TOWEFO (Toward Effluent Zero) EVALUATION OF THE EFFECT OF THE IPPC APPLICATION ON THE SUSTAINABLE WASTE MANAGEMENT IN TEXTILE INDUSTRIES	IDENTIFICATION CODE: **TW-505-001** (Including TE-505-001)	DIS.: **PU**	PAG.: **1**	OF PAG.: **85**
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TITLE:

DELIVERABLE 10: AN ON-LINE TEXTILE WASTEWATER CHARACTERISATION TECHNIQUE

(THIS DOCUMENT INCLUDES DELIVERABLE 13)

KEY WORDS

WASTEWATER CHARACTERISATION, ON-LINE TECHNIQUE, RESPIROMETRY, TEXTILE EFFLUENTS, DEGRADABILITY TEST, NEURAL NETWORK, SHORT-TERM BOD, INFRARED SPECTROMETRY

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Preface

This investigation was carried out as part of the project TOWEF0 (Towards Effluent 0): Evaluation of the effect of the IPPC application on the sustainable wastewater management in textile industries. Towef0 is a research project supported by the European Commission under the Fifth Framework Programme and contributing to the implementation of the Key Action "Sustainable Management and Quality of Water" within Energy, Environment and Sustainable Development (Contract n°: EVK1-CT-2000-00063). A more detailed project description can be found on the project's homepage: http://spring.bologna.enea.it/towefo. This research is part of workpackage 5. For LeAF, the main activity in Work package 5 of the project is developing online textile wastewater characterisation techniques. A summary from the project proposal:

"In WP5 a strategy will be developed to support the decision for the best (pre) treatment scenario out of a given set of available scenarios. The aim will be to meet effluent standards and to obtain optimum recovery of specific compounds and re-use of process water in order to realise sustainable waste management. Existing wastewater characterisation techniques will be improved and adapted to the measurement of textile process wastewater streams. The techniques will enable the on-line measurement of key variables for the biological and physico/chemical treatment of the wastewater such as toxicity, nutrient deficiency and degradability. The techniques will be based in the first instance on respirometry, i.e. the measurement of the oxygen uptake rate of biomass in contact with waste water under well defined measuring conditions. A comparison with micro-calorimetry will also be undertaken. From the comparison of thermograms evaluated in both the absence and the presence of particular compounds, it will be possible to reach a better comprehension of the effect of toxicity, nutrient deficiency and degradability on the metabolic activities of micro-organisms (activated sludge). Moreover, in WP5 a protocol will be developed to determine the optimal composition of the wastewater produced in the factories in terms of treatment performance. To fully develop the "waste design" concept for finishing textile industries, a network of "on-line" sensors will be designed, in order to allow a real time monitoring and control of wastewater characteristics. The task of the "on-line" sensor is to inform waste producers, treatment plant and industrial operators when and how to discharge into the sewer or a specific pre-treatment or, alternatively, continue to re-use water in production process. The protocol will be based on the on-line information and should also include the means of feeding back the information on the optimal composition to the production units. In collaboration with WP4 the Water Pinch technology approach will be integrated with the characterisation and design of wastewater as far as treatability is concern. Treatability will be used as an index for understanding how many recycling loops wastewaters can undergo before being discharged from the process and disposed of at satisfying grade of treatability."

This report includes (part of) the work specified with the following jobs:
- wp05.01.5 (Literature review on textile industry wastewater characterisation)
- wp05.02.5 (Development of on line wastewater characterisation techniques)
- wp05.04.5 (Respirometric on-line tests) and
- wp05.08.5 (Protocol for wastewater design in terms of treatability and reusability).

This study was conducted in co-operation with Dr. Jean-Philippe Steyer and Dr. Jean-Claude Bouvier of the Laboratory for Environmental Biotechnology of the INRA in Narbonne (France) for the part of on-line COD analysis, and Dr. Karel Keesman of the Systems and Control Group of Wageningen University for the part on neural networks.

Incorporation of Deliverable 13

This report is a combination of two deliverables, namely D10 ("An on-line textile waste water characterisation technique") and D13 ("A protocol to determine the optimum composition of the wastewater streams of the different process units"). During the work for D10 it was recognised a combination of on-line respirometry and on-line COD analysis would provide a novel on-line monitoring technique for the assessment of biochemical treatability of textile process effluents, thereby allowing the implementation of automatic control in treatment and reuse schemes. To develop this combined monitoring technique an additional two months work input to wp05.02.5 was requested, and it was approved by the project coordinator to reallocate this time from wp05.08.5 (Protocol for wastewater design in terms of treatability and reusability). The latter was justified by the consideration that for LeAF less effort was anticipated to carry out the work in wp05.08.5, because much of this work was already dealt with by Vito under activity WP05.07.04 (Integrated methodology for water pinch and wastewater design).

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1 INTRODUCTION

1.1 GENERAL CONTEXT

The textile industry comprises a great number of processes. Each process and even each process step generates a different kind of wastewater. For all those streams decisions have to be taken: immediate reuse, biological treatment, chemical (pre-)treatment, etc. Respirometry in combination with an on-line COD measurement could provide a value for the aerobic biological treatability of a wastewater in the form of a BOD_{ST}/COD value. Typically, a low ratio indicates that only a very small fraction of the organic wastewater content is aerobically biodegradable, whereas a higher ratio indicates the opposite. An (extremely) low value for both COD and BOD_{ST} can indicate that the wastewater is relatively clean, and therefore suitable for reuse. In this way, the combined methods can work like a decision making tool of what to do with which wastewater stream. In Figure 1 the proposed set-up is shown.

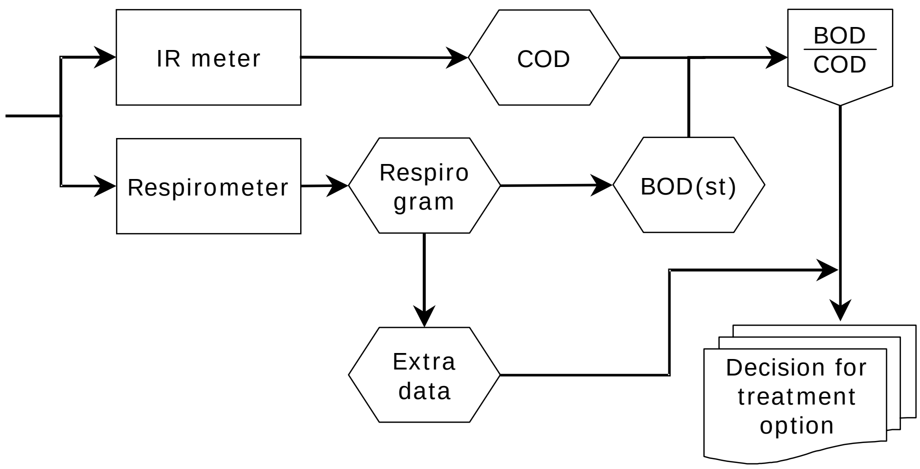


Figure 1, Scheme of the proposed on-line treatability measurement

The BOD/COD ratio is a number in the range from 0 to a value between 0.5 and 1. (because the BOD can never be higher than the COD), and is a measure for the treatability of the wastewater: the higher the number, the higher the wastewater treatability. Determination of COD values using infrared spectrometry will be discussed in chapters 2.6 and 5.

1.2 RESPIROMETRY

Degradation of organic matter by activated sludge can be monitored with respirometry, obtaining kinetic information about the sludge and information on the biodegradability of the organic matter. Respirogram shape (steepness, shoulders, etc) and area are important for estimation of involved compounds and parameters. One technique is based on measurement of the oxygen concentrations of sludge that enters and leaves a respiration chamber, and with those values the respiration rate is calculated. Respirometry can be used for monitoring the activity of activated sludge, toxicity effects of wastewater, etc. Figure 2 shows a schematic set-up of a respirometer of the static gas, flowing liquid type (Spanjers et al., 1998).

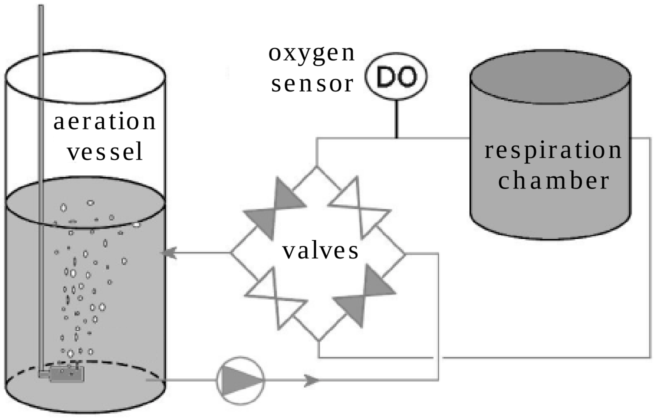


Figure 2, Schematic representation of respirometer. The aeration vessel is filled with sludge, which is constantly pumped around to the respiration chamber and back again.

Aeration, pH and temperature are controlled. The respiration chamber is where the oxygen concentrations are measured. By using the pair of valves only one oxygen probe needs to be used: the valves cause the flow to intermittently pass the electrode on the way in and the way out. Figure 3 is a photo of the respirometer used in the majority of the experiments.

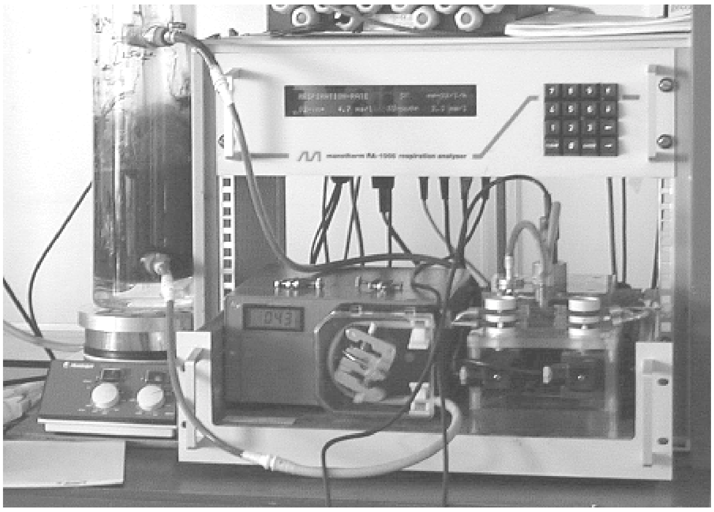


Figure 3, RA1000 respirometer used in Biotechnion

1.3 RESPIROMETRY AS CHARACTERISATION METHOD FOR TEXTILE WASTEWATER

Research on respirometry as a tool in the area of textile wastewater has been conducted mainly by the group of Derin Orhon of the Environmental Engineering Department of Istanbul Technical University. Their work, however, concentrates on the assessment of biodegradability and model parameters by using off-line respirometry. Germirli Babuna and co-workers (1998) stated that parameter assessment is a prerequisite for evaluation of the biological treatability of textile wastewaters.

1.4 RESPIROGRAM ANALYSIS

Figure 4 is an example of a respirogram. Graphically (see Figure 5), several characteristics of a respirogram can be determined:

height	→	Maximum exogenous respiration rate: maximum respiration rate minus endogenous respiration rate
length	→	Time elapsed between beginning and completion of degradation
slope	→	Indicating degradation kinetics
area below the respirogram	→	short term BOD
shoulders	→	Indicating the presence of multiple compounds

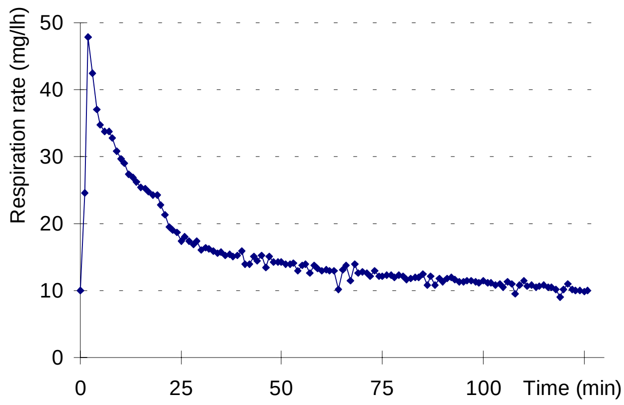


Figure 4, Respirogram

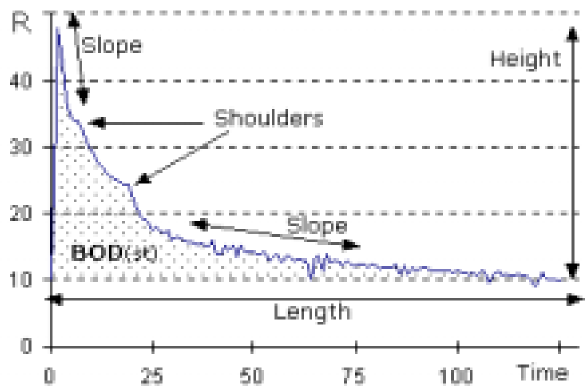


Figure 5, Graphical respirogram analysis

1.5 USING RESPIROMETRY FOR BOD$_{ST}$ ASSESSMENT

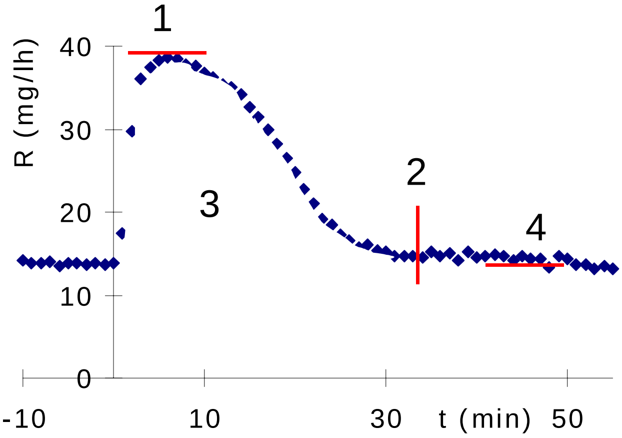
To assess the short-term BOD of a wastewater, respirometry is a useful tool (Spanjers et al., 1999). The area under the respirogram (see Figure 6) is the value of the short-term BOD (BOD$_{ST}$). To be able to calculate the area, several points need to be known:

Begin point of exogenous respiration rate – this is known, because the time of addition is known.
Measuring points – these are known, because the measurements are recorded
End point of exogenous respiration rate – this is not known and has to be determined to make area calculation possible

When all characteristics are known, the area can be calculated. The calculated BOD$_{ST}$ is an important parameter for the assessment of the biodegradability of a wastewater.

1.6 END-POINT DETECTION

For the expert it is relatively easy to determine the end point of exogenous respiration in a respirogram. That is: the instant where the substrate is exhausted and the metabolism changes into endogenous respiration (Spanjers et al., 1999). In Figure 6 the four steps of how an expert would analyse a respirogram are represented. This is an example of a "standard" easy respirogram.



1) The height can easily be seen

2) The end point as well

3) When the end is known we calculate the area

4) Just a last check to see whether no strange things happen to the endogenous respiration rate

Figure 6, Respirogram analysis by the expert

Due to many possible shapes of respirograms, it is not an easy task to develop an algorithm that can evaluate a respirogram the same way as an expert. A "normal" model would not be effective because it would need strict indications and boundaries to do its job properly. Step 2 in figure 2 is the most difficult for a computer. How to tell it why the end point is in the indicated spot and not five points to the left or ten points to the right? The expert uses a great deal of knowledge to judge the many characteristics and anomalies that may occur in respirograms. The expert's brain processes all information in the image and of previously seen respirograms and takes a decision. In Figure 7 two examples of the possible difficulties that can arise are given. The picture on the left shows a very common pattern of a respirogram of a wastewater containing also slower biodegradable material. The respiration rate will be horizontal while the bacteria are degrading this component at their maximum speed. But a model told that the end point is where the respirogram is horizontal will make a mistake. On the right an example of a toxic substrate is shown. The endogenous respiration rate drops under the initial rate. A model told to take a straight line form the initial rate and take the end-point where that line crosses the respirogram will make a mistake.

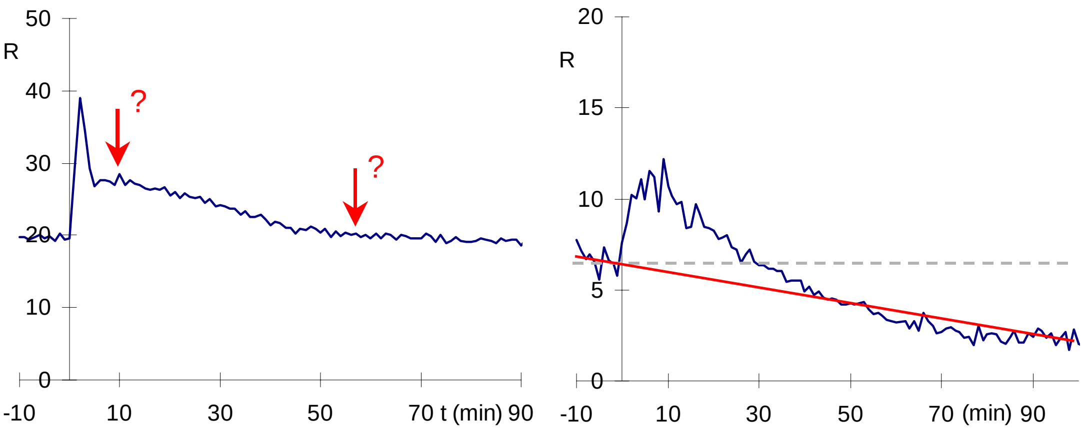


Figure 7, Two examples of difficulties for automated respirogram analysis.

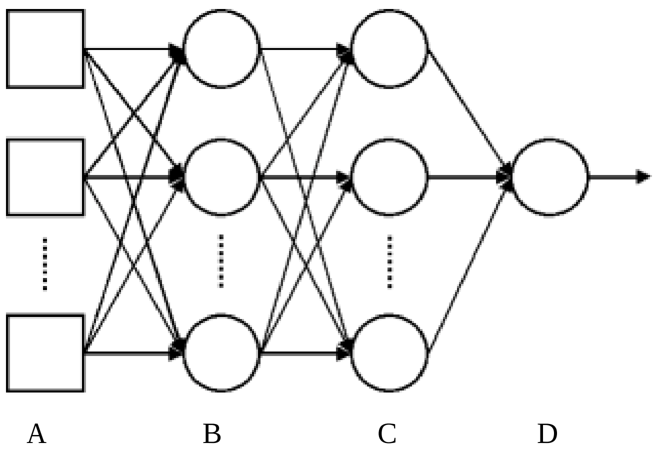
Apart from these two examples there are many more that make it difficult to develop an automatic procedure that can analyse respirograms. Neural network might be the solution. A neural network (NNW) is a tool used for those situations where no strict boundaries are present and deterministic models are not successful. Therefore in theory it is a perfect tool for the end point determination of respirograms.

1.7 NEURAL NETWORKS

A neural network consists of various layers: an input layer, one or more hidden layers and an output layer. Each layer consists of a number of neurons. The user can define the number of neurons, but in fact the NNW is a "black box". It cannot be told what to do exactly, or where to look for the solution. An explanation by Seliger (2003), adapted to the topic of respirogram analysis:

"Artificial neural nets derive their name from the fact that they are made up by a number of highly interconnected, rather simple non-linear information processing elements, the artificial neurons, which are supposed to work in a simplified fashion similarly to their natural counterparts in the brain. In the context of this project, an artificial neural net is just a black box that produces the end point of a given respirogram. That is to say, the neural net takes a respirogram as input and somehow comes up with an end point as output. Mathematically speaking, it performs a non-linear map on an input pattern, which represents the input position."

Data that is loaded into the neural network is divided in a part for training and a part for validation. Each layer of neurons is connected to the next by what are called "weights". The training data are analysed by the network and it tries to adjust its weights to fit the offered training data. An example by NeuroSolutions (2003) explains the structure of NNW's into more detail:



Block diagram of a two hidden layer multiplayer perceptron (MLP). The inputs are fed into the input layer [A] and get multiplied by interconnection weights as they are passed from the input layer to the first hidden layer [B]. Within the first hidden layer, they get summed then processed by a nonlinear function (usually the hyperbolic tangent). As the processed data leaves the first hidden layer, again it gets multiplied by interconnection weights, then summed and processed by the second hidden layer [C]. Finally the data is multiplied by interconnection weights then processed one last time within the output layer [D] to produce the neural network output.

