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On-line data-based process monitoring of aerobic wastewater treatment processes

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Abstract

Why the ability to estimate both the COD loads in different parts of a system and the Oxygen Uptake Rate (OUR) is important for a sufficient operation of an activated sludgy system? It is the question, which was posed for the conducted study. An importance of the consistent methods for an OUR estimation and an ability to tract variations of biological processes based on the treatment technologies applied, they both contribute to a sufficient operation of an activated sludge system.

This report gives an overview of the study research conducted in the Process Engineering (Eng) Department at the Eawag. The topic of the study was “On-line data-based process monitoring of aerobic wastewater treatment processes”. The study was made as a part of a master degree level project at ETH Zurich over the course of seven weeks.

Three sections of the study were defined. In the first section the mass of the unbiodegradable organic, which was removed from the wastewater with the filter application, was defined. The BOD test was complete in order to determine the fractionation of unbiodegradable organic in different parts of the system. In the second section the effect of the filtration unit, which is installed prior to the SBR, on the sludge composition in the SBR was simulated. The simulation was carried out in Berkeley Madonna software. Within the third section of the study several methods allowing an on-line estimation of a OUR were developed. The modeling was carried out in MatLab software.

Information, which was obtained in the results of this study, can contribute to the further scientific studies related to the biological treatment processes. The results of Section 1 and Section 2 will contribute to the degradation studies in the PhD of Ing. Jonathan Habermacher. The results of Section 3 can help to improve and analyse the computational methods for an OUR estimation, which are investigated by Kris Villez, Group Leader of the research group Spike at the Eawag.

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1 Introduction

Wastewater treatment in activated sludge systems is based on a process for treating sewage using air and a biological floc composed of bacteria and protozoa. The oxygen uptake rate (OUR) is the microorganism oxygen consumption per unit time and is one of the few accessible parameters to quantify the metabolism rate of the activated sludge. The OUR is proportional to the microorganism concentration and depends on the quality of the incoming wastewater. The estimation of the oxygen uptake rate by aerobic bacteria has a crucial importance for the wastewater treatment operations. It is a measure for the quality of the activated sludge and an presence indicator of high loads of organic matter or of toxic materials in the influent. Correct identifications of the OUR variations, being done on time, allow the correct actions to ensure good effluent quality at minimal costs. (Gautam Chalasani 2007)

What are the current procedures, which are able to estimate the variation of OUR on-line? How precise they are? What are their pros and cons? **The aim of the first part of the current study** is to be able to answer these questions and to provide methods. The methods are robust and can deal with imperfections, which are due to the rapid changes in the OUR, imperfect aerations or dissolve oxygen (DO) censors. Moreover, they are able to monitor and characterize the non-linear effects of DO profiles, which are caused by these imperfections.

The second part of the study, which is dedicated to the characterization of an experimental Wastewater Treatment (WWT) system composed of a Filter and Sequencing Batch Reactor (system Filter-SBR), gives an insight on the changing of an activated sludge composition due to applied treatment technologies. The Filter receives primary effluent and retains particles with a size larger than 100 um. The purpose of this filter is to remove unbiodegradable particulate organics ($X_{U,Inf}$) from the primary effluent. The filter-permeate flows to the SBR, which produces a sludge of mainly microbial origin. This specific sludge will be characterized and used for degradation studies in the PhD of Ing. Jonathan Habermacher.

Oxygen uptake rate measurements can provide valuable information about the biodegradation characteristics of wastewaters received by activated sludge processes. (Young 1999) The changing in the activated sludge compositions, which are the focus of the second part of the current study, can be tracked using the methods obtained in the first part of the study. Hence, the both parts together contribute to the overall goal of the study to be able to identify the OUR variations due to changing in the characteristics of the influent wastewater in the SBR.

1.1 Scope of the project/Project limitations

A master project with 7 weeks duration is the first opportunity for master students to apply on practice the knowledge they gained during classes. The master project allows independent work, the aims of which is an ability to deal with incomplete and inaccurate data, an assessment of uncertainty of available data, practice of a team work and oral presentations, handling of professional literature and engineering reports, etc.

The current master project consists of the two parts: the part, which was related to laboratory experiments, and the part, which was aiming to develop different methods for the OUR estimation.

Within the experimental part of the project the Filtration-SBR Unit was studied. Wastewater, which was used for the experiments, is pumped from the Zurich sewage system to the laboratory facilities of Eawag, where it passes through primary treatment ("Sandfang" and primary clarifier with the particular up-flow velocity [m/hr]). After primary treatment a part of the primary effluent is directed to the Filtration-SBR unit. The sequencing batch reactor (SBR) has the reaction volume of 200 liters (max capacity is 400 liters) and it is supposed to remove the biodegradable COD from the

wastewater. It does not provide the full treatment of the wastewater (e.g. nutrients removal), but rather the conditions for the sludge production.

The main steps of the SBR cycle include 5 phases, which are presented in the Table 1. They are filling phase; nitrification phase, which processes with relative extent of the completeness (including aeration and mixing), settling phase and effluent removal. Filling of the SBR has a duration of an hour. A few of the first seconds of SBR filling phase wastewater, which is coming after the primary sedimentation, goes directly to the drain bypassing the filter (phase number 1). The water flows out of the reactor under gravity forces. Aeration is provided only for the biomass oxidation purposes, but not for the complete nitrification. The sludge age of 5 days does not provide required conditions for nitrification processes. Excess sludge is withdrawn from the SBR once a day. To prevent overfilling of the SBR tank the safety pipe is mounted.

Table 1. Cycles of biological wastewater treatment in the SBR.

N	Name of period	Boundary value			Duration [sec]	
		Min	Max	Unit	Min	Max
1	Flush				10	10
2	Influent flow	50	250	Volume in liters	600	3600
3	Nitrification	2	2.3	Dissolved oxygen concentration in [mg/L]	2400	2400
4	Settling				1500	1500
5	Effluent flow	150	500	Volume in liters	20	3600

For research purposes the filtration step was implemented in the treatment system and placed just before SBR. The sketch of the operated system is presented in Figure 1. The filtration system does not work constantly during the filling phase, but rather switching on and off for the backwashing. As it was mentioned before, the SBR filling phase continues for an hour and consists of sequential actual fillings alternating with the periods of the filter backwashing and drainage of backwashed water.

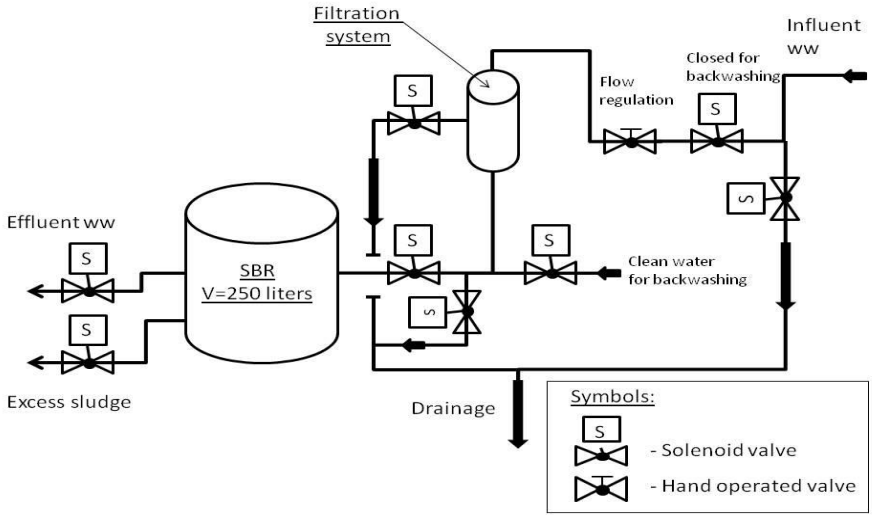


Figure 1. Principal scheme of the treatment system with the filtration system.

Another part of the master project is aiming to develop methods for the OUR estimation. The reliable methods allow correct estimation of the OUR parameter, which is crucial for the efficient operation of the wastewater treatment facilities. The methods can be also applied for the estimation of other parameters, such as the mass transfer coefficient (k_La). The existing procedures to estimate these parameters describe an oxygen profile by a linear equation. The non-linear seg-

ments are ignored, when these procedures are applied. Not considering the data in non-linear segments can lead to losses of consequential information.

The methods were developed in MatLAB software and are based on the measured data, which is provided from the study within PhD of Ing. Jonathan Habermacher. The study is carried out using 6 SBRs, each with the volume of 12 liters.

1.2 Goals of the project

The filtration system, which is placed prior to the SBR, has the average retention capacity of 100 µm and removes inert organics ($X_{U,Inf}$) and inert inorganics ($X_{U,IG,}$). The influent wastewater of SBR consists mainly from biodegradable organics (X_{Bio}), which might contain endogenous residues ($X_{U,E}$), see Figure 2. Assuming that all biodegradable organic is eliminated from wastewater during biological treatment in SBR, the effluent of SBR contains only endogenous residues. Analysis of these residues can give information about their composition and their degradation pathways.

As it was mentioned before the conducted experiments are aiming to assess removal performance of the filtration system in terms of unbiodegradable (inert) influent organics (later used $X_{U,Inf}$ as an abbreviation) and investigate its effect on the sludge composition in SBR. Though it is worthy to mention that 100 µm pore size of the filter might also retain some biodegradable organics. It means that rejected part of waste water compounds unbiodegradable (inert) but also biodegradable organics, see Figure 2.

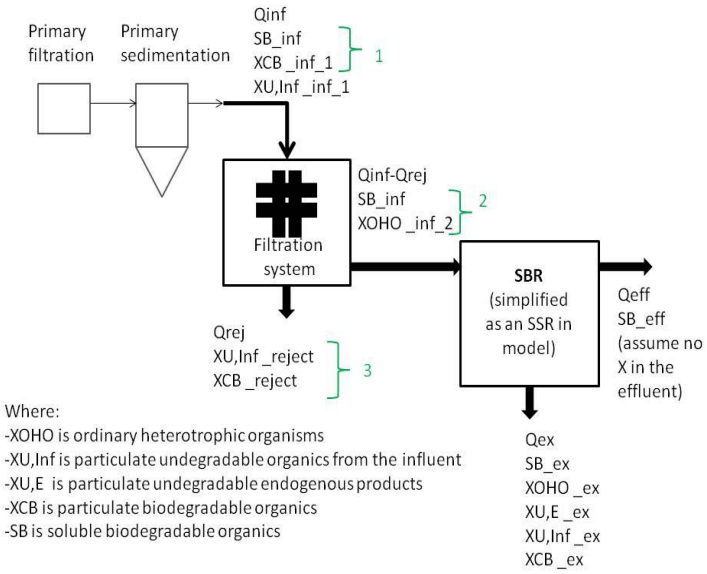


Figure 2. Flow diagram of the of the treatment system and the associated relevant variables.

Section 1. The main task in Section 1 was to determine a fractionation of the COD loads into biodegradable and unbiodegradable parts, depending on a presence/non-presence of the filtration system prior to the SBR. Additionally the mass of the non-biodegradable particulate organic, which was removed by the filter, was defined.

Section 2. The aim of Section 2 was to determine the effect of the filtration system on the sludge composition in the SBR. In order to do it the processes of aerobic treatment, which are taking place in the SBR, were simulated. A simple model of the SBR as a CSTR with internal recirculation was made in Berkeley Madonna program, using an appropriate biokinetic model, which includes growth and decay process(es) of hetero-trophic microorganisms.

Section 3. The section is dedicated to implementation of the original standard method for online OUR estimation (Method 1) and, additionally, three state-of-the-art methods (Method 2-3), which are assuming non-linear effects in the DO profile. Afterwards, the root mean square error (RMSE) of the each method is defined and the OUR estimation results of these methods are compared between each other.

In the conclusion the following question will be answered - Why the ability to estimate both the COD loads in different parts of a system and the Oxygen Uptake Rate (OUR) is important for the sufficient operation of an activated sludgy system? Conclusions of all Sections contribute to this answer.

2 Material and methodology of the work

Chapter 2 aims to give an understanding of the methods and procedures, which were used in order to achieve particular goals of each section and finally come to the final goal of the project. All standard methods, equipment and software, which were used for the experiment are mentioned here.

2.1 Section 1

2.1.1 Fractionation of the COD loads into biodegradable and unbiodegradable parts

For the purpose of defining a fractionation of the main organic fluxes into biodegradable and non-biodegradable COD, the COD- and the ultimate BOD-measurements were carried out.

COD measurement. Three samples of wastewater were taken on the 11th of April: 1. Before the filter, 2. After the filter, 3. From the Filter Cake. It was assumed that the parameters of the wastewater taken that day will be at the same range with the ones for the sample which will be taken for the later BOD measurements (on the 15th of April). Total and soluble COD was determined for these samples, in order to have an understanding of the range for the BOD which will be measured further. Defined COD value of the sample also allows to determine the content of the elements crucial for the biomass.

Equipment. Syringe filters Nanocolor, with 0.7 and 0.45 µm subsequent pore sizes; Dr. Lange Tests. **Procedure of the COD measurements.** Total and soluble COD was determined for the all taken samples. For the soluble COD measurements the wastewater was filtered prior to measurement through syringe filters Nanocolor, with 0.7 and 0.45 µm subsequent pore sizes. Dr. Lange Tests can be used for the COD mass balances of the SBR. To conduct Dr. Lange Test, only few things have to be available. One needs a Dr. Lange Test tube including the direction from the manufacturer and all chemicals required (the chemicals are part of the Dr. Lange Test-box).

Dr. Lange Test tubes for COD assess the COD according to the Standard Methods 2005. Predefined amount of sample has to be added to the test tube, which already contains most of the analytical chemicals needed. Dr. Lange Tests also have to be heated in customized ovens. After the chemical reaction in the test tubes is finished, the tubes can be inserted into a device that measures the photometric absorptivity. Since this device is also a product of the Dr. Lange manufacturer, it is already calibrated for the standard Dr. Lange Tests and returns the concentration in the sample directly by reading the barcode on the test's tube.

The BOD test. Equipment. System OxiTop® . **Procedure of the ultimate BOD** or, in other words, measurements of biodegradability, allow a determination of the amount of molecular oxygen utilized during specified incubation period for biological degradation of organic material and the oxygen used to oxidize inorganic material. For this study respirometric method of BOD measurement was applied. The BOD measurements were carried out according to Standard Methods 2005, 5210 D (Andrew D. Eaton et al. 2005). The main principle of the method, as well as some precisions on open points in the protocol, are listed in the following. The method allows measures of oxygen uptake rate in a closed vessel under conditions of constant temperature and agitation, these measures are continuous over time. System OxiTop® from WTW was used for BOD measurements in this study.

Three samples of the tested wastewater were taken on the 15th of April: 1. Before the filter, 2. After the filter, 3. From the Filter Cake.. The volume of each sample is approximately 1 liter. Three additional samples were taken to allow direct comparison between taken samples: glucose, acetate and seed blank sample.

