Addiquat su 321. PH 7,6 was measured in presence of 10g/m3 addiquat su 321.

Final BOD drop from 550 at 0,1 to 430 mgO_2/lat 10g/m^3

4.2.2.3 Analysis of Titan Hypo results.

Table 16 : OUR and inhibition analysis in presence of Titan Hypo

solution		blank (0)	0,1	1	10
	1	7,01	1,91	6,57	6,30
	2	11,26	5,86	7,11	2,29
	3		5,82	4,93	5,50
average		9,13	4,53	6,20	4,70
std dev		3,01	2,27	1,13	2,12
std error		2,13	1,31	0,66	1,23
inhibition based			72,71	6,25	10,03
on BL1			16,37	-1,49	67,36
			16,97	29,62	21,56
average			35,35	11,46	32,98
inhibition based			83,01	41,66	44,01
on BL2			47,96	36,84	79,69
			48,33	56,20	51,18
average			59,77	44,90	58,29

Table 16 and figure 11 show how the microorganisms reacts in presence of 0,1 to 10 g/m^3 of Titan Hypo. Ph of 7,6 was measured in 10g/m3 samples. The final BOD decrease from 510-400 at 0,1 to 370mgO_2/l at 10 g/m^3

4.2.2.4 Climax TK results.

Table 17 : OUR and inhibition analysis in presence of Climax TK

Solution		blank (0)	0,1	1	10
	1	6,22	8,22	8,06	7,19
	2	5,98	8,68	7,61	7,00
	3		7,43	6,92	4,12
Average		6,10	8,11	7,53	6,10
std dev		0,17	0,63	0,57	1,72
std error		0,12	0,36	0,33	0,08
inhibition based			-32,09	-29,53	-15,55
on BL1			-39,40	-22,19	-12,43
			-19,36	-11,22	33,74
Average			-30,28	-20,98	1,92
inhibition based			-37,45	-34,78	-20,24
on BL2			-45,06	-27,15	-16,99
			-24,20	-15,73	31,05
Average			-35,57	-25,89	-2,06

Figure 12 and table 17 show how the microorganisms reacts in presence of 0,1 to 10 ml/m^3 of Climax tk . pH in the 10 ml/m^3 samples was 7,5.

During this test the Oxitop heads stop after 8000min. This problem happened 2 more time.

Final BODs for Climax tk are decreasing from 500 to 400 after 8000 mins.

4.2.2.5 Alkades results.

Table 18 : OUR and inhibition analysis in presence of Alka des

solution	blank (0)	0,1	1	10
1	6,68	7,26	8,76	9,11
2	6,43	8,84	9,11	9,12
3		7,95	6,87	6,84
average	6,55	8,01	8,25	8,35
std dev	0,17	0,79	1,21	1,31
std error	0,12	0,46	0,70	0,76
inhibition based		-8,69	-31,25	-36,38
on BL1		-32,38	-36,50	-36,53
		-19,08	-2,84	-2,52
average		-20,05	-23,53	-25,14
inhibition based		-12,79	-36,21	-41,53
on BL2		-37,38	-41,65	-41,68
		-23,57	-6,72	-6,39
average		-24,58	-28,19	-29,87

Figure 13 and table 18 show how the microorganisms reacts in presence of 0,1 to 10 ml/m^3 of Alka des . pH of 7,5 was measured in presence of 10 ml/m^3.

Final BOD is decreasing from 550 to 500mg/l with increasing concentration.

4.2.2.6 Titan 951 results.

Table 19 : OUR and inhibition analysis in presence of Titan 951

solution	blank (0)	0,1	1	10
1	7,10	1,08	5,51	5,49
2	6,86	3,32	4,78	2,96
3		4,14	4,65	4,86
average	6,98	2,84	4,98	4,44
std dev	0,17	1,58	0,47	1,31
std dev in% av	0,12	0,91	0,27	0,76
inhibition based		84,82	22,37	22,74
on BL1		53,27	32,70	58,28
		41,74	34,58	31,50
average		59,94	29,88	37,51
inhibition based		84,28	19,63	20,01
on BL2		51,61	30,31	56,80
		39,68	32,26	29,07
average		58,53	27,40	35,30

Figure 14 and table 19 show how the microorganisms reacts in presence of 0,1 to 10 g/m^3 of Titan 951. Ph of 7,5 measured for concentration 10 g/m^3.

At the concentration of 0,1 g/m^3 the 3 parallels gave very different results but repetability became better at higher concentrations.

As the variation between initial OUR is very large for titan 951, the final BOD follow the same rule. Final BODs values are between 420 and 500 except.

4.2.2.7 Addi 932 results.

Table 20 : OUR and inhibition analysis in presence of Addi 932

solution	blank (0)	1	10	100
1	5,91	5,94	6,83	6,93
2		7,15	8,09	7,07
3		5,80	5,98	6,11
average		6,29	6,97	6,70
std dev		0,75	1,06	0,52
std dev in% av		0,43	0,61	0,30
inhibition based		-0,39	-15,56	-17,16
on BL1		-20,93	-36,76	-19,50
		1,98	-1,10	-3,37
average		-6,45	-17,80	-13,34

Figure 15 and table 20 show how the microorganisms react in presence of 1 to 100 g/m^3 of Addi 932. Ph of 7.9 was measured at 100g/m^3.

As we get only one blank for this test, the inhibitory results for Addi 932 and titan Kassevask XL cannot be verified. This absence of blank is due to the stop of the 3rd chemical's (Ecofoam CL) test bottles after 2000 minutes.

The curves from addi 932 are different from previous ones, we can see an increase of the OUR in the second part of the curve. This increase of OUR could be explain by the biodegradation of the chemical.

4.2.2.8 Titan Kassevask XL results.

Table 21 : OUR and inhibition analysis in presence of Titan Kassevask XL

solution	blank (0)	1	10	100
1	6,42	3,97	7,10	6,45
2		5,52	6,61	3,84
3		2,61	6,17	5,16
average		4,03	6,63	5,15
std dev		1,46	0,46	1,31
std error		0,84	0,27	0,75
inhibition based		38,23	-10,53	-0,42
on BL1		13,99	-2,98	40,24
		59,30	3,93	19,69
average		37,17	-3,19	19,84

Figure 16 and table 21 show how the microorganisms react in presence of 1 to 100 g/m^3 of Titan Kassevask XL. pH of 8.1 was measured at 100 g/m^3.

Final BOD are respectively, 350, 440 and 340 mg/l.

4.2.2.9 Mip EA results.

As the previous test, this test has only one blank. But this time only one blank were used because there were no magnet in the other one.

Table 22 : OUR and inhibition analysis in presence of Mip EA

solution	blank (0)	0,1	1	10
1		4,90	5,55	3,99
2	8,52	4,44	5,33	3,85
3		6,71	5,30	4,32
average		5,35	5,39	4,05
std dev		1,20	0,13	0,24
std dev in% av		0,69	0,08	0,14
inhibition based		42,48	34,85	53,21
on BL2		47,87	37,40	54,78
		21,23	37,75	49,23
average		37,19	36,67	52,41

Figure 17 and table 22 show how the microorganisms react in presence of 1 to 10 g/m^3 of Mip EA. pH 7.6 was measured at the concentration of 10g/m^3. In the blank start with Mip Ea, no magnet was present. This absence results in low oxygen consumption and the values were not usable.

Final BODs have no sign of biodegradation and decrease from 350 to 300mgBOD/l with increasing concentration.

4.2.2.10 Basol M results.

Table 23 : OUR and inhibition analysis in presence of Basol M

solution	blank (0)	0,1	1	10
1		8,02	7,24	8,56
2	8,11	7,24	7,77	8,73
3		6,36	6,77	5
average		7,21	7,26	8,14
std dev		0,83	0,51	0,871
std error		0,48	0,29	0,50
inhibition based		1,06	10,72	-5,53
on BL2		10,73	4,13	-7,71
		21,56	16,54	11,86
average		11,12	10,46	-0,46

Figure 18 and table 23 show how the microorganisms react in presence of 1 to 10 g/m^3 of Basol M. measured ph of 7.5 was found in presence of 10 g/m^3.

Final BODs are stable around 400 mg/l

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4.2.2.11 ACO hygene skum Alkaklor results.

Table 24 : OUR and inhibition analysis in presence of ACO hygene skum alkaklor

solution	blank (0)	1	10	100
1	6,20	5,99	6,04	5,72
2	5,84	6,05	6,58	5,68
3		5,93	6,57	5,25
4				
average	6,02	5,99	6,40	5,55
std dev	0,25	0,06	0,31	0,26
std error	0,18	0,04	0,18	0,15
inhibition based		3,27	2,60	7,65
on BL1		2,34	-6,26	8,40
		4,32	-6,05	15,33
average		3,31	-3,24	10,46
inhibition based		-2,68	-3,39	1,97
on BL2		-3,67	-12,80	2,77
		-1,57	-12,57	10,12
average		-2,64	-9,59	4,95

Figure 19 and table 24 show how the microorganisms react in presence of 1 to 100 g/m^3 of ACO hygene skum alkaklor. In 100g/m3 samples, ph of 9 was measured.

The final BODs vary decrease 450 to 350 with increasing concentration.

4.2.2.12 TP66 results.

Table 25 : OUR and inhibition analysis in presence of TP 66

solution	blank (0)	10	100	1000
1	2,83	1,21	3,89	0,49
2	4,08	2,89	4,62	0,56
3		4,02	3,58	0,57
4				
average	3,46	2,71	4,02	0,54
std dev	0,89	1,41	0,54	0,04
std error	0,63	0,82	0,31	0,02
inhibition based		57,22	-36,59	82,52
on BL3		-1,97	-63,22	80,35
		-42,12	-26,40	80,03
average		4,37	-42,07	80,97
inhibition based		70,34	5,31	87,88
on BL4		29,31	-13,15	86,38
		1,48	12,38	86,16
average		33,71	1,51	86,81

Figure 20 and table 25 show how the microorganisms react in presence of 10 to 1000 ml/m^3 of TP 66. In presence of 1000ml/m3, the measure ph was 9,2.

For the first time at 1000ml/ m^3 a really strong inhibition can be observed with 80-90% inhibition. From 1000ml/m3 samples, we can also observe a sudden increase of OUR after 2000 min. this increase results in the BOD to reach the same value as the blanks at 3000 min. So the inhibition is more like a lag phase of 2000mins

The final BOD for all samples is stable around 350mg/l.

The sudden increase of the BOD at the highest concentration can be linked to the degradation of the inhibitor.

4.2.2.13 Ecofoam CL results.

This test is the first one using the sludge from Grødaland wwtp.

Table 26 : OUR and inhibition analysis in presence of Ecofoam CL

solution	blank (0)	1	10	100
1	5,29	7,14	6,44	5,38
2	7,37	7,74	7,06	5,37
3		6,68	6,36	4,73
average	6,33	7,19	6,62	5,16
std dev	1,46	0,53	0,38	0,37
Std error	1,04	0,31	0,22	0,21
inhibition based		-34,93	-21,67	-1,58
on BL1		-46,14	-33,29	-1,34
		-26,09	-20,08	10,69
average		-35,72	-25,01	2,59
inhibition based		3,02	12,55	26,99
on BL2		-5,04	4,19	27,16
		9,37	13,69	35,81
average		2,45	10,14	29,98

Figure 21 and table 26 show how the microorganisms react in presence of 1 to 100 g/m^3 of Ecofoam CL. Ph of 8 was measure for 100g/m3 samples. The final BOD is stable for all samples around 300 mg/l

4.2.2.14 Topactive DES results.

Table 27 : OUR and inhibition analysis in presence of Topactive des

solution	blank (0)	1	10	100
1	5,83	6,15	6,80	6,32
2	5,53	6,76	6,88	6,51
3		5,06	5,78	4,77
average	5,68	5,99	6,49	5,87
std dev	0,21	0,86	0,61	0,95
std error	0,15	0,50	0,35	0,55
inhibition based		-5,56	-16,60	-8,45
on BL1		-15,96	-18,04	-11,63
		13,20	0,83	18,18
average		-2,77	-11,27	-0,63
inhibition based		-11,20	-22,84	-14,25
on BL2		-22,17	-24,36	-17,60
		8,56	-4,48	13,80
average		-8,27	-17,23	-6,02

Figure 22 and table 27 show how the microorganisms react in presence of 1 to 100 g/m^3 of Topactive des. At the concentration of 100g/m3, a ph of 7,5 was measured.