Prerequisite for application of a neural network is a close resemblance of the training and validation data, and the success depends on the quality of the data set used for training (Linko et al., 2000).

Whether or not neural networks are able to determine the end point of respirograms was investigated using the neural network toolbox of Matlab.

1.8 THE INFRARED TECHNIQUE DEVELOPED AT INRA

Infrared spectrometry is normally used for measuring separate compounds in for instance chemical reactions. In the case of INRA a method was developed that uses infrared spectrometry for monitoring of an anaerobic fixed bed reactor treating vinasses wastewater. Parameters that can be measured with this infrared technique are COD, VFA, TOC, and partial and total alkalinity. The most crucial aspect of the technique is the calibration. The amount of samples that has to be analysed to be able to make a reliable calibration depends on how constant the process is. For the vinasses calibration about 20 samples were used. In any case enough samples have to be used to cover the whole range of measurements. Every wastewater stream has a different matrix ("background composition"), that causes the infrared light to absorb in a different way. Hence, the infrared absorption spectra for a wastewater will be typical for that particular stream. Therefore, when measuring a stream different from the one the calibration was made with, resulting values will often mean nothing. A different stream similar to the one used for calibration can give useful results, if the matrices are very much alike.

A correction has to be made for the presence of water, as water shows strong absorption in the infrared area. The spectrum of water is subtracted from the spectrum of the sample, and then the remaining "compound-spectrum" is validated using the calibration. Determination of different parameters is done using different parts of the spectrum.

The purpose of this study is to determine whether or not this technique can be used for online monitoring of process streams in textile factories. The study was done within the framework of the EU project "TOWEF0". Decisions on the fate of the streams (direct reuse or treatment) would be then be directly taken based on the results of the infrared measurements. As the textile industry requires a very good water quality for almost all of the processes, the accuracy of the technique when it comes to low values is important. With the infrared method used by INRA it is difficult to measure below certain values. The minimum concentration is about 500 mg COD/l, whereas better results will be obtained above 1000 mg COD/l.

Total costs of the Infrared spectrometer (including computer and IR software) are around 30.000 Euro. For a filtration unit, pumps and controlling software similar to what is used at INRA, another 10.000 Euro should be counted (at maximum). When there is no need for a very fine filtration, the price will be much lower. As the effluent of an anaerobic reactor contains a lot of bacteria, without ultra-filtration biomass will start to grow in tubes with risk of clogging of the system. Textile wastewater does not contain bacteria, so a less fine filtration will likely be enough to remove for instance textile fibres and prevent clogging.

Figure 8, Experimental setup in the technical hall of INRA.

1. Anaerobic reactor treating vinasses wastewater

2. Infrared spectrometer
(→ COD, TOC, VFA, PA, TA)

3. Computer connected to infrared spectrometer

4. Titrimetric Sensor (→ pH, VFA, PA, TA)

5. Computer connected to titrimetric sensor

6. TOC sensor (accessible from other side)

7. Monitoring of complete installation: all data are shown together

2 MATERIALS AND METHODS

2.1 RESPIROMETERS

Bennekom (used February – March)

The respirometer that was used in the technical hall in Bennekom is a RA1000 meter. It was only available for one day per week, because this was the only possibility during that period. Sludge and wastewater were left in the technical hall for the time between measurements. Technical specifications of the conducted experiments were (based on water and sludge characteristics):

- Volume respiration vessel: 0.728 litre
- Initial sludge volume: 1,5 litres
- Pump position: 2 (54)
- Flow at that position: average 24 l/h
- Temperature: 20°C
- pH: 7.4 – 7.6
- Used solutions: Acetate (1 g COD/l) and ammonium (1 g COD/l)

Sludge was always sieved before use to prevent clogging etc.

Respirometer Biotechnion (used April – present)

The respirometer used in lab 726 in the Biotechnion in Wageningen is also a RA1000 meter. Technical specifications of the conducted experiments were (based on water and sludge characteristics):

- Volume respiration vessel: 0.728 litre
- Initial sludge volume: 1,5 litres
- Pump position: 2 (43/44)
- Flow at that position: average 17 l/h
- Temperature: 20°C
- pH: depends on the pH of the sludge (7 or 8)
- Used solutions: Acetate (1 g COD/l) and ammonium (1 g COD/l)

Remarks:
The flow stored in the RA1000 was not calibrated, and therefore not useful. Instead, the flow was measured manually and used for calculation of respiration rate off-line. Therefore only the calculated respirogram was correct in terms of absolute values, and the measured rate was only used to check the calculated respirogram.

2.2 SLUDGES

Most sludge was sent to our lab by the Italian company Lariana Depur, from different WWTPs. Some data were provided by Lariana with each sludge (see table 1). In addition, sludge from the wastewater treatment plant of a Belgian textile factory (here called factory B-01) and sludge from the municipal WWTP of Bennekom, The Netherlands, was used. TS and MLVSS were almost always measured during each experiment, as the solids amount changes during aerated storage due to evaporation and samples addition. The values between which the solids varied when looking at all the experiments with a certain sludge, are mentioned in Table 1 as well.

Table 1 , The used activated sludges. Solids in g/l, settled volume in ml/l in 30 minutes.

	Alto Seveso	Factory B-01	Livescia	Alto Seveso	
Sample date	23-1/5-3 ‘02	19-4-2002	6-6-2002	25-6-2002	
pH	7.52	8	7	7.42	7*
MLVSS	6.73	2.2-2.9*	2.8-4.3*	6.46	2.7-4.5*
MLSS	-	-	-	8.28	-
T (°C)	15	-	-	-	-
Settled Volume	990	-	-	990	-
kg COD/kg sludge.d	0.22	-	-	-	-

* Analysis at LeAF

The Italian sludges (from the Alto Seveso and Livescia plants) were grown on a mixture of domestic wastewater and textile industry wastewater (30% and 70% respectively). Factory B-01 has its own wastewater treatment plant, so that sludge was grown exclusively on textile wastewater.

Sludge was stored at room temperature during the whole experiment, and continuously aerated. At times it was fed with small amounts of textile wastewater (although not enough to keep up its original loading) to slow down its loss of activity. During each experiment an automatic pH controller was used, to maintain pH. The pH controller was always set at the original pH of the sludge.

2.3 TEXTILE EFFLUENTS

Most textile effluents were provided by the Italian company Lariana Depur, which is based in Como. Wastewater and sludge samples were sent to Wageningen. The Belgian textile organisation Centexbel facilitated availability of other samples that came from Belgian factories. They were collected there by us and taken back to Wageningen.

Within the Towef0 project, Lariana Depur was gathering information on processes and wastewater production in different Italian textile factories. The obtained data is reported in a document called “PIDACS” (Process Identification and DAta Collection Sheet). For every factory a separate document is made. In the PIDACS document of a factory, data can be found on water use, chemical use, wastewater production, etc. Most of the values reported in this paragraph come from the PIDACS documents. Specific wastewater samples were not analysed prior to shipment, as the PIDACS values are supposed to be typical for the processes. However, most of the samples were analysed after receiving them, to check for possible variations.

All the factories co-operating in Towef0 were assigned a number, to keep the information gathered in this project confidential (both Italian and Belgian factories). These codes are I-02, I-06, I-09, B-01 and B-02. In the Italian PIDACS documents, the different textile processes have been given a code (F.4.2, G.7.2, etc). The combination of the factory number and the process code provides a unique code for each wastewater. These codes are mentioned in the tables with wastewater data. The Belgian wastewaters do not have process codes.

Textile effluents were stored at 4°C during the whole experimental period.

2.3.1 Wastewater received from Lariana Depur, Como, Italy

1. Textile factory final mixed effluent (equalisation tank factory I-06)

   Sample dates: 15-01-2002 and 07-03-2002

2. I-06 / F.4.2-1: Double scouring in Torpedo – Bath 1

   - Sample date: 05-06-2002
   - Type of fabric: usually cotton/polyester or silk/polyester
   - Process temperature and time: 60°C for 40 minutes, indirect heating
   - Ingredients reported in PIDACS: Non ionic surfactant (1058)=5 g/l
     Sequestering agent (1071)=0,5 g/l

3. I-06 / F.4.2-2: Double scouring in Torpedo – Bath 2

   - Sample date: 05-06-2002
   - Type of fabric: usually cotton/polyester or silk/polyester
   - Process temperature and time: 60°C for 40 minutes, indirect heating
   - Ingredients reported in PIDACS: Non ionic surfactant (2057)=4,5 g/l

4. I-06 / G.7.2-1: Light reactive dyeing in overflow – Bath 1

- Sample date: 05-06-2002
- Type of fabric: usually cotton/polyester or silk/polyester
- Process temperature and time: 60°C for 90 minutes, indirect heating
- Ingredients reported in PIDACS: Sodium solphate (2008) = 50 g/l
  Soda solvay (1016) = 3 g/l
  Detergent (2046) = 0,5 g/l
  Dispersant agent (2058) = 0,5 g/l
  Lubricating agent (1057) = 2 g/l
  Reactive dyestuffs < 0,05%

Table 2, Analysis data for mixed wastewater and separate wastewaters of factory I-06. Data sources are mentioned in the second row. Values are in (mg/l), except for conductivity (mS/cm) or mentioned otherwise.

	(1)	(2) I-06 / F.4.2-1		(3) I-06 / F.4.2-2		(4) I-06 / G.7.2-1	
	Mixed effluent	Double scouring		Double scouring		Light reactive	
	Provided by Lariana	Pidacs	LeAF	Pidacs	LeAF	Pidacs	LeAF
COD	778	2650	445	5250	6500	750	675
BOD_5	271	-	-	-	-	-	-
TSS	176	75	-	25	-	21	-
N-org	18	-	-	-	-	-	-
conductivity	-	0.45	-	0.37	-	1.8	-
pH	7	9.8	6.3	9.05	6.4	7.4	10.5
$T_{discharge}$ (°C)	-	59	-	50	-	51	-
acetate	-	-	-	-	-	-	9.6
propionate	-	-	-	-	-	-	2.6
n-butyrate	-	-	1.6	-	-	-	1.5

5. I-09 / F.3.1-1: Degumming – Bath 1

- Sample date: 20-06-2002
- Type of fabric: Silk fabric
- Process temperature and time: 60°C for 40 minutes, indirect heating
- Ingredients reported in PIDACS: Sequestering agent (10382) = 2 g/l
  Sequestering agent (10433) = 1 g/l
  Detergent (10347) = 1 g/l

6. I-09 / G.6.2-1: Dark Reactive Dyeing – Bath 1

- Sample date: 20-06-2002
- Type of fabric: Silk yarn
- Process temperature and time: 80°C for 120 minutes, indirect heating
- Ingredients reported in PIDACS: Sequestering agent (10263)= 1 g/l;
  Sodium chloride (10181)= 70 g/l;
  Sodium bicarbonate (10104)=6 g/l;
  Sodium carbonate (10175)= 5 g/l;
  Reactive dyestuffs >1,5%

7. I-09 / G.9-1: Dark Acid Dyeing – Bath 1

- Sample date: 20-06-2002
- Type of fabric: Silk yarn
- Process temperature and time: 80°C for 40 minutes, indirect heating
- Ingredients reported in PIDACS: Acid buffer (10178)= 1,5 g/l;
  Equalising agent (10029)= 0,75%;
  Antifoaming agent (10404)= 0,5 g/l;
  Sequestering agent (10263)= 0,8 g/l;
  Acid dyestuffs > 1,5%

Table 3, Analysis data for wastewaters of factory I-09. Data sources are mentioned in the second row. Values are in (mg/l), except for conductivity (mS/cm) or mentioned otherwise.

	(5) I-09 / F.3.1-1		(6) I-09 / G.6.2-1		(7) I-09 / G.9-1	
	Degumming		Dark reactive		Dark Acid	
	Pidacs	LeAF	Pidacs	LeAF	Pidacs	LeAF
COD	3220	3400	2660	3900*	2070	2300
TSS	300	-	230	-	35	-
conductivity	0.39	-	48	-	1.11	-
pH	6.95	6.4	9.12	9.0	4.96	6.5
$T_{discharge}$ (°C)	60	-	80	-	78	-
acetate	-	2.9	-	73.3	-	3.5
propionate	-	-	-	3	-	1.5
n-butyrate	-	8.9	-	-	-	-

* I-09 / G.6.2-1 COD is difficult to measure because of precipitation of a component. So results not completely reliable.

2.3.2 Wastewater received from Belgium

1. Scouring (Factory B-01)

- Sample date: 19-04-2002
- Type of fabric: Indigo dyed cotton (jeans)
- Process temperature and time: no data given by B-01
- Ingredients mentioned: no data given by B-01

2. Black Sulphur Dyeing (Factory B-01)

- Sample date: 19-04-2002
- Type of fabric: Cotton
- Process temperature and time: no data given by B-01
- Ingredients mentioned: no data given by B-01

3. Bleaching and desizing (Factory B-01)

- Sample date: 19-04-2002
- Type of fabric: Cotton
- Process temperature and time: no data given by B-01
- Ingredients mentioned: no data given by B-01

4. Sizing liquid (Factory B-02)

- Sample date: February 2002
- Type of fabric: Cotton
- Process temperature: 95°C
- Amounts: 700 litres used per day, 120 litres wasted.
- Ingredients mentioned: 500 litres water
  40 kg (potato) starch
  1 kg solid fat ('Sapolive')

This leads to a composition of: 2 kg/m^3 wax, 35 kg/m^3 starch (data from Centexbel)

Table 4, Analysis data for wastewaters of factory B-01 and B-02. Analyses were done by LeAF. Values are in (mg/l), except when mentioned otherwise.

	Scouring	Black Sulphur Dyeing	Bleaching	Sizing liquid
pH	5.5	4.6	10.5	8.3
COD_{tot}	11574	6027	13012	64760
COD_{ss}	3137	594	1961	0
COD_{filter}	8437	5433	11051	
$COD_{colloidal}$	654	566	1307	7191
$COD_{soluble}$	7783	4867	9744	57570
COD_{VFA}	1520	4489	241	
SS	504	513	562	4
VFA (C2)				242
NH_4-N	4.98	5.14	7.74	
$NO_{2/3}$-N	4.11	2.8	8.34	
NO_2	0.3	0.3	1.79	
PO_4-P	3.58	4.03	40.21	
Colour 220 nm	2.675			
Colour 500 nm	0.4275			

2.4 EXPERIMENTAL CONDITIONS - SUMMARISING TABLE FOR CHARACTERISATION EXPERIMENTS

An overview of experimental conditions is given in Table 5. Given values all correspond to the conditions at the beginning of the experiment. Below the table an explanation of the various experimental factors can be found.

*Table 5, Experimental conditions. Experiment 1-5 were conducted in the experimental hall in Bennekom, the other experiments in Biotechnion (building where LeAF is situated). The VSS*1.4 value will be used in modelling. Exp = experiment number, SD = sludge sample date.*

Exp	Date	Sludge	SD	pH	VSS (g/l)	VSS*1.4 (COD)	Q (l/h)
1	February 8	Alto Seveso	23-1	7.5	3.77 ± 0.34	5.28	-
2	February 15	Alto Seveso	23-1	7.5	4.61 ± 0.12	6.45	23.92 ± 0.20
3	February 25	Alto Seveso	23-1	7.5	4.45 ± 0.14	6.23	24.46 ± 0.14
4	March 8	Alto Seveso	5-3	7.5	5.95 ± 0.11	8.33	23.92 ± 0.12
5	March 15	Bennekom	15-3	7.5	- [1]	-	-
6	April 25	B-01	19-4	8	-	-	-
7	April 26	B-01	19-4	8	-	-	-
8	May 2	B-01	19-4	8	2.54 ± 0.03	3.56	17.09 ± 0.19
9	May 3	B-01	19-4	8	-	-	16.86 ± 0.12
10	May 14	B-01	19-4	8	2.87 ± 0.13	4.02	-
11	May 16	B-01	19-4	8	2.89 ± 0.10	4.05	17.09 ± 0.19
12	May 29	B-01	19-4	8	2.71 ± 0.17	3.79	16.79 ± 0.05
13	May 30	B-01	19-4	8	2.29 ± 0.05	3.21	16.81 ± 0.04
14	June 4	B-01	19-4	8	2.82 ± 0.07	3.95	-
15	June 7	B-01	19-4	8	2.18 ± 0.05	3.05	16.67 ± 0.06
16	June 12	Livescia	6-6	7	4.25 ± 0.06	5.95	16.67 ± 0.07
17	June 17	Livescia	6-6	7	3.19 ± 0.06	4.47	16.57 ± 0.08
18	June 18	Livescia	6-6	7	2.79 ± 0.08	3.91	16.26 ± 0.06
19	June 19	Livescia	6-6	7	3.03 ± 0.04	4.24	-
20	June 24	B-01	19-4	8	-	-	-
21	June 27	Alto Seveso	25-6	7	-	-	16.43 ± 0.09
22	July 1	Alto Seveso	25-6	7	4.52 ± 0.05	6.33	16.43 ± 0.06
23	July 2	Alto Seveso	25-6	7	3.65 ± 0.22	5.11	-
24	July 3	Alto Seveso	25-6	7	3.94 ± 0.02	5.52	16.36 ± 0.03
25	July 4	Alto Seveso	25-6	7	-	-	16.47 ± 0.07
26	July 8	Alto Seveso	25-6	7	2.73 ± 0.04	3.82	16.50 ± 0.05
27	July 9	Alto Seveso	25-6	7	2.69 ± 0.46	3.77	-
28	July 19	Alto Seveso	25-6	7	-	-	-

[1] The respirometer could only be used once a week, crucibles got lost.

Acetate and ammonium were used as reference compounds during the respirometric experiments. At the beginning of each measurement acetate was added to the sludge, to check the activity of the sludge. After each textile wastewater addition, acetate was added again, to check for changes in sludge activity. Changes are related to properties of the wastewater: it can be toxic, but it can also have a positive effect on the activity. When the wastewater has a slight toxic effect for example, the maximum respiration rate on acetate will be lower than before wastewater addition. From the acetate response the biomass yield can be assessed. The yield for acetate is usually between 0.6 and 0.7 g Biomass-COD per g Acetate-COD, depending on the history of the sludge. If this value changes the sludge was probably affected by the wastewater additions. Ammonia was used for a similar check, but on nitrifying bacteria. The shape of the ammonia oxidation respirogram is quite characteristic, and for each gram of ammonia about 4 grams of oxygen are needed. If either one of these two characteristics changes, then the nitrifying bacteria were affected by the additions.

2.5 NEURAL NETWORK

Neural networks need to be trained for every job. It was planned to use only “real” recorded respirograms for training and validation of the network. Due to problems with the respirometer and samples that were too diluted, not enough respirograms could be gathered. Using the ASM1 model, respirograms were generated after calibration based on a limited set of real respirograms from acid dyeing wastewater to be sure to have enough respirograms. The respirogram data were put in excel files that could be read by Matlab, and various combinations of training data and validation data were tried.

2.5.1 The neural network as used in this study

Matlab is a well-known computer program for all kinds of mathematical exercises, based on matrices (MatLab = Matrix Laboratorium). It includes a neural network toolbox that can be configured according to the data that needs processing. The toolbox itself is a black box, which makes it ideal for applications that require application of a “standard” NNW. Using the Matlab Neural Network Toolbox a two-layer network was created by Dr. Keesman. This was used as such, with minor adaptations according to the data that had to be processed. The complete transcription is given in appendix 1.

By running the m-file certain functions of the neural network toolbox are called and executed. Examples of changes that can be made in the net are changing the number of input neurons, and the amount of noise applied to the simulated data. For training, the network can be given a goal (e.g. 0.01), which indicates the maximum difference between the training set and the result of adaptation by changing the weights. When no goal is set, the network will keep trying by adjusting its weights to get the exact training value.