If it would be impossible to start analysis of the wastewater samples after 2 hours of collection, then the sample should be stored at a temperature below 4°C. The quality control measures have to be taken prior to BOD measurements in order to provide the correct measurements results. The results of the BOD measurements will be correct, only if:

a. a population of microorganisms is capable of oxidizing the biodegradable organic matter (unless seed should be added);
b. a nutrient availability is not limited (unless nutrients should be added);
c. nitrification does not occur and oxygen is consumed only for the biomass oxidation (unless the nitrification inhibitors should be added, e.g. allythiourea (ATU));
d. there is enough constituents crucial for the biomass (as nitrogen, phosphorous, etc.) (unless specific reagents should be added);
e. there is enough high pH capacity (pH buffer should be added).

Based on the measured COD values the sample of the filter cake was diluted to allow the reduction of COD from the value of 5'500 mg COD/l down to 366.67 mgCOD/l, which is in the range of all other wastewater samples taken for the BOD test.

The pH level in all samples was measured and if it needed pH in the sample was justified to pH 7.0 by adding solution of 7.5% H_2SO_4 or solution of 1M NaOH. Initial pH level of all wastewater samples was in the range between 7.6-7.7 pH. Oxygen concentration of the wastewater samples was not adjusted. Initial oxygen concentration of the taken samples was assumed to be not lower and not higher than the desired concentration.

Ammonium powder was added to the samples to provide a COD:N:P ratio of 100:5:1. The amount of powder added to each sample was 0.1 – 0.12 g.

Phosphate buffer (NaH_2PO_4) was added to the samples in order to provide the proper COD:N:P ratio and also to allow pH buffer capacity to the sample. It will eliminate the possibility of pH to be a limiting factor for the test. The amount of phosphate buffer which was added to each sample was 8 ml.

Nutrients and minerals requirements were met by adding the following dosages of the chemicals to each of 12 bottles: 1 ml of iron solution; 2 ml of the trace-compounds; 1 ml of ATU.

After addition of all chemicals all samples were shacked by hands. Further the samples were seeded into an airtight BOD bottles with 1.0 L capacity (see Table 2). The volume of the sample inside each bottle is 97 ml (according manufacturer's instructions).

Table 2. 12 BOD test bottles with the wastewater samples and control samples (are setted on the 15th of April).

Bottle number	Sample description	Bottle number	Sample description
1	Filter cake 1 (FC 1)	7	Wwaf 3
2	FC 2	8	Wastewater before filter 1 (Wwbf 1)
3	FC 3	9	Wwbf 2
4	FC 4	10	Glucose control
5	Wastewater after filter 1 (Wwaf 1)	11	Acetate control
6	Wwaf 2	12	Seed black sample

Seeding procedure was done by adding the seed culture in the form of activated sludge (taken the same day from the SBR) in order to prevent major lags in the oxygen uptake reaction. The volume of the activated sludge was 0.2 ml.

Afterwards the bottles were transported in the special premises where the constant temperature of 20°C (+/- 2°C) is maintained. Before the oxygen measurements all samples were mixed with the opened lid, that allows to bring temperature and oxygen concentration of the sample to an equilibrium with the environment. After mixing each bottle was closed with the special lid which

can track the oxygen level inside the bottle during the specified period of time (27 days for this study) and recorder these measures so they can be later extracted and assessed.

The rest of the wastewater samples, which were taken in the morning, was brought to the experimental hall. The total COD was measured (by Dr. Lange Tests) for each of three of them. Also the certain amount of wastewater from each of three samples was filtered through 0.45 µm Glasfiber filter, so the NH4, NO2 and N03 concentrations of this filtered wastewater can be measured in the laboratory.

2.1.2 Measurement of the COD loads towards the filter and in the filter cake

To determine the part of the solids, being removed from the wastewater by filter application, the COD loads in the wastewater towards the filter and in the filter cake were measured on the 30th of April. Also TSS- and VSS-measurements were done for the same taken samples.

Equipment. Syringe filters Nanocolor, with 0.7 and 0.45 µm subsequent pore sizes; Dr. Lange Tests. **Procedure of the COD measurements.** The total COD was determined using Dr. Lange Test tubes and according to the Standard Methods 2005, Method 410.1 (Andrew D. Eaton et al. 2005). The procedure of the COD test was described in the previous chapter and more details were given.

The measurements were taken within the period of three days (from the 28th of April until the 30th of April). During this period the same filter bag was used for the filtration unit. After 3 days of operation the filter bag was taken out of the filter, all solids were collected and diluted in 5 liters of groundwater. The samples of the wastewater towards to the filter were taken every day within this 3-day period (see Table 3). In total five samples of the wastewater prior to the filter were taken. Sampling wastewater prior to the filter every day within the 3-day period allows the understanding of the parameters of the wastewater coming in the treatment unit during the specified period.

Table 3. Samples, which were taken to define the COD loads on the 28th-30th of April.

Sample ID	Sample	Name of COD test with the range [mg/l]
Wwbf (1)	Wastewater before filter, 28.04.2014, time 16:30	LCK 114 150-1'000
Wwbf (2)	-//-, 29.04.2014, time 07:35	-//-
Wwbf (3)	-//-, 29.04.2014, time 11:25	-//-
Wwbf (4)	-//-, 29.04.2014, time 13:45	-//-
Wwbf (5)	-//-, 30.04.2014, time 10:00	-//-
FC	-//-, 30.04.2014, time 10:00	LCK 014 1'000-10'000

In order to analyze the COD loads in SBR, the volume of water inside the system should be defined. For this reason all volumes of wastewater coming in SBR during the same 3 days (the 28-30th of April) were summed up.

The TSS-VSS measurements. Equipment. Volumetric pipette 50 ml; Fisherbrand Silicone Bulb-Type Safety Pipette Filler; glass fiber filter MN GF-5 with the pore size 0.45 µm; filtration apparatus - membrane filter funnel; filter flasks; vacuum pump; drying oven, for operation at 103 to 105 °C; analytical balance.

Procedure of the TSS-VSS measurements. Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) measurements were made for the filter cake sample, which was taken on the 30th of April. The TSS-measurements were done according to the Standard Methods 2005, 2540D. (Andrew D. Eaton et al. 2005). The sample volume of 60 ml was filtered through a glass fiber filter MN GF-5 with the pore size 0.45 µm. The filters were preheated since the 28th of April at 550°C oven and afterwards cooled down by keeping the filters for 15 minutes at the room temperature. Additionally the TSS-measurements were taken for the blank sample (60 ml of groundwater).

The samples of the wastewater were filtered through the filters, the filters were then dried in the oven at the temperature of 103-105°C. The residue retained on the filter indicated the total non-filterable suspended solids in the sample.

After the TSS- the VSS-measurements were done for the same samples. The TSS-measurements were done according to the Standard Methods 2005, 2540E (Andrew D. Eaton et al.

2005). Volatile suspended solids data is critical for determination the operational behavior and biological concentration throughout the system. The filters used for the TSS-measurements were taken out of the oven and were kept for 5 minutes at the room temperature in order to cool them down. Then they were ignited at 550 °C for 2-3 hours. The weight lost on ignition of the solids represents the volatile solids in the samples.

2.2 Section 2

The model of the SBR was made in Berkeley Madonna program in order to define a composition of the activated sludge in the SBR depending on a presence/non-presence of the filtration system prior to the SBR. For the simplification purposes the SBR was modeled as a CSTR with internal solids recirculation. Two scenarios were modeled in Berkeley Madonna software. The first scenario is made, assuming the filtration unit prior to the SBR, the second one – without the filtration unit.

The biokinetic model, which was applied, includes growth and decay processes of heterotrophic microorganisms and hydrolysis processes as well. All processes are presented in the Table 4.

Table 4. Biokinetic model chosen for the simulation model.

	S_B	$X_{U,Inf}$	XC_B	X_{OHO}	$X_{U,E}$	Process rate
Aerobic growth of heterotrophs	$-1/Y_{OHO}$			1		$\mu_{OHO,Max}*[S_B/(K_{SB,OHO}+S_B)]*X_{OHO}$
Decay of heterotrophs			$1-f_{XU\_Bio,lys}$	-1	$f_{XU\_Bio,lys}$	$b_{OHO}*X_{OHO}$
Hydrolysis of entrapped organics	1		-1			$q_{XCB\_SB,hyd}*[(XC_B/X_{OHO})/(K_{XCB,hyd}+XC_B/X_{OHO})]*X_{OHO}$

All stoichiometry and kinetic parameters were chosen according to ASM 1 model. ASM 1 model, which was applied in the study, is the simplified corrected version 19/01/2013 of ASM 1 with original application by (Henze M. 2000).

The source of the information is a spreadsheet by Hélène Hauduc. For the convenience the parameters with their abbreviation according to the standardised notation rules (Corominas et al. 2010) and their abbreviation in the simplified corrected version of the ASM 1 are listed in the Table 5.

Table 5. State variables, stoichiometric and kinetic parameters chosen for the model.

		Parameter **	Standardised notation	unit	Value* T=20°C
State Variables	Soluble biodegradable organics	S_S	S_B	g COD.m^{-3}	
	Particulate biodegradable organics	X_S	XC_B	g COD.m^{-3}	
	Particulate undegradable organics from the influent	X_I	$X_{U,Inf}$	g COD.m^{-3}	
	Particulate undegradable endogenous products	X_P	$X_{U,E}$	g COD.m^{-3}	
	Ordinary heterotrophic organisms	$X_{B,H}$	X_{OHO}	g COD.m^{-3}	
Stoichiometry	Yield for X_{OHO} growth	Y_H	Y_{OHO}	g X_{OHO}.g XC_B^{-1}	0.67
	Fraction of X_U generated in biomass decay	f_P	$f_{XU\_Bio,lys}$	g X_U.g X_{Bio}^{-1}	0.08
Kinetic	Maximum specific hydrolysis rate	k_h	$q_{XCB\_SB,hyd}$	g XC_B.g X_{OHO}^{-1}.d^{-1}	3
	Saturation coefficient for X_B/X_{OHO}	K_X	$K_{XCB,hyd}$	g XC_B.g X_{OHO}^{-1}	0.03
	Maximum growth rate of X_{OHO}	μ_H	$\mu_{OHO,Max}$	d^{-1}	6
	Half-saturation coefficient for S_B	K_S	$K_{SB,OHO}$	g S_B.m^{-3}	20
	Decay rate for X_{OHO}	b_H	b_{OHO}	d^{-1}	0.62

*For the fraction of Xu,inf generated in biomass decay the value 0.20 [g XU.g XBio-1] from ASM3 was applied (instead of 0.08 [g XU.g XBio-1] from ASM1 given in the Table 5).

For the simulation model the following assumptions were made and the following input parameters were applied. SBR was simulated as a CSTR with complete solids recirculation. The hy-

draulic residence time of 0.25 day (volume of 0.2 m³ and flow rate is 0.1 [m³/day/cycle] with 8 cycles per day) and the solid retention time of 5 days enable the recirculation of solids. For the soluble organic only Soluble biodegradable organic SB was considered and it is 150 [gCOD/m³] defined from the measurements of the 11th of April. No biomass was assumed in the influent in the SBR, it means that the total COD is equal to the sum of SB, XCBin, XU_Infin and XU_E. COD in the effluent of the SBR is negligible. The endogenous residues XU,E are modeled separately from the inert unbiodegradable solids XU_Inf. Total COD in the influent of the SBR is 360 [gCOD/m³] (from the measurements of the 11th of April). The unbiodegradable particulate organic in the influent of the SBR will be defined based on the results of the BOD test, which is aiming to determine a fraction of XU_Inf in total COD. The complete text of the code, which was used for simulation is given in the Appendix 1.

2.3 Section 3

The section is dedicated to implementation of the original standard method for on-line Oxygen Uptake Rate (OUR) estimation (Method 1, a and b versions) and, additionally, two state-of-the-art methods (Method 2), which are assuming non-linear effects in the DO profile. Afterwards, the root mean square error (RMSE) of the each method is defined and the OUR estimation results of these methods are compared between each other.

Modeling was carried out based on the measured data, which was collected during scientific experiments with 12 liter SBRs within the PhD study of Ing. Jonathan Habermacher. It is very important to mention that the SBR, which was studied for Section 1 and 2 is not the same as SBRs, which provided data for Section 3. A set of parameters of biological treatment processes were measured, but only data of Dissolved Oxygen concentration [mg/l] and aeration signal ("1"- when aeration is turned on and "0" – when aeration is off) was used for modeling. Modeling was carried out in MathLab R2013a simulation software. All the scripts, which were written to allow modeling, are presented in the appendixes of the report.

Figure 3 shows variations of dissolved oxygen concentration and aeration signal within one batch cycle, which was measuremed on the 21st of March 2013. With aeration signal data the start and end of non-aerated period of the cycle can be determined. The dissolved oxygen concentration was maintained between 2 and 4.5 mg O2/L. The dissolved oxygen concentrations were measured with constant time interval with the help of oxygen sensors and each non-aerated period has the particular number of measured oxygen concentrations. The non-aerated periods in the beginning of a cycle have less points with measured oxygen concentration than the others in the end of a cycle, where the endogenous respiration takes place.

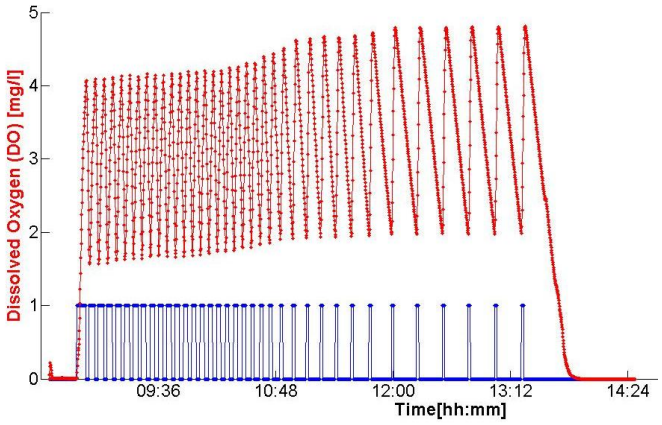
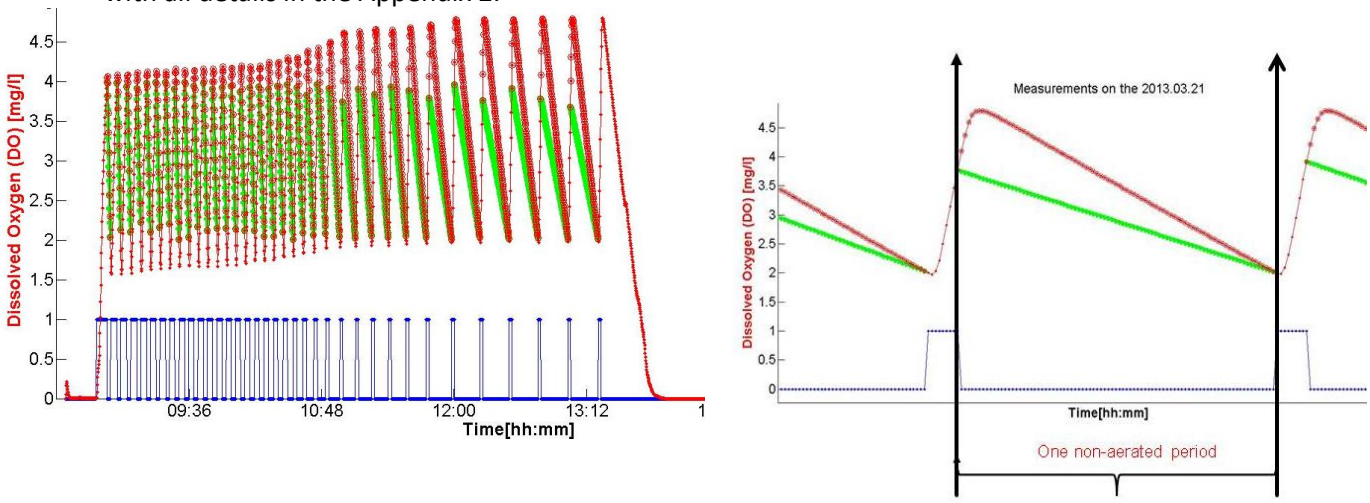


Figure 3. Variations of dissolved oxygen concentration and aeration signal for the batch measurements on the 2013.03.21.