The final BODs are stable for all samples around 300 mg/l.

4.2.2.15 TP 36 results.

Table 28 : OUR and inhibition analysis in presence of TP 36

solution	blank (0)	1	10	100
1	6,76	6,68	5,53	4,60
2	6,42	5,88	0,34	5,47
3		5,33	5,15	4,67
average	6,59	5,96	3,67	4,91
std dev	0,24	0,68	2,89	0,48
std error	0,17	0,39	1,67	0,28
inhibition based		1,21	18,15	31,89
on BL1		13,04	95,00	19,13
		21,10	23,88	30,89
average		11,79	45,68	27,30
inhibition based		-4,03	13,81	28,27
on BL2		8,42	94,73	14,83
		16,91	19,84	27,22
average		7,10	42,79	23,44

Figure 23 and table 28 show how the microorganisms react in presence of 1 to 100 g/m^3 of TP36. The PH of 9 was measures in the most concentrated samples.

From figure 21, we can see at a concentration of 10 g/m^3 one of the samples was strongly inhibited (as tp66 1000ml/m^3). But as this effect appears only on this sample and not event at higher value this measurement is probably an error.

Final BODs are stable for all samples around 300 mg/l except for the second sample of 10g/m3 that is a bit lower.

4.2.2.16 Cip Acid FA results.

Table 29 : OUR and inhibition analysis in presence of Cip acid Fa

solution	blank (0)	0,1	1	10
1	7,61	8,85	8,02	7,16
2	7,81	8,94	8,13	7,20
3		7,80	7,14	7,52
average	7,71	8,53	7,77	7,29
std dev	0,14	0,63	0,54	0,20
std error	0,10	0,36	0,31	0,11
inhibition based		-16,14	-5,35	6,02
on BL1		-17,40	-6,80	5,44
		-2,45	6,19	1,27
average		-12,00	-1,99	4,24
inhibition based		-13,24	-2,72	8,37
on BL2		-14,47	-4,14	7,80
		0,11	8,53	3,73
average		-9,20	0,56	6,63

Figure 24 and table 29 show how the microorganisms react in presence of 0,1 to 10 ml/m^3 of Cip acid fa. PH 8 was measured in 10ml/l cip acid fa sample.

The final BOD is stable for all samples between 350 and 400 mg/l

4.2.2.17 Addi 931 results.

Table 30 : OUR and inhibition analysis in presence of Addi 931

solution	blank (0)	0,1	1	10
1	7,08	7,73	7,79	8,01
2	6,55	7,43	7,68	7,68
3		7,17	7,30	6,43
average	6,81	7,44	7,59	7,37
std dev	0,38	0,28	0,25	0,83
std error	0,27	0,16	0,15	0,48
inhibition based		-9,18	-10,01	-13,11
on BL1		-5,00	-8,54	-8,54
		-1,33	-3,19	9,14
average		-5,17	-7,24	-4,17
inhibition based		-18,05	-18,94	-22,30
on BL2		-13,53	-17,35	-17,35
		-9,56	-11,57	1,76
average		-13,71	-15,96	-12,63

Figure 25 and table 30 show how the microorganisms react in presence of 0,1 to 10 g/m^3 of Addi 931. In presence of 10 g/m3 the pHof the solution was 8.

Final BODs are stable as for cip around 350 and 400mg/l.

4.2.3 Evolution of inhibition in function of concentration.

Inhibition has been calculated from the variation of OUR between samples and blanks.

As we saw in the theory section, the inhibition typical curve consist in a stable part with no inhibition, one increasing part and another stable part with complete inhibition.

Inhibition average was plot against concentration for all tested detergents in order to see how inhibition varies in function of concentration. 3 graphs have been done according to the 3 ranges of concentration.

Based on the model maximum concentrations, maximum inhibitions corresponding have been plotted on the graphs (black arrows).

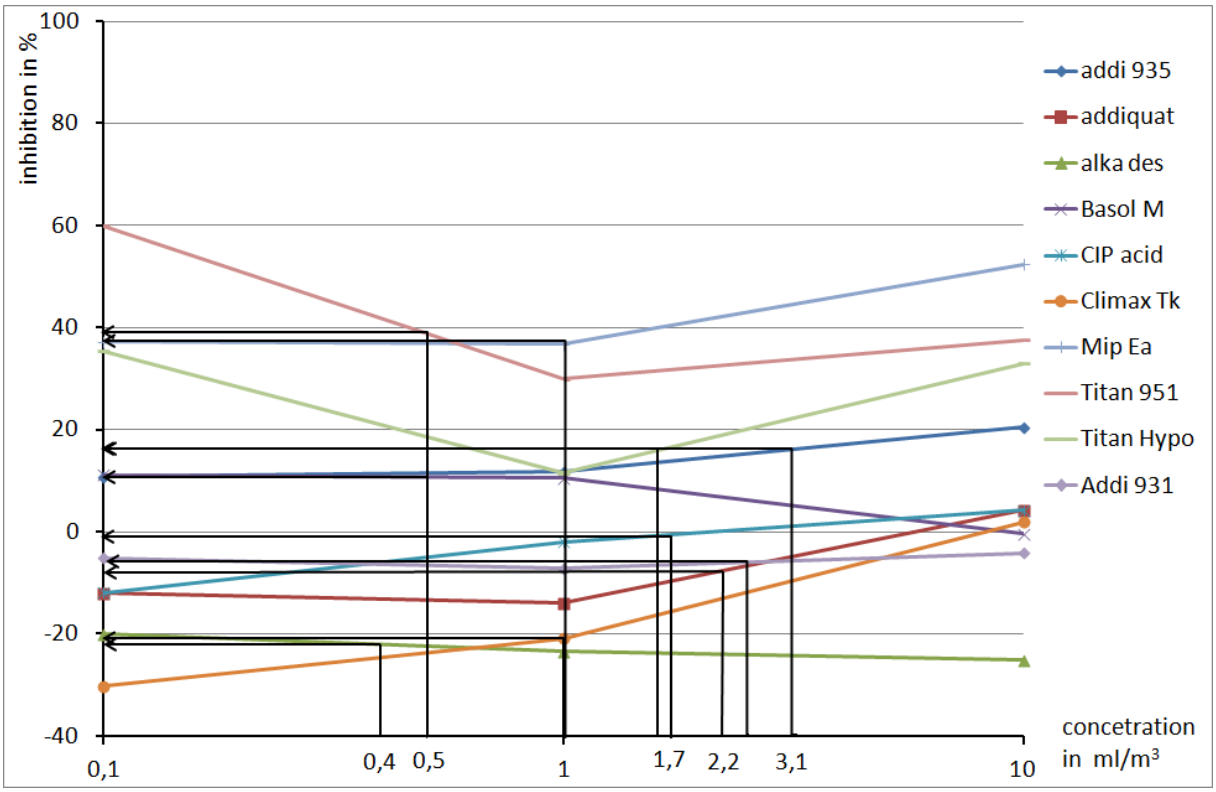

Figure 6: effect of concentration on inhibition in the range of 0,1-10.

Figure 6 show how inhibitory effect of the different compounds test in the range of 0,1 to 10 ml/m3 or g/m3. From this figure, we can observe that from one chemical to the other, the initial inhibition is highly changing. But by looking at the inhibition variations with increasing concentration, we can see that there is no proper tendency. As there is only 3 concentration, it is difficult to status properly if the variations especially increases are due to the variability or to the chemical dose. Climax TK is the only chemical to show a constant increase with the concentration (30% within the 2 decades).

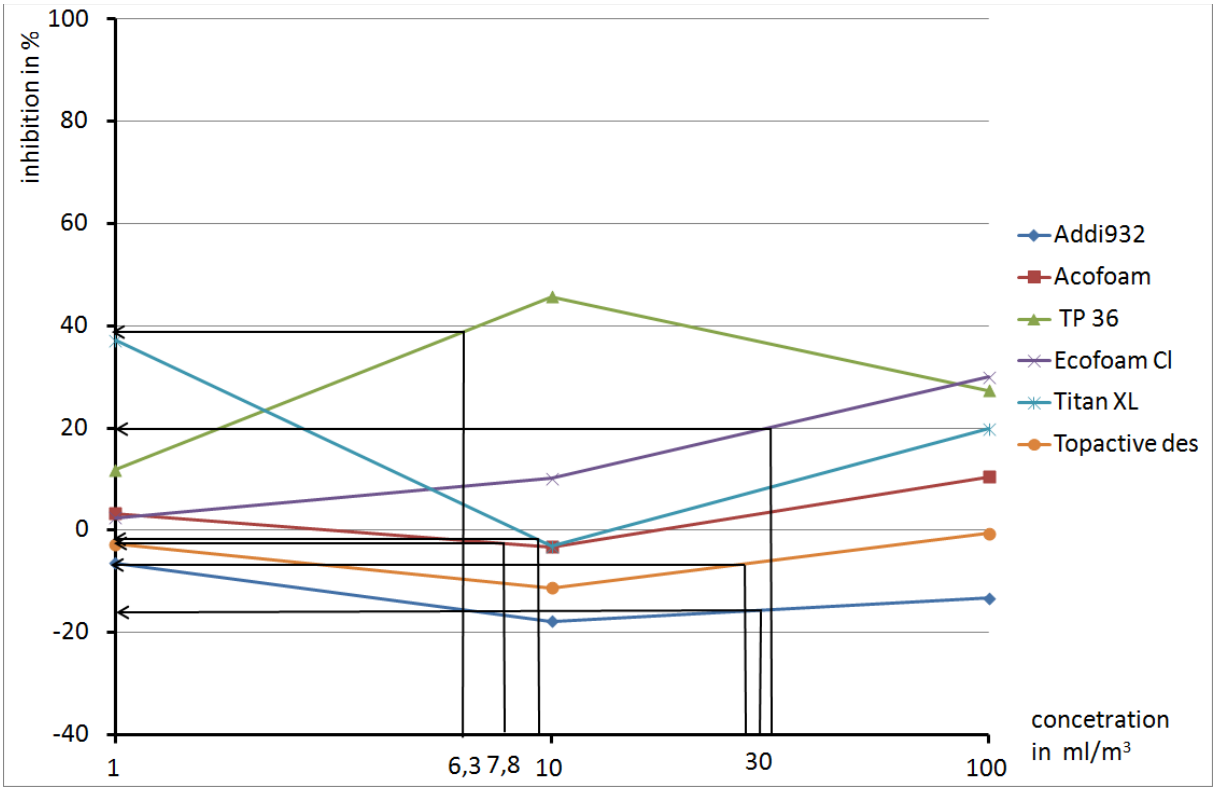

Figure 7: effect of concentration on inhibition in the range of 1 -100.

Figure 7 the inhibition variation in the range of 1 to 100 ml/m3 or g/m3.

From this figure, we can observe that inhibition is stable with increasing concentration for Addi 932, Topactive des, Acofoam. Ecofoam is the only chemical to show constant increase in inhibition with increasing concentration (appox 30% increase for 2 decades). Tp36 and titan XL are the 2 chemical with the highest variability.