2.5.2 Textile wastewater respirograms for usage with neural network

During the TOWEF0 project many respirograms were recorded. Samples came form all kinds of textile processes, and had many different shapes. To train the neural network a set of similar respirograms was needed. After evaluating the shapes of the available respirograms it was decided that samples from a dyeing process would be best. The different steps of the dyeing processes would give variations on the same basic respirogram shape.

Samples from different steps of five acid dyeing processes were used. Apparently the rinsing steps are very efficient, because many of the rinsing samples were too diluted to give a useful response. Characteristics of the samples that did give a usable response are given in Table 6 (rows 1-4). Due to the limited available data set, respirograms that had been recorded in the past were included in the set (rows 5-14).

Table 6, Used respirograms and their characteristics. Sample volume in ml, COD in mgO_2/l, BOD_{ST} in mgO_2/l (calculated from respirogram), height in mg $O_2/l.h$, length in min (rounded off on 5 min)

Respirogram	Sample volume	COD	BODst	Height	Length
Acid dyeing 52	50	3816	194	56	50
Acid dyeing 203	50	1871	340	47	80
Acid dyeing C	50	1530	334	57	70
Acid dyeing 106	50	5244	222	51	40
Indigo cotton scouring	5	11574	2025	52	70
Black sulphur dyeing	5	6027	2495	87	45
Bleaching	5	13012	2407	41	75
Size	2.5	64760	2866	27	75
Light reactive dyeing	100	675	157	25	100
Silk degumming	20	3400	685	60	60
Silk degumming 2	10	3400	716	54	60
Dark acid dyeing	10	2300	791	39	60
Dark acid dyeing 2	20	2300	787	45	70
Dark reactive dyeing	50	2660	359	65	70

2.5.3 Simulated respirograms for usage with neural network

To create a set of similar respirograms three of the newest recorded ones were selected and using the ASM1 model in SIMNON a fit was made for each one of them. Then the amount of easily biodegradable material was changed and the model was run again. In this way 21 respirograms were simulated, three fits and their variations. In Table 7 the most important parameters for these simulations are given.

Table 7, Parameters for the simulated respirograms. Respirograms used for calibration were Acid dyeing 106, 203 and 52

Respirogram	Initial states		Parameters			
	X_s	S_s	K_s	μ_m	K_h	K_x
106 –50%	180	5	0.1	1.6	11	0.05
106 –20%	288	8	0.1	1.6	11	0.05
106 –10%	324	9	0.1	1.6	11	0.05
106	360	10	0.1	1.6	11	0.05
106 +10%	396	11	0.1	1.6	11	0.05
106 +20%	432	12	0.1	1.6	11	0.05
106 +50%	540	15	0.1	1.6	11	0.05
203 –50%	225	20	0.1	1.4	10	0.1
203 –20%	360	32	0.1	1.4	10	0.1
203 –10%	405	36	0.1	1.4	10	0.1
203	450	40	0.1	1.4	10	0.1
203 +10%	495	44	0.1	1.4	10	0.1
203 +20%	540	48	0.1	1.4	10	0.1
203 +50%	675	60	0.1	1.4	10	0.1
52 –50%	90	75	0.5	1.7	10	0.08
52 –20%	144	120	0.5	1.7	10	0.08
52 –10%	162	135	0.5	1.7	10	0.08
52	180	150	0.5	1.7	10	0.08
52 +10%	198	165	0.5	1.7	10	0.08
52 +20%	216	180	0.5	1.7	10	0.08
52 +50%	270	225	0.5	1.7	10	0.08

X_s = Slowly biodegradable substrate
S_s = Readily biodegradable substrate
K_s = Half saturation heterotrophic growth
μ_m = Maximum heterotrophic growth rate
K_{h}_x = Maximum specific hydrolysis rate
K_x = Half saturation hydrolysis

2.5.4 Preparation of the data

All columns of the excel worksheet had to be even in length. The respirograms were lined up on the last value (taking the largest respirogram as “standard”) and the empty cells at the beginning of each column was filled in with the average of the endogenous respiration rate (see Figure 9A). This approach was chosen because the difficulty in respirogram analysis is determining the end of exogenous respiration. Also the other way around was tried out, lining up all respirograms on the first value and filling in at the bottom with the last number (see Figure 9B).

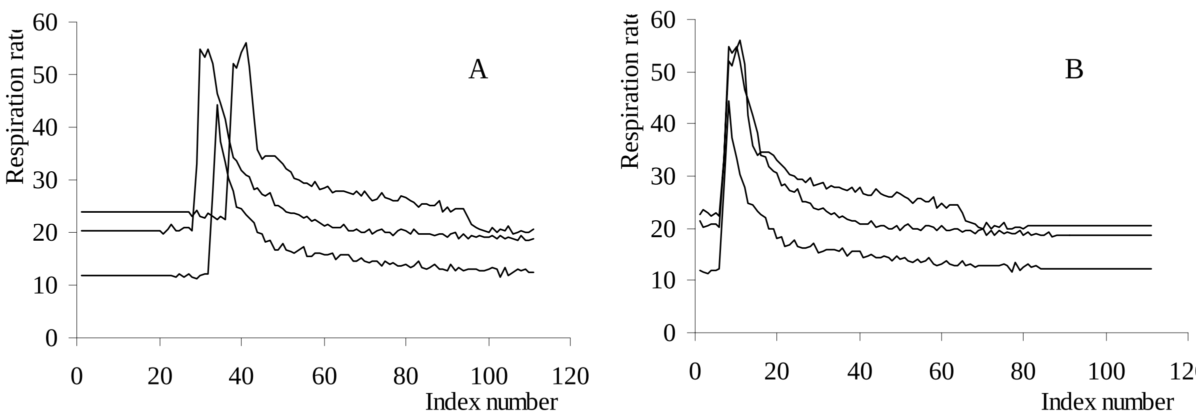


Figure 9 , Preparation of the data sets. A= Respirograms are lined up on the last value, the average of the endogenous respiration rate is used to fill up the beginning, B=Respirograms are lined up on the first value, the average of the endogenous respiration after addition is used to make all respirograms the same length.

In all cases in the last row the manually determined end points were given. As all respirograms had a different duration in time, they were different in length. The Excel sheet row number is not the same as the time in the respirogram. So, a manually determined end-point that is for example minute 58 can be row number 95 in the file. The outcome of the neural network is the row-number, not the time. In an excel data file all respirograms that will be used in a test have to be present. In the Matlab neural network file it has to be indicated how many columns of that excel file the net has to take for training. Automatically the rest will be used for validation.

2.5.5 Overview of the performed trials with the neural network

An overview of the performed calculations with the neural network is given in Table 8. Not all combinations were tested, this table does not represent an experimental planning. The decision for testing a new combination of factors was taken after evaluating the result of the previous calculation.

After each calculation the average error in end-point detection was calculation by taking the standard deviation.

Table 8, Result table of performed experiments. Result "x-y" is average error in end-point detection (x) and number of end-points within 5 points of manually determined end-point (y).

Goal	Off	On	On	On	On	On	On	On	On	On	On	On	On	On
Neuron	5	5	5	5	4	4	3	3	2	2	6	6	7	7
Noise	0	0	0.05	0.1	0	0.1	0	0.1	0	0.1	0	0.1	0	0.1
Data 1a	17-3	20-0	17-0	16-4	nd.	15-5	nd.	17-2	nd.	nd.	nd.	nd.	nd.	20-4
Data 1b	10-3	9-4	nd.	7-7	nd.	11-5	nd.	20-3	nd.	nd.	nd.	20-2	nd.	10-3
Data 2a	nd.	9-3	nd.	nd.	11-2	nd.	nd.	nd.	nd.	nd.	11-3	nd.	nd.	nd.
Data 2b	nd.	10-2	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.
Data 3a	0.5-9	0.5-9	0.5-9	0.7-9	0.9-9	0.6-9	0.4-9	1.3-9	2-8	2.7-8	0.6-9	0.7-9	0.5-9	0.4-9
Data 3b	0.5-9	0.9-9	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	0.4-9	nd.
Data 4a	nd.	3.5-12	nd.	nd.	3.3-10	nd.	2.6-12	nd.	nd.	nd.	3-9	nd.	3-13	nd.
Data 4b	3.8-10	3.3-10	nd.	nd.	1.8-12	nd.	nd.	nd.	nd.	nd.	3.2-11	nd.	2.2-12	nd.

a = lined up last row (top-filled in) and b = lined up first row (= bottom filled in)
Data-set 1 = Training with 21 simulated respirograms, validation with 14 real respirograms
Data-set 2 = Training with 7 real respirograms, validation with other 7 respirograms
Data-set 3 = Training with 12 simulated respirograms "50%" and "10%", validation with 9 resp "0%" and "20%"
Data-set 4 = Training with 14 real respirograms multiplied by a random factor, validation with 14 original respirograms
nd. = not determined, no calculation performed

2.6 INFRARED SPECTROMETRY COD MEASUREMENT

2.6.1 Sampling

At INRA, sampling of the anaerobic reactor is done automatically every half-hour. To avoid clogging of the tubes due to bacterial growth, the sample is filtered using ultrafiltration before analysis. With the same filtered effluent, measurements are done with a TOC analyser, the titrimetric analyser and the IR spectrometer. Filtration is also required because solids influence the infrared absorption of the sample.

2.6.2 Calibration and measuring

In fact the principle of calibration of the IR method is the same as for any calibration line (see Figure 10). Spectra are taken from the samples used for calibration, and the same samples are analysed in the lab using conventional methods. Many different compounds can be determined, but for this purpose only COD was considered. The COD values that were measured in the lab using standard methods are assigned to the samples, as are the 'COD - IR values' resulting from analysis of the spectra. Certain areas of the spectra are evaluated to determine a COD value from an IR spectrum, but the exact calibration process is confidential. With the "lab-value" and the "IR spectrum value" a calibration line can be made (Figure 10). This calibration line can than be validated with the spectrum of sample not used for calibration.

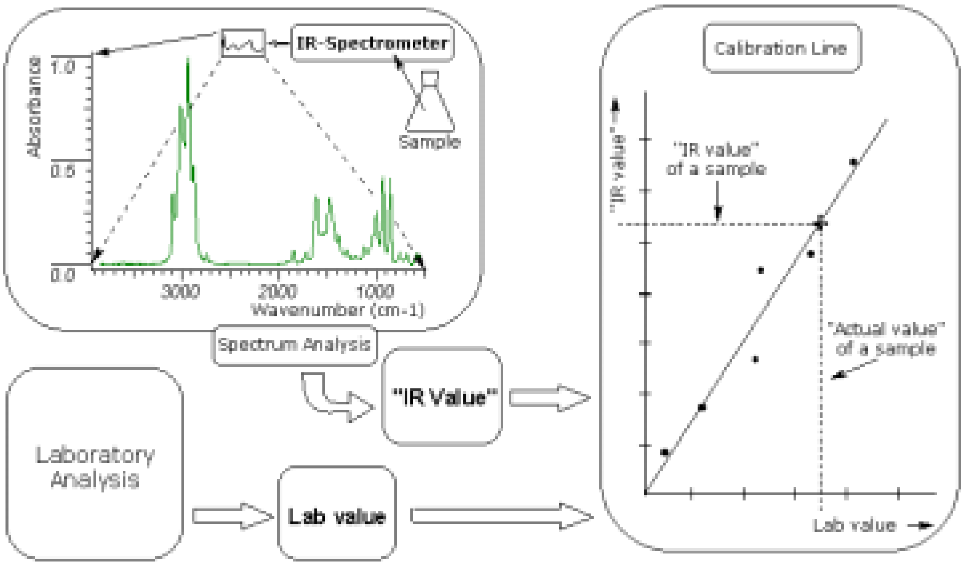


Figure 10, Schematic representation of the calibration procedure

3 RESULTS OF RESPIROMETRY

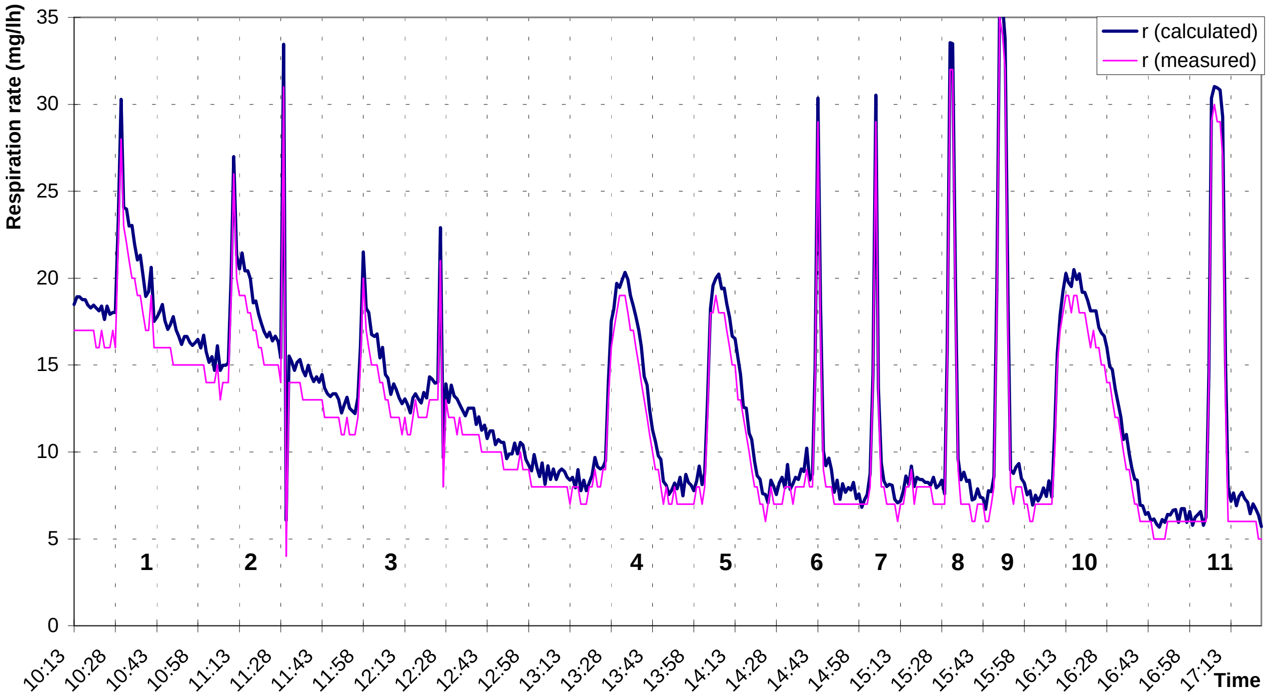
Only the calculated respiration rate should be considered as this is done by using the instrument's DO values with a higher resolution and is based on the correct pump calibration values. The (non-calibrated) instrument values just serve to check the correct positioning of the calculated respirograms.

3.1 RESPIROGRAMS RECORDED OF DIFFERENT TEXTILE WASTEWATERS

3.1.1 Alto Seveso sludge and mixed textile wastewater

3.1.1.1 Experiment 1

Solids determination: ML VSS = 3.77 ± 0.34 g/l (TS = 7.61 ± 0.57 g/l)



Observations:

- Wastewater causes foaming, this leads to loss of sludge
- The peaks at 11:35 and 12:28 are erroneous measurements
- NH_4 respirograms have an uncommon shape; normally they are more "square"
- A strong decrease of endogenous activity with wastewater additions

Yields and O/N-ratios:

Table 9, Calculated results from experiment 1. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

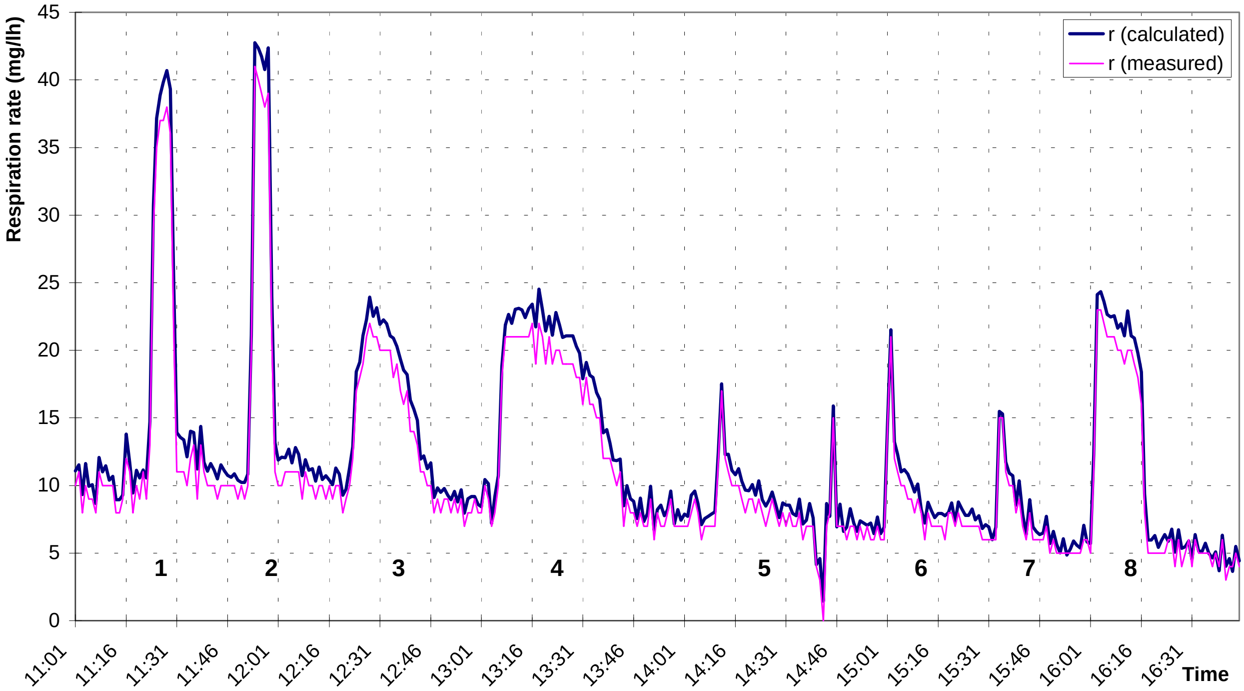
Additions	1	2	3	4	5	6	7	8	9	10	11
Substrate	Ww	Ww	Ww	NH_4	NH_4	Ac	Ac	Ac	Ac	NH_4	Ac
Concentration				175	175	1000	1000	1000	1000	175.3	1000

Volume added	0.050	0.050	0.050	0.005	0.005	0.005	0.005	0.010	0.015	0.010	0.020
Total volume	1.550	1.600	1.650	1.655	1.660	1.665	1.670	1.680	1.695	1.705	1.725
Endog. resp.	18.50	15.59	13.58	8.56	8.13	8.44	7.54	7.77	7.51	6.84	6.77
BOD_{st}	24	31	17	821	774	236	221	213	215	783	197
Y or O/N				4.68	4.41	0.76	0.78	0.79	0.79	4.46	0.80

3.1.1.2 Experiment 2 – Repetition

To check for toxic effects of the wastewater, and for changes in the wastewater due to storage time, experiment 1 was repeated. The sludge had been hardly aerated for part of the week between the experiments, because of problems with the air pump.