Method 1a is a standard method of OUR estimation, it determinates dissolved oxygen concentrations based on the values in two time points: one in the beginning of a non-aerated period and

another one in the end of a non-aerated period. Computing the slope of the line, which is passing through these both points, the OUR can be quantified (Jansen 2007). The method assumes the linearity of oxygen profile. The oxygen concentration in the beginning of a non-aerated period is not the highest within the entire non-aerated period (as it is shown in the Figure 4 (a,b)). The oxygen concentration is still increasing due to some processes, which are happening in the wastewater (e.g. some air bubbles are left after aeration was turned off). The computation procedure is provided with all details in the Appendix 2.



a) **b)**

Figure 4. Principle of the Method 1a: a)whole cycle; b) one non-aerated period.

Method 1b is a version of Method 1a. It is also based on the assumption of a linearity of a oxygen profile. But the computation of OUR value is based not on two points any more, but takes into consideration all oxygen concentrations, which were measured within a non-aerated period. The computation procedure is based on the least squares method. The least squares method solves over-defined systems of linear equations (see the Equation 1). The method defines an x so the equations fit to the measured data as well as possible. Residual vector (r=b-Ax), which is calculated for that, should then has a minimal length.

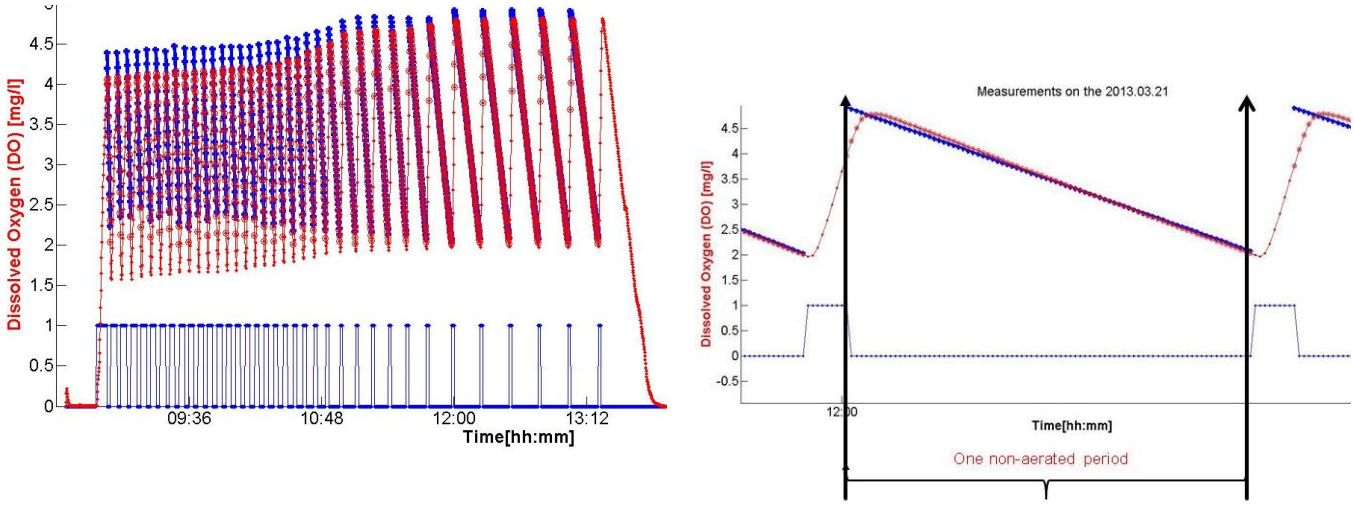
$$Ax = b, \in R^{mxn}, x \in R^{n}, b \in R^{m}$$

Equation 1. Systems of linear equations, which are solved by the least squares method.

The Figure 5 (a,b) illustrates the oxygen concentration, which are modeled using Method 1b. All details of the Method 1b procedure are given in the Appendix 3. There a linear polynomial line with equation $p(x) = a1 + a2 * x$ was computed, so that p(xi) ≈f(xi), i=1…n and Equation 2 is valid (Arbenz 2007-2008).

$$\left\| \begin{bmatrix} 1 & x1 \\ 1 & x2 \\ 1 & xn \end{bmatrix} \begin{pmatrix} a1 \\ a2 \end{pmatrix} - \begin{pmatrix} f(x1) \\ f(x2) \\ f(xn) \end{pmatrix} \right\| 2 = minimal$$

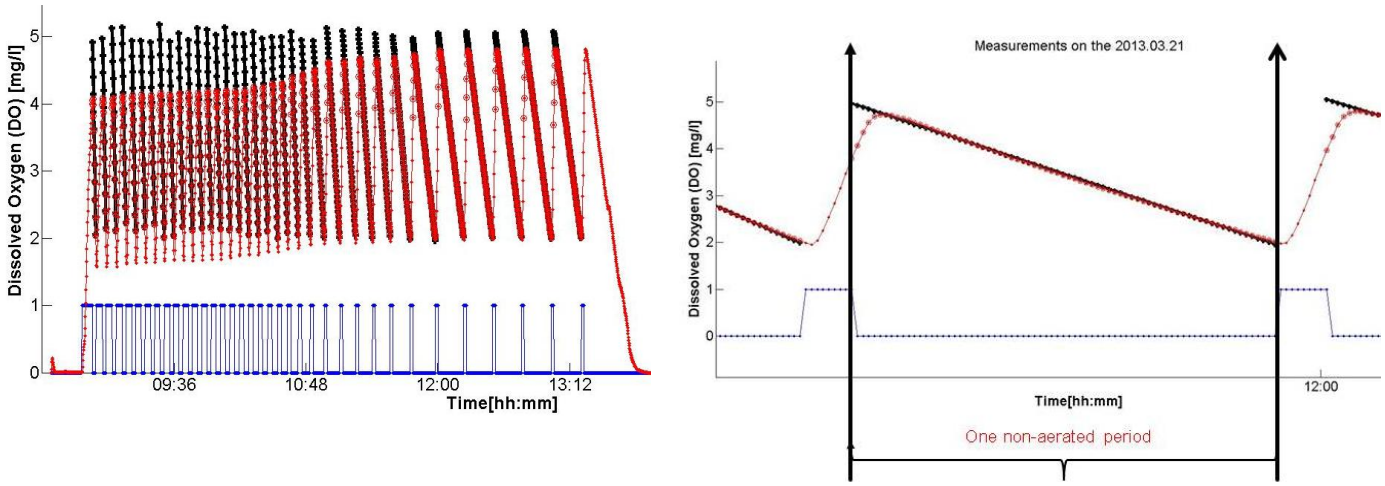
Equation 2. Principle of the least squares computation.



a) b)

Figure 5. Principle of the Method 1b: a)whole cycle; b) one non-aerated period.

Method 2 does not assume the complete linearity of oxygen profile. The method finds a linear segment in the oxygen profile by adjusting time window. All measured data points are used for modeling using Method 2. The slope of regression between each pair of measured values are computed. Afterwards the longest series of slopes within specified Maximum and Minimum values (in this study, 0 and minus infinity, respectively) were found. This series is assumed to be linear. The first three measured points within the found series are taken out from further modeling in order to improve the correctness of the results (see the Appendix 4 and Appendix 5 for more details). The Figure 6 (a,b) illustrated the oxygen concentration, which are modeled using Method 1b.



a) b)

Figure 6. Principle of the Method 2: a)whole cycle; b) one non-aerated period.

Evaluation and comparison of the quality of OUR estimation was carried out by computing the Sum-of-Squared-Residuals (SSR) statistic (or particularly Root Mean Square Error (RMSE) for the current study) for each non-aerated period and for each applied method. For the computation of RMSE the Equation 3 was used. Applying this equation two assumptions were made, they are the following: the errors are unbiased and follow a normal distribution. Using the RMSE helps to provide a complete picture of the error distribution (T. Chai et al. 2014).

$$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n} e_i^2}$$

Equation 3. Computation of the Root Mean Square Error (RMSE)

Where n is an amount of measured data points; e is the difference between measured and modeled data values.

3 Results

In this section of the report the results of the conducted measurements are described. No interpretations are added to the pure facts.

3.1 Section 1

3.1.1 Fractionation of the COD loads into biodegradable and unbiodegradable parts.

The BOD values were measured after 27 days of on-going BOD test (see the Table 6).

Equipment, which was used for the BOD test, allows continuous measurements of BOD values and plots them as a graph on the screen. It is very useful for comparative analysis of the collected data. For instance, it helps identification of the nitrification processes going inside a bottle. Identification of presence of the nitrification is very important for the calculation of un- and biodegradable part of organic.

The sudden increase of BOD concentration level (after seemed to be stabilized period) identified that the nitrification process was going on inside some samples despite the fact that the nitrification inhibitor was added to the sample before test started. The nitrogenous part of the measured BOD value should then be determined. For this purpose, nitrite (NO2) and nitrate (NO3) concentrations were measured in the samples at the time when the BOD test started and after 27 days of the running BOD test. Based on the difference between initial and final the amount of oxygen, which was consumed for the conversion of nitrogen, can be determined [reference]. Calculations were done using the following coefficients: 3.43 mg BOD is needed per 1 NO2-N formation and 4.57 mg BOD - per 1 g NO3-N formation. The results of the calculations are given in the Appendix 6. Carbonaceous part of the measured BOD can be calculated by substituting the nitrogenous BOD from the total measured BOD.

The biodegradable part of the total COD in the sample in the beginning of the BOD test was defined according to the procedure described in (Mecalf & Eddy 2004), using the Equation 4 (is based on the equation 8-1 in (Mecalf & Eddy 2004)) and coefficients from the Table 5. The unbiodegradable part of the COD is defined by substituting the biodegradable part from the total amount of COD. The actual values of un- and biodegradable COD [mg COD/m3] and their fractions in the total COD are given in the Table 6.

$$bCOD = UBOD/(1.0 - Y\_OHO * f\_(XU\_Bio))$$

Equation 4. Determination of the biodegradable part of the total COD [mgCOD/m³].

Where bCOD is the biodegradable part of the total COD [mg COD/m³]; UBOD is the measured ultimate BOD [mg BOD/l]; Y_OHO and f_XU_bio are the stoichiometric coefficients from the Table 5.

Table 6. The results of the BOD test (on the 13th of May) and the fractionation of the total COD.

Name of the sample	COD initial [mg O2/l]	BOD_ 27 days [mg O2/l]	Nitrogenous part of the BOD [mg BOD/l]	Carbonaceous part of the BOD [mg BOD/l]	Biodegradable COD (bCOD) [mg COD/m³]	Unbiodegradable COD (nbCOD) [mg COD/m³]	Fraction of biodegradable bCOD f(bCOD)	Fraction of unbiodegradable nbCOD f(nbCOD) or f_XU,inf
Filter Cake (FC)	460	428	90	338	391	69	0.85	0.15
WW after filtration (WWaf)	351	327	6	321	370	-19	1.05	-0.05
WW before filtration (WWbf)	435	428	36	392	453	-18	1.04	-0.04
Glucose	379	417	56	361	417	-38	1.10	-0.10
Acetate	758	732	-5	737	851	-93	1.12	-0.12
Seed blank sample	8	107	47	60	69	-62	9.21	-8.21

In the majority of the taken samples the concentration of the unbiodegradable organic is negative (see the Table 6). It means, there might be some inaccuracy in the measuring or calculation procedure. The measured BOD value for the seed blank sample is equal to 107 [mg COD/m3] instead of being almost negligible. The “error BOD” value can be introduced in order to correct the measured values of the BOD in the samples. This value is equal to the difference between the measured BOD and theoretical maximum of BOD for the seed blank sample. The theoretical maximum of BOD can be determined as a part of COD, which does not contribute to the oxygen equivalent of the cell debris (Mecalf & Eddy 2004), see Equation 5. The “error BOD” is equal to 53.5 [mg COD/m³].

Theor. Max.BOD = CODtot_in * (1-Y_OHO*f_XU_Inf)

Equation 5. Determination of the theoretical maximum BOD [mgBOD/m³] for the seed blank sample.

Where Theor.Max.BOD is the theoretical maximum BOD [mg BOD/m³], CODtot_in is initial total COD, measured in the sample [mg COD/m³]; Y_OHO and f_XU_bio are the stoichiometric coefficients from the Table 5.

The rough assumption can be done , that the same “error BOD” is valid for all samples. Most probably there were not the same misleading processes in the measuring or calculation procedure in the all samples, but there is no way to quantify the difference between them. The new values of the carbonaceous part of the BOD were calculated for all samples. These values were applied for the calculation of “corrected” values of un- and biodegradable COD in each sample [mg COD/m3] and their fractions in the total COD. The results are presented in the Table 7.

Table 7. The corrected results of the BOD test and un/biodegradable COD.

Name of the sample	COD initial [mg O2/l]	BOD_ 27 days [mg O2/l]	Nitrogenous part of the BOD [mg BOD/l]	Carbonaceous part of the BOD [mg BOD/l]	Carbonaceous part of the BOD [mg BOD/l] corrected with "error BOD"	Biodegradable COD (bCOD) [mg COD/m³]	Unbiodegradable COD (nbCOD) [mg COD/m³]	Fraction of biodegradable bCOD f(bCOD)	Fraction of unbiodegradable nbCOD f(nbCOD) or f_XU,inf
					Corrected with "error BOD" values				
Filter Cake (FC)	460	428	90	338	285	329	131	0.71	**0.29**
WW after filtration (WWaf)	351	327	6	321	267	308	43	0.88	**0.12**
WW before filtration (WWbf)	435	428	36	393	339	391	44	0.90	**0.10**
Glucose	379	417	56	361	308	355	24	0.94	**0.06**
Seed blank sample	7.53	107	47	60	6.5	7.5	0.0	1.00	**0.0**

3.1.2 Measurement of the COD loads towards the filter and in the filter cake

The results of the COD-measurements for the five samples of the wastewater before the filter and one filter cake sample are presented in the Table 8.