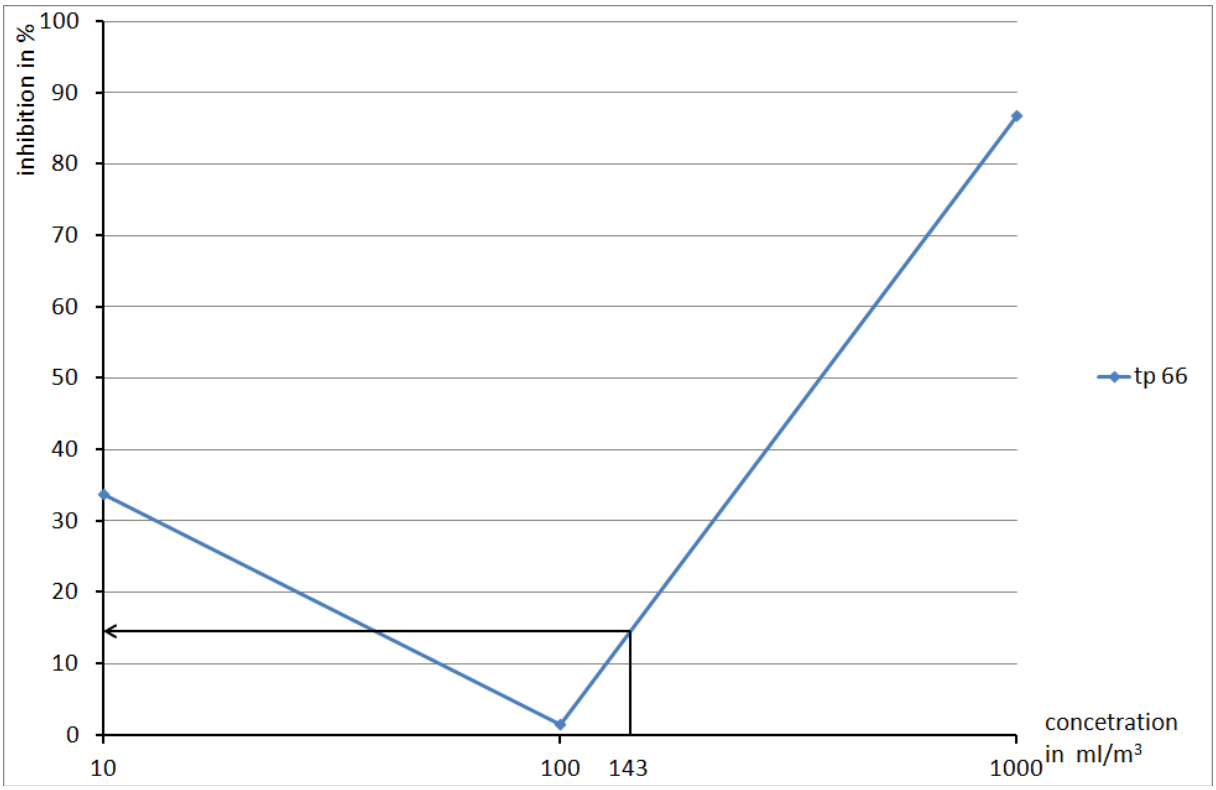

Figure 8: effect of concentration on inhibition in the range of 10-1000.

Figure 9 show as the effect of increase doses of TP66. This time the range is 10-1000ml/m3. On this graph, we can observe for the first time a clear increase of the inhibition from a dosage of 100 to 1000ml/m3.

5. DISCUSSION

A model was created based on Grødaland wwtp specificities in case of low water loading to obtain the most concentrated conditions.

Respirometric tests provided the BOD in function of time and based on these datas, secondary results were calculated as the initial OUR and the inhibition. Finally the inhibition was plotted in function of the chemical concentration.

5.1 Discussion on inhibition results

From BOD curves, we saw that the phase change between growth and maintenance appears after 1000min with a BOD value between 100 and 150 mgO_2/l which correspond to ½ of the easily biodegradable COD introduced in the bottles.

During different test, the final BOD has drop from 500 to 300 mgO_2/l.

This decrease in the final BOD value came progressively during the different runs of respirometic tests and no observation on final BOD or on the OUR have been observed after the change of sludge.

The results on the OURs show to be repeatable between the parallels, except few cases like Titan 951 with the 3 samples at $0.1g/m^3$ that were completely different or the presence of a probable outlier with Tp 36.

Furthermore, the OURs values are remaining stable with increasing concentration. Only Ecofoam cl and climax tk have a continuous increase of inhibition with concentration (around 30% within 2 decade for both).

TP 66 is the only chemical that has a strong inhibitory effect at the high concentration with a peek in the inhibition value of 86% at $1000ml/m^3$.

The low variation in inhibition with increasing concentration can highlight only a non inhibitory condition because in case of complete inhibition, the inhibition value should be higher. Furthermore, the maximum concentration is between 3 and 20 time higher than the maximum model reactor concentration.

This low effect of the chemicals is linked to the tested range of concentration. Indeed, on OUR 17 detergents, 10 were tested within the range of 0,1-10, 6 in the range 1-100 and 1 in the range of 10-1000 while OECD 209 advice for preliminary concentrations the range of 10-1000. From Bodik et al., we can see that the inhibition becomes high within this range and according to tp66 this range appears to be confirmed.

5.2 Limit of static respirometic tests.

Inhibition tests have been performed in close bottle system, only the chemical effects on the oxygen uptake have been remarked. But chemicals and especially surfactant can have effect at the macroscopic level. In 2006, Liwarska et al. observed that inionic surfactant and especialy LAS were affecting the shape and the size of flocs [40]. This variation are linked to the settlability of flocs and as the size is reduced, the settling velocity is reduced also. Causing a lower effluent quality due to the presence of biomass and a lower treatment efficiency due to this biomass loss.

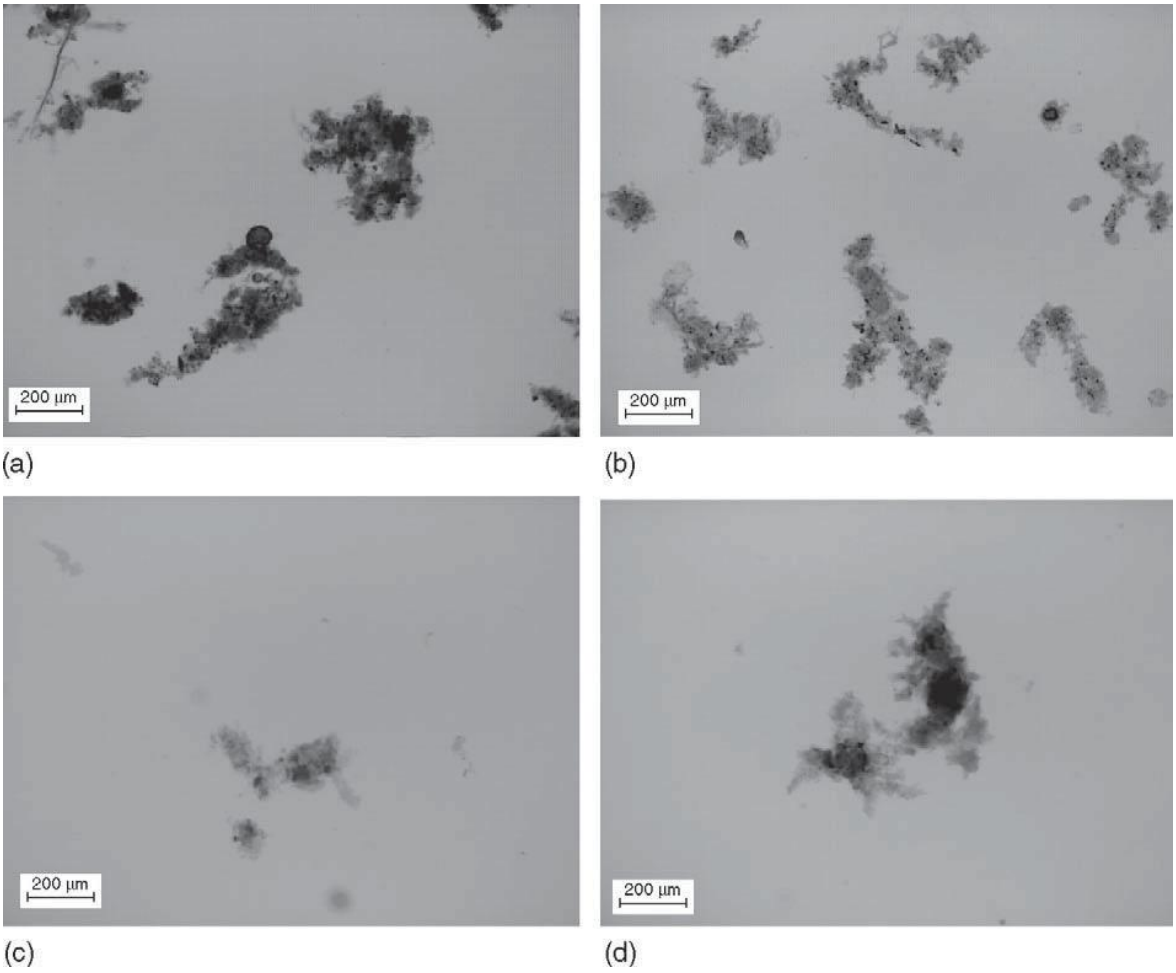

Figure 9: effect of anionic surfactant on flocs shape and size[40].

Figure 9 shows the variation of flocs size between the control (a), in poresence of Alkyl sulphate (b), Linear alkylbenzene sulphonate (c) and Alkylpolyoxyethylene sulphate (d). from this figure, the impact on the flocs size is very clear with a large decrease especially in presence of LAS. As anionic surfactant and LAS are present in the tested detergents, the impact on the flocs size is a important subject to study.

5.3 Further experiments

In order to have a better understanding of the possible effects of the chemicals on activated sludge, more test can be performed. Indeed, during the experiments only individual chemicals effects were tested. But the wwtp receive all the chemicals during the same period of time especially because those chemicals are cleaning agent. So test with multiple chemicals should be performed in order to look for the possible synergetic effects and other interactions between chemicals.

Furthermore, as the chemicals may also affect the microbial arrangement in flocs, pilot plant testing and flocs analysis can also be a good step.

6. CONCLUSION

The main objective of this project was to find if the high load of detergents in Grødaland treatment plant can have an effect on the treatment. Based on this objective, concentration in the wwtp was model and respirometric test were performed for each chemicals.

Results on this inhibition tests show that most of the chemical are not inhibiting the process to a large extent but Tp66 which is the most concentrated chemical could have high impact with concentration approaching 1000ml/m^3 but as this concentration is approximately 10 times higher than the maximum model concentration, no effects at the wwtp should appear.

To conclude, according to OUR measurements, the presence of chemical should not have any notable effect on the waste water treatment process. But as these tests are looking at only single chemicals, some complementary test especially with plural chemicals and on flocs level should be performed.