Solids determination: MLVSS = 4.61 ± 0.12 g/l (TS = 9.17 ± 1.09 g/l)



Observations:

- Wastewater causes foaming
- Last acetate respirogram much lower than first ones, and also the endogenous respiration is lower than before. This is probably a toxicity effect from the wastewater

Yields and O/N-ratios:

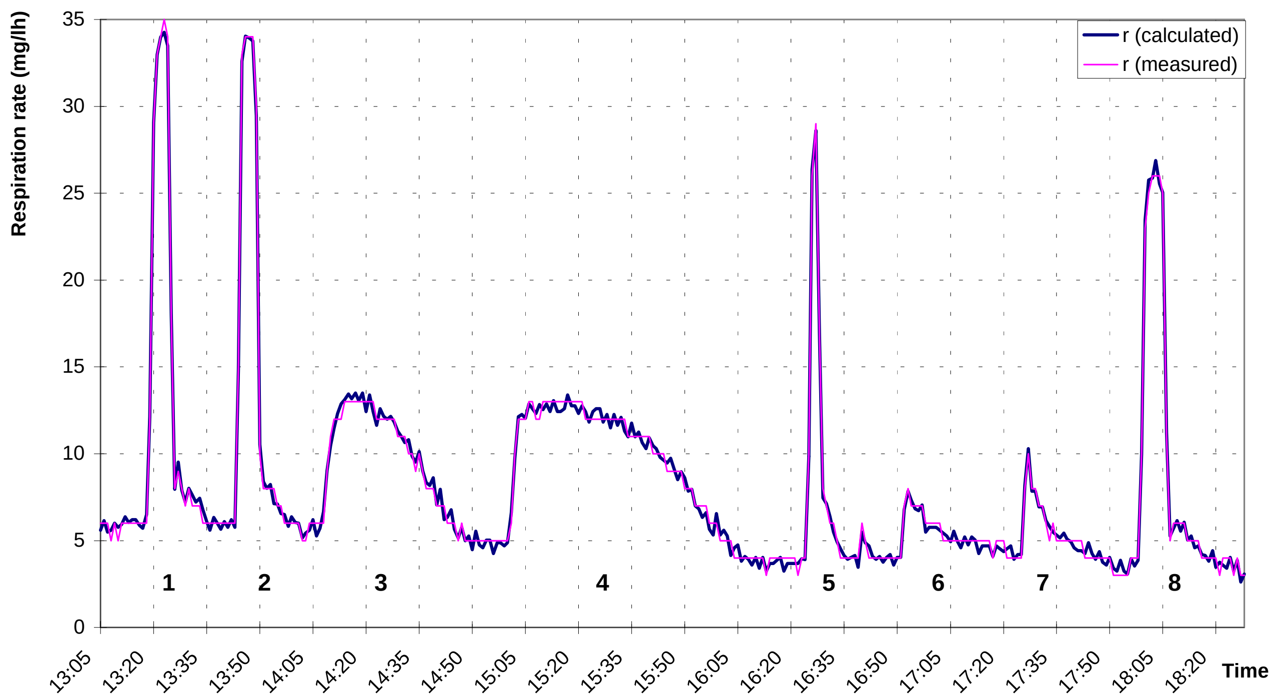
Table 10, Calculated results from experiment 2. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4	5	6	7	8
Substrate	Ac	Ac	NH_4	NH_4	Ww	Ww	Ww	Ac
Concentration	1000	1000	175	175				1000
Volume added	0.025	0.025	0.010	0.020	0.050	0.100	0.150	0.040
Total sludge volume	1.525	1.550	1.560	1.580	1.630	1.730	1.880	1.920
Endogenous respir.	11.05	10.58	10.11	8.95	704	7.63	7.07	5.72
BOD_{st}	197	204	498	511	38	13	5	193
Y or O/N	0.80	0.80	2.84	2.92				0.81

3.1.1.3 Experiment 3 – Repetition

Wastewater composition can change over time. A second repetition was done to see effects of storage after some time.

Solids determination: ML VSS = 4.45 ± 0.14 g/l (TS = 7.25 ± 0.06 g/l)



Observations:

- Wastewater causes foaming, foam is brownish
- No big decrease of endogenous activity with wastewater additions, but acetate respirogram gets lower

Yields and O/N-ratios:

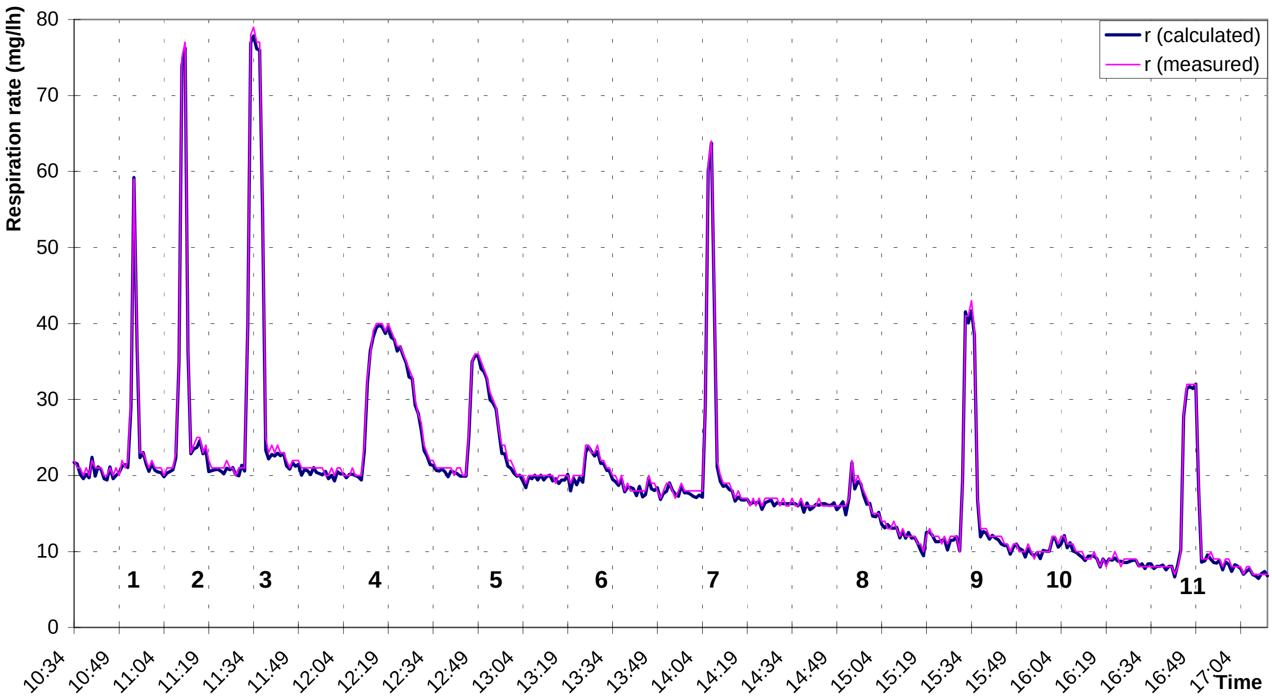
Table 11, Calculated results from experiment 3. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4	5	6	7	8
Substrate	Ac	Ac	NH_4	NH_4	Ac	Ww	Ww	Ac
Concentration	1000	1000	175	175	1000	-	-	1000
Volume added	0.020	0.020	0.010	0.020	0.01	0.050	0.100	0.020
Total volume	1.520	1.540	1.550	1.570	1.580	1.630	1.730	1.750
Endogenous resp.	6.02	5.80	5.45	4.49	4.16	3.99	4.32	3.60
BOD_{st}	212	206	497	480	199	24	8	238
Y or O/N	0.79	0.79	2.83	2.74	0.80	-	-	0.76

3.1.1.4 Experiment 4 – New sludge and wastewater

New sludge and wastewater were received on 07-03-2002. The sludge was aerated from 18.00 h that day until the measurements so it was still fresh.

Solids determination: ML VSS = 5.95 ± 0.11 g/l (TS = 8.37 ± 0.26 g/l)



Observations:

- New wastewater gives small respirograms, and a lot of foaming
- Old wastewater gives almost no respirogram, and less foam than with new water
- Decrease of endogenous activity with wastewater additions, acetate respirogram gets lower, this indicates a toxic effect of the wastewater on the sludge

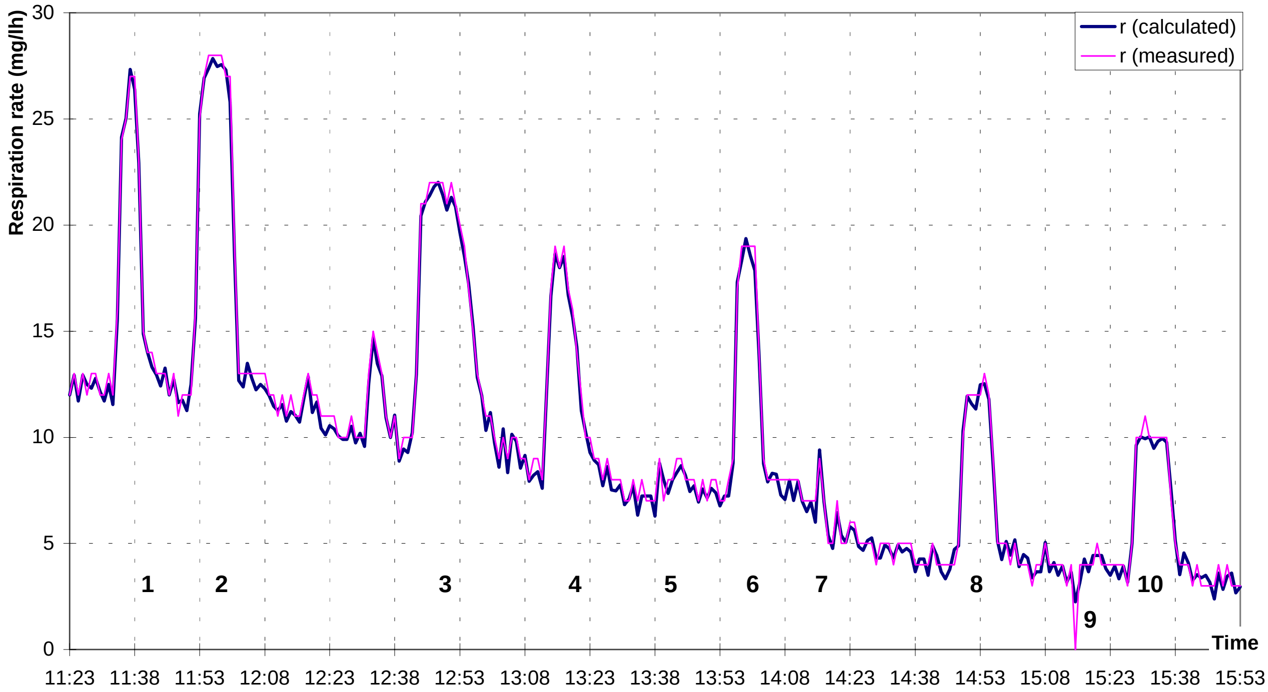
Yields and O/N-ratios:

Table 12, Calculated results from experiment 4. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4	5	6	7	8	9	10	11
Substrate	Ac	Ac	Ac	NH_4	NH_4	Lar_{new}	Ac	Lar_{new}	Ac	$Lari_{old}$	Ac
Concentration	1000	1000	1000	175	175	-	1000	-	1000	-	1000
Volume added	0.010	0.020	0.040	0.020	0.010	0.050	0.02	0.050	0.020	0.050	0.020
Total volume	1.510	1.530	1.570	1.590	1.600	1.650	1.670	1.700	1.720	1.770	1.790
Endog. resp.	20.59	20.51	20.50	20.35	19.76	19.07	16.77	14.03	10.70	9.41	8.15
BOD_{st}	175	204	195	391	368	14	197	16	205	6	191
Y or O/N	0.83	0.80	0.80	2.23	2.10	-	0.80	-	0.79	-	0.81

3.1.2 Experiment 5 – Bennekom sludge and mixed wastewater

Sludge taken on the same day from Bennekom municipal WWTP.



Observations:

- Respirograms seem to be somewhat noisy, but this is mainly due to scale.
- Wastewater gives no respirograms, but foaming is the same as always
- Foam is colourful like soap instead of brownish: Bennekom sludge seems to have better resistance to surfactants than Lariana sludge (although both receive municipal wastewater)
- Acetate respirograms lower and change shape after wastewater addition

Yields and O/N-ratios:

Table 13, Calculated results from experiment 5. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

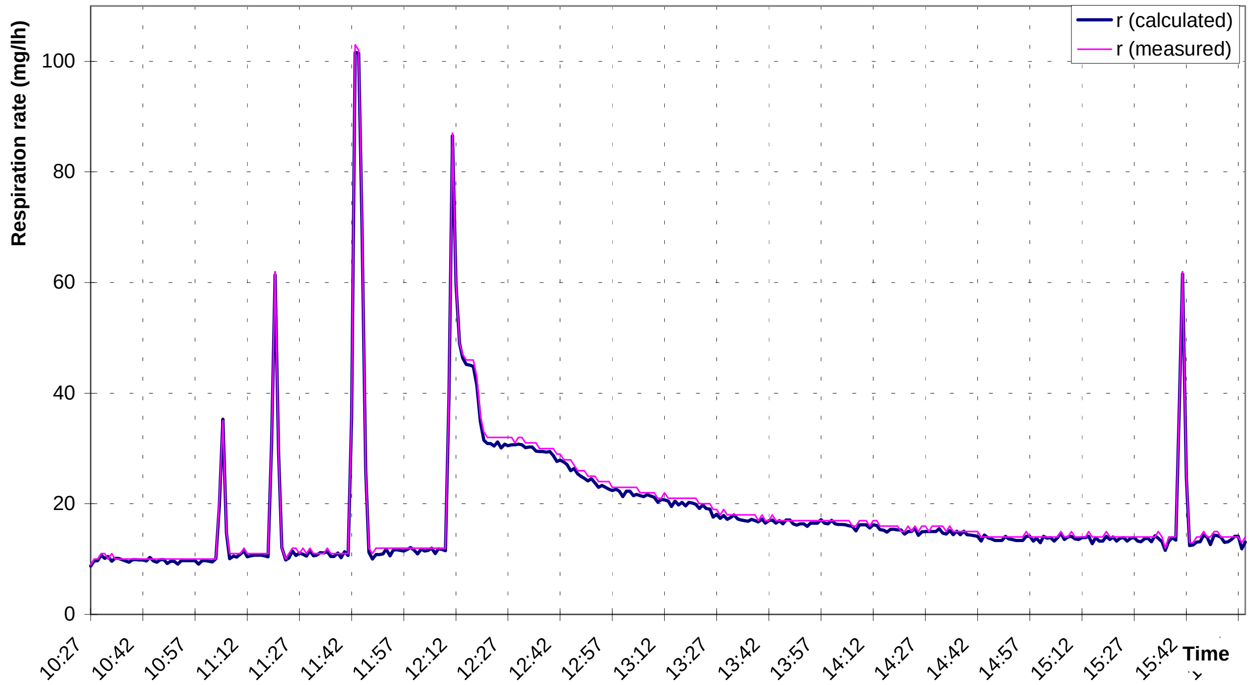
Additions	1	2	3	4	5	6	7	8	9	10
Substrate	Ac	Ac	NH_4	NH_4	Lar_{new}	Ac	Lar_{new}	Ac	Lar_{old}	Ac
Concentration	1000	1000	175	175		1000		1000		1000
Volume added	0.010	0.020	0.010	0.005	0.050	0.010	0.05	0.010	0.050	0.010
Total volume	1.510	1.530	1.540	1.545	1.595	1.605	1.655	1.615	1.665	1.675
Endog. resp.	11.73	11.49	9.64	7.65	n.d.	6.17	n.d.	3.98	n.d.	3.54
BOD_{st}	208	183	366	413	n.d.	226	n.d.	172	n.d.	159
Y or O/N	0.79	0.82	2.09	2.36		0.77		0.83		0.84

n.d. = could not be determined, no respirograms.

3.1.3 B-01 sludge and wastewater

3.1.3.1 Experiment 6 – Scouring wastewater

Experiment 6 was a test to determine the quantity of scouring wastewater that would be best for respirometric experiments.



Observations:

- Too much scouring wastewater added, respirogram still not finished after 3 hours
- Respirogram has two shoulders

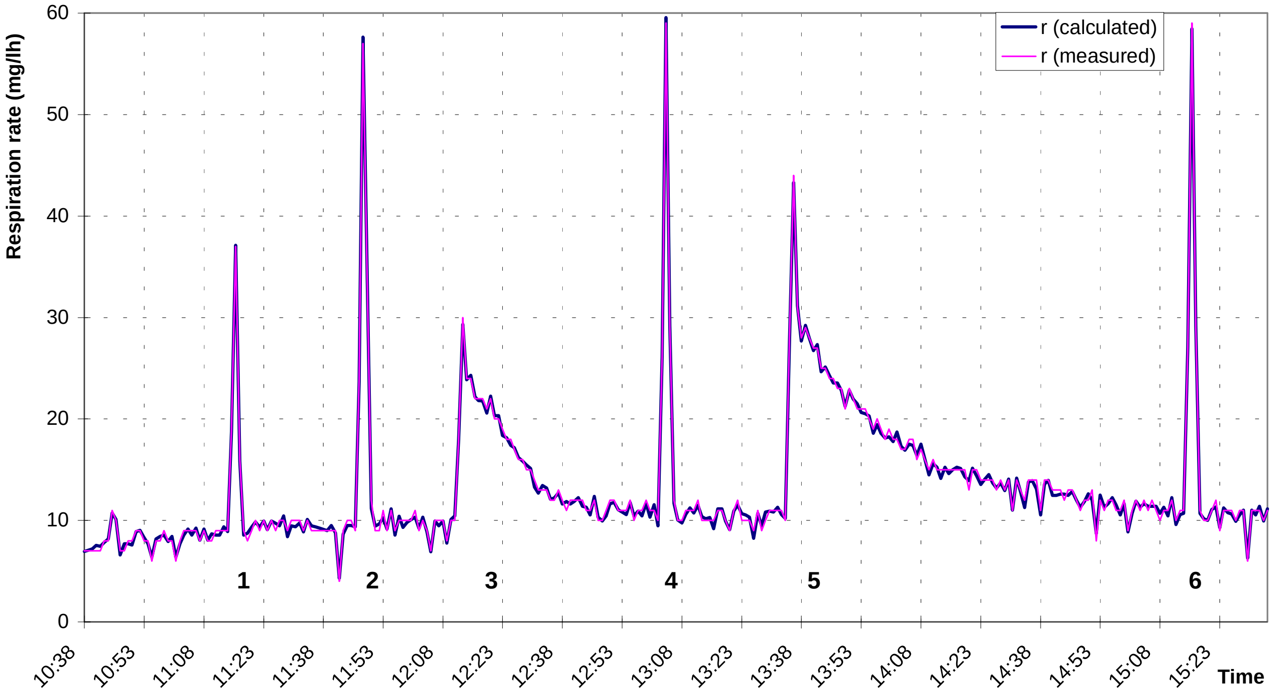
Yields and O/N-ratios:

Table 14, Calculated results from experiment 6. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4	5
Substrate	Ac	Ac	Ac	Scouring	Ac
Concentration	1000	1000	1000		1000
Volume added	0.005	0.010	0.025	0.025	0.010
Total volume	1.755	1.765	1.790	1.815	1.825
Endogenous respiration	10.24	10.74	11.07	12.38	13.21
BOD_{st}	230	265	334	1862	264
Y or O/N	0.77	0.74	0.67		0.74

3.1.3.2 Experiment 7 – Repetition scouring wastewater

Test with smaller amounts of wastewater.



Observations:

- Respirogram a bit less smooth than on April 25.
- Respirograms not fully completed before additions of next substrate
- Respirograms do not have two shoulders. Amounts too small or the compound that caused it has disappeared?