The total volume of wastewater, which entered the system during the specified period (from the 28 until the 30th of April), were defined and it is equal to 971 liter of wastewater.

With simple calculations the mass of the organics, which entered the system after 3 days of operation, can be determined. 971 liters of the wastewater with the average (over the 3-day period) COD concentration of 384.8 [mgCOD/l] brought into the system 373'750 mg of the total COD. At the same time the amount of the total COD rejected from the filter after the 3-day period is 19'515 mg of the total COD.

With an application of the fraction coefficient, which was determined in the previous section, the mass of the undegradable particulate organic in the wastewater prior to the filter and in the wastewater rejected from the filter can be determined. 10.0% of undegradable organic in the wastewater prior to the filter gives 37'375 [mgCOD], which entered the system after 3 days of operation. At the same time 28.5% of undegradable particulate organic in the filter cake sample gives 5'560 [mgCOD] of undegradable organic, which was removed from the wastewater by filter application. Hence, 15% of all particulate undegradable organic, which entered the system, were retained in the filter.

Table 8. Mass of the total COD and of the Xu,inf for the samples, which were taken on the 28th-30th of April.

Sample ID	Measured COD [mg/l]	Average COD [mgCOD/L]	Volume of the wastewater[l]	Mass of COD [mg COD]	f(XU,Inf)	Mass of Xu,inf [mg COD]	fraction of the inluent Xu,inf [%]
Wwbf (1)	355						
Wwbf (2)	311						
Wwbf (3)	489						
Wwbf (4)	437						
Wwbf (5)	332	385	971	373'750	0.100	37'375	100%
FC	3'903	3'903	5	19'515	0.285	5'560	15%

The results of the TSS- and VSS-measurements are given in the Appendix 7. The concentration of the total suspended solids, measured for the filter cake sample diluted in the 5 liters of

groundwater is 2.63 [g/l]. It leads to the conclusion, 2.63 [h/l]*5[l] = 13.15 [g] of total suspended solids were retained in the filter bag after 3 days of operation. 93.2% of total suspended solids are determined to be volatile suspended solids, their amount is equal to 12.25 [g]. Almost negligible results of TSS- and VSS-measurements for the blank sample state for the correct measurement results of the filter cake sample.

3.2 Section 2

The results for the 2 simulation scenarios are presented in this section.

The first scenario assumes the absence of the filter before the SBR. The value for the fraction of the unbiodegradable organic in the total influent COD was taken from the results of section 3.1.1. Two versions of the first scenario were made. In version 1 the unbiodegradable fraction (F_XU_Inf=0.15), which was determined based on uncorrected with "error BOD" values, was applied. In version 2 the fraction of unbiodegradable organic (F_XU_Inf=0.29), which was determined based on corrected with "error BOD" values of measured BOD, was used.

In the second scenario the biological processes inside the SBR were simulated, considering the filter before the SBR. Also two version of the second scenario were made. Version 1 assumes the fraction of unbiodegradable organic (F_XU_Inf=0.12) in the influent in the SBR according to the results of section 3.1.1. Version 2 assumes the absence of unbiodegradable organic in the influent wastewater, such a "best case" scenario.

The results of the simulation of the activated sludge composition in the SBR according to four different scenario are given in the Table 9. The simulation was run for 30-day period of operation, which is slightly longer than three times SRT the system, when a system comes to the equilibrium.

Table 9. The results of the simulation of the activated sludge composition in the SBR according to four different scenario.

										Fraction of the XT total solids		
Scenario	**Comment**	**Simulation time [days]**	**Initial total COD [gCOD/m3]**	**Fraction* of unbiodegradable organic f_XU_Inf**	**Total solids concentration (XT) [gCOD/m3]**	**Concentration of unbiodegradable particulate organic (XU_Inf) [gCOD/m3]**	**Concentration of slowly biodegradable organic (XCB) [gCOD/m3]**	**Concentration of endogenous residue (XU_E) [gCOD/m3]**	**Concentration of heterotrophic biomass (XOHO) [gCOD/m3]**	**Fraction of unbiodegradable particulate organic (F_XU_Inf)**	**Fraction of endogenous residue (F_XEnd)**	**Fraction of heterotrophic biomass (F_XOHO)**
1.1	unbiodegradable organic and without BOD error	40	360	0.15	3815	1080	20	1039	1676	0.28	0.27	0.44
1.2	With unbiodegradable organic and with BOD error	40	360	0.29	4370	2088	15	868	1400	0.48	0.2	0.32
2.1	With filter, with 12% of unbiodegradable organic in the influent	40	310	0.12	3182	744	17	926	1495	0.23	0.29	0.47
2.2	without unbiodegradable organic in the influent	40	310	0	2770	0.028	21	1052	1698	1.00E-05	0.38	0.61
* calculated in section 3.1.1												

3.3 Section 3

Section 3.3 gives the results, which were obtained for the OUR estimation and RMSE between modeled and measured oxygen concentrations using Method 1a, 1b and 2.

Figure 7 illustrates OUR, which have values calculated according to three methods separately. OUR are given for four different days of measurements, these days are chosen in the beginning, middle and in the end of all measuring company.

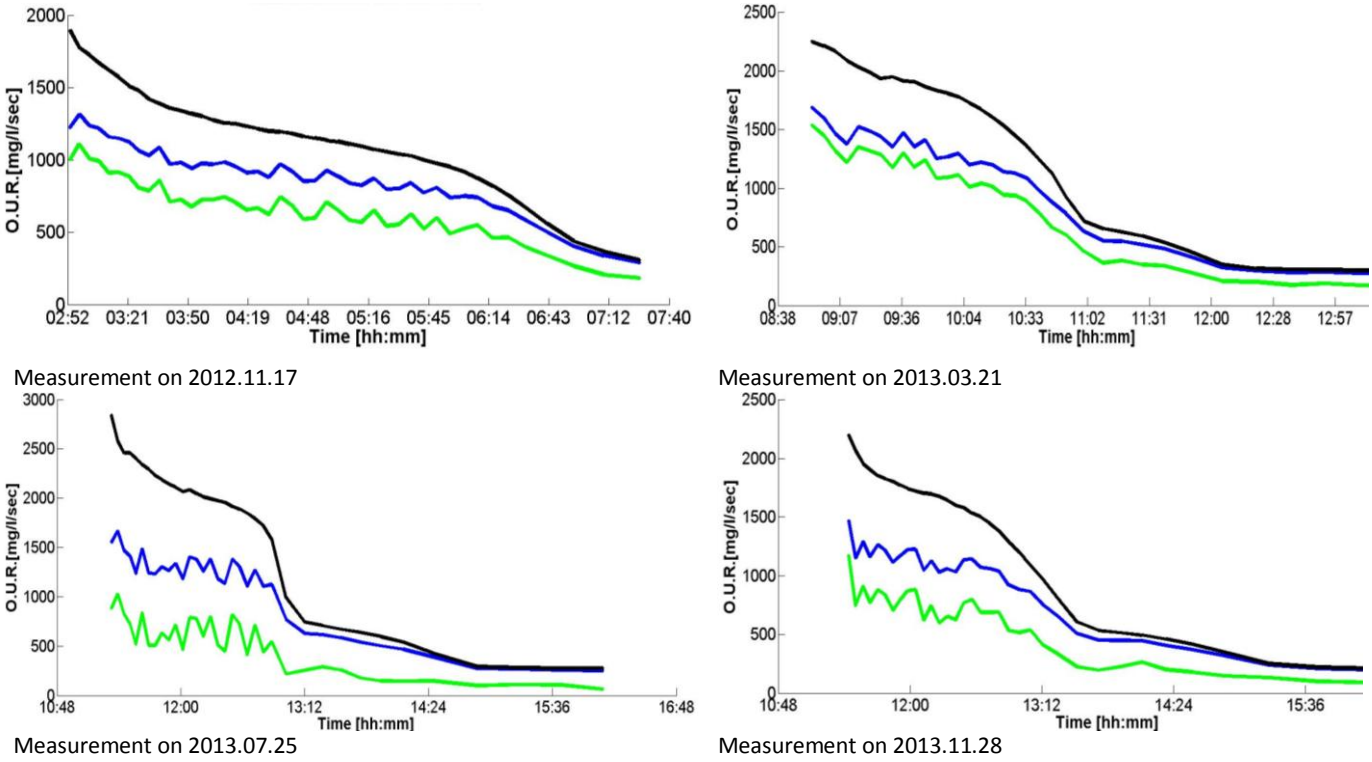


Figure 7. OUR computation results for Methods 1a (green), 1b (blue) and 2 (black).

Figure 8 illustrates RMSE values, which were defined using three Methods (described in section 2.3). As it can be seen from the graph, Method 1b has the lowest RMSE values (in the range between 0.05 and 0.78 [mg O2/l]) and Method 1a has the highest RMSE values (in the range between 0.17 and 2.23 [mg O2/l]). RMSEs for Method 1a are about two orders of magnitude higher than others for Method 1b. Though the RMSE curves for three different methods have similar shape.

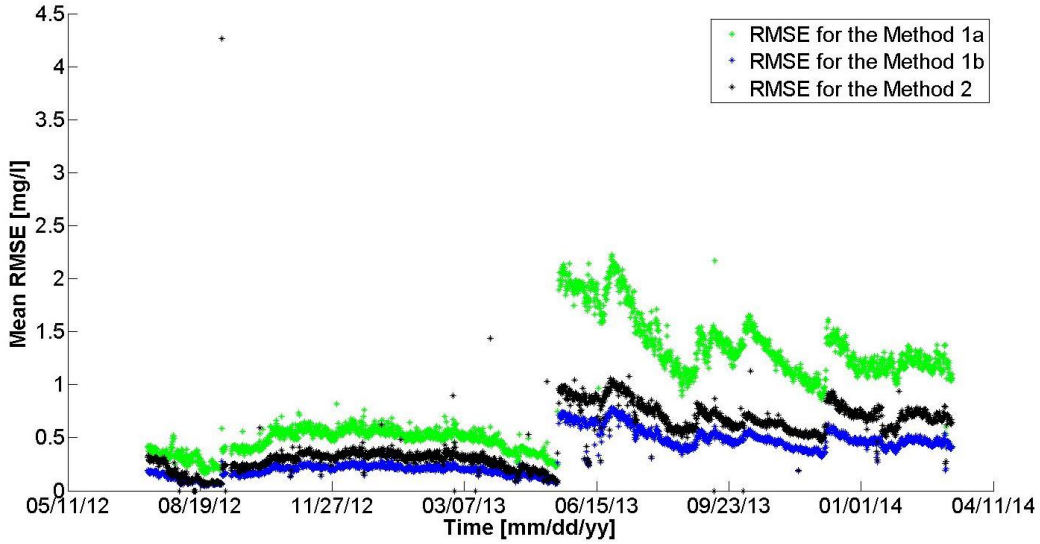


Figure 8. RMSE values, which are computed for Methods 1a (green), 1b (blue) and 2 (black).

There are some unusual time periods when RMSE values changed a lot. Information about some processes or event, which might be carried out or happened at the same time periods, was tried to be found. It might be very important for further interpretation of the results. The information, which was found are presented in **Table 10.**

Table 10. Information concerning events and processes, which were at the same time periods with the sudden increases or RMSEs.

Date, when the sudden increase in RMSE occurred	Information about processes/event, which occurred at the date
2013.06.27	In reactor number 5 ("R5") I had increased the aeration step from 17220 sec length to 38820 sec, since I had the impression that the substrate oxidation wasn't complete.
2013.05.15	The air-flow rate in the Reactor 1, 3 and 5 is increased from 80 to 150 mg O2/l. This new setting was kept from that moment on.
2013.08.18	nothing exceptional reported
2013.09.01	nothing exceptional reported
2013.10.13	nothing exceptional reported
2012.08.29	Ordinary reactor cleaning is done, in all reactors. Some sludge is transferred from the SBRs to the SSRs, or vice versa. Especially 1 l of sludge is transferred from R1 to R2.
2012.09.18	Ordinary reactor cleaning is done, in all reactors. Some sludge is transferred from the SBRs to the SSRs, or vice versa.
2012.08.2	Cleaning of the O2-sensor of R5. Electricity failure.

4 Discussion

Discussion gives the interpretations of the collected results. Some hypotheses are stated and reasoned with stringent arguments and concrete data.

4.1 Section 1

4.1.1 Fractionation of the COD loads into biodegradable and unbiodegradable parts.

In the BOD test it was determined that unbiodegradable part of organic in the filter is equal to 28.5% [131 mg COD/m³] of the total COD. A unbiodegradable organic part in the wastewater towards the filter is 10% [44 mg COD/m³] and a part in the wastewater after the filter is 12% [43 mg COD/m³] of the total COD. The difference between the fraction values of unbiodegradable organic in the samples of wastewater before and after the filter is almost negligible. Through generally the obtained results seem to be logical, as a fraction of unbiodegradable organic in the wastewater after the filter is larger than in the wastewater prior to the filter. There is a removal of unbiodegradable organic from the wastewater.

The percentage of the biodegradable organic in the filter cake is close to 71%, that prove the assumption, which was made in Section 1.2, that the filter with pore size of 100 µm retains also some biodegradable organic. The following fact can contribute to the substantial content of biodegradable organic in the filter. Before taking a sample of the filter cake for the BOD analysis the filter was operated under the normal conditions for 3 days. During this period the backwashing mode was activated. It means that after several minutes of a period, when wastewater was passing through the filter, the filter bag was washed up with clean water. As a result of it the part of solids was removed each time and may decrease the content of solids in the filter cake.

Despite the fact that the BOD measurements were carried out according to the standardized method, there is **an uncertainty of the BOD measurements**. Common problems of the BOD test can lead to different results and decrease the accuracy of the test:

- Dilution water without any chlorine, toxic, etc. elements;
- Adding the right amount of seed;
- D.O. membranes and probe performance;
- Poor precision;
- Nitrification;

- Sample toxicity;
- Improper interpretation of results; etc. (George Bowman et al. 2004)

Some possible problems, which might contribute to the accuracy of the BOD test results, are described further in the report.

CO2 stripping. The changes of pH level can give an insight into some unconsidered processes going on during the BOD test. Prior to the start of the BOD test the phosphate solution was added in order to provide sufficient buffer pH capacity. The following day after the start of the test (on 16th of April) pH level started to increase, see the Appendix 8. It can be explained by CO2 stripping processes, which were carried out inside the BOD bottles. Being in a gas phase, CO2 could contribute to the pressure inside the bottles and effect the measured values (as a manometric type of BOD measuring equipment was applied for the test).

In order to mitigate the effect of CO2 gas on the measurement results, the manufacturers of the BOD bottles provide NaOH in solid form in the filter, which is placed in the bottleneck. NaOH captures CO2 according to (V. Nikulshina a 2008/140). The Several pills of NaOH were placed inside each BOD bottle. There was no calculations done to define the required amount of NaOH for each samples and to assess the amount of NaOH, which is high enough to capture all formed CO2 (see the Equation 6.

$$2NaOH(s) + CO2(g) = Na2CO3(s) + H2O(g)$$

Equation 6. CO2 capture by NaOH.