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8. APPENDIX

8.1 Appendix 1 : BOD curves

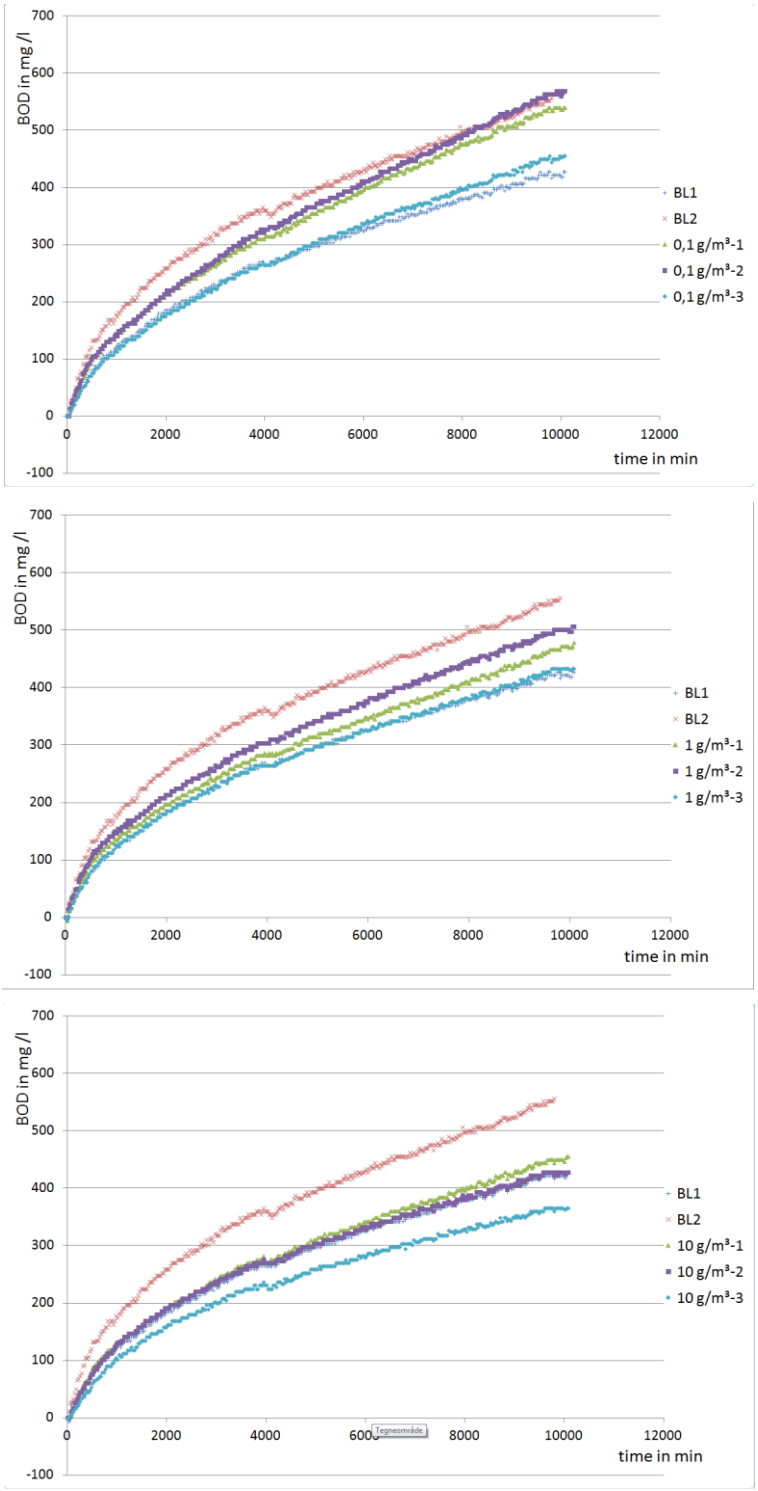

Figure 10: respirometric curve for Addiquat su 321.

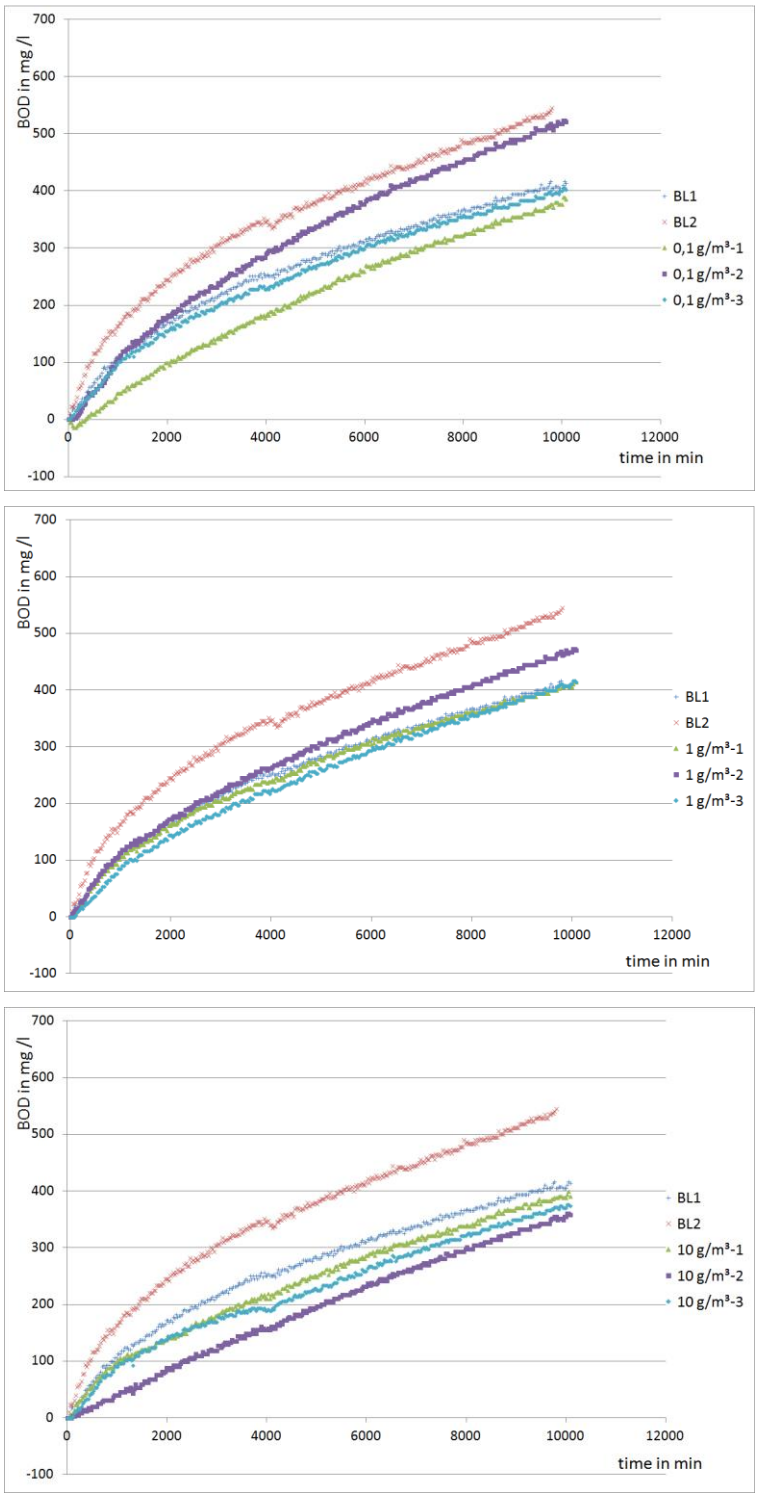

Figure 11: respirometric curve for Titan Hypo.

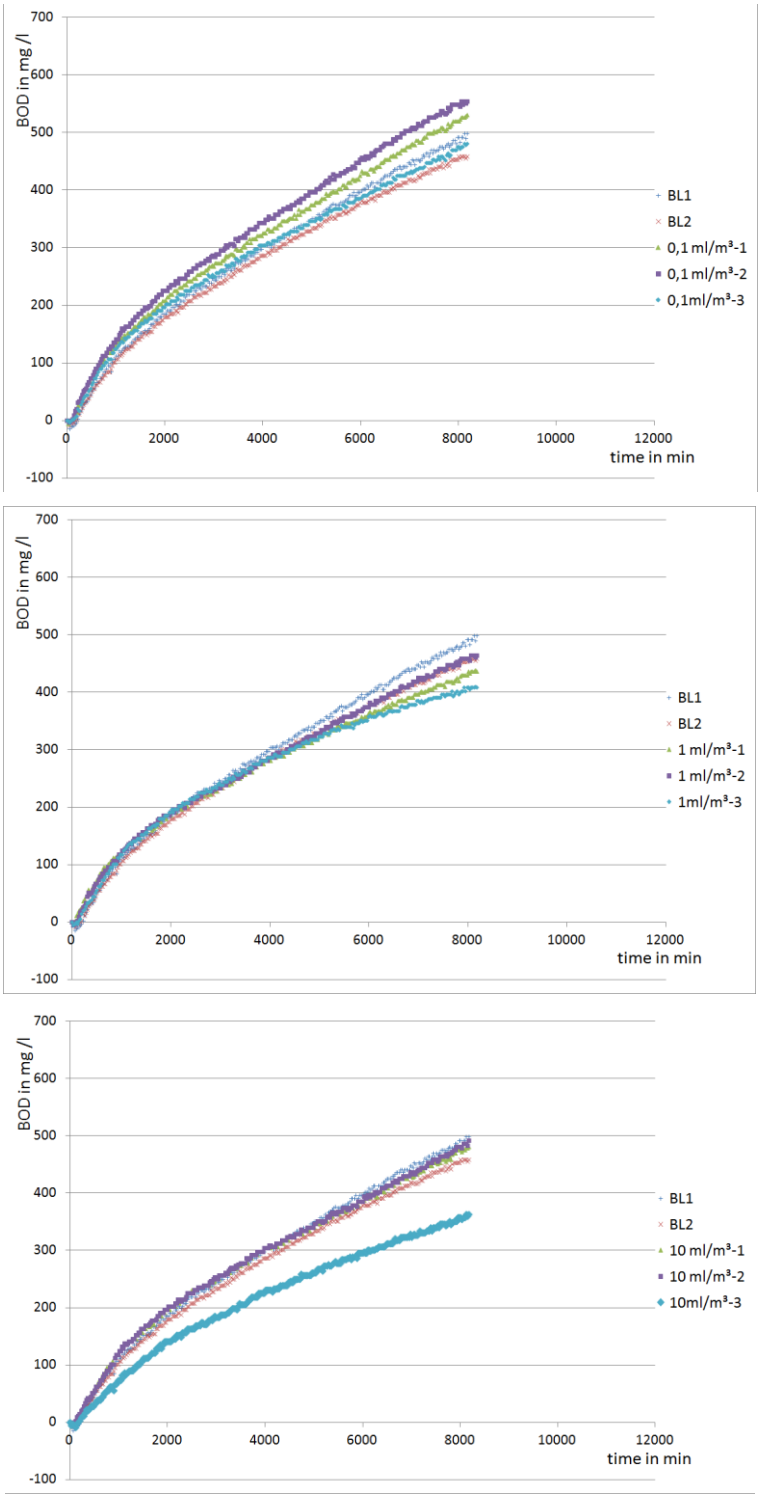

Figure 12: respirometric curve for Climax TK.