Yields and O/N-ratios:

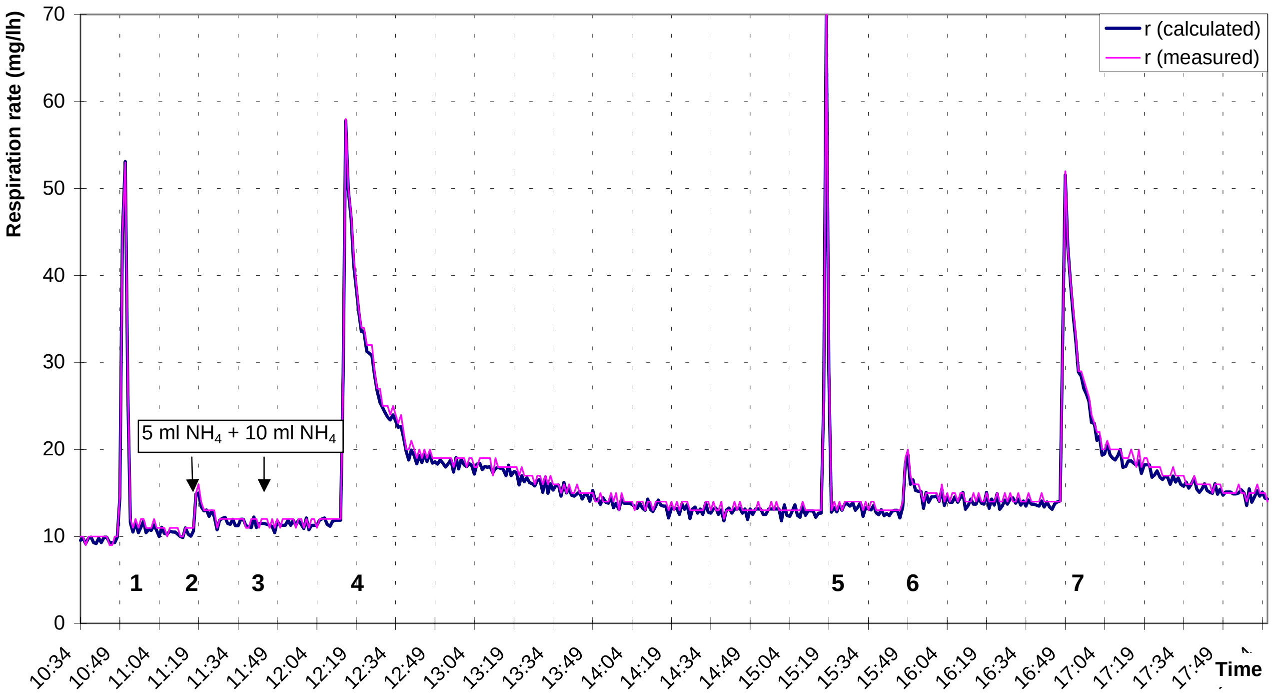
Table 15, Calculated results from experiment 7. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4	5	6
Substrate	Ac	Ac	Scouring	Ac	Scouring	Ac
Concentration	1000	1000		1000		1000
Volume added	0.005	0.010	0.005	0.010	0.010	0.010
Total volume	1.505	1.515	1.520	1.530	1.540	1.550
Endogenous respiration	9.16	8.65	10.98	10.57	10.74	10.67
BOD_{st}	237	272	916	210	1366	210
Y or O/N	0.76	0.73		0.79		0.79

3.1.3.3 Experiment 8 – Repetition scouring wastewater

Respirograms seemed not completely finished in experiment 7, therefore repeated with the same amounts of scouring wastewater. Now more time after each respirogram.

Solids determination: ML VSS = 2.54 ± 0.03 g/l (TS = 8.17 ± 0.18 g/l)



Observations:

- Second ammonium addition does not give a respirogram, so small peak at 5 ml probably due to increased activity as a result of nutrient addition. Sludge had apparently lack of nitrogen.
- Although baseline already very flat, it appears that the first wastewater respirogram was not finished yet. Or endogenous respiration became higher?
- After wastewater respirogram, 10 ml ammonium does give response. Sludge ran out of N?
- The second wastewater respirogram was not completed.

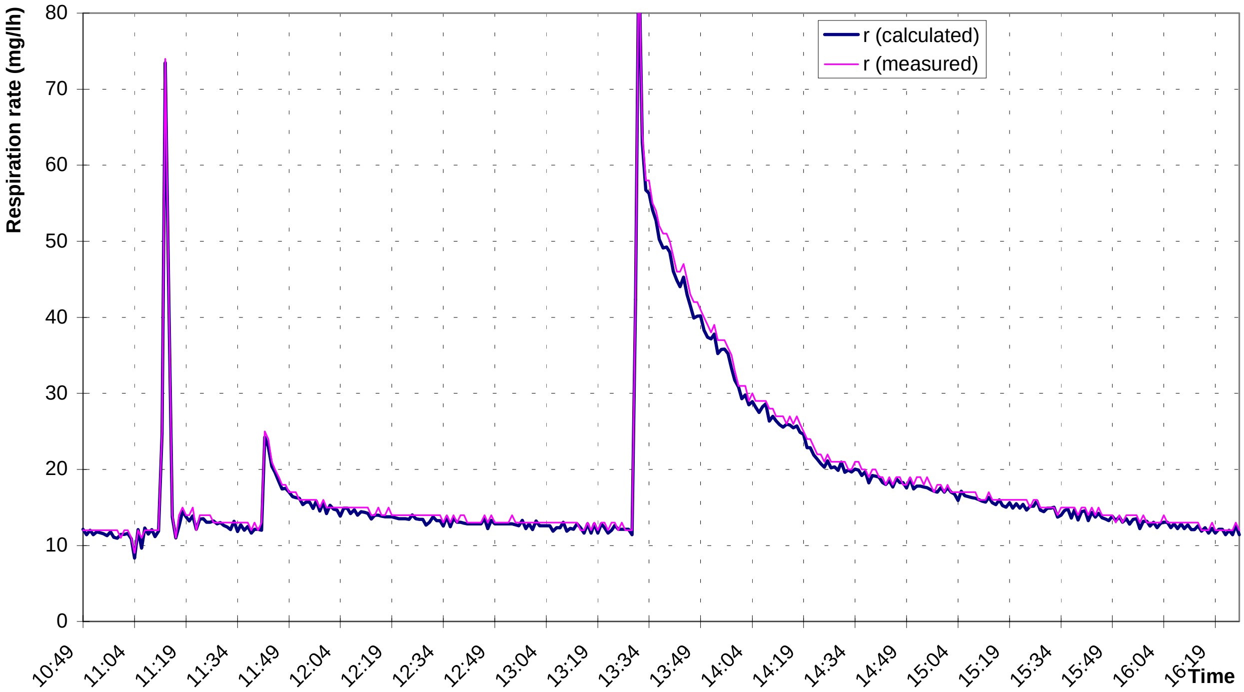
Yields and O/N-ratios:

Table 16, Calculated results from experiment 8. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4	5	6
Substrate	Ac	NH_4	Scouring	Ac	NH_4	Scouring
Concentration	1000	292		1000	292	
Volume added	0.010	0.005	0.010	0.010	0.010	0.005
Total volume	1.510	1.515	1.525	1.535	1.545	1.550
Endogenous respiration	9.89		12.19	12.89		14.19
BOD_{st}	291		2280	220		2025
Y or O/N	0.71			0.78		

3.1.3.4 Experiment 9 – Repetition scouring wastewater

Respirograms in experiments 7 and 8 do not show exactly the same shape as in experiment 6. Repetition with larger amount to check for shoulders.



Observations:

- Large amount of wastewater resulted in an extended respirogram. Shoulders not as clear as in experiment 6.
- Ammonium generates a response but since the shape is not typical nitrification, this is probably due to an increase in carbonaceous respiration as a result of nitrogen nutrient addition.
- Difficult to determine the end of a long respirogram. Now stopped too early.

Yields and O/N-ratios:

Table 17, Calculated results from experiment 9. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

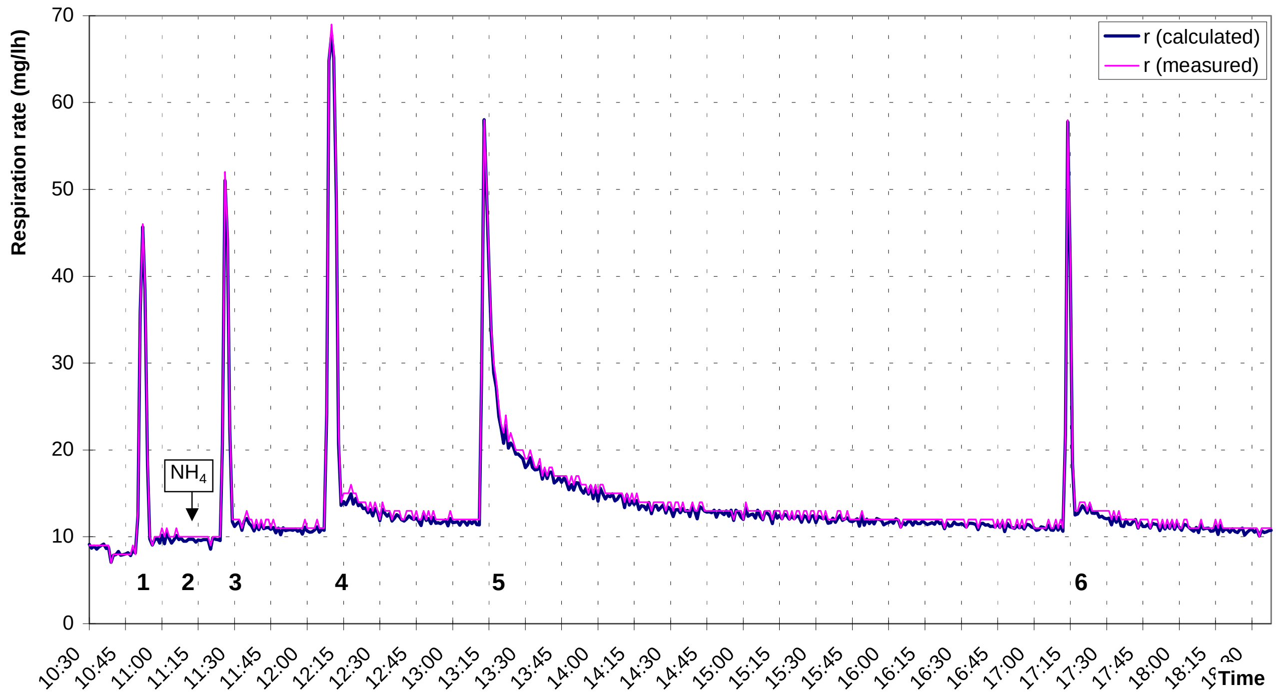
Additions	1	2	3
Substrate	Ac	NH_4	Scouring wastewater
Concentration	1000	292	
Volume added	0.010	0.010	0.020
Total volume	1.510	1.520	1.540
Endogenous respiration	13.17	12.16	12.74
BOD_{st}	246	524*	2442
Y or O/N	0.75	1.80*	

* Respirogram not typical ammonium oxidation respirogram

3.1.3.5 Experiment 10 - Repetition scouring wastewater

In all experiments respirograms seem not to finish. Now test with small amount and very long time to check if endogenous respiration can come back to value before addition.

Solids determination: ML VSS = 2.87 ± 0.13 g/l (TS = 9.69 ± 0.03 g/l)



Observations:

- Ammonium addition does not give a response
- Endogenous respiration increases slightly after ammonium addition. This indicates an effect of nitrogen nutrient addition.
- Scouring respirogram completely finished. This time long enough, endogenous respiration rate after addition is the same as before.

Yields and O/N-ratios:

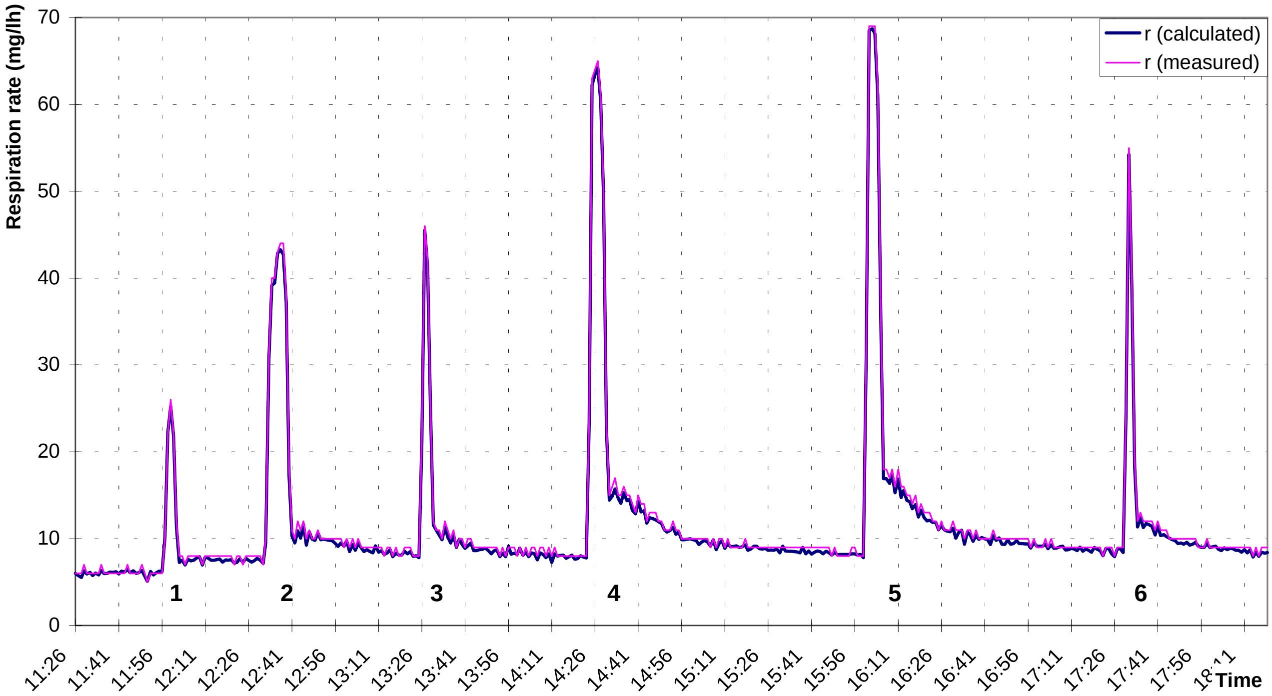
Table 18, Calculated results from experiment 10. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4	5
Substrate	Ac	Ac	Ac	Scouring wastewater	Ac
Concentration	1000	1000	1000		1000
Volume added	0.010	0.010	0.020	0.005	0.010
Total volume	1.810	1.820	1.840	1.845	1.855
Endogenous respiration	8.83	10.15	12.47	11.71	11.35
BOD_{st}	321	365	332	3429	353
Y or O/N	0.68	0.64	0.67		0.65

3.1.3.6 Experiment 11 – Black sulphur dye wastewater

Other type of wastewater.

Solids determination: ML VSS = 2.89 ± 0.10 g/l (TS = 9.31 ± 0.03 g/l)



Observations:

- Sludge has not been fed with sulphur dye water since sampling (19 April)
- Endogenous respiration does not decrease after wastewater addition, no toxic effect visible.

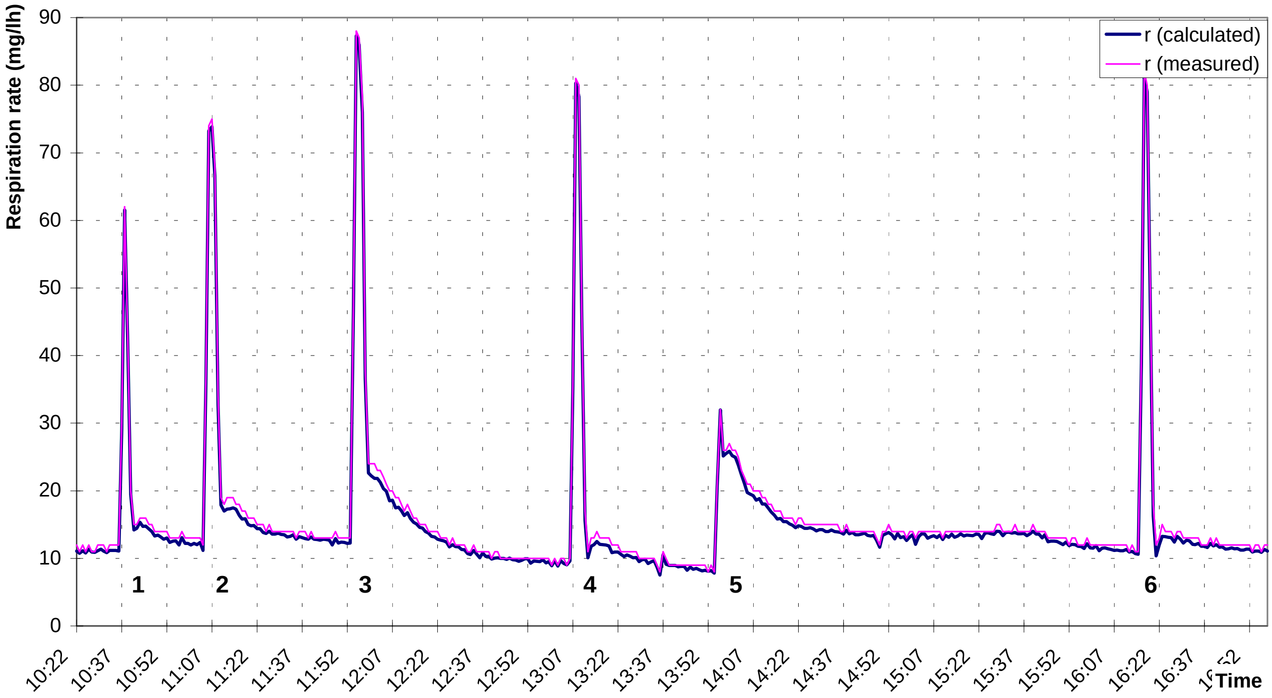
Yields and O/N-ratios:

Table 19, Calculated results from experiment 11. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4	5	6
Substrate	Ac	Ac	Ac	Sulphur dye ww	Sulphur dye ww	Ac
Concentration	1000	1000	1000			1000
Volume added	0.005	0.020	0.010	0.005	0.005	0.010
Total volume	1.805	1.825	1.835	1.840	1.845	1.855
Endogenous respiration	7.00	8.00	7.96	7.99	8.44	8.63
BOD_{st}	413	425	432	2855	2792	440
Y or O/N	0.59	0.57	0.576			0.56

3.1.3.7 Experiment 12 – Repetition black sulphur dye wastewater

Solids determination: ML VSS = 2.71 ± 0.17 g/l (TS = 10.58 ± 0.04 g/l)



Observations:

- Sludge was fed with sulphur dye wastewater
- Sizing liquid takes a long time, seemed already finished on the computer.
- Next time with less, and longer time running.

Yields and O/N-ratios:

Table 20, Calculated results from experiment 12. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

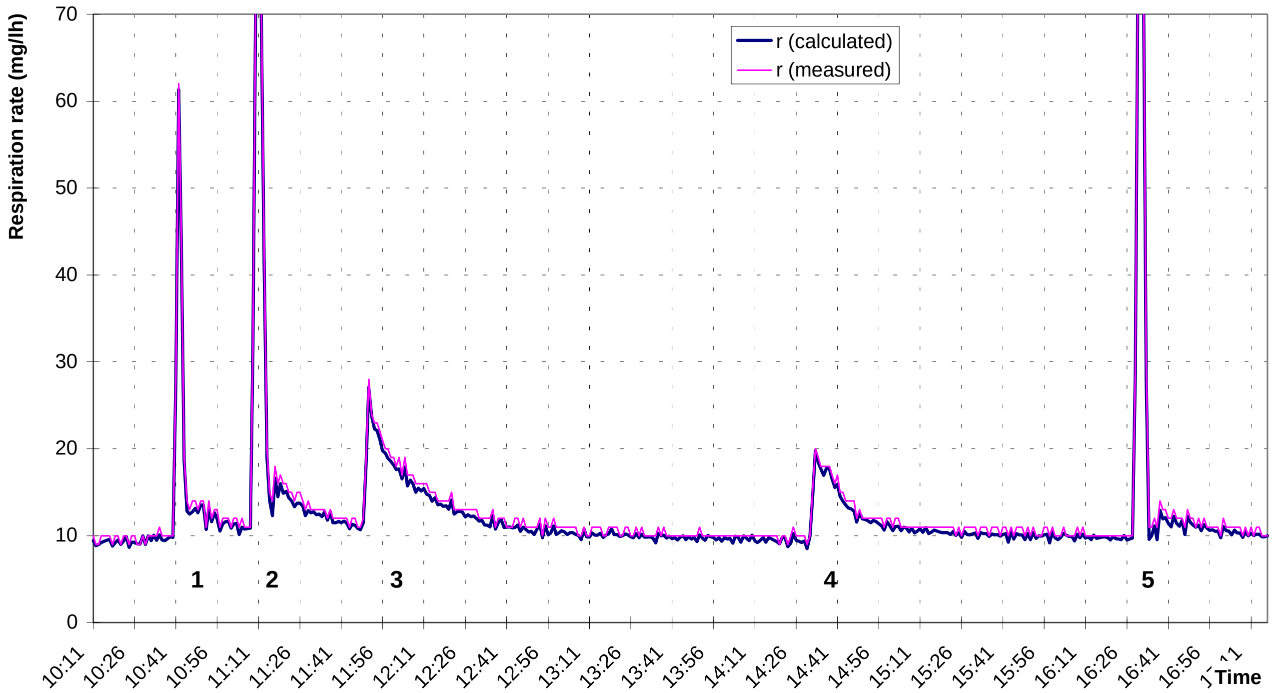
Additions	1	2	3	4	5	6
Substrate	Ac	Ac	Sulphur dye	Ac	Sizing liquid	Ac
Concentration	1000	1000		1000		1000
Volume added	0.010	0.020	0.005	0.020	0.005	0.020
Total volume	1.810	1.830	1.835	1.855	1.860	1.880
Endogenous respiration	11.64	12.20	10.81	8.75	n.d.	11.00
BOD_{st}	404	445	2495	386	n.d.	371
Y or O/N	0.60	0.56		0.61		0.63

n.d. = could not be determined, respirogram seemed to have ended but r was still decreasing.