Biological processes inside the BOD bottles result in the formation of CO2. If there is high BOD concentration, there are good conditions for CO2 formation (Alan Bowers 2003). Decrease in alkalinity and increase in pH level, both follow the CO2 stripping. These processes are described by the Equation 7.

$$CO2+H2O=H2CO3$$
$$H2CO3=HCO3^{-}+H^{+}$$

Equation 7. Formation of H^+ ions due to CO2 stripping.

The increase of pH level indicates insufficient buffer capacity of the tested samples. The buffer capacity measure of ability of the sample to resist changes in pH level. Quantitatively, buffering capacity is defined as the number of moles of a strong acid or strong base that are required to change the pH of 1 liter of the solution by 1 pH unit (Lee 1997). The procedure of quantitative assessment is quite simple and can be described as following. The number of drops of 0.1 mL HCl has to be defined, which are changing pH level by 1 pH unit, by measuring the difference between initial pH of the sample and pH after adding the HCl acid. Afterwards the buffering capacity of the sample can be defined with the Equation 8.

$$\text{Buffering capacity} = \frac{\#\text{drops HCl}}{\text{Vsample(mL)}} \text{x} \frac{0.067\text{mL}}{1\text{dropHCl}} \text{x} \frac{1\text{L}}{1000\text{mL}} \text{x} \frac{0.1\text{moleH}+}{1\text{L HCl}}$$

Equation 8. Buffering capacity of the sample.

Where 0.067 mL is the volume of one drop of HCl acid, 0.1 mole H+ has 1 L of HCl. (Lee 1997)

Nitrification. As a result of CO2 stripping, pH level increased from 7.0 up to 7.5 and created optimal conditions for a nitrification (see Figure 9).

The nitrification was detected in almost all samples, except samples with the wastewater after the filter (see results of the Table 7 and Appendix 6). The COD content there was the lowest among all tested samples. It might be a reason, why nitrification did not occur there. Due to going on nitrification the nitrate stripping took place in the BOD bottles. It decreased the pH level and values of pH for the tested samples are given in the Appendix 9. The range of pH level for the samples, where the nitrification was identified, after 27 days of running test stayed at the level 7.5-7.7. The samples with wastewater after the filter (thus without nitrification) has 9.0-9.5 pH. Nitrification process is an oxygen consumption process. The part of BOD, which was measured in the BOD test contributes to the conversion of nitrogen in forms of nitrite and nitrate. The correct determination

of the nitrogenous BOD can effects the accuracy of the carbonaceous BOD value and introduce additional uncertainty in the results.

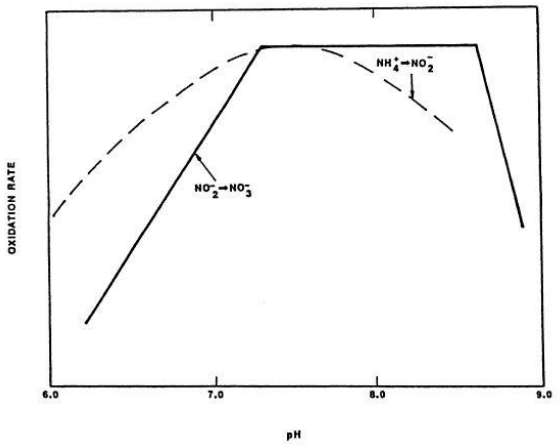


Figure 9. Effect of pH on ammonia oxidation (Sedlak 1991).

Excessive chloride content in dilution water. The fact that ground water, which was used for dilution of the samples, contains about 50[mg/l] of chloride can also explain inaccuracy of the BOD test results. This value is several orders of magnitude larger than maximum residual disinfectant level of 4 [mg/l] (provided by EPA agency) (EPA 2014). According to the standardized method the water, which is used for dilution, must be free from chlorine, chloramines, or acids. The measures to decrease or eliminate chloride content in the groundwater were not carried out.

The uncertainty of the results of the conducted BOD test was defined. The measurements of the BOD were done for the 12 samples, which were taken from the wastewater in different parts of the activated sludge system and for three samples for comparison (Glucose, Acetate and Seed Blank samples). The several samples, which were taken 4 times for filter cake, three times for the wastewater after the filter and 2 times for the wastewater before the filter). The several samples allows several measurements and thus allows computation of the uncertainty of the results. The results are presented in the Appendix 10.

4.1.2 Measurement of the COD loads towards the filter and in the filter cake

In section 3.1.2 the actual mass of the unbiodegradable organic, which was retained in the filter, was determined. The mass is equal to 5’560 mg COD and accounts for 15% of total mass of unbiodegradable organic entering the system.

15% of unbiodegradable organic, which were retained in the filter bag, can lead to the conclusion regarding to not high efficiency of the applied filter. But the following fact should be taken into consideration during an interpretation of the results. The assumption was made in the beginning that the fraction coefficients of the unbiodegradable part of organic in the samples, which were used for the mass calculations, can be used as those, which were calculated in section 3.1.1. Though determination of the fraction coefficients in section 3.1.1 was done based on the measurements of COD and BOD of the sample, which were collected while a backwashing mode of the filter filling phase was activated. Afterwards due to the lack of time for the laboratory work, these coefficients were applied for the mass calculations in section 3.1.2, where COD measurements were collected while a backwashing mode was inactivated. For the more precise calculations of the unbiodegradable organic mass these coefficients also have to be determined for the inactivated mode of filter filling.

As a result of the TSS measurements the fact that 13.15 [g] of total suspended solids were retained in the filter bag after 3 days of operation can be stated. VSS was determined to account for 93.2% of TSS, it means that content of organic solids is substantially higher than content of inorganic solids in the samples.

4.2 Section 2

Though four scenarios were made, the main focus is on the scenario (Scenario 1.2) with the filter prior to the SBR and 29% of unbiodegradable organic in the influent and on the scenario (Scenario 2.1) without the filter and with 12% of unbiodegradable organic in the influent.

The comparison between these two scenarios helps to understand the effect of the filter on the sludge composition in the SBR. The fractions of different microorganism groups in the total solids concentration are presented in the Table 9.

It is worth to mention again that the inert and endogenous parts of unbiodegradable organic were simulated separately. The inert part was assumed to accumulate in the sludge and the endogenous part was formed due to decay of bacteria.

In Scenario 1.2 the concentration of unbiodegradable organic (2088 [gCOD/m3]) contributes a lot to the total solids concentration (4370 [gCOD/m3]) and it is equal to a half of the total solids concentration. In Scenario 2.1. with the filter the content of unbiodegradable organic is twice lower (23% of the total solids concentration versus 48% in Scenario 1.2). The effect of the filter, which is installed prior to the SBR, is clear and has a positive influence.

The concentration of the heterotrophic biomass for both scenarios is the same and it is equal to about 1400 [gCOD/m3]. The unbiodegradable organic in the sludge just accumulates there and does not transform into other biological active forms. It contributes to the total solids content and thus the mass of the sludge. Decreasing the amount of unbiodegradable organic in the sludge allows usage of the less amount of the sludge while having the same amount of active biomass.

In Scenario 1.1, where the filter prior to the SBR was not considered, the fraction coefficients for unbiodegradable organic were applied without “error BOD” correction. Since the unbiodegradable fraction in the influent wastewater is 15% (which is lower than in Scenario 1.2 with 28%), the unbiodegradable fraction in the sludge accounts to 28%. These results cannot be treated as a consistent results, since they were not corrected with “error BOD” value and thus doubt their correctness.

In Scenario 2.2 the “best case” scenario was simulated. The 100% efficiency of the filter was assumed and a total removal of unbiodegradable organic for the influent wastewater was suggested. The fraction of unbiodegradable organic in the sludge is negligible for this scenario. The concentration of the heterotrophic biomass in the sludge stays at the same level as for other scenarios and it is even a bit higher (1700 gCOD/l). The highest heterotrophic fraction and the lowest mass of the total solids in the sludge makes this scenario the most efficient among others, though it is almost impossible to achieve.

4.3 Section 3

4.3.1 Method 1a, Method 1b and Method 2 for the OUR estimation

Section 3.3 contains the results of the OUR estimation using three different methods (Method 1a, Method 1b and Method 2), which were developed in MatLab software. RMSE values of these methods, or with other words, a fit to the measured data, differentiate between methods.

Method 1b has the lowest RMSE value, while Method 1a shows the highest RMSE values. It is logical, because the Method 1a operates only with two values of dissolved oxygen concentration (one concentration in the beginning and one in the end of non-aerated period) and thus cannot be consistent. While not considering the majority of the data, which was collected during a non-aeration period, it might creates a bias in the results. Methods 1b and 2 consider all measured dissolved oxygen concentrations and have two orders of magnitude lower RMSE values.

More problematic to explain why the RMSE values of Method 1b are lower than those for Method 2. Method 1b considers all measured dissolved oxygen concentrations, assuming linearity of oxygen profile. At the same time, Method 2 doubts a linearity of the entire oxygen profile and looks for the linear parts of the profile. During this computation procedure, some oxygen concentrations can also be not considered. Thus some information losses in Method 2 lower the preciousness of the results, as the RMSE values appear to be higher there.

The profiles of the OUR values, which were estimated using three different methods, are presented in the Figure 11. Since the RMSE value for the method 1b is the lowest, the OUR values for this method should be closest to the right estimation. The OUR values, which were computed using Method 2, are higher than the right estimation of Method 1b. But the OUR profile of Method 2 is much smoother than other profiles and does not have so rapid alliterations in values from one non-aerated period to another. The OUR profiles of Methods 1a and 1b have fluctuations and the results computed using these profiles can vary depending on the chosen non-aerated period.

Based on the OUR profiles, Method 2 might be assumed to be the best, since its OUR estimation results does not changes so much from period to period. Though Method 1b should be considered as the most consistent among all three tested methods. Assessing consistency of the computation methods with RMSE is more reliable, since RMSE was computed using all the data: modeled and measured concentrations.

As it was mentioned before, apart from the fact that the RMSE values of all three methods are different their shape is very similar. This fact enables to discuss interesting trends and parts of the RMSE profile for all methods simultaneously. Three different phases can be allocated in the RMSE profile and they are presented in Figure 10.

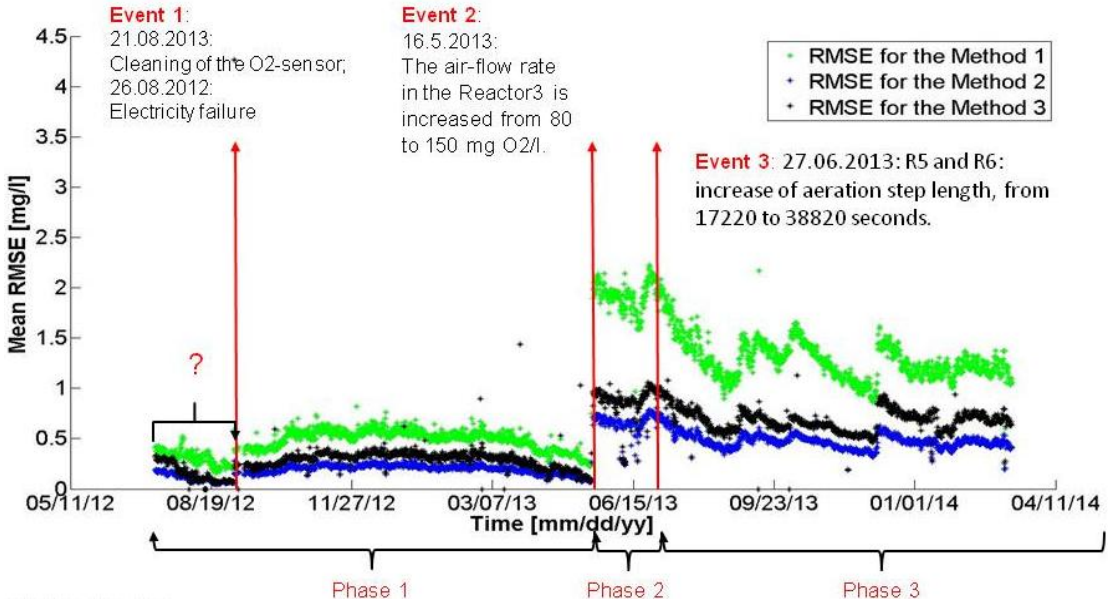
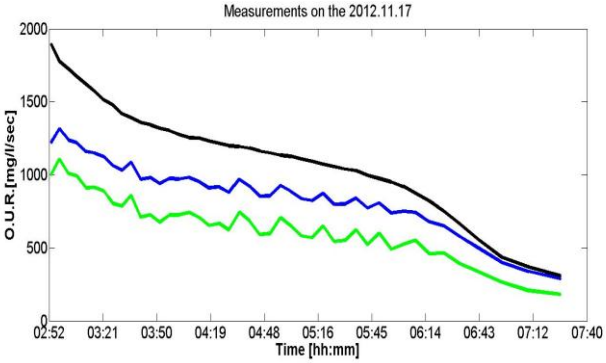


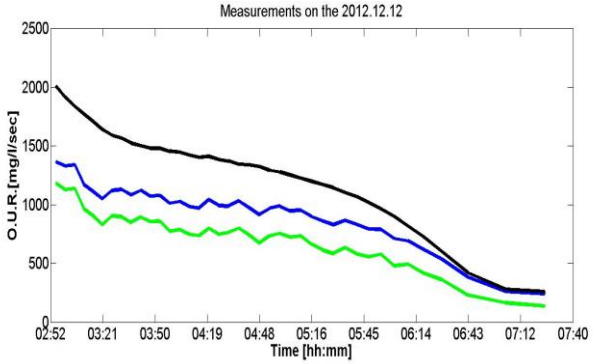
Figure 10. Differentiation of three phases in the RMSE profile.

Phase 1 corresponds to the period before the changing of air-flow rate in the reactors (see Event 2 in the Figure 10), which was made on the 16-17th of May 2013. The air-flow was increased from 80 up to 150 [mg O2/l]. The changes in the OUR profile and in the Dissolved Oxygen profile (see Figure 11 and Figure 12) can be seen after this event. RMSE value suddenly increased from about 0.3 up to almost 2 [mg O2/l] (for Method 1a). Before the air-flow rate was changed, the OUR profile was flash and smooth. The part of endogenous respiration was short comparing to the entire duration of the cycle. The values of OUR from comparatively constant in the phase before, were decreasing during endogenous respiration and achieving their minimum at the end. After the 16th of May 2013 (Event 2) the OUR profile has two pronounced parts, their durations are almost equal. The first part of the OUR profile correspond to the aerobic respiration phase, while the second part – to the endogenous respiration. The endogenous respiration phase became longer than it was in Phase 1 (before the air-flow rate was changed), since more oxygen is available in

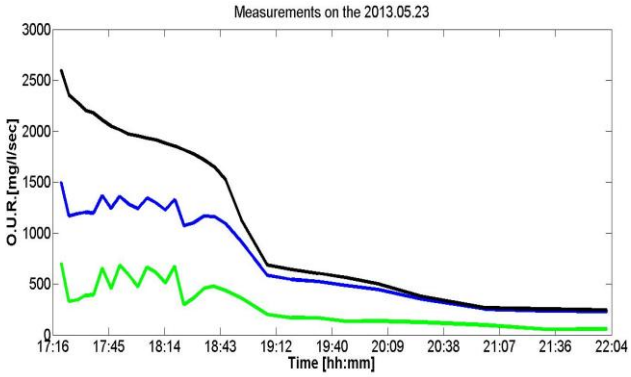
wastewater (Dissolved Oxygen concentration in wastewater increased) and substrate is oxidized faster and decay phase starts sooner. During the second half of a cycle, supplied oxygen is almost not consuming, which makes this operation mode inconsistent.