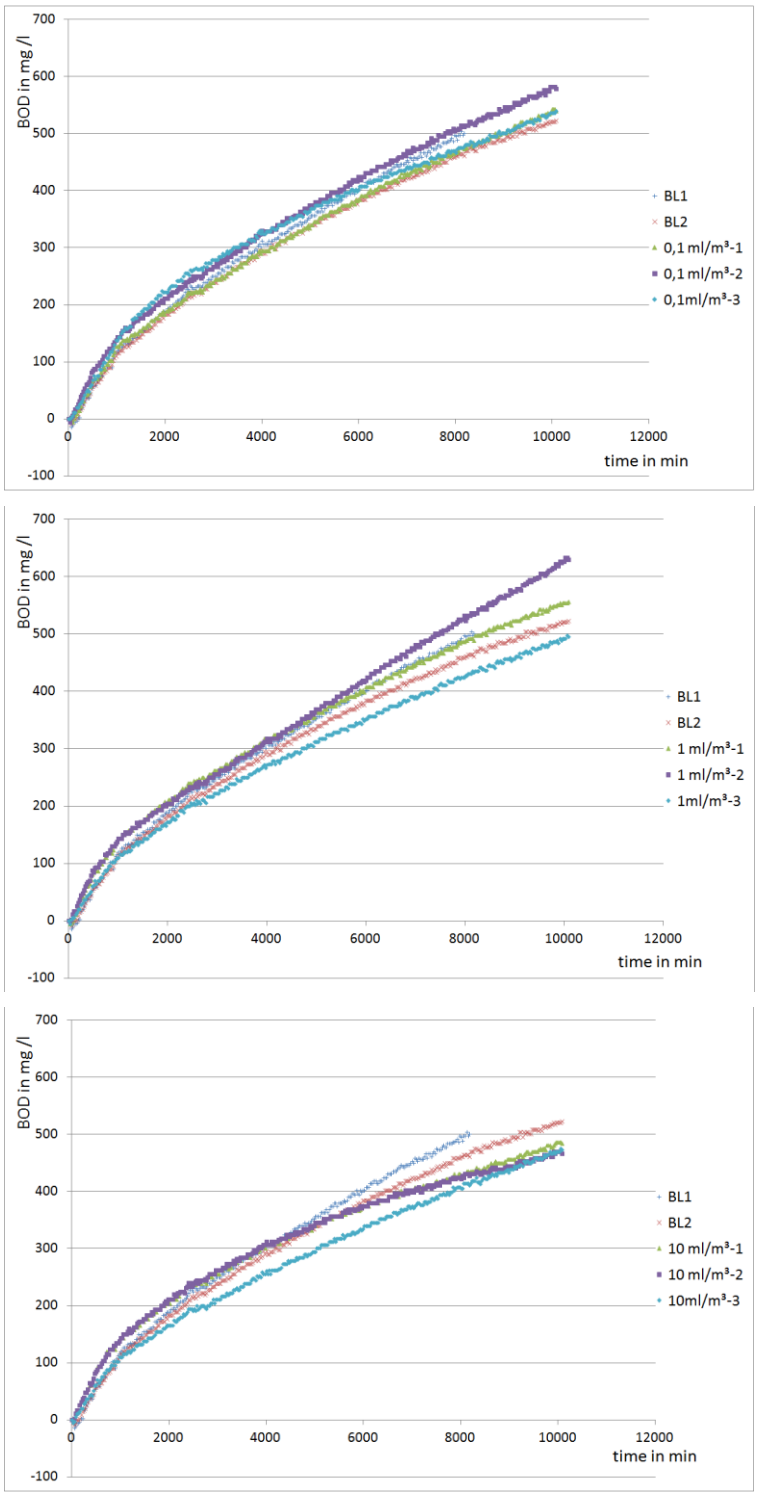

Figure 13: respirometric curve for Alka des.

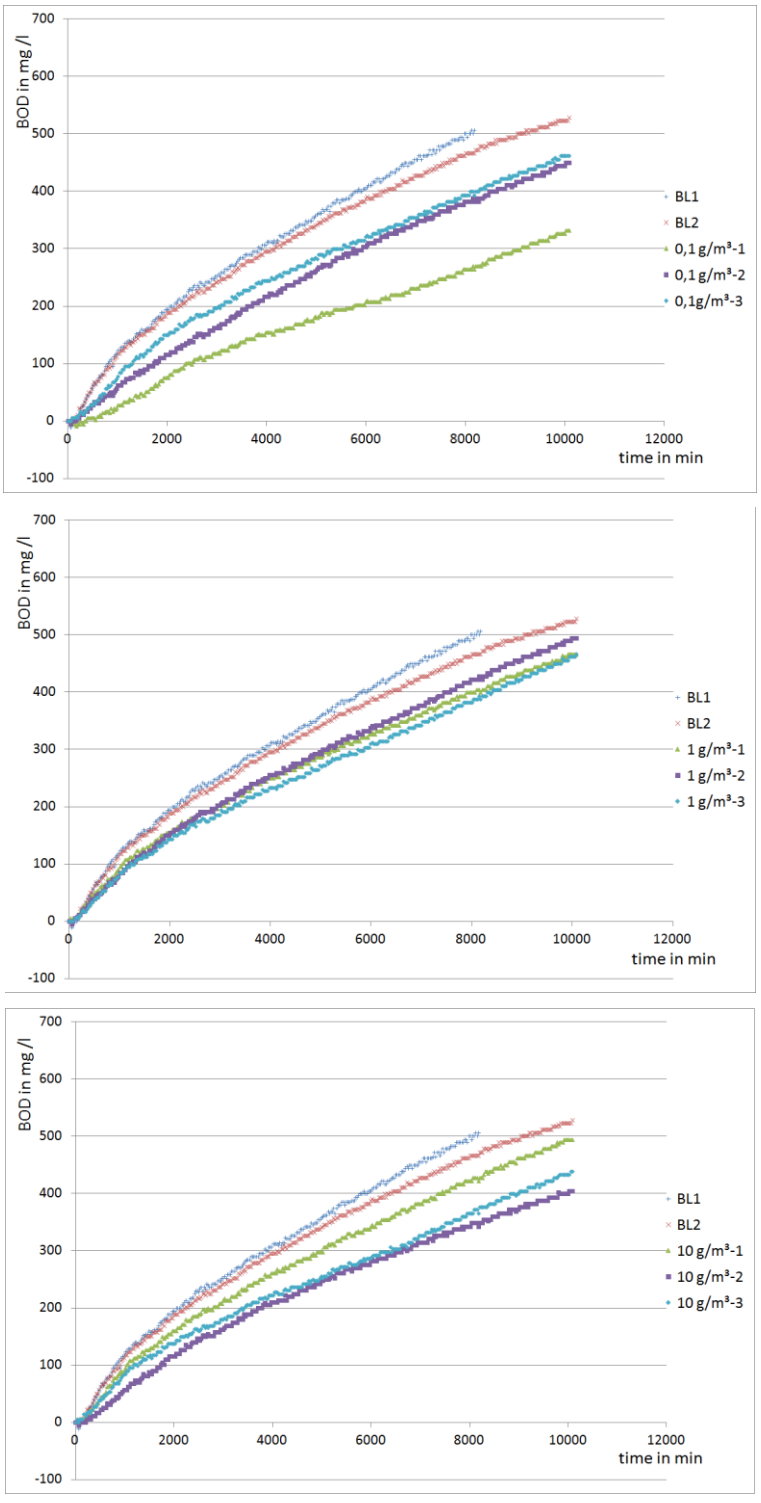

Figure 14: respirometric curve for Titan 951.

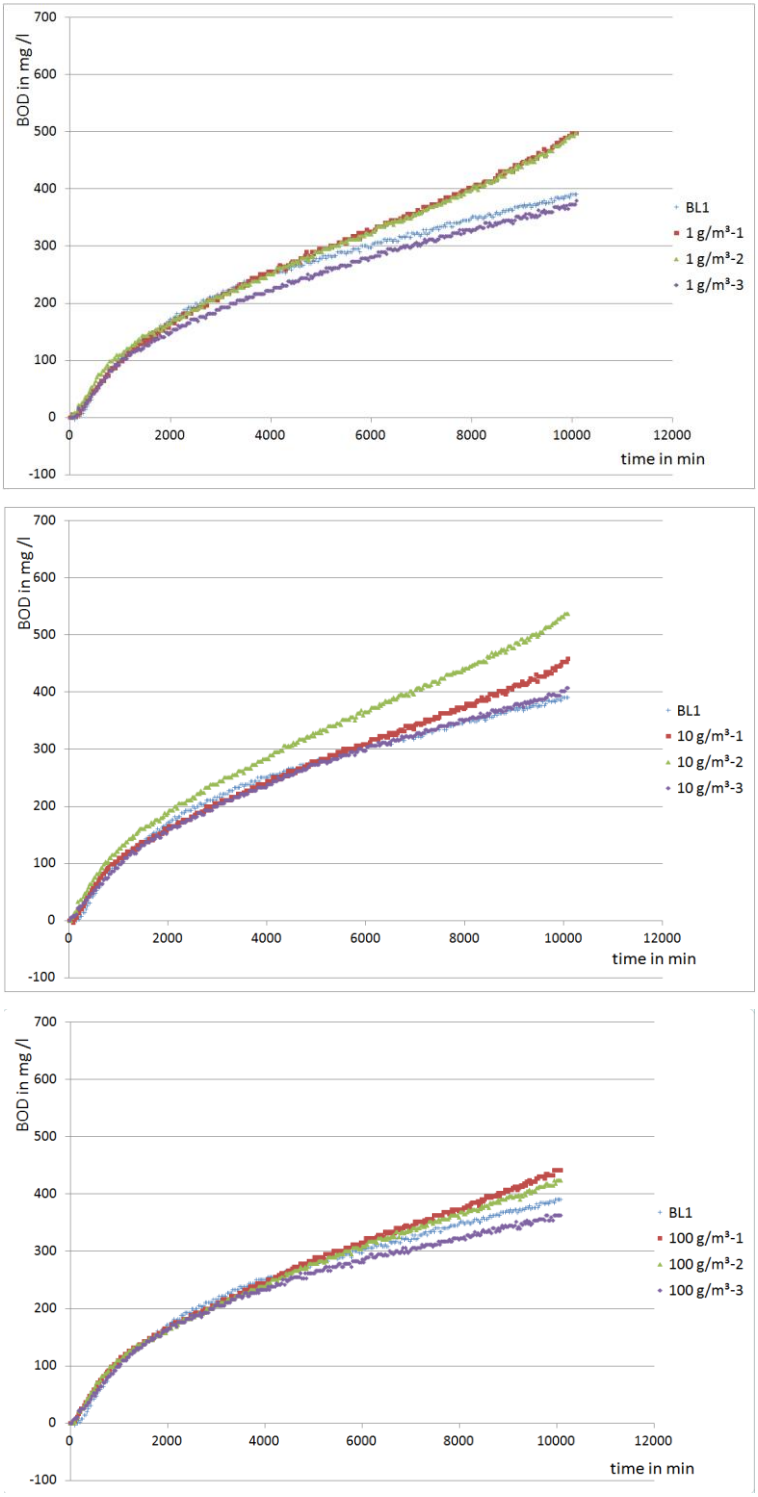

Figure 15: respirometric curve for Addi932.

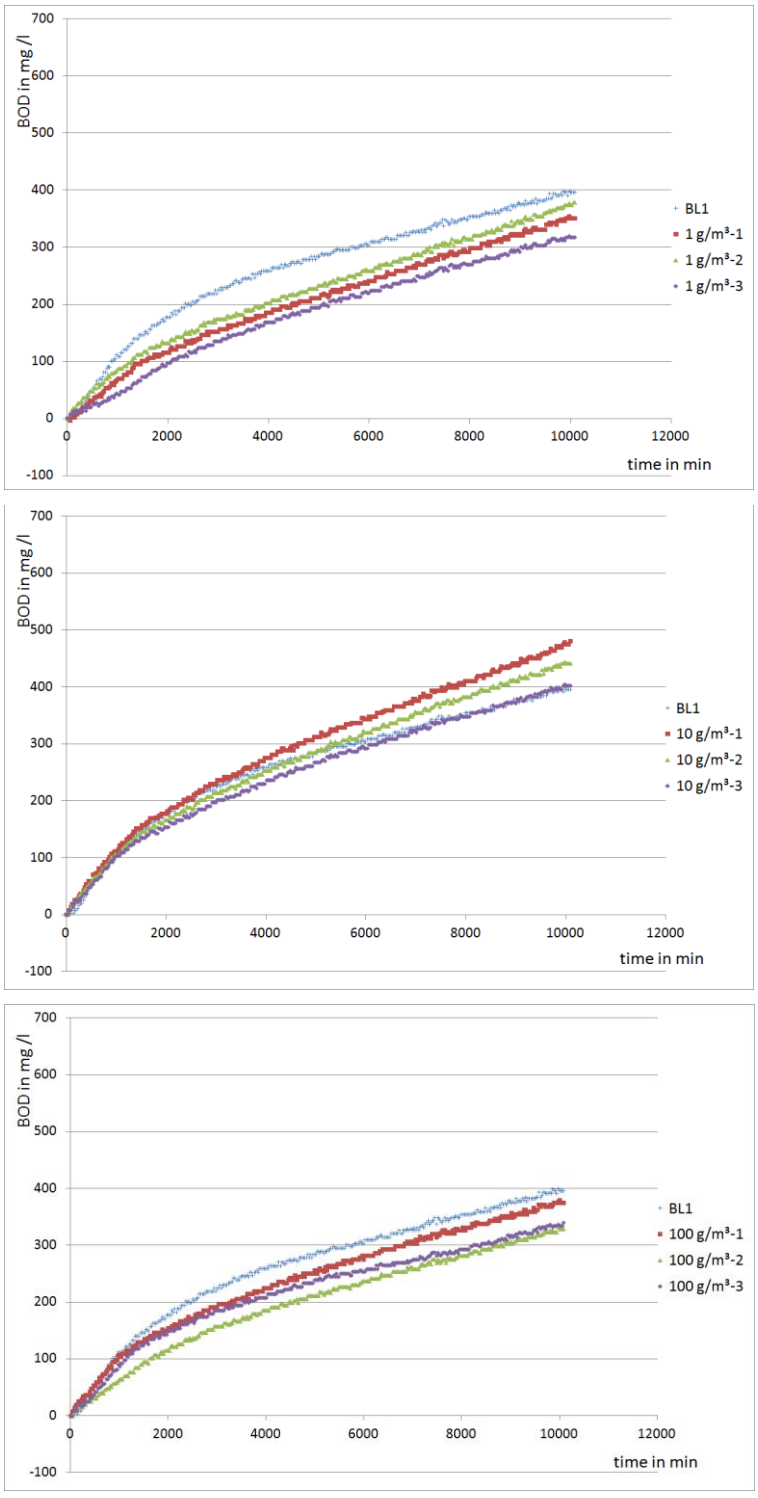

Figure 16: respirometric curve for Titan Kassevask XL.