3.1.4 Experiment 13 – B-01 sludge and B-02 Sizing liquid

There was no sludge available that was adapted to sizing liquid, so sludge of B-01 was used.

Solids determination: ML VSS = 2.29 ± 0.05 g/l (TS = 10.61 ± 0.11 g/l)



Observations:

- 2.5 ml sizing liquid seems appropriate quantity (respirogram not high, but needs still 1 hour)
- Third acetate respirogram (20 ml) slightly higher than second (20 ml)
- Endogenous activity very constant, no toxic effect of sizing liquid

Yields and O/N-ratios:

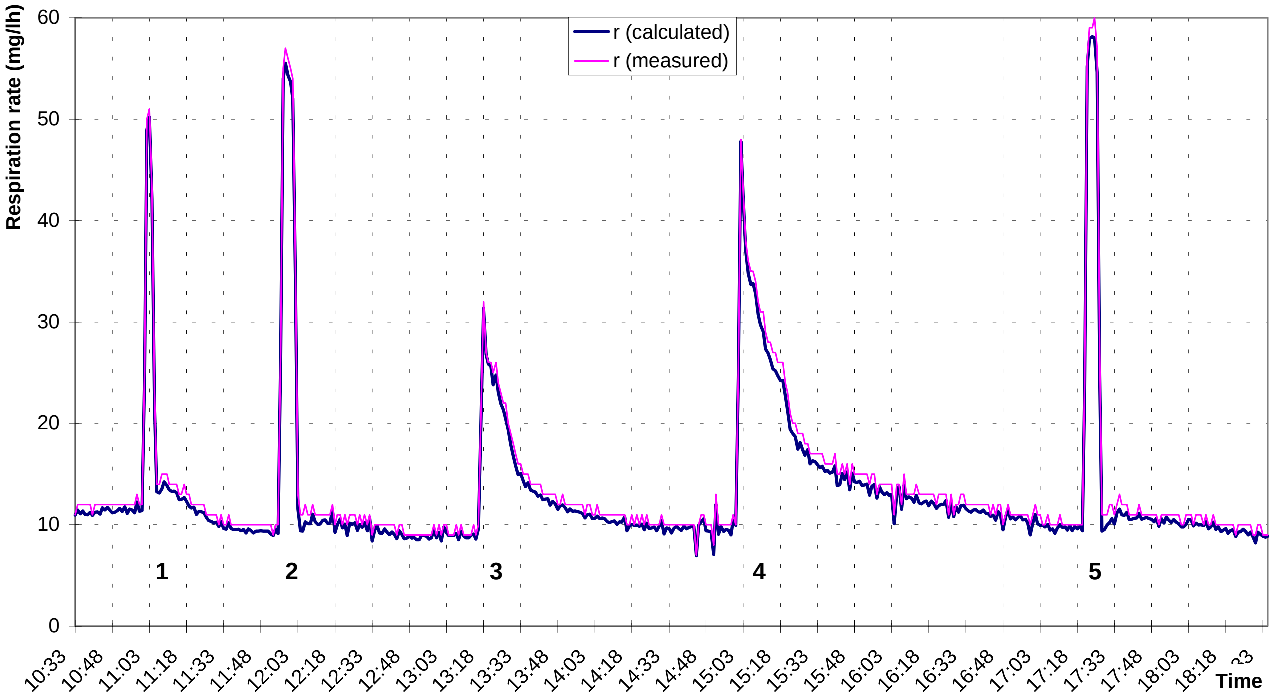
Table 21, Calculated results from experiment 13. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4	5
Substrate	Ac	Ac	Sizing liquid	Sizing liquid	Ac
Concentration	1000	1000			1000
Volume added	0.010	0.020	0.0025	0.001	0.020
Total volume	1.810	1.830	1.833	1.834	1.854
Endogenous respiration	11.21	11.66	10.58	9.82	10.09
BOD_{st}	322	419	2866	3661	395
Y or O/N	0.68	0.58			0.60

3.1.5 B-01 sludge and wastewater

3.1.5.1 Experiment 14 – Bleaching wastewater

Solids determination: ML VSS = 2.82 ± 0.07 g/l (TS = 10.74 ± 0.05 g/l)



Observations:

- 5 ml Bleaching wastewater is appropriate quantity
- Third acetate respirogram (20 ml) slightly higher than second (20 ml)
- Endogenous activity very constant, no toxic effect of bleaching wastewater

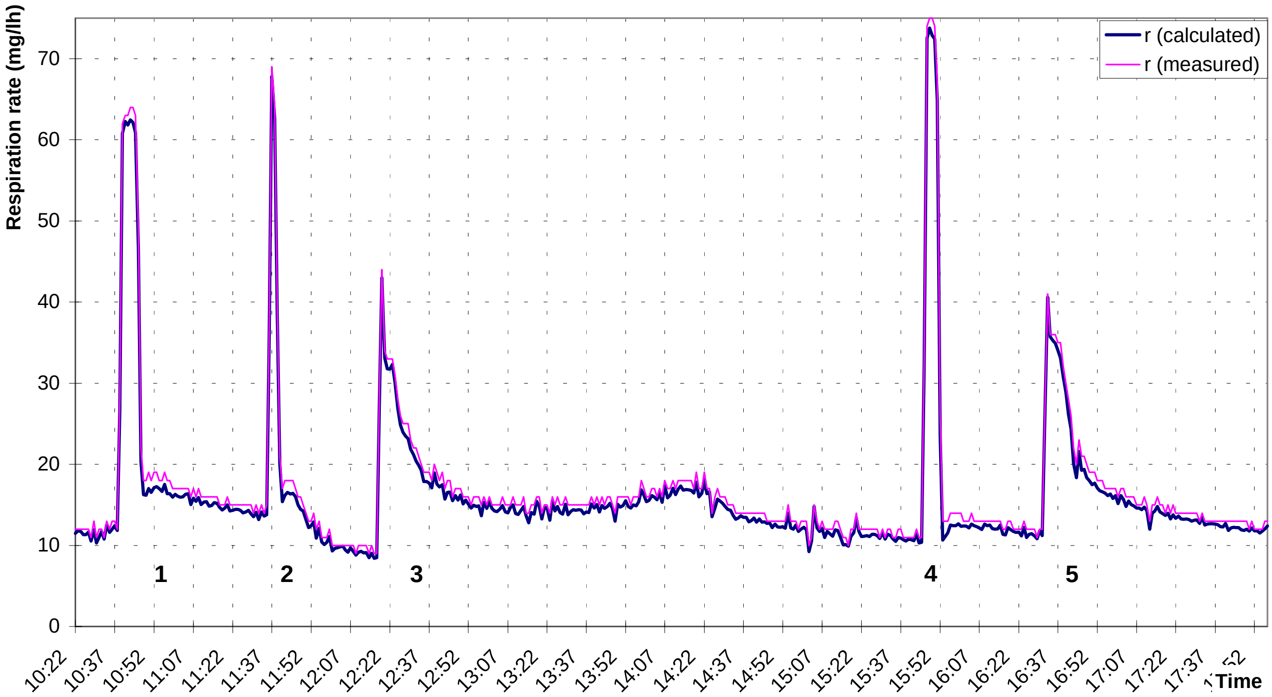
Yields and O/N-ratios:

Table 22, Calculated results from respiration experiment 14. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{ST} for the added solution in mg O_2/l.

Additions	1	2	3	4	5
Substrate	Ac	Ac	Bleaching ww	Bleaching ww	Ac
Concentration	1000	1000			1000
Volume added	0.010	0.020	0.005	0.010	0.020
Total volume	1.760	1.780	1.785	1.795	1.815
Endogenous respiration	11.47	9.33	9.20	9.83	9.79
BOD_{st}	448	427	1959	2168	399
Y or O/N	0.55	0.57			0.60

3.1.5.2 Experiment 15 - Bleaching wastewater and B-02 Sizing liquid

Solids determination: ML VSS = 2.18 ± 0.05 g/l (TS = 10.46 ± 0.12 g/l)



Observations:

- Endogenous respiration rate varies a lot, results probably not reliable. Also the yield for acetate (see table 19) is very low compared to previous experiments (±0.5 instead of ±0.7)
- The 5 ml Bleaching wastewater is good quantity
- Sizing respirogram strange shape, 5 ml is really too much because after 2 hours not finished

Yields and O/N-ratios:

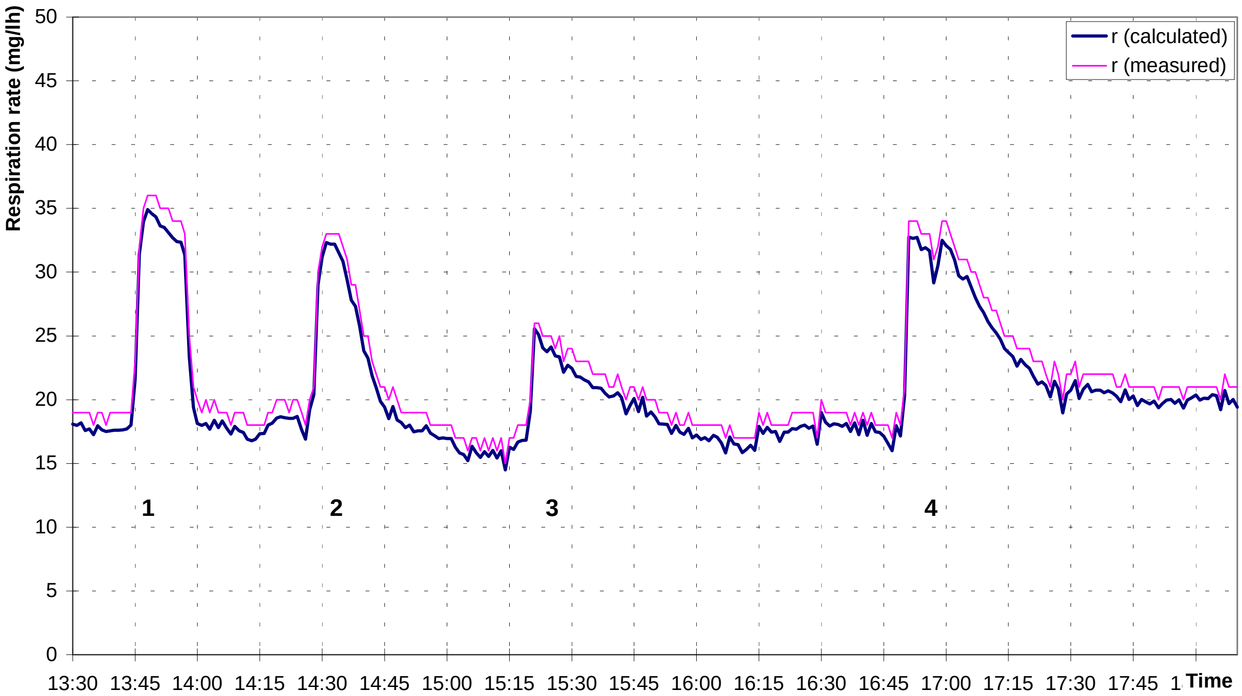
Table 23, Calculated results from respiration experiment 15. Substrate conc. are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4	5
Substrate	Ac	Ac	Sizing liquid	Ac	Bleaching ww
Concentration	1000	1000		1000	
Volume added	0.020	0.010	0.005	0.020	0.005
Total volume	1.770	1.780	1.785	1.805	1.810
Endogenous respiration	14.36	13.38	9.74	11.16	11.61
BOD_{st}	494	527	6196	503	2407
Y or O/N	0.51	0.47		0.50	

3.1.6 Livescia sludge and I-06 wastewater

3.1.6.1 Experiment 16 – Reactive dyeing and double scouring wastewater.

Solids determination: ML VSS = 4.25 ± 0.06 g/l (TS = 10.89 ± 0.03 g/l)



Observations:

- Sludge had been fed once between sampling and experiment with wastewater from double scouring process (0.5 litre on 5 litre sludge)

Yields and O/N-ratios:

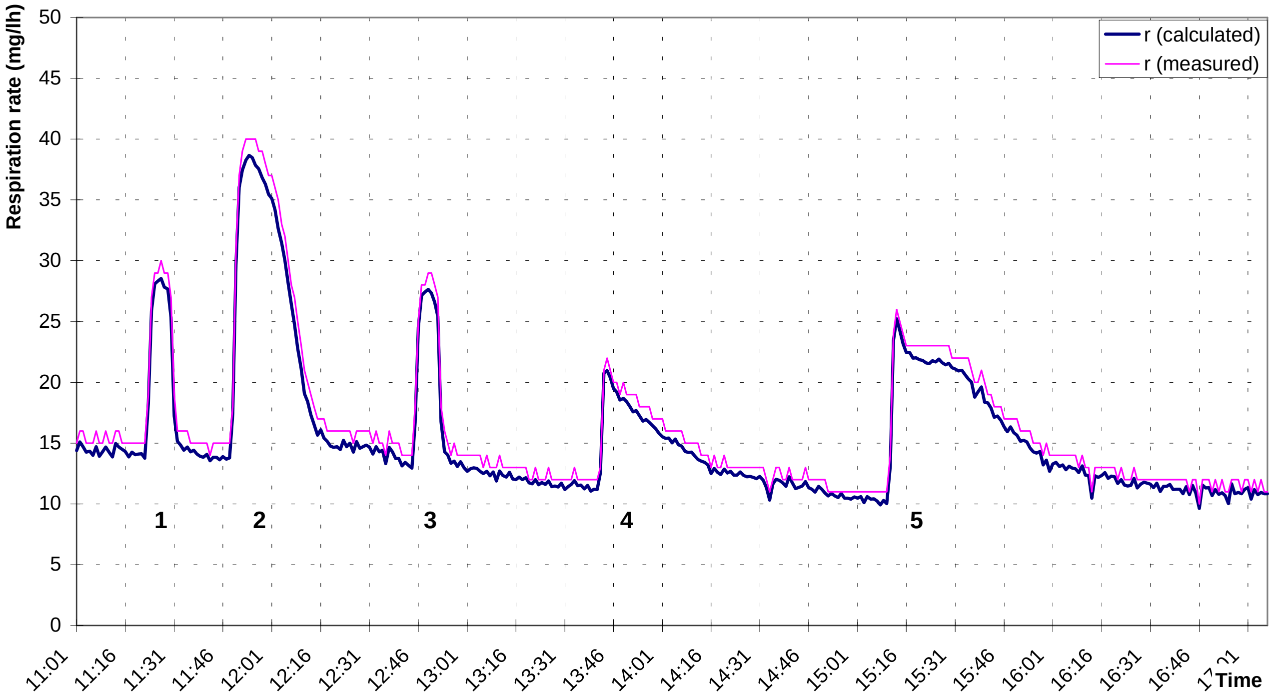
Table 24, Calculated results from respiration experiment 16. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4
Substrate	Ac	NH4	Light reactive dyeing ww	Double scouring 2nd bath
Concentration	1000	1000		
Volume added	0.020	0.005	0.050	0.050
Total volume	1.770	1.775	1.825	1.875
Endog. respiration	17.64	17.12	16.36	17.05
BOD_{st}	294	1003	104	309
Y or O/N	0.71	3.44		

3.1.6.2 Experiment 17 – Repetition light reactive dyeing wastewater

Small wastewater respirogram in experiment 16 so check with higher amount.

Solids determination: ML VSS = 3.19 ± 0.06 g/l (TS = 9.09 ± 0.04 g/l)



Observations:

- Endogenous respiration rate decreased during the experiments
- good response to wastewater
- No effect yet of wastewater addition

Yields and O/N-ratios:

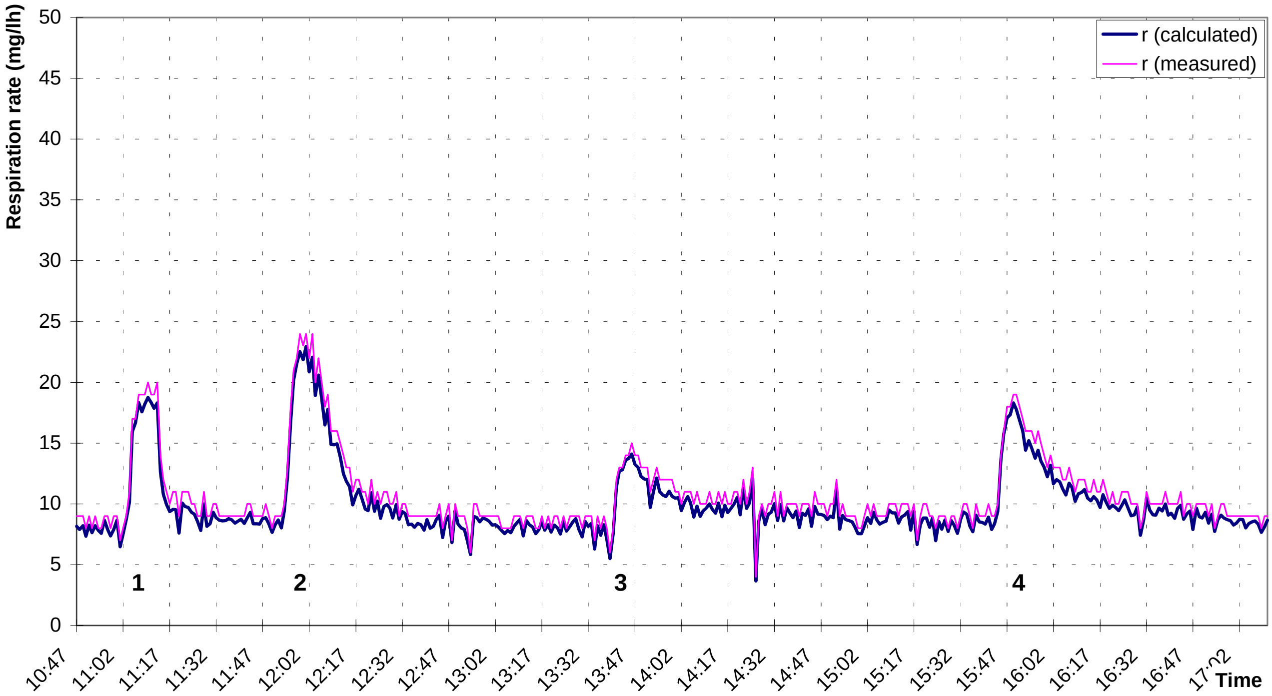
Table 25, Calculated results from respiration experiment 17. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O2/l.h, and BODst for the added solution in mg O2/l.

Additions	1	2	3	4	5
Substrate	Ac	NH_4	Ac	Light reactive dyeing ww	Light reactive dyeing ww
Concentration	1000	1000	1000		
Volume added	0.010	0.005	0.010	0.050	0.100
Total volume	1.760	1.765	1.775	1.825	1.925
Endog. respiration	13.92	14.18	13.11	10.71	10.55
BOD_{st}	311	1235	278	142	157
Y or O/N	0.69	4.32	0.72		

3.1.6.3 Experiment 18 – Double scouring wastewater

This time the scouring wastewater from the first bath was tested.