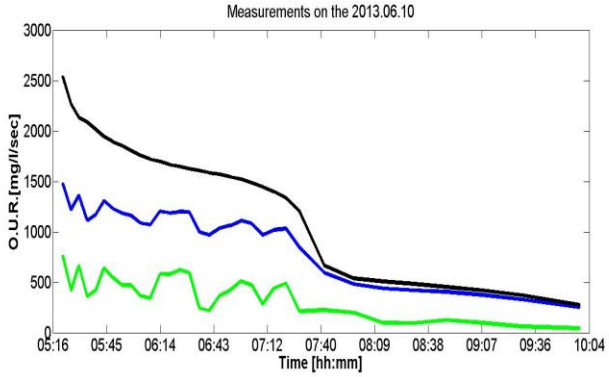
A month later, the aeration step was increased from 17220 to 38820 seconds on the 27th of June 2013. It was made, since the incomplete substrate oxidation was suggested. This event corresponds to the Event 3 in the Figure 10 and Phase 3 began after it. The RMSE values after Event 3 started to decrease and from closed to 2 [mg O2/l] values declined to the range 1-1.5 [mg O2/l] (for Method 1a). The OUR and Dissolved Oxygen profiles changed their shape comparing to Phase before. There is more time now for the substrate oxidation. The endogenous respiration part is still considerably long (at least longer than in Phase 1), but does not equal to the half of the cycle any more. The OUR profile for Phase 3 is not so flash as during Phase 1, it is declining within endogenous part. But the change of the OUR profile slope is not so prompt and there an intermediate phase exists between anaerobic and endogenous respirations. Due to this fact and also due to decreased RMSE value, the decision to increase the aeration step was done correctly.



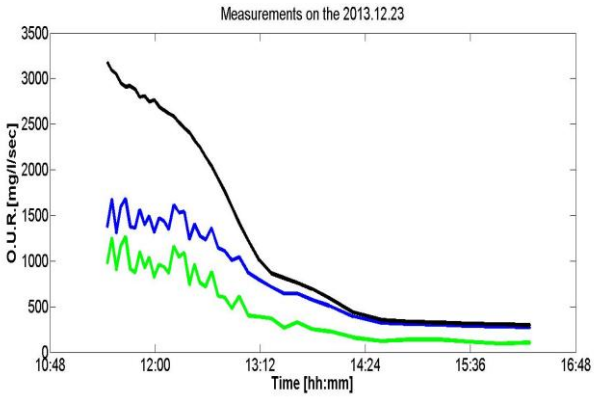


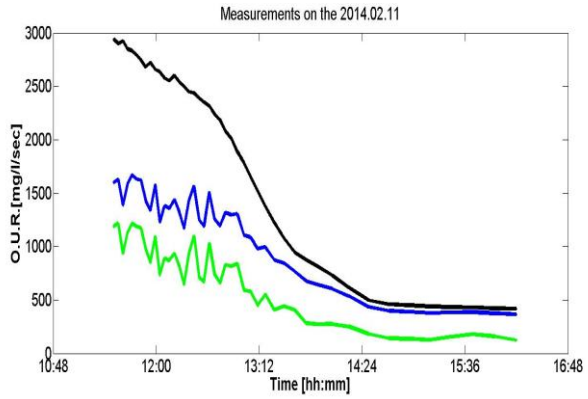
Phase 1: OUR before a increase in flow rate on the 2013.05.16





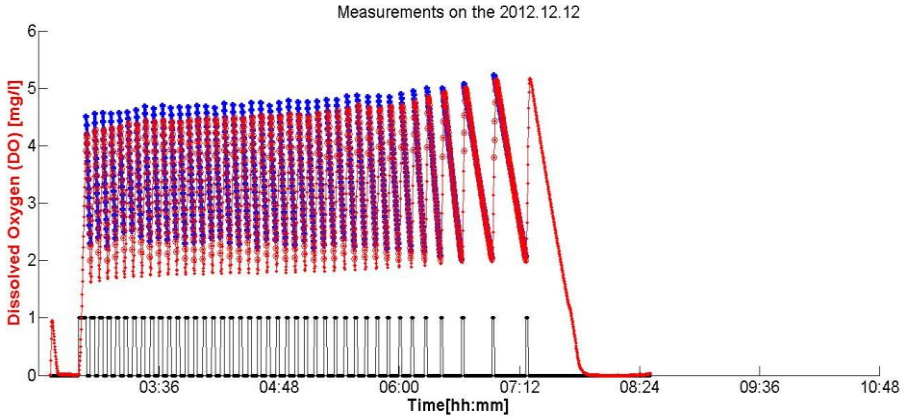
Phase 2: OUR after a increase in flow rate on the 2013.05.16



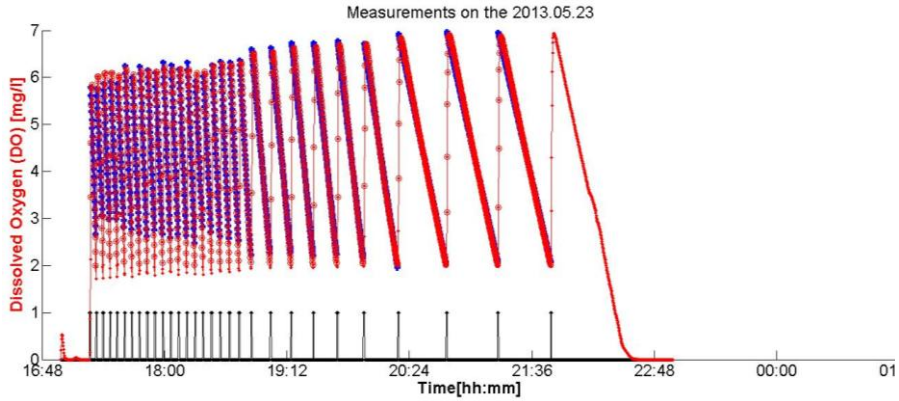


Phase 3: OUR after a increase in aeration step on the 2013.06.27

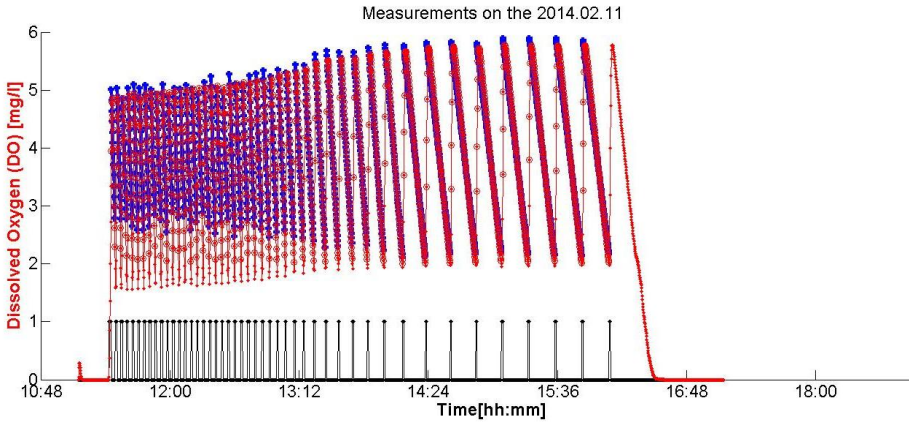
Figure 11. OUR estimation results for Methods 1a (green), 1b (blue) and 2 (black) and for 3 Phases.



Phase 1: OUR before a increase in flow rate on the 2013.05.16



Phase 2: OUR after a increase in flow rate on the 2013.05.16



Phase 3: OUR after a increase in aeration step on the 2013.06.27

Figure 12. Dissolved Oxygen profiles for Methods 1a (green), 1b (blue) and 2 (black) and for 3 Phases.

There is also one interesting change of the RMSE profile (see Event 1 in the Figure 10), which happened in the end of August 2012. The RMSE values from very low (range 0.1-0.25 [mg O2/l] increased up to the range of 0.5 [mg O2/l]. O2 sensors were cleaned on the 21st of August. But this procedure is done regularly (every 2 weeks) and can not affect OUR estimation results so much. Furthermore the electricity failure occurred on the 26th of August 2012. It was summer time and the air temperature can be high enough, plus without electricity supply aeration and temperature control of the reactor were not available for some time. It might affect the microorganisms inside the reactors and lead to the changes in the activity of biomass and thus oxygen consumption.

4.3.2 Method 3 for the OUR estimation

Additionally Method 3 for the OUR estimation was implemented.

Methodology.

This state-of-the-art method does not assumes the linearity of a oxygen profile. It fits a non-linear function to the oxygen profile of the measured data. All the oxygen concentrations, which were measured during a non-aerated period, are considered. The methods is based on the principle of split the oxygen profile into two distinct segment – concave and convex segment. An intersection point of these segments is an inflection point. The estimated OUR value is a tangent in this inflection point. The method is experimental at this stage.

Results and Discussion.

For the simplification purposes and due to a long computation time of the method, only each 10th Batch and the last Batch was tested. The determined results show that the RMSE values, which are valid for this method, are substantially lower than those for Methods 1 and 2. Method 3 has the RMSE in the range from 0.00091 to 0.022 [mg O2/l], while the RMSE values for Method 1b (which was assumed to be the most consistent) are in the between 0.05 and 0.78 [mg O2/l].

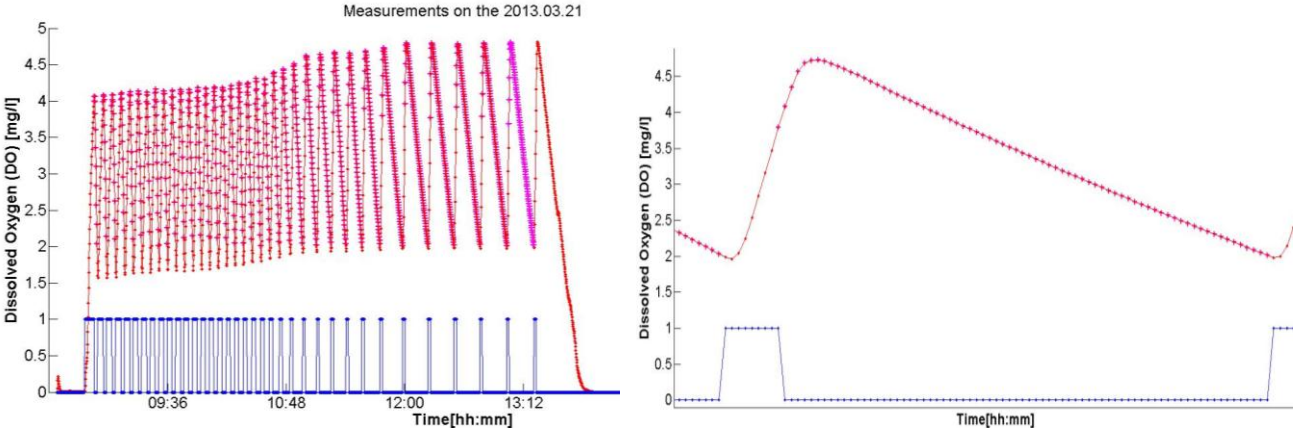


Figure 13. Principle of the Method 3: a)whole cycle; b) one non-aerated period.

The Figure 13 (a,b) illustrates the oxygen concentration, which are modeled using Method 3. It is clear that the modeled oxygen concentration values have a close fit to the measured concentrations.

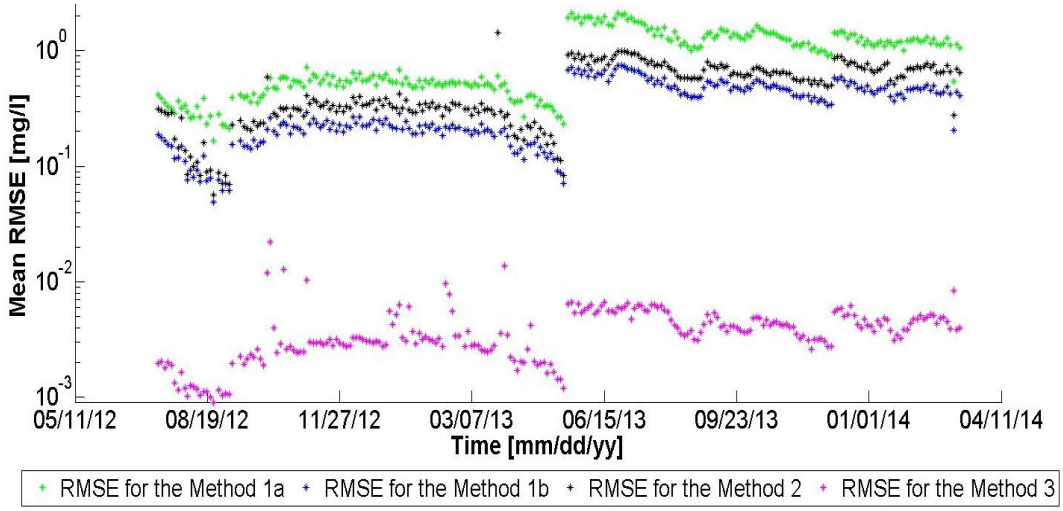


Figure 14. RSME of the Method 1, 2 and 3 for the OUR estimation

Though the RMSE values for Method 3 are several orders of magnitude lower than those of Methods 1 and 2, they are following the similar trends. In the Figure 14 The RMSE values for all methods are plotted in logarithmic scale, which allows to see and compare the shape of their profiles. The shapes are more or less identical, except the fact that Method 3 has a bit more out-of-scale values, when for specific Batches it suddenly increases.

The lowest among all tested method RMSE value of Method 3 can lead to an assumption about the highest consistency of the method comparing to all others. Assuming the non-linearity of the oxygen profile and the attempt to model the measured data using a non-linear function advances in the best fit of the model to the measured data.

5 Conclusion

The laboratory measurements and simulations, which were performed within the study, help to understand biological processes in an activated sludge treatment system. The questions, which were posed in the beginning of the study, and the answers contribute to the knowledge, which is useful for developing consistent operation modes of biological treatment facilities and evaluate the efficiency of treatment processes.