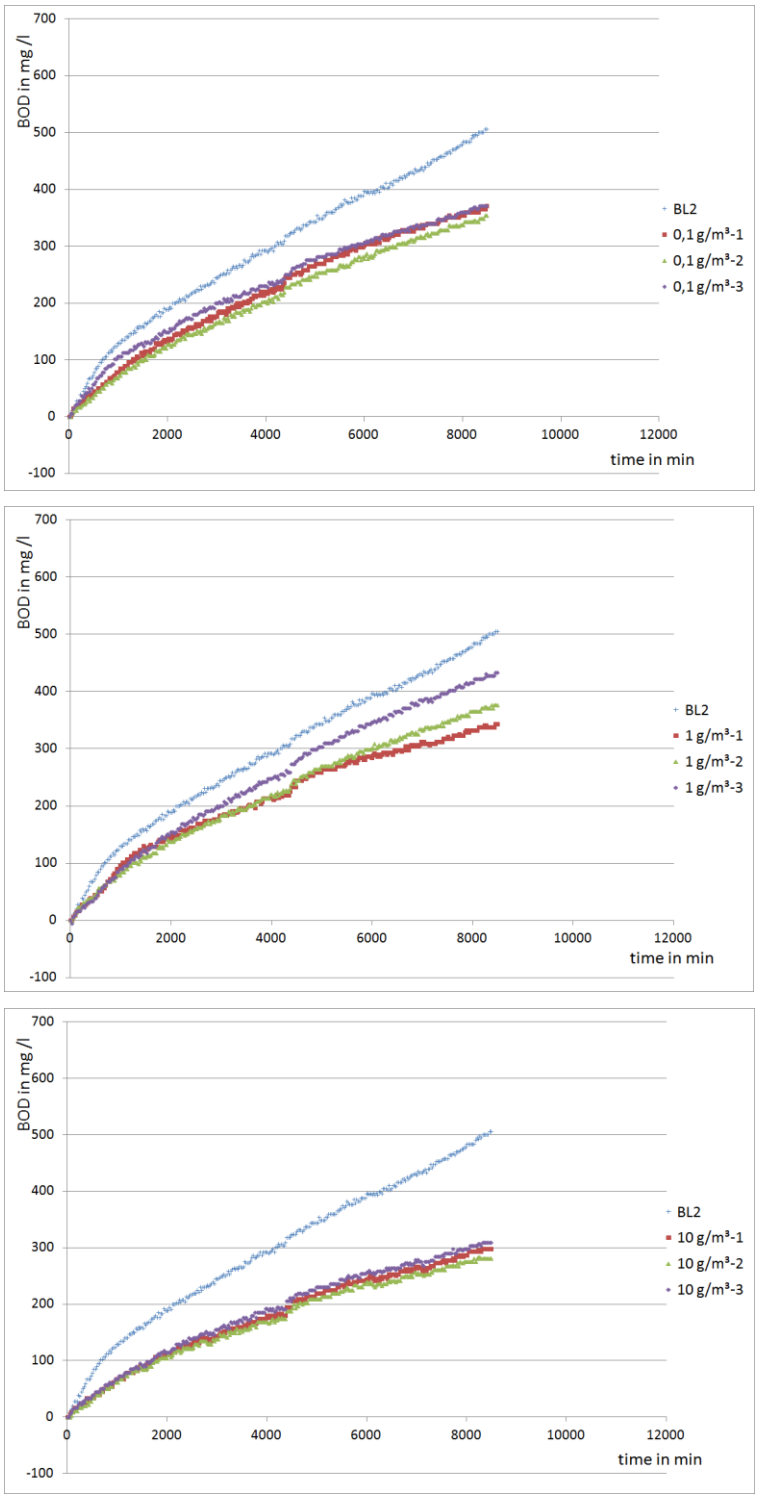

Figure 17: respirometric curve for Mip EA.

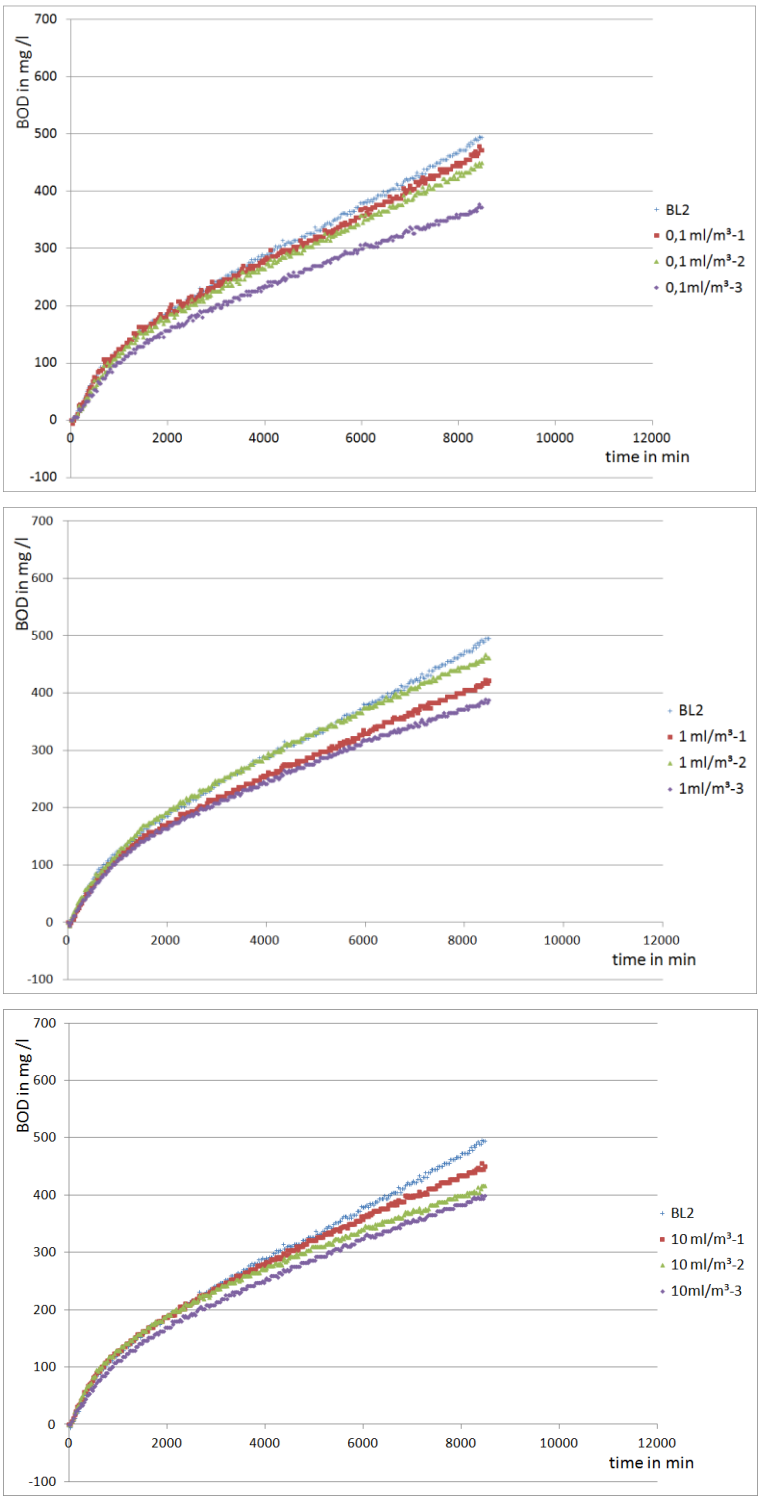

Figure 18: respirometric curve for Basol M.

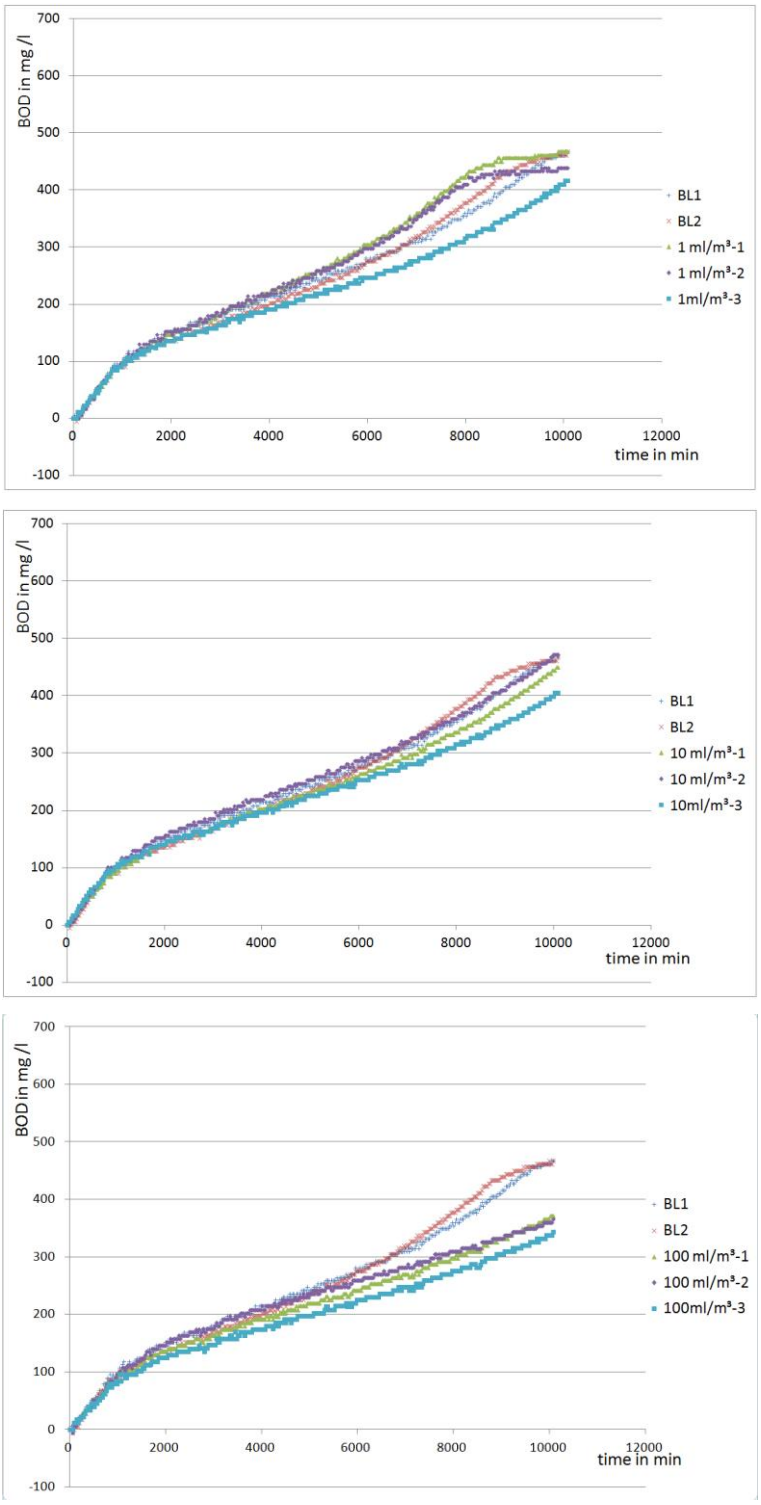

Figure 19: respirometric curve for ACO hygene skum alkaklor.