Solids determination: ML VSS = 2.79 ± 0.08 g/l (TS = 9.57 ± 0.06 g/l)



Observations:

- The course of r is more stable than before, with respect to value for endogenous respiration
- Good response to wastewater, strange dip just before respirogram

Yields and O/N-ratios:

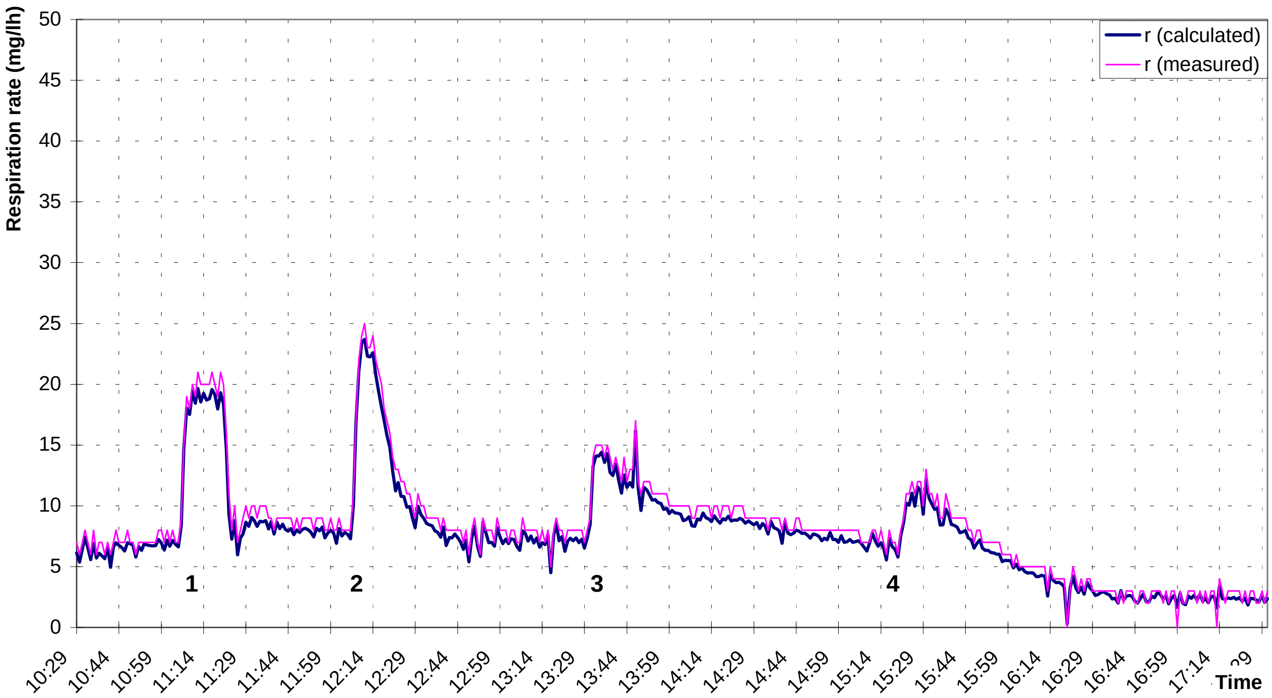
Table 26, Calculated results from respiration experiment 18. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4
Substrate	Ac	NH_4	double scouring (bath 1)	double scouring (bath 1)
Concentration	1000	1000		
Volume added	0.010	0.005	0.050	0.100
Total volume	1.760	1.765	1.815	1.915
Endog. respiration	8.10	8.23	7.94	8.34
BOD_{st}	357	1318	107	63
Y or O/N	0.64	4.51		

3.1.6.4 Experiment 19 – Repetition double scouring wastewater

In experiment 18 the respirograms were rather noisy, repetition to check the form of the respirograms.

Solids determination: ML VSS = 3.03 ± 0.04 g/l (TS = 9.74 ± 0.05 g/l)



Observations:

- Good response to wastewater, but after addition of 100 ml the sludge seems to be affected.
- Double scouring (bath 2) wastewater seems to be toxic to the sludge
- A lot of foaming, not surprising as the wastewater contains surfactants

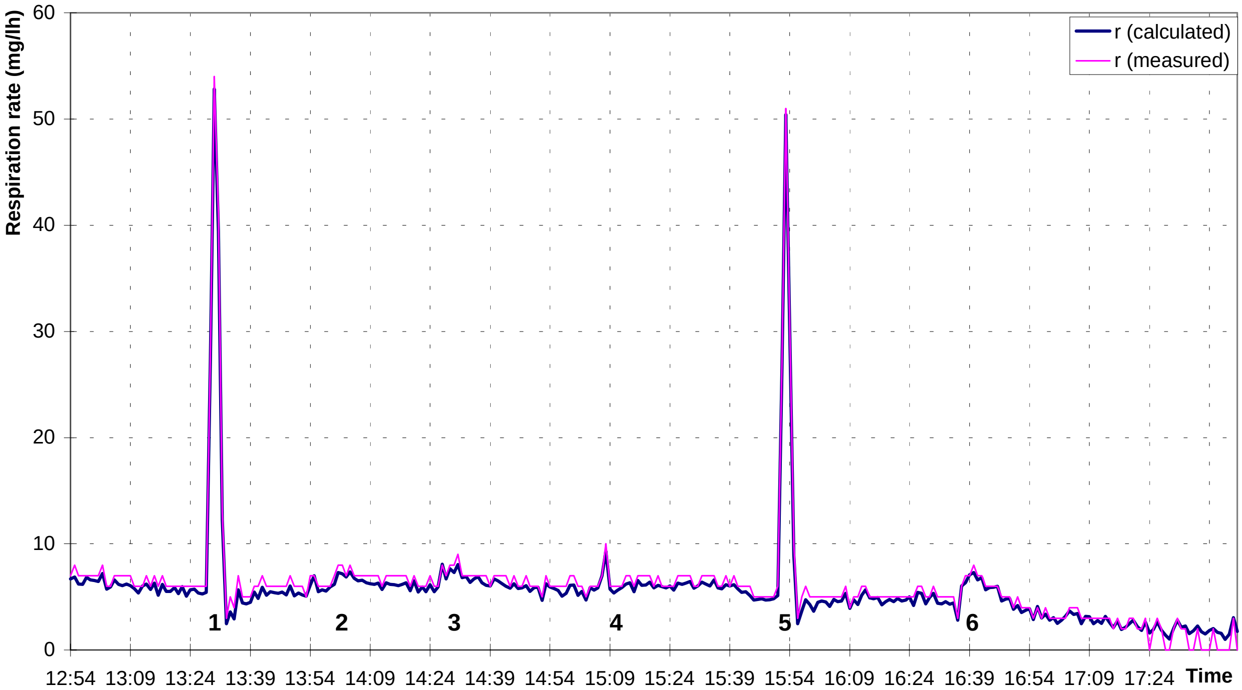
Yields and O/N-ratios:

Table 27, Calculated results from respiration experiment 19. Substrate conc. are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4
Substrate	Ac	NH_4	double scouring (bath 2)	double scouring (bath 2)
Concentration	1000	1000		
Volume added	0.020	0.005	0.050	0.100
Total volume	1.770	1.775	1.825	1.925
Endogenous respiration	7.42	7.53	7.09	-
BOD_{st}	284	1173	122	-
Y or O/N	0.72	4.02		

3.1.7 Experiment 20 – B-01 sludge and I-06 wastewater

Checking response of B-01 sludge to unknown wastewater.



Observations:

- B-01 sludge reacts good to acetate
- Almost no response to wastewater, seems not to be degradable for B-01 sludge.
- Maybe sludge needs to be acclimatised to these types of textile wastewater?
- Double scouring (bath 2) wastewater seems to be toxic to the sludge
- Less foaming than with Livescia sludge

Yields and O/N-ratios:

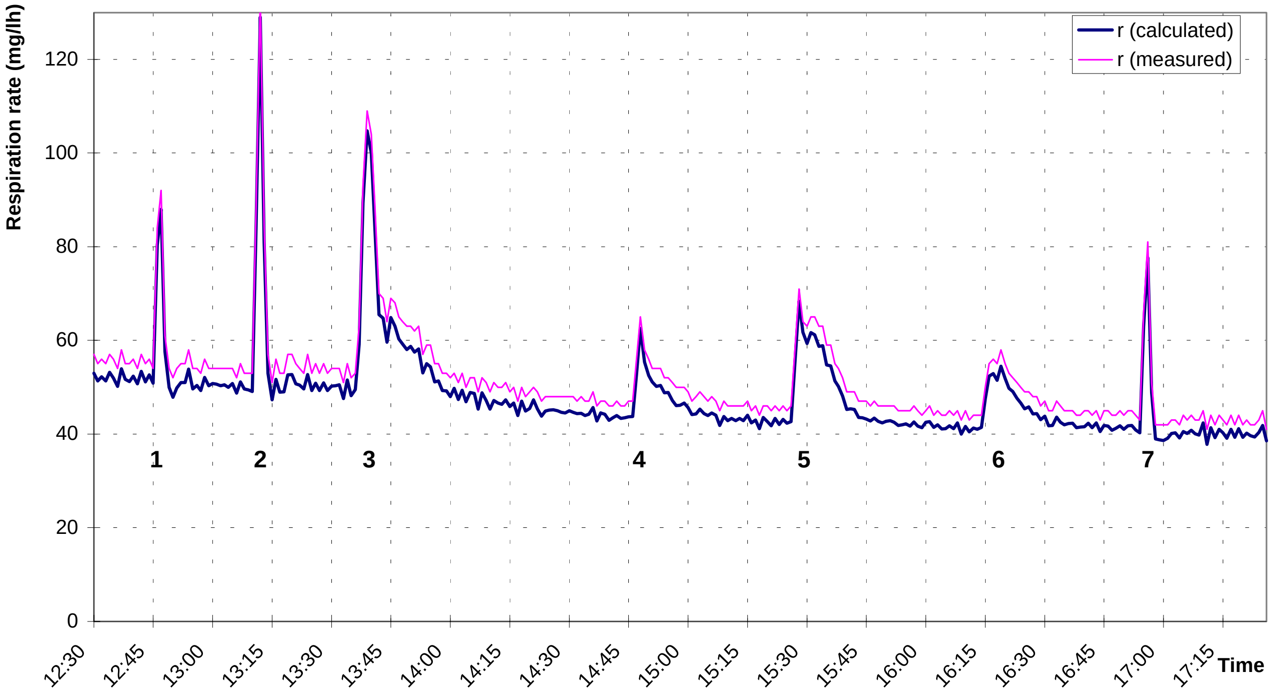
Table 28, Calculated results from respiration experiment 20. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4	5	6
Substrate	Ac	Light reactive dyeing	Light reactive dyeing	Scouring bath 1	Ac	Scouring bath 2
Concentration	1000				1000	
Volume added	0.010	0.020	0.050	0.050	0.010	0.050
Total volume	1.760	1.780	1.830	1.880	1.890	1.940
Endog. respiration	5.43	5.53	5.73	5.30	4.73	3.07
BOD_{st}	294	32	12	18	290	14
Y or O/N	0.71				0.71	

Calculations could only be done satisfactorily for the acetate respirograms, the wastewater respirograms are too small. The resulting values are very low.

3.1.8 Alto Seveso sludge and I-09 wastewater

3.1.8.1 Experiment 21 – All three I-09 wastewaters



Observations:

- This test was done to determine wastewater amounts for next experiments.
- Alto Seveso sludge reacts good to acetate and ammonium
- Good response to wastewaters.
- Tested wastewater amounts are appropriate, but larger amounts would be better.
- No toxicity effect observed, but the respiration rate is very high in the beginning and decreases a bit. Probably a lot of degradable matter is present in the sludge and this causes a high respiration rate.

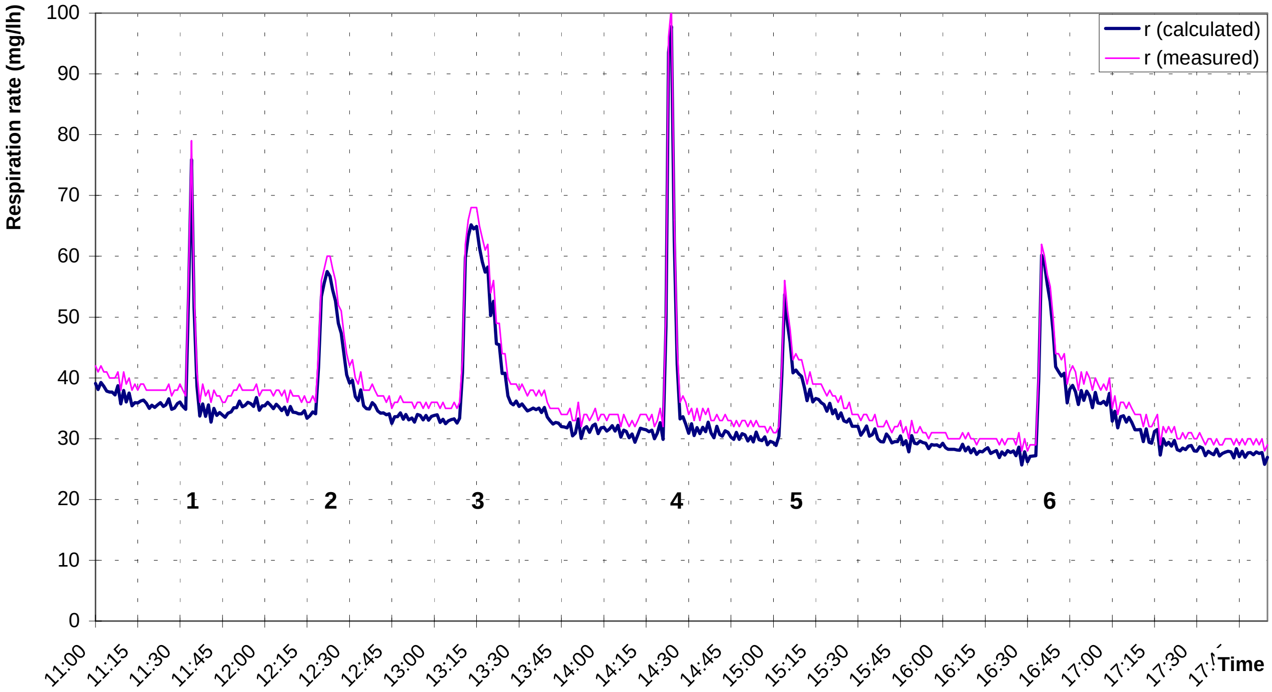
Yields and O/N-ratios:

Table 29, Calculated results from respiration experiment 21. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O2/l.h, and BOD_{ST} for the added solution in mg O2/l.

Additions	1	2	3	4	5	6	7
Substrate	Ac	Ac	NH_4	Degumming	Acid dyeing	Reactive dyeing	Ac
Concentration	1000	1000	1000				1000
Volume added	0.010	0.020	0.010	0.005	0.010	0.010	0.010
Total volume	1.760	1.780	1.790	1.795	1.805	1.815	1.825
Endog. respiration	51.10	49.80	48.94	43.46	42.37	41.18	40.65
BOD_{st}	193	232	962	610	629	372	181
Y or O/N	0.81	0.77	3.29				0.82

3.1.8.2 Experiment 22 – Degumming wastewater

Solids determination: ML VSS = 4.52 ± 0.05 g/l (TS = 6.39 ± 0.05 g/l)



Observations:

- Used amounts of degumming wastewater are appropriate, would be interesting to test 50 ml as well.

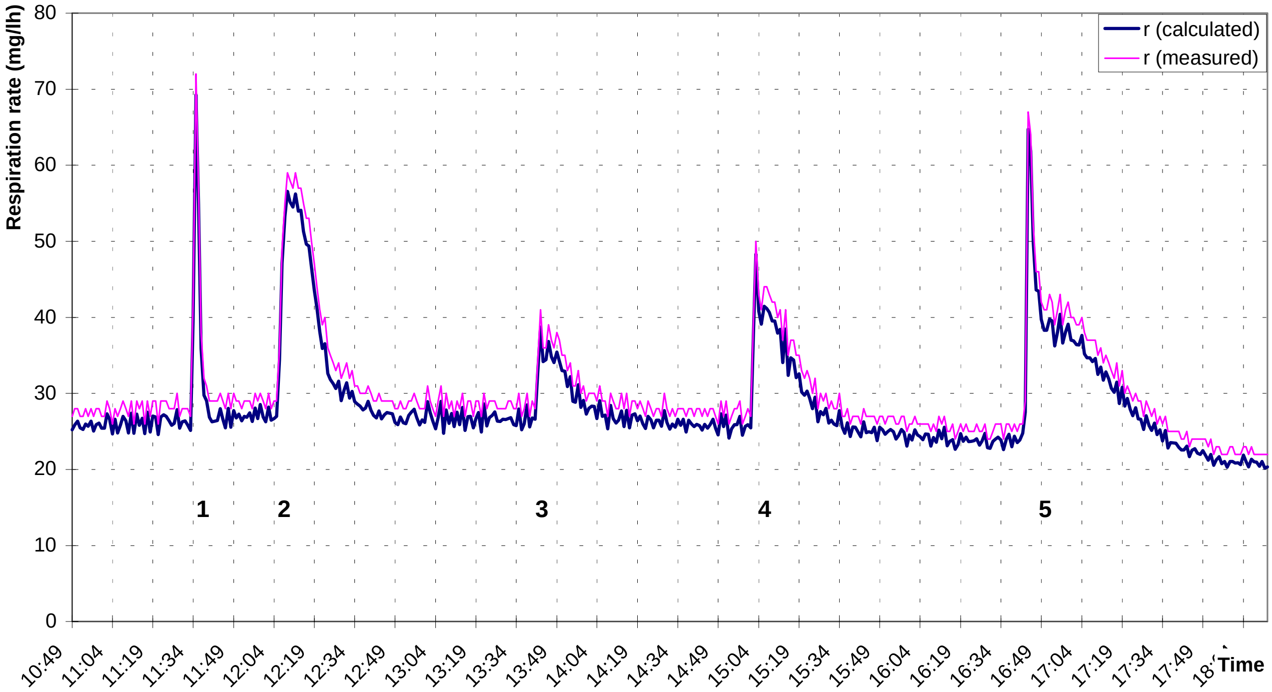
Yields and O/N-ratios:

Table 30, Calculated results from respiration experiment 22. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O_2/l.h, and BOD_{st} for the added solution in mg O_2/l.

Additions	1	2	3	4	5	6
Substrate	Ac	NH_4	NH_4	Ac	Degumming wastewater	
Concentration	1000	1000	1000	1000		
Volume added	0.010	0.005	0.010	0.020	0.010	0.020
Total volume	1.760	1.765	1.775	1.795	1.805	1.825
Endog. respiration	35.20	33.82	32.04	31.18	28.00	27.06
BOD_{st}	203	1232	1206	304	716	685
Y or O/N	0.80	4.22	4.13	0.70		

3.1.8.3 Experiment 23 – Dark reactive dyeing wastewater

Solids determination: ML VSS = 3.65 ± 0.22 g/l (TS = 6.23 ± 0.05 g/l)



Observations:

- Used amounts of dark reactive dyeing wastewater are good.
- Heights of acetate and ammonium respirograms are the same as on July 1st.
- Would be nice to test 50 ml again because at the end of the respirogram the respiration rate drops further than before.