Section 1, where the BOD test was conducted, determined the fractionation of the COD loads in the treatment system. The results conclude that the filter, which is installed prior to the SBR, removes a part of unbiodegradable organic, but also some biodegradable part of the total COD. Though the filter retains 15% of total mass of unbiodegradable organic entering the system, the unbiodegradable fractions in the samples with wastewater before and the filter are just slightly differentiate between each other.

The BOD test, which was done in order to answer the posed questions, showed an uncertainty of the defined results. BOD test is a method, which has a set of drawbacks, it is hard to get precise results using it (it requires a lot of practice), time period between collecting the samples and receiving the results might be too long in some cases. Though following to the standardized procedure and being precise with a preparation and handling of the tested samples, the consistent and precise BOD results can be achieved. Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) tests are the alternatives to BOD test, but they are not sensitive to changes in the chemical composition of wastewater (these tests measure oxygen, which was consumed for the oxidation of all constituents in the wastewater).

Section 2 simulated the biological processes inside the SBR and defined the composition of the activated sludge in the SBR. The SBR, which was simulated as a CSTR with internal recirculation, has a smaller part of unbiodegradable organic in the scenario with the filter (Scenario 2.1). Without the filter prior to the SBR (Scenario 1.2) the content of unbiodegradable organic in the sludge was twice higher. Thus it was concluded that the filtration of unbiodegradable organic out of the wastewater entering the SBR has a substantial impact on the sludge composition and helps to improve system operation. The amount of heterotrophic biomass for the scenarios with and without the filter is equal, so the filter allows usage of less amount of the sludge having the same amount of heterotrophic biomass.

Section 3 developed different methods for OUR estimation. Methods 1a and 1b assume linearity of the oxygen profile, Methods 2 tries to find linear segments in the oxygen profile and Method 3 fits the oxygen profile to a non-linear function. Methods 3 is considered to be the most precious, since it has the lowest RMSE values. This Method is experimental and was not tested in this study with details. Among Methods 1a, 1b and 2, Method 2 has the lowest RMSE value and was assumed to be more consistent among others methods.

The questions, which were answered in all three sections, give an insight to the importance of oxygen uptake processes for the sufficient operation of an activated sludge system. Reliable methods, which allow an on-line estimation of an OUR, can help to discover and eliminate/prevent undesirable processes on time. On the other hand, the additional treatment steps in the system, can

have a substantial effect on the composition of the COD in different parts of the system and thus change oxygen consumption of organic. All processes happening inside the operated system are strongly related to each other, that is why it is very important to be able to tract the variations of all of them. At the same time, this knowledge allow close mass balance in the system, e.g. ThOD mass balance, and discover parts of the system working insufficiently.

6 Literature

Alan Bowers, W Wesley Eckenfelder. *Industrial Wastewater and Best Available Treatment Technologies.* DEStech Publications, Inc, Jan 1, 2003, 2003.

Andrew D. Eaton et al., Lenore S. Clesceri, Eugene W. Rice. «Standard Methods for the Examination of Water & Wastewater.» *Centennial Edition. 21st edition.* 2005. 5.7 - 5.13.

Arbenz, Peter. *Introduction to Matlab.* Zürich : ETH Zurich, Computer Science Department, 2007-2008.

Corominas et al., L., Rieger, L., Takács, I., Ekama, G., Hauduc, H., Vanrolleghem, P.A., Oehmen, A., Gernaey, K.V., van Loosdrecht, M.C.M. and Comeau, Y. *New framework for standardized notation in wastewater treatment modelling.* 61(4), 841-857, Water Science & Technology, 2010.

EPA. «Basic Information about Disinfectants in Drinking Water: Chloramine, Chlorine and Chlorine Dioxide.» *EPA. United States Environmental Protection Agency.* 2014. http://water.epa.gov/drink/contaminants/basicinformation/disinfectants.cfm (Zugriff am 20. May 2014).

Gautam Chalasani, Weimin Sun. "A Report on Measurements of Temperature Effects on Oxygen Uptake Rate in Activated Sludge System." Michigan: Michigan Satet Unviersity College of Engineeering, 2007.

George Bowman et al., Rick Mealy. «BOD Analysis. Basics and Particulars.» Wisconsin State Laboratory of Hygiene, 2004.

Henze M., Grady C. P. L. Jr, Gujer W., Marais G. v. R. and Matsuo T. *Activated Sludge Model No. 1.* Scientific and Technical Report No. 9, London IWA: IWA Publishing, 2000.

Jansen, Marinette Hagman and Jes La Cour. *Oxygen uptake rate measurements for application at wastewater treatment plants.* Vatten 63:131-138, Lund: Water and Environmetal Engineering/Dep. of Chemical Engineering, Lund University, 2007.

Lee, Luann Christensen. «pH and Buffering Capacity of Seawater and Fresh Water.» *Chemicals and Laboratory Supplies.* 1997. http://www.kyantec.com/Tips/phbuffering.htm (Zugriff am 20. May 2014).

Mecalf & Eddy, Inc. *Wastewater Engineering. Treatment and Reuse.* USA: Fourth Edition, 2004.

Sedlak, Richard. *Phosphorus and Nitrogen removal from municipal wastewater: principles and practice .* USA: Lewis Publishers, 1991.

T. Chai et al., and R. R. Draxler. *Root mean square error (RMSE) or mean absolute error (MAE)?* USA: Published by Copernicus Publications on behalf of the European Geosciences Union., 2014.

V. Nikulshina a, N. Ayesa a, M.E. G´alvez a, A. Steinfeld. «Feasibility of Na-based thermochemical cycles for the capture of CO2 from air—Thermodynamic and thermogravimetric analyses.» *Chemical Engineering Journal*, 2008/140: 62-70.

Young, James C. «Oxygen Uptake Rate as a Monitoring and Control Parameter for Activated Sludge Processes.» Indianapolis, IN: Hyatt Regency Indianapolis, 1999. 5-6.

7 Appendix

Appendix 1. The Berkeley Madonna Code for the simulation of aerobic treatment processes in the SBR as a CSTR with internal recirculation.

```
STARTTIME = 0
STOPTIME = 150
DT = 0.00125

;--------Assumptions----------------------------------------------------------
; 1. Sorgtot = SBin+ SUin, where SUin is assumed to be 0, so Sorgtot = SBin
; 2. No biomass was assumed in the influent in SBR, it means CODtotin=Sorgtot+ XCBin+XU_Infin+XU_E
; 3. CODorg in the effluent equals to 0
; 4. XU,E: endogenous residues, will be modeled separatedly from the influent unbiodegradable solids
;--------Design parameters----------------------------------------------------

V = 0.2                    ;volume (in m3); 200 liters
SRT = 5                    ;solid retention time [day] - sludge age
n=8                        ;number of cycles per day
Qinf_c=0.100               ;volume of ww coming in each cycle [m3]
Q=n*Qinf_c                 ;inflow [m3/day]
HRT = V/Q          ;hydraulic retention time [day] - 0.25 day
;---------Measured influent parameters-----------------------------------------------------------
; for the 1st  scenario ----------------------------------------------
CODtotin = 360          ;[gcod/m3]; Measurement of 11.04.2014
; for the 2nd scenario ----------------------------------------------------------
;CODtotin = 310          ;[gcod/m3]; Measurement of 11.04.2014
Sorgtot = 150           ;[gcod/m3; Measurement of 11.04.2014
SUin = 0                ;[gcod/m3] concentration SI in the inflow; neglected
SBin = Sorgtot          ;[gcod/m3] soluble COD in the inflow
XOHO_in =0                  ;[gcod/m3] biomass in the inflow in SBR
XU_E_in=0               ;[gcod/m3] Endogenous residues in the influent

Xu_Inf_in = fract* CODtotin         ;[gcod/m3] inert particulate COD in the inflow

;---------Scenario 1, version_1_with nbCOD without BOR error------------
;fract=0.15; for the version with BOD test without BOD-error correction
;---------Scenario 1,version_2_with nbCOD with BOR error------------
fract=0.29; for the version with BOD test with BOD-error correction
;---------Scenario 2, version 1_with filter, with some nbCOD ------------
;fract=0.12; for the scenario with the filter before the SBR
;---------Scenario 2, version 2_with filter, without nbCOD ------------
;fract=0; for the scenario with the filter before the SBR


XCBin = CODtotin-Sorgtot-XU_E_in-XU_Inf_in ;[gcod/m3] slowly biodegradable COD in the inflow

;---Model parameters at 20 0C, according to ASM 1 (without oxygen inhibition or anoxic considerations) ----------------------------------------------------------------------------------------------------------

Y_OHO= 0.67       ; [g XOHO.g XCB-1] Yield for XOHO growth
mohomax = 6             ;[1/day] Maximum growth rate of XOHO
KS_OHO = 20                 ;[gcod/m3] Half-saturation coefficient for SB
q_XCB_SB= 3                     ;[g XCB.g XOHO-1.d-1] Maximum specific hydrolysis rate
b_OHO = 0.62                ;[1/day] Decay rate for XOHO
```

```
f_XU_bio = 0.20                    ;[ g XU.g XBio-1] Fraction of XU generated in biomass decay
K_XCB=0.03                  ; [g XS-COD/g XH-COD] Saturation coefficient for XB/XOHO
;---------Initial conditions----------------------------------------------------------
init XOHO = 100
init XU_Inf= 100
init XCB = 100
init SB = 100
init XU_E=100
;---------System limitations (aim - no negative concentrations)-----------------------------------------------
limit XOHO >= 0
limit XU_Inf >= 0
limit XCB >= 0
limit SB >= 0
;---------Mass balance equations (around CSTR boundaries)-----------------------------------------------
d/dt(XOHO) = (1/HRT)*XOHO_in - (1/SRT)*XOHO + mohomax*(SB/(KS_OHO+SB))*XOHO - b_OHO*XOHO ;mass balance equation for biomass
d/dt(XCB) = (1/HRT)*XCBin - (1/SRT)*XCB - q_XCB_SB *((XCB/XOHO)/(K_XCB+(XCB/XOHO)))*XOHO+ (1-f_XU_bio) *b_OHO*XOHO ;mass balance equation for XCB
d/dt(XU_Inf) = (1/HRT)*XU_Inf_in - (1/SRT)*XU_Inf ;mass balance equation for XU_Inf
d/dt(XU_E)= f_XU_bio *b_OHO*XOHO - (1/SRT)*XU_E ;mass balance equation for XU_E
d/dt(SB) = (1/HRT)*SBin- (1/SRT)*SB - (mohomax/Y_OHO)*(SB/(KS_OHO+SB))*XOHO+ q_XCB_SB *((XCB/XOHO)/(K_XCB+(XCB/XOHO)))*XOHO ;mass balance equation for SB, also the removal of SB by the effluent is neglected, since in a SBR it is assumed that the SB is negligible, at the moment the excess sludge is removed.

XT = XOHO+XCB+XU_Inf+XU_E ;total MLVSS concentration [gCOD/m3]
XT_VSS=XT/1.42             ; total MLVSS concentration [gVSS/m3]
F_Xu_Inf=XU_Inf/XT                 ; fraction of XU_Inf over total solids
F_XCB=XCB/XT               ; fraction of XCB over total solids
F_Xend=XU_E/XT             ; fraction of XU_E over total solids
F_XOHO=XOHO/XT                 ; fraction of XOHO over total solids
```

Appendix 2. Matlab Function for the Method 1a.

```
function [Mean_RMSE] = calc_our_method_1a_analytical_method (ncycles, CurrentFile,t_nonaer_end,t_nonaer_st, DO_nonaer_st, DO_nonaer_end, data, zero_time)
%METHOD 1A. ANALYTICAL SOLUTION

% TO PLOT ALL CYCLES FOR THE BATCH - FIRST IN THE GENERAL FILE CHOOSE THE NUMBER OF THE BATCH
%Also the script calculates RMSE values (Error between measured
%Dissolved Oxygen (DO) concentrationvalues  and values defined using
%analytical computation method). Parameter "Mean_rmse" gives the mean value for each SBR.

M=zeros(ncycles,2)                ;%Matrix to save the value of slopes in each nonaeration period
Mrmse=zeros(ncycles,1)             ;%Matrix to save the value of RMSE in each nonaeration period

% ========================================================================
% RUN IT FOR ALL NUMBER OF CYYLES OF NONAERATION

for  i=1:ncycles
    % COMPUTE SLOPE

    x=[t_nonaer_st(i,:) t_nonaer_end(i,:)]                          ;%X values of the two points of start and end of nonaer period
    y=[DO_nonaer_st(i,:) DO_nonaer_end(i,:)]                        ;%Y values of the two points of start and end of nonaer period
```

```
       slope=(y(1)-y(2))/(x(1)-
x(2))                                   ;%Computation of the slope
       a=y(1)-slope*x(1)                                                    ;%y-
intercept value
       M(i,1)=slope                                                        ;%Matrix
M with the slopes values
       M(i,2)=a                                                            ;%Matrix
M with the y-intercept values

       % EQUATION OF THE LINE DISCRIBING "DO" OVER TIME BASED ON THE MODEL_1a
       Time=data(:,1);
       Interval_incl=and(Time>=t_nonaer_st(i,:),Time<=t_nonaer_end(i,:));%Time in-
terval between start and end of nonaer period
       x_new=Time(Interval_incl)                                          ;%X (time)
values inside "Interval_incl" time interval
       y_new=a+slope*x_new                                                 ;%DO con-
centrations for X (time) values, which were calculated based on the model_1

       % COMPUTE RMSE
       data_for_y_new=data(Interval_incl, 12)                              ;%y meas-
ured inside interval of interest
       I = ~isnan(data_for_y_new) & ~isnan(y_new); % delete records with NaNs in
both datasets first
       data_for_y_new = data_for_y_new(I); y_new = y_new(I);% delete records with
NaNs in both datasets first
       RMSE=sqrt(sum((data_for_y_new(:)-y_new(:)).^2)/numel(data_for_y_new));%Root
mean square  error for i loop
       Mrmse(i,1)=RMSE                                                     ;%Matrix
to save the values of RMSE in each nonaeration period
       Mean_RMSE=mean(Mrmse)                                               ;%mean
value of RMSE
   %                                                                        %
==========================================================================
   %     % IMPORTANT !!!!! ACTIVE ONLY WHEN THE PARTICULAR BATCH IS SPECIFIED
   %      x_new_n=x_new+zero_time;
   %      Time_n=Time+zero_time;
   %            %                                                          %
==========================================================================
   % %     % PLOT ALL CYCLES - MEASURED DATA AND MODELLED RESULTS
   % %     % IMPORTANT !!!!! ACTIVE ONLY WHEN THE PARTICULAR BATCH IS SPECIFIED
   %     hold on
   %     plot(x_new_n, y_new,'g+-', 'LineWidth', 3);
   %     plot (x_new_n, data_for_y_new, 'ro')
   %     plot(Time_n,data(:,3),'b.-')
   %     plot(Time_n,data(:,12),'r.-')
   %     dateaxis('x', 15)
   %     set(gca,'fontsize',18)
   %     xlabel('Time[hh:mm]','FontSize',18,'FontWeight','bold','Color','k')
   %                                  ylabel('Dissolved       Oxygen       (DO)
[mg/l]','FontSize',18,'FontWeight','bold','Color','r')
   %     title({['Measurements on: ' CurrentFile]},'interpreter','none')

   end
   end
```