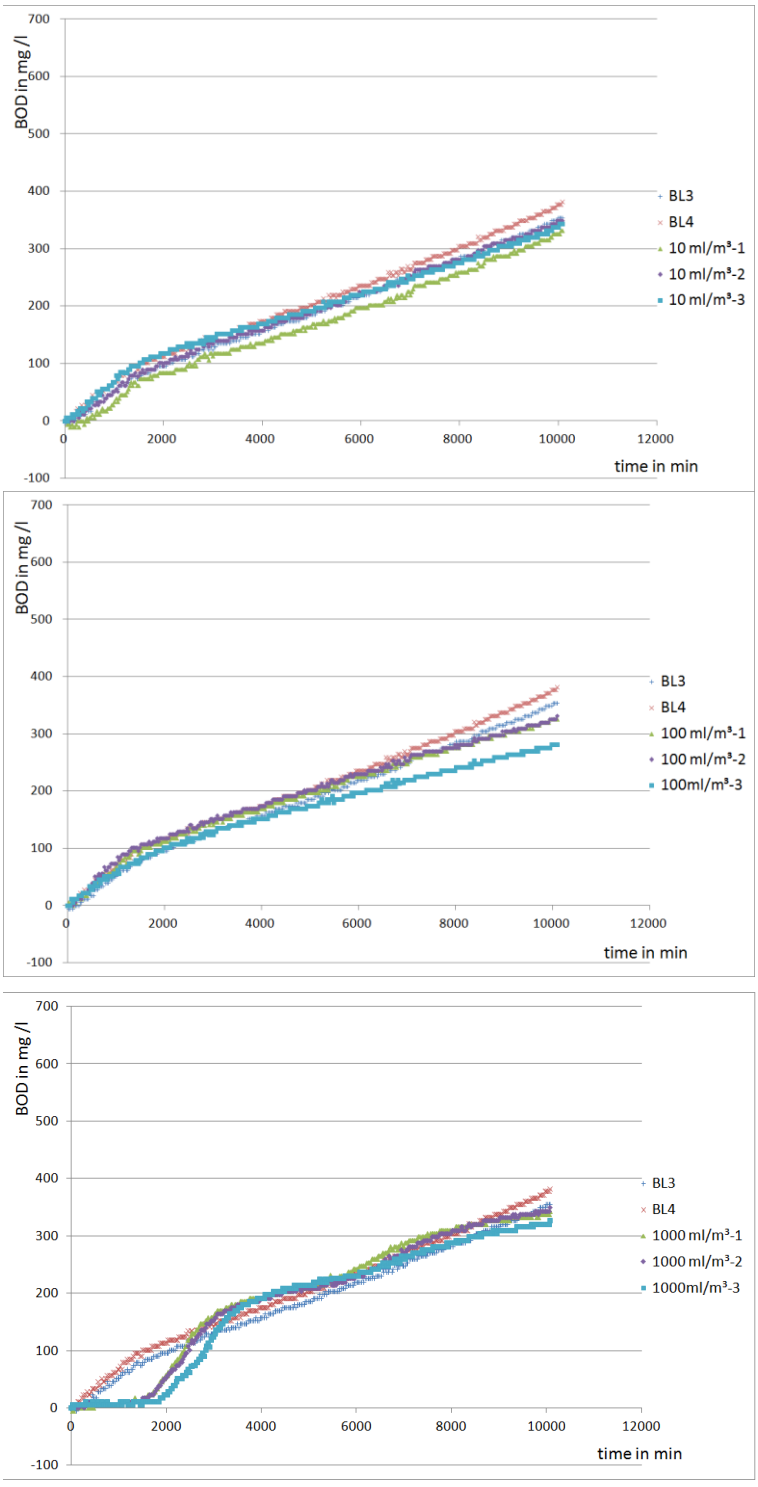

Figure 20: respirometric curve for TP 66.

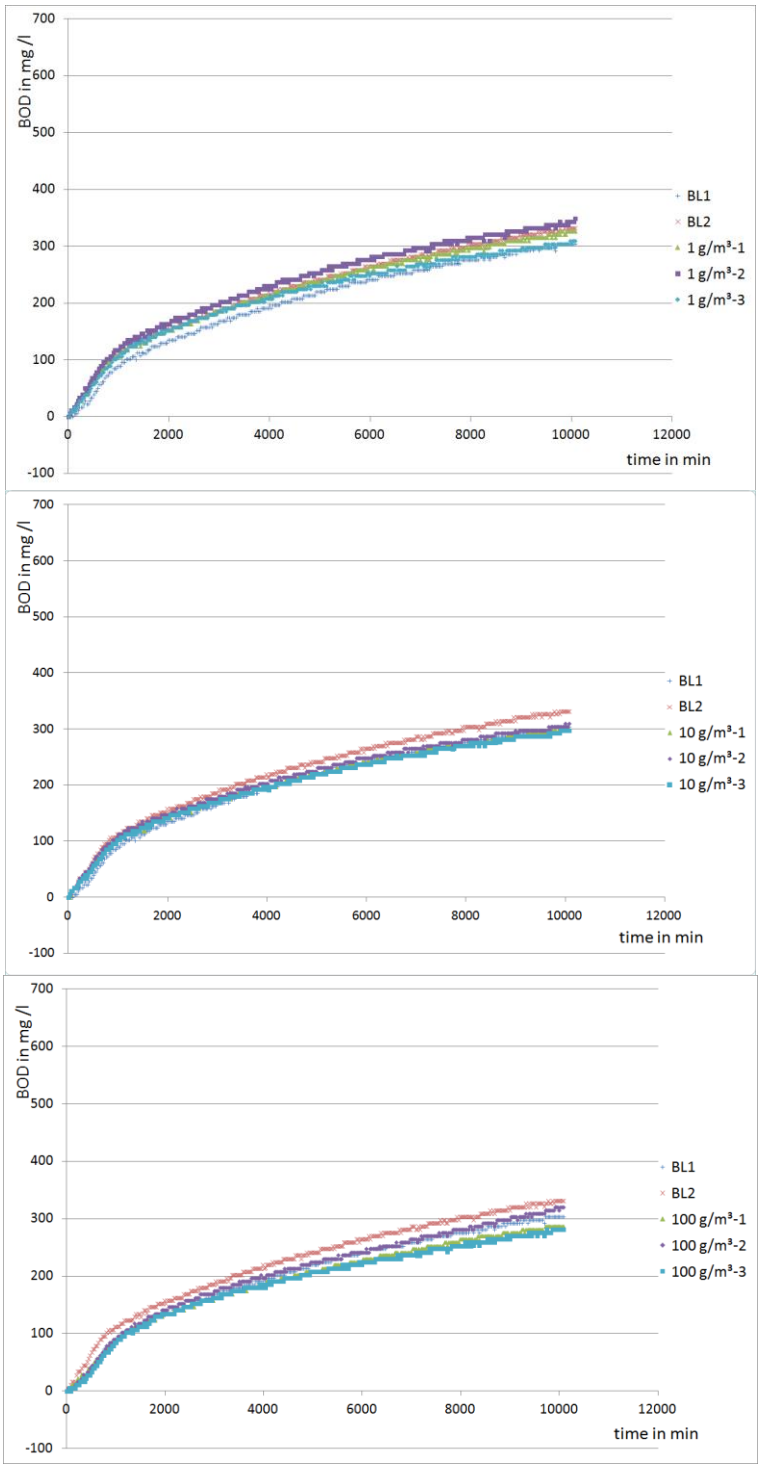

Figure 21: respirometric curve for Ecofoam CL.

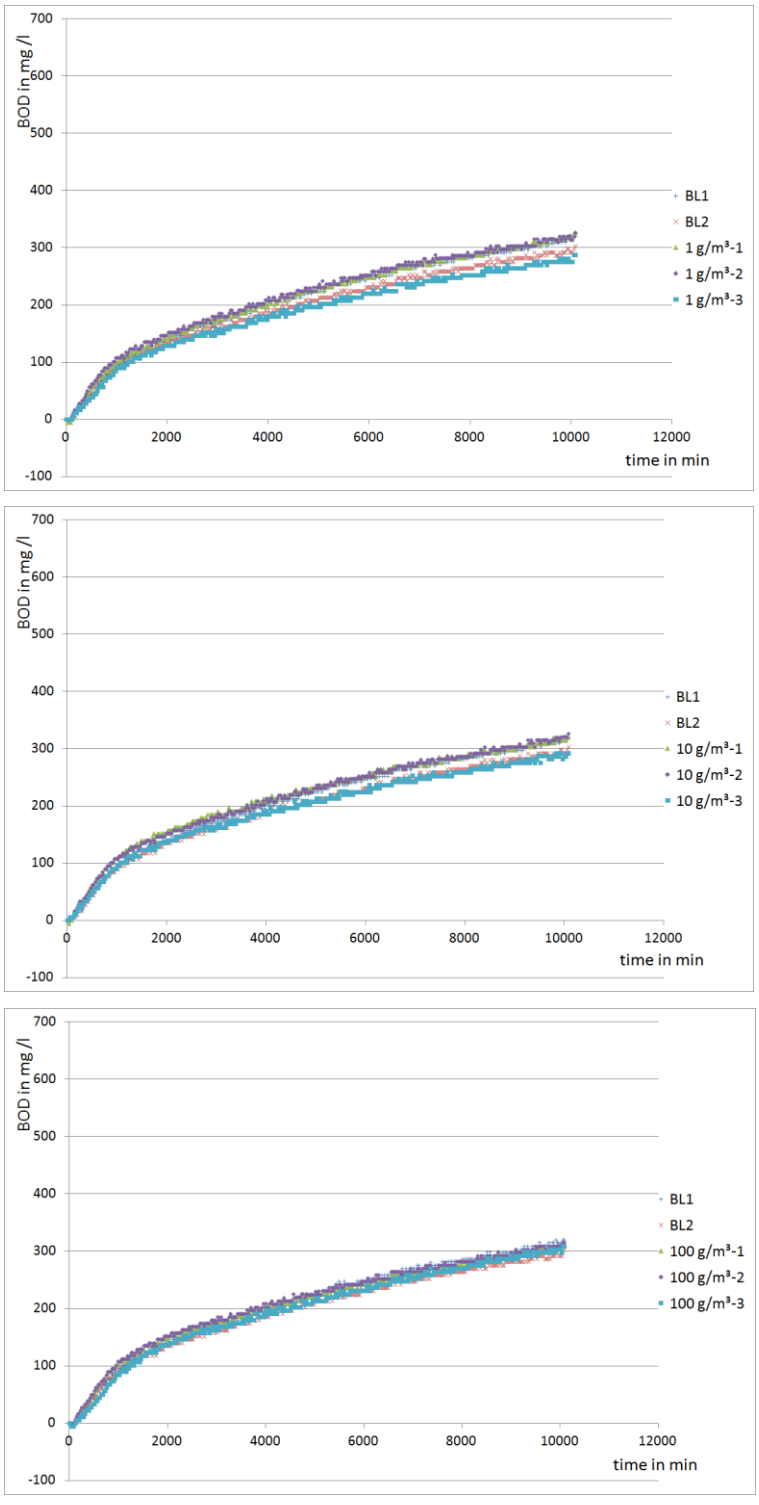

Figure 22: respirometric curve for Topactive des.