Appendix 3. Matlab Function for the Method 1b.

```
   function      [Mean_RMSE,      OUR,      t_our,      y_new,      data_for_y_new]=
calc_our_method_1b_analytical_solution  (iBatch,  nBatch,  Time,data,t_nonaer_end,
t_nonaer_st, zero_time, CurrentFile)
   % ==========================================================================
   % METHOD 1B. ANALYTICAL SOLUTION
   % TO PLOT ALL CYCLES FOR THE BATCH - FIRST IN THE GENERAL FILE CHOOSE THE
NUMBER OF THE BATCH

   % COMPUTATION OF O.U.R.
   % COMPUTATION OF RMSE VALUES FOR "DO" CONCENTRATIONS
   % EMPTY MATRICES
   ncycles=size(t_nonaer_end,1)       ;%Number of batches
```

```
   M=zeros(ncycles,2)                 ;%Matrix to save the value of slopes in each
nonaeration period
   Mrmse=zeros(ncycles,1)              ;%Matrix to save the value of RMSE in each
nonaeration period

   % ========================================================================
   % RUN IT FOR ALL NUMBER OF CYYLES OF NONAERATION

   for  i=1:ncycles
       % COMPUTE SLOPE
       Interval_incl=and(Time>=t_nonaer_st(i,:),Time<=t_nonaer_end(i,:));%Time in-
terval between start and end of nonaer period
       x=data(Interval_incl,1)                                  ;%X values of the two
points of start and end of nonaer period
       y=data(Interval_incl, 12)                                ;%Y values of the two
points of start and end of nonaer period
       x_design=ones(size(x));
       x_design(:,2)=x;
       x_design(:,1)=1;
       beta=x_design\y;
       beta=transpose(beta);
       M(i,1:2)=beta;
       % ========================================================================
       % COMPUTE O.U.R. FOR EACH 500TH BATCH REACTOR
       OUR(i,1)=beta(2)*(-1);
       t_our=((t_nonaer_end-t_nonaer_st)/2)+t_nonaer_end    ;%Middle of the time
interval for which OUR was calculated
       t_our=t_our+zero_time;
       % EQUATION OF THE LINE DISCRIBING "DO" OVER TIME BASED ON THE MODEL_1a
       Interval_incl=and(Time>=t_nonaer_st(i,:),Time<=t_nonaer_end(i,:));%Time in-
terval between start and end of nonaer period
       x_new=Time(Interval_incl)                                ;%X (time)
values inside "Interval_incl" time interval
       y_new=M(i,1)+M(i,2)*x_new                                ;%DO
concentrations for X (time) values, which were calculated based on the model_1
       % COMPUTE RMSE
       data_for_y_new=data(Interval_incl, 12)                   ;%y meas-
ured inside interval of interest
       I = ~isnan(data_for_y_new) & ~isnan(y_new); % delete records with NaNs in
both datasets first
       data_for_y_new = data_for_y_new(I); y_new = y_new(I);% delete records with
NaNs in both datasets first
       RMSE=sqrt(sum((data_for_y_new(:)-y_new(:)).^2)/numel(data_for_y_new));%Root
mean square  error for i loop
       Mrmse(i,1)=RMSE                                          ;%Matrix
to save the values of RMSE in each nonaeration period
       Mean_RMSE=mean(Mrmse)                                    ;%mean
value of RMSE


   %                                                                        %
========================================================================
   %     % IMPORTANT !!!!! ACTIVE ONLY WHEN THE PARTICULAR BATCH IS SPECIFIED
   %     x_new_n=x_new+zero_time;
   %     Time_n=Time+zero_time;
   %                                                                        %
========================================================================
   %     % PLOT ALL CYCLES - MEASURED DATA AND MODELLED RESULTS
   %     % IMPORTANT !!!!! ACTIVE ONLY WHEN THE PARTICULAR BATCH IS SPECIFIED

   %         hold on
   %     plot(x_new_n, y_new,'b+-', 'LineWidth', 3);
   %     plot (x_new_n, data_for_y_new, 'ro')
   %     plot(Time_n,data(:,3),'k.-')
   %     plot(Time_n,data(:,12),'r.-')
   %     dateaxis('x', 15)
   %     set(gca,'fontsize',18)
   %     xlabel('Time[hh:mm]','FontSize',18,'FontWeight','bold','Color','k')
```

```
   %                                    ylabel('Dissolved       Oxygen       (DO)
[mg/l]','FontSize',18,'FontWeight','bold','Color','r')
   %     title({['Measurements on: ' CurrentFile]},'interpreter','none')
   %

   end

   end
```

Appendix 4. Matlab Function for the Method 2.

```
   function [ Mean_RMSE, OUR, t_our]= calc_our_method_2 (ncycles, CurrentFile,
Time,data, t_nonaer_end, t_nonaer_st, zero_time)
   % ========================================================================
   % METHOD 1B. ANALYTICAL SOLUTION
   % TO PLOT ALL CYCLES FOR THE BATCH - FIRST IN THE GENERAL FILE CHOOSE THE
NUMBER OF THE BATCH

   % Mean_RMSE - mean values of root mean square error for OUR computation method
   % OUR - O.U.R. values of all batches
   % t_our - time corresponding to a O.U.R.

   % ========================================================================
   % RUN IT FOR ALL NUMBER OF CYYLES OF NONAERATION
   for  i=1:ncycles
       % ====================================================================
       % COMPUTE SLOPE
       % INPUTS

Interval_incl=and(Time>=t_nonaer_st(i,:),Time<=t_nonaer_end(i,:))           ;%Time
interval between start and end of nonaer period

x=data(Interval_incl,1)                                                     ;%X val-
ues of the two points of start and end of nonaer period
       y=data(Interval_incl,
12)                                                ;%Y values of the two points of
start and end of nonaer period
       [xyVector]              =       xyvector       (Time,       data,       i,
t_nonaer_st,t_nonaer_end)         ;%Vector of input data
       dn                                                                   =
2                                                          ;%number of points
(delta) to identify the slope
       SlopeMin                                          =                 -
inf                                                ;%minimal slope for data
subset recognition
       SlopeMax                                                             =
0                                                  ;%maximal slope for data
subset recognition
       graph=1;
       %OUTPUTS
       [beta]                                                               =
calc_beta(xyVector,SlopeMin,SlopeMax,dn,graph)                    ;%1x2 vector con-
sisting of the intercept and slope
       beta=transpose(beta);
       M(i,1:2)=beta;
       % ====================================================================
       % COMPUTE O.U.R.
       OUR=(-1)*M(:,2);
       t_our=((t_nonaer_end-
t_nonaer_st)/2)+t_nonaer_end                          ;%Middle of the time interval
for which OUR was calculated
       t_our=t_our+zero_time;
       % ====================================================================
       % EQUATION OF THE LINE DISCRIBING "DO" OVER TIME BASED ON THE MODEL_1a

x_new=Time(Interval_incl)                                                   ;%X (time)
values inside "Interval_incl" time interval

y_new=M(i,2)*x_new+M(i,1)                                                   ;%DO con-
centrations for X (time) values, which were calculated based on the model_1
```

```
        % ========================================================================
        % COMPUTE RMSE
        data_for_y_new=data(Interval_incl, 12)                              ;%y meas-
ured inside interval of interest
        I = ~isnan(data_for_y_new) & ~isnan(y_new); % delete records with NaNs in
both datasets first
        data_for_y_new = data_for_y_new(I); y_new = y_new(I);% delete records with
NaNs in both datasets first
        RMSE=sqrt(sum((data_for_y_new(:)-y_new(:)).^2)/numel(data_for_y_new));%Root
mean square  error for i loop
        Mrmse(i,1)=RMSE                                                     ;%Matrix
to save the values of RMSE in each nonaeration period
        Mean_RMSE=mean(Mrmse)                                               ;%mean
value of RMSE
    %                                                                       %
========================================================================
    %     % IMPORTANT !!!!! ACTIVE ONLY WHEN THE PARTICULAR BATCH IS SPECIFIED
    %     x_new_n=x_new+zero_time;
    %     Time_n=Time+zero_time;
    %                                                                       %
========================================================================
    %     % PLOT ALL CYCLES - MEASURED DATA AND MODELLED RESULTS
    %     % IMPORTANT !!!!! ACTIVE ONLY WHEN THE PARTICULAR BATCH IS SPECIFIED
    %     hold on
    %     plot(x_new_n, y_new,'k+-', 'LineWidth', 3);
    %     plot (x_new_n, data_for_y_new, 'ro')
    %     plot(Time_n,data(:,3),'b.-')
    %     plot(Time_n,data(:,12),'r.-')
    %     dateaxis('x', 15)
    %     set(gca,'fontsize',18)
    %     xlabel('Time[hh:mm]','FontSize',18,'FontWeight','bold','Color','k')
    %                                     ylabel('Dissolved       Oxygen       (DO)
[mg/l]','FontSize',18,'FontWeight','bold','Color','k')
    %     title({['Measurements on: ' CurrentFile]},'interpreter','none')
    end
    end
```

Appendix 5. Additonal Matlab Function for the Method 2.

```
    function [beta] = calc_beta(xyVector,SlopeMin,SlopeMax,dn,graph)
    %function to fit a linear regression within the slope boundaries
    %   xyVector:   Vector of input data
    %   SlopeMin:   minimal slope for data subset recognition
    %   SlopeMax:   maximal slope for data subset recognition
    %   dn:         number of points (delta) to identify the slope
    %   noPlot:     set to any value to avoid plotting data and regression

    if nargin<5 || isempty(graph)
        graph = false ;
    end

    dx=mean(diff(xyVector(:,1)));   %mean increment of x
    dMin=SlopeMin*dx*dn;            %minimal difference of y(n+dn)-y(n)
    dMax=SlopeMax*dx*dn;            %maximal difference of y(n+dn)-y(n)
    dy=xyVector(dn:end,2)-xyVector(1:(end-dn+1),2);   %differences of y vector
    %adrMinMax=[0,find(dy>=dMin  &  dy<=dMax),numel(dy)+1];  %positions  where  the
slope is within boundaries
    adrMinMax=find(dy>=dMin  &  dy<=dMax); %positions  where  the  slope  is  within
boundaries
    if isempty(adrMinMax)
       beta=[NaN, NaN]; pos=[];
    else
        gaps=[0;find(diff(adrMinMax)>1);numel(adrMinMax)];     %find  positions  of
gaps within adrMinMax
        adr_ini=adrMinMax(gaps(1:(end-1))+1);       %addresses of the beginning of
the series
        adr_end=adrMinMax(gaps(2:end));        %addresses of the end of the series
        adr_pos=find((adr_end-adr_ini)==max(adr_end-adr_ini));   %find  position  of
longest series
```

```
        pos=(adr_ini(adr_pos)+3):adr_end(adr_pos);   %find addresses of values of
the longest series
    %    pos=(adr_ini(adr_pos)):adr_end(adr_pos);  %find addresses of values of the
longest series
        if isempty(pos)
           beta=[NaN, NaN];
        else
           beta=glmfit(xyVector(pos,1),xyVector(pos,2));    %make linear regression
of the longest series
        end
    end
    if (beta(2)<SlopeMin | beta(2)>SlopeMax)
        disp('FitLinReg: Steigung ausserhalb Erwartungsbereich')
    end
    end
```

Appendix 6. Calculation of the nitrogenous part of the BOD (measured on the 13th of May).

	NO2-N in the beginning of the BOD test [mg NO2-N/l]	NO2-N in the end of the BOD test [mg NO2-N/l]	NO2-N produced during the BOD test [mg NO2-N/l]	NO3-N in the beginning of the BOD test [mg NO3-N/l]	NO3-N in the end of the BOD test [mg NO3-N/l]	NO3-N produced during the BOD test [mg NO3-N/l]	BOD for NO2-N formation [mg BOD/l]	BOD for NO3-N formation [mg BOD/l]	BOD for NO2-N and NO3-N transformation [mg BOD/l]
Filter Cake (FC)	0.5	21.0	20.0	3.0	7	4.0	70	20.0	90
WW after filtration (WWaf)	0.2	1	1.0	0.2	1	1.0	3	4.0	6.5
WW before filtration (WWbf)	0.2	9.5	9.0	0.2	1	1.0	32	4.0	35.5
Glucose	0.5	12.0	12.0	3.0	6.0	3.0	42	14.0	56
Acetate	0.2	1.5	1.0	3.0	1	-2.0	4.5	-10.0	-5
Seed blank sample	0.2	13.5	13.0	3.0	4.0	0.5	46	1.5	47.0

Appendix 7. The results of the mass of unbiodegradable particulate organic, which is removed by the filter application.

Filter label	Filter ID	Volume of the sample added [l]	Weight of the filter before filtering [g]	Weight of the filter after filtering and following it drying [g]	Filter ash, Weight of the filter after ignition at 550 °C [g]	TSS [g]	TSS [g/l]	VSS [g]	VSS [g/l]	Average TSS [g/l]	Average VSS [g/l]
J3	Filter Cake in 5 l. of groundwater, non-diluted	0.03	0.7066	0.785	0.7099	0.079	2.64	0.072	2.39		
J4	Filter Cake in 5 l. of groundwater, non-diluted	0.03	0.7019	0.7807	0.7054	0.079	2.63	0.075	2.51	2.63	2.45
J8	Blank sample, 60 ml of groundwater	0.03	0.7102	0.7094	0.706	0.00	0.00	0.00	0.00	0.17	0.00

* TSS- and VSS-measurements results were corrected with the values of the blank sample test

Appendix 8. pH measurements in the sample with wastewater after the filter (which were made for the BOD test).

day	time	pH
16.04.2014	14:00	7.8
	21:00	8.22
17.04.2014	10:00	8.33
	17:00	8.2
19.04.2014	18:35	8.48
22.04.2014	07:30	8.53
	17:30	8.51
24.04.2014	10:10	8.62
13.05.2014	09:50	9.45

Appendix 9. pH measurements in all samples on the 13th of May (the day of the end of the BOD test).

N	BOD bottle with the sample	pH value	N	BOD bottle with the sample	pH value
1	FC (1)	7.56	7	Wwaf (3)	9.43
2	FC (2)	7.73	8	Wwbf (1)	9.06
3	FC (3)	7.55	9	Wwbf (2)	9.33
4	FC (4)	7.58	10	Glucose	7.85
5	Wwaf (1)	9.45	11	Acetate	9.69
6	Wwaf (2)	9.37	12	Seed blank	8.23

Appendix 10. Uncertainty of the BOD test results

N	**Measured concentration [mgBOD/L]**	**Average measurement result [mgBOD/L]**	**Standard deviation [mgBOD/L]**	**Variance [mgBOD/L]**
Filter cake				
1	428			
2	389			
3	355			
4	377	387.25	30.59	702
Wastewater after filtration				
1	327			
2	327			
3	315	323	6.93	32
Wastewater before filtration				
1	428			
2	383	405.5	31.82	506.25