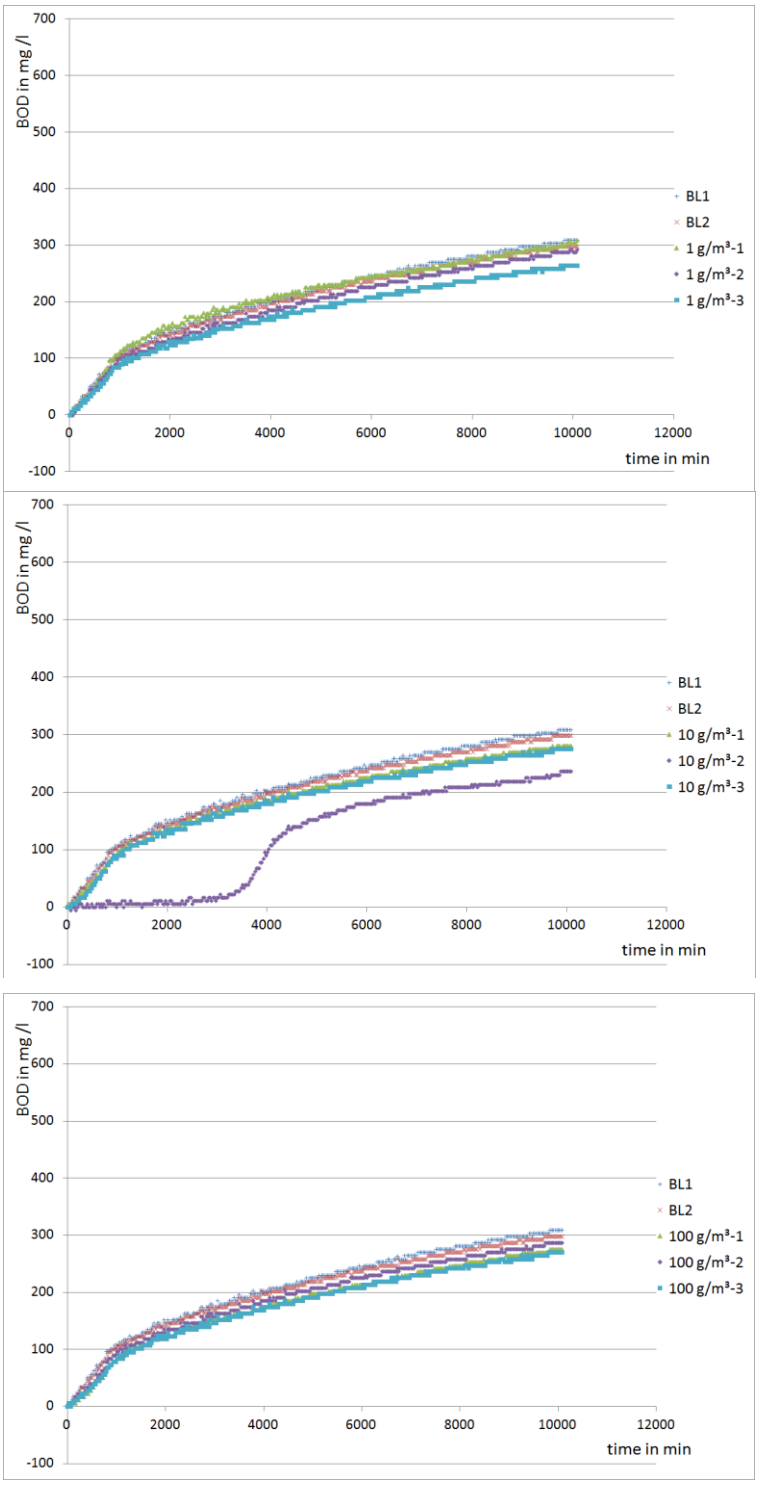

Figure 23: respirometric curve for TP 36.

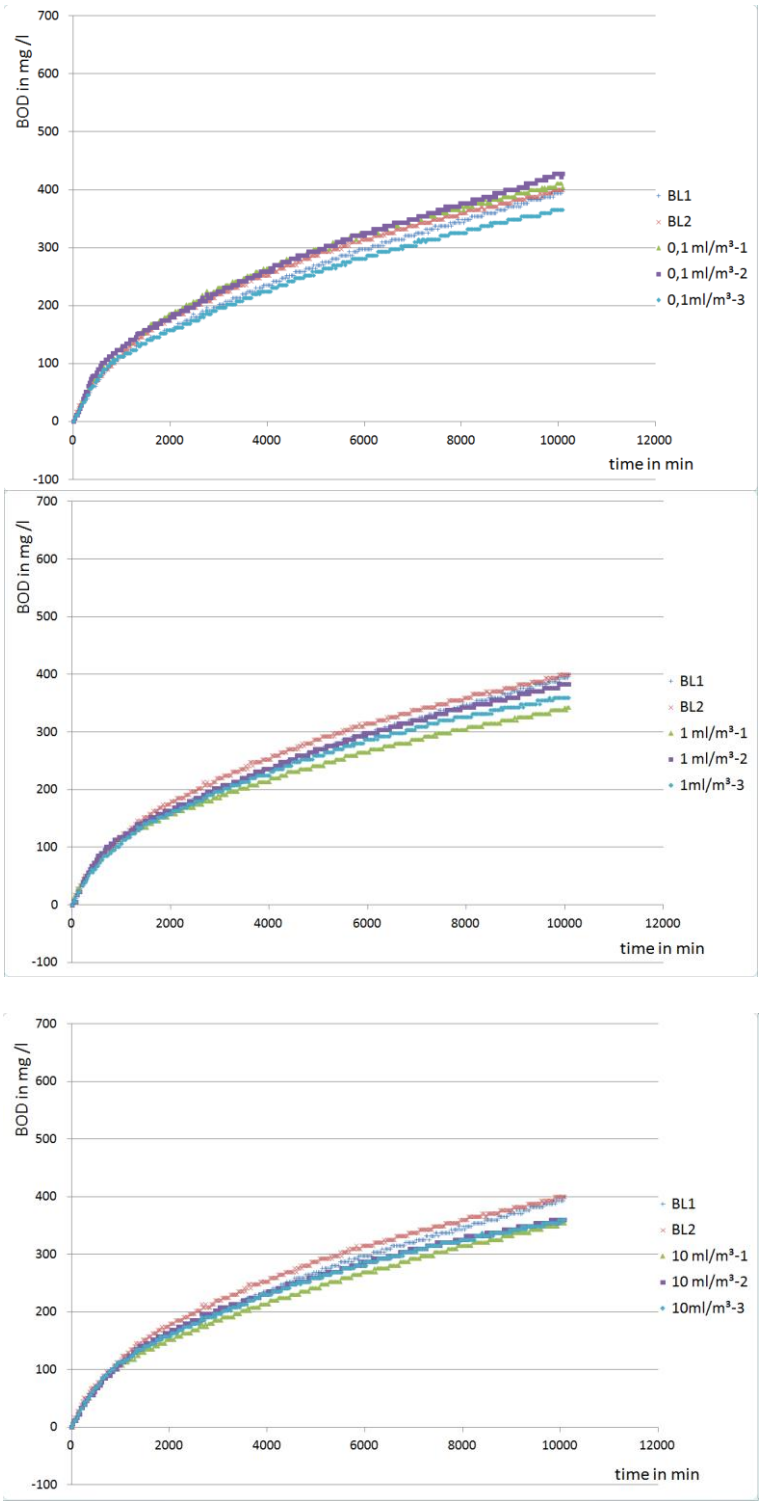

Figure 24: respirometric curve for Cip acid fa.

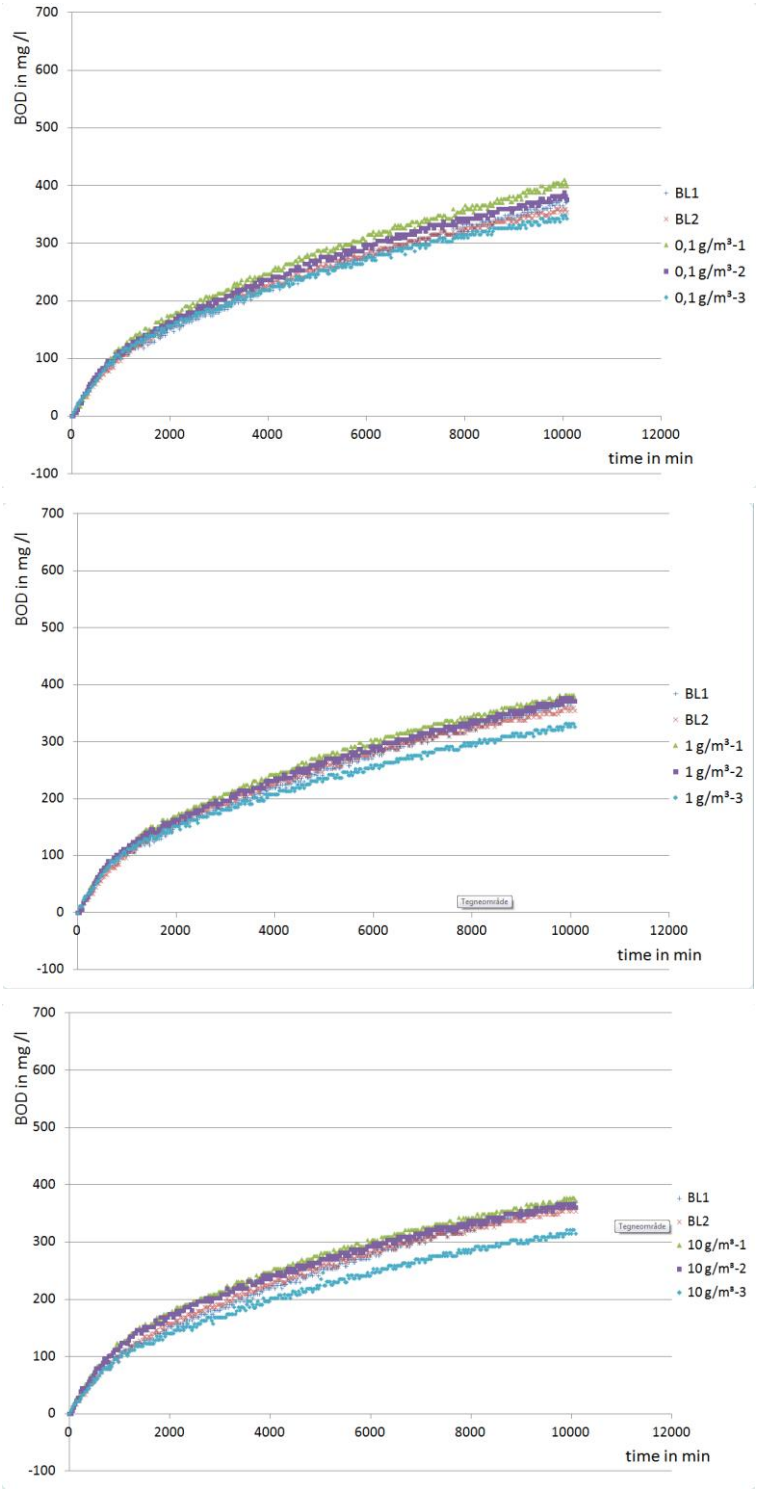

Figure 25: respirometric curve for Addi931.