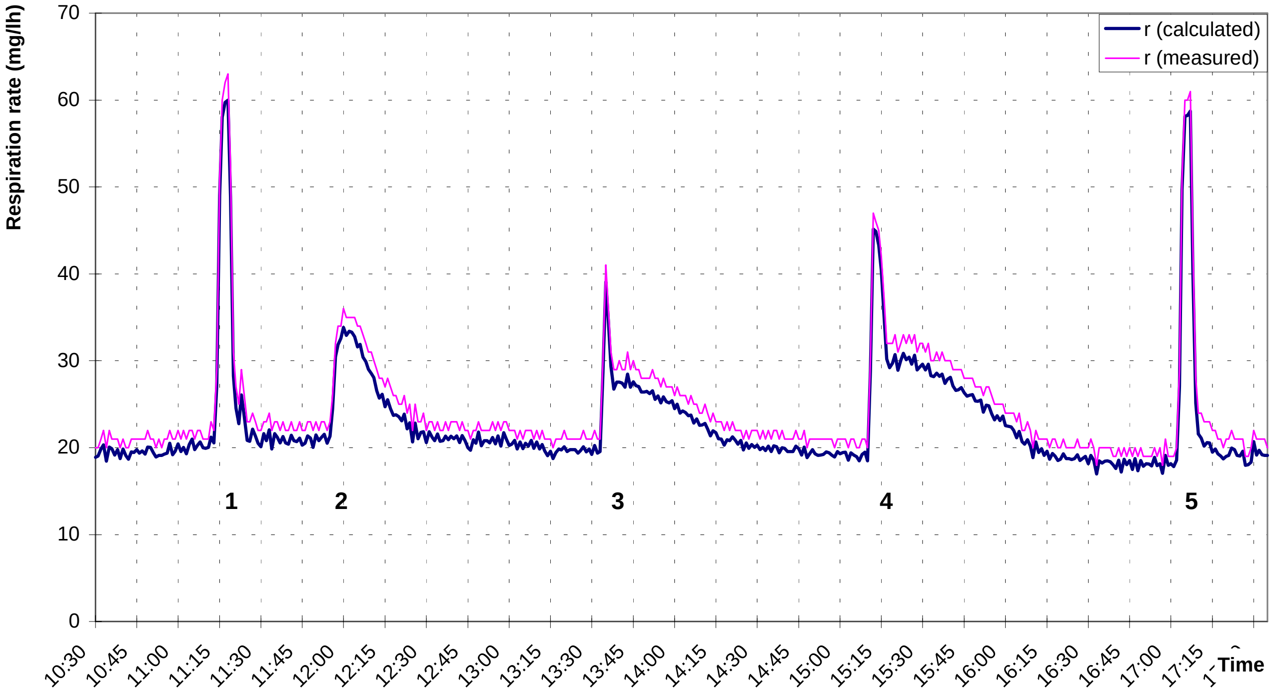
Yields and O/N-ratios:

Table 31, Calculated results from respiration experiment 23. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O2/l.h, and BODst for the added solution in mg O2/l.

Additions	1	2	3	4	5
Substrate	Ac	NH_4	Dark reactive wastewater		
Concentration	1000	1000			
Volume added	0.010	0.010	0.010	0.020	0.050
Total volume	1.760	1.770	1.780	1.800	1.850
Endog. respiration	26.47	26.67	26.37	25.24	22.21
BOD_{st}	303	1284	389	400	359
Y or O/N	0.70	4.40			

3.1.8.4 Experiment 24 – Dark acid dyeing wastewater

Solids determination: ML VSS = 3.94 ± 0.02 g/l (TS = 6.53 ± 0.05 g/l)



Observations:

- Used amounts of dark acid dyeing wastewater are good.
- Height of acetate and ammonium respirogram are the same as on July 1st.
- Would be nice to test 50 ml to see patterns.
- Readily degradable matter present in wastewater.

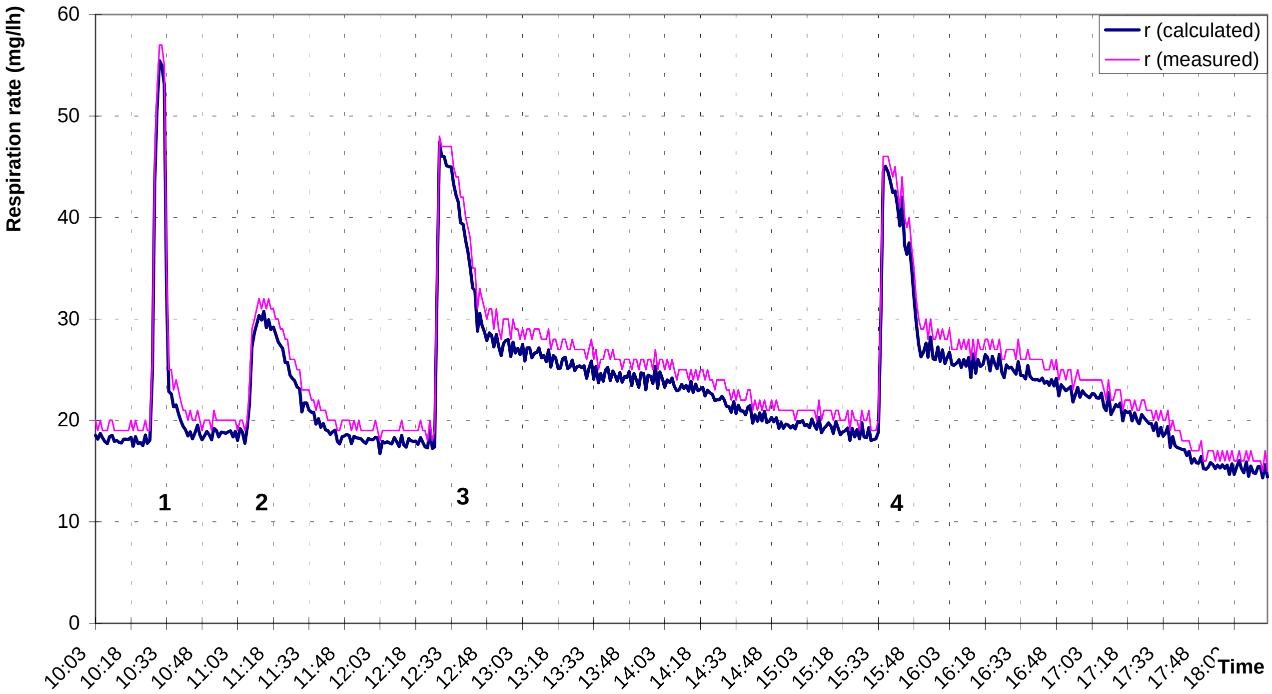
Yields and O/N-ratios:

Table 32, Calculated results from respiration experiment 24. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O2/l.h, and BOD_{st} for the added solution in mg O2/l.

Additions	1	2	3	4	5
Substrate	Ac	NH_4	Dark Acid dyeing ww		Ac
Concentration	1000	1000			1000
Volume added	0.020	0.005	0.010	0.020	0.020
Total volume	1.770	1.775	1.785	1.805	1.825
Endog. respiration	20.58	20.68	19.80	18.89	18.59
BOD_{st}	309	1321	791	787	314
Y or O/N	0.69	4.52			0.69

3.1.8.5 Experiment 25 – Degumming and acid dyeing wastewater

To compare respirograms with and without addition of ATU first a reference respirogram was recorded with two different wastewaters. In the next experiment the same wastewaters will be tested, but in the presence of ATU, a compound that inhibits nitrification.



Observations:
- I09 sludge does not seem to be a problem for the Alto Seveso sludge

Yields and O/N-ratios:

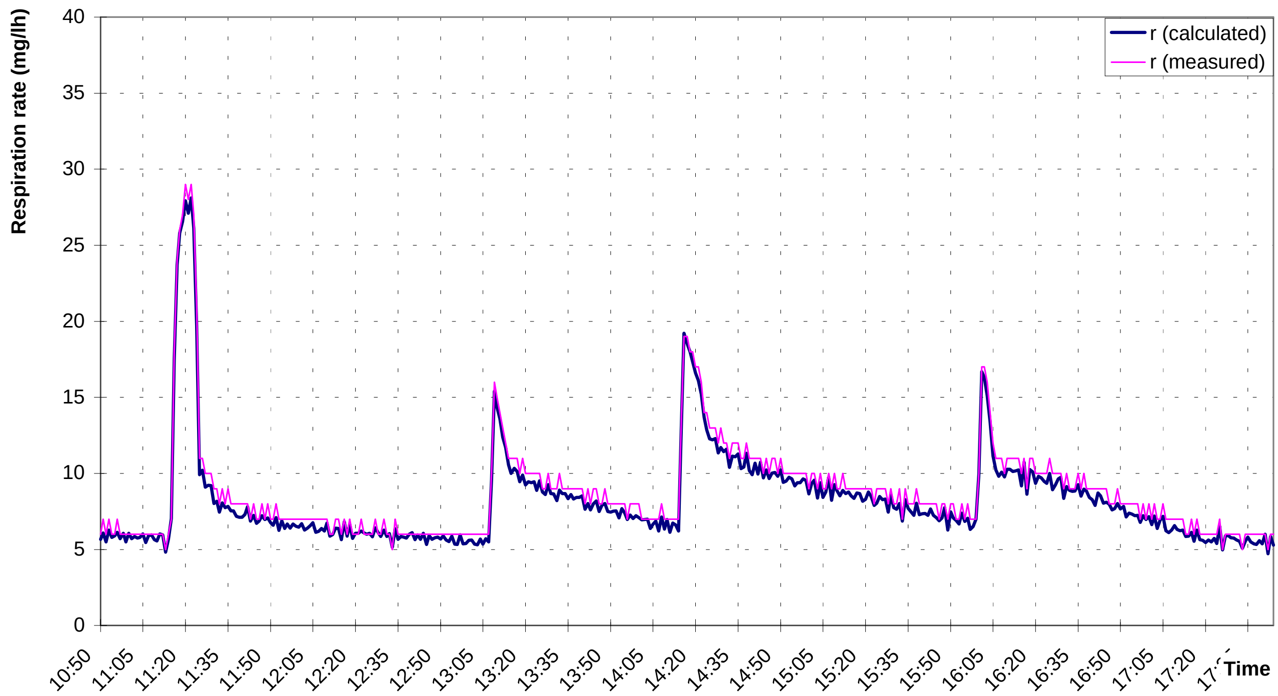
Table 33, Calculated results from respiration experiment 25. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O2/l.h, and BODst for the added solution in mg O2/l.

Additions	1	2	3	4
Substrate	Ac	NH4	Degumming	Dark Acid
Concentration	1000	1000		
Volume added	0.020	0.005	0.050	0.050
Total volume	1.770	1.775	1.825	1.875
Endog. respiration	18.25	18.47	18.04	16.77
BOD_{st}	322	1259	745	650
Y or O/N	0.68	4.31		

3.1.9 Alto Seveso sludge and I-09 wastewater – Using ATU

3.1.9.1 Experiment 26 – Degumming and acid dyeing wastewater

Solids determination: ML VSS = 2.73 ± 0.04 g/l (TS = 4.95 ± 0.01 g/l)



Observations:

- Looks reasonable, but not good yet. Has to be repeated.
- At ~12.30 5 ml NH_4 was added. No peak, so ATU has effect.
- Respirograms are lower than in experiment 25, because of ATU inhibiting the nitrification.
- Apparently the wastewaters contained ammonium, but maybe the respiration rate is lower because ATU is toxic to bacteria in general?

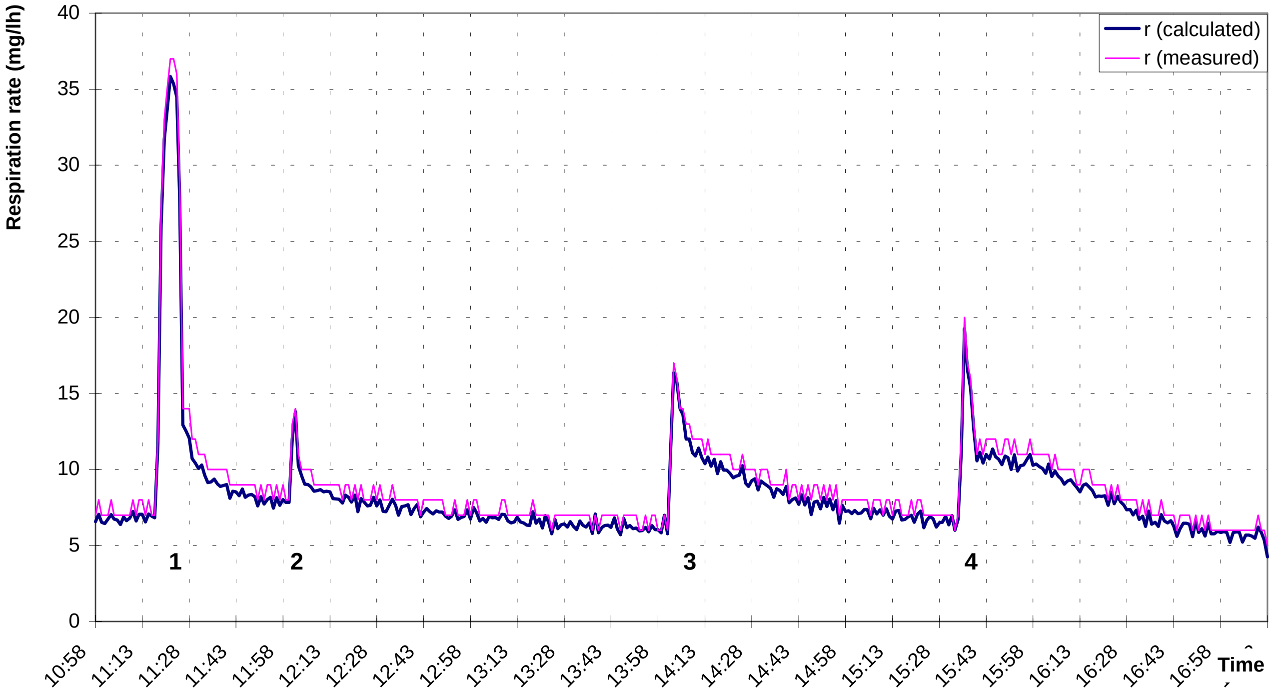
Yields and O/N-ratios:

Table 34, Calculated results from respiration experiment 26. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O2/l.h, and BOD_{st} for the added solution in mg O2/l.

Additions	1	2	3	4	5
Substrate	Ac	NH4	Degumming	Degumming	Dark acid
Concentration	1000	1000			
Volume added	0.020	0.005	0.010	0.020	0.020
Total volume	1.770	1.775	1.785	1.805	1.825
Endog. respiration	6.10	no peak	6.02	6.64	6.09
BOD	315		477	457	549
Y or O/N	0.68				

3.1.9.2 Experiment 27 – All three I-09 wastewaters

Solids determination: ML VSS = 2.69 ± 0.46 g/l (TS = 5.66 ± 0.31 g/l)



Observations:

- No ammonium has been added. The low degumming respirogram may be a result of nutrient deficiency.

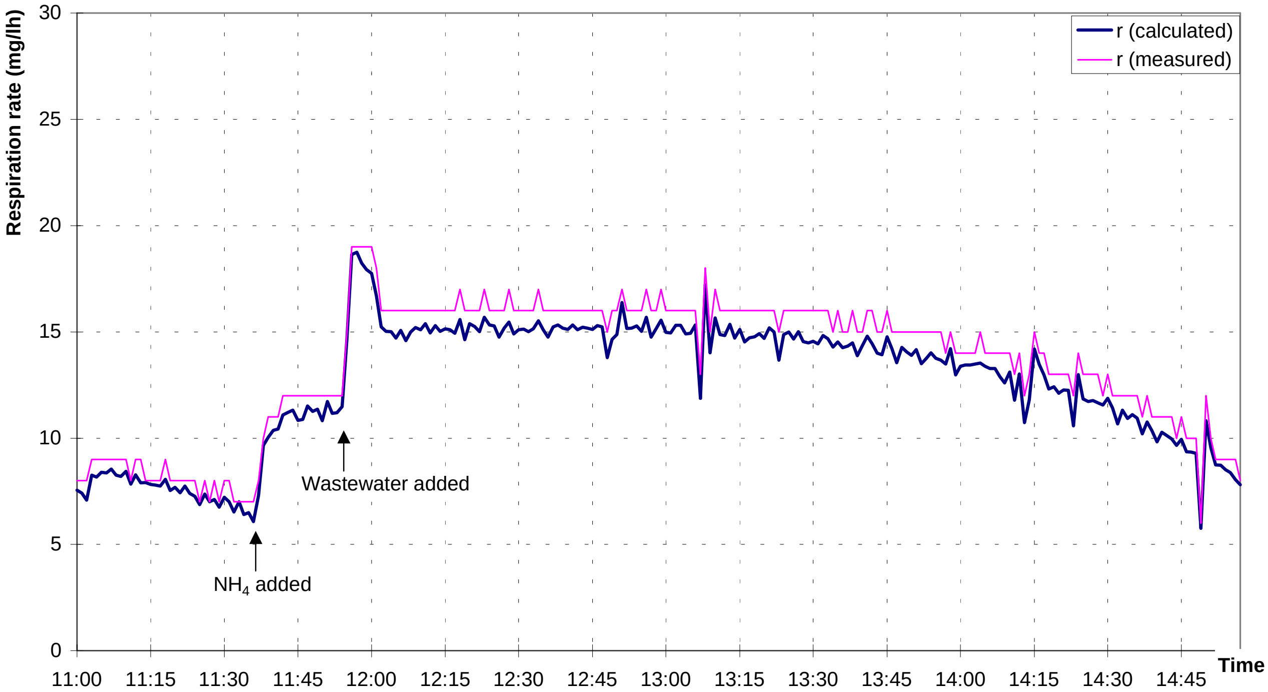
Yields and O/N-ratios:

Table 35, Calculated results from respiration experiment 27. Substrate concentrations are in mg COD/l or mg N/l. Volumes are in l, respiration in mg O2/l.h, and BOD_{st} for the added solution in mg O2/l.

Additions	1	2	3	4
Substrate	Ac	Degumming	Reactive dyeing	Dark Acid dyeing
Concentration	1000			
Volume added	0.020	0.010	0.010	0.010
Total volume	1.770	1.780	1.790	1.800
Endog. respiration	7.39	7.79	6.35	6.22
BOD_{st}	340	75	589	642
Y or O/N	0.66			

3.1.10 Experiment 28 – Alto Seveso sludge and I-09 wastewater. During maximum nitrification.

Instead of using ATU to inhibit nitrification in this experiment a high dose of ammonium was added to the aeration vessel, as to saturate the liquid with ammonium. When the maximum respiration rate was reached and constant, dark acid dyeing wastewater was added. In this way, if ammonium was present in the wastewater it will not contribute to the respiration rate due to nitrification, as this process is already running at maximum rate. Any increase in respiration rate will be solely due to oxidation of other (organic) compounds in the wastewater.



Observations:

- In the beginning a peak can be seen on top of the ammonium respirogram.
- After a long time, the respiration rate starts dropping and keeps dropping.
- Graph in general too noisy, the sludge is old and the electrode might need cleaning again.
- Interesting to repeat with new sludge, possibly Bennekom sludge.

3.2 RESULTS: SUMMARISING TABLES FOR GRAPHICAL METHOD

Exp. = experiment number. Length is the length of the response in minutes, height is the maximum respiration rate reached during a response.

3.2.1 Sizing (B-02)

Sludge	ML VSS (g/l)	Exp	Date	Sample (ml)	BOD (mg/l)	Length (min)	Height (r)
B-01	2.29 ± 0.05	13	May 30	2.5	2866	83	16.5
B-01	2.29 ± 0.05	13	May 30	1	3661	65	9.95
B-01	2.18 ± 0.05	15	June 7	5	6196*	202	33.3

*strange shape

3.2.2 Scouring (B-01)

Sludge	ML VSS (g/l)	Exp.	Date	Sample (ml)	BOD (mg/l)	Length (min)	Height (r)
B-01	-	6	April 25	25	1865	204	74.2
B-01	-	7	April 26	5	916	45	18.4
B-01	-	7	April 26	10	1366	95	32.6
B-01	2.54 ± 0.03	8	May 2	10	2280	178	45.6
B-01	2.54 ± 0.03	8	May 2	5	2025	74	37.4
B-01	-	9	May 3	20	2442	139	75.8
B-01	2.87 ± 0.13	10	May 14	5	3429	159	46.3

3.2.3 Black Sulphur Dyeing (B-01)

Sludge	ML VSS (g/l)	Exp.	Date	Sample (ml)	BOD (mg/l)	Length (min)	Height (r)
B-01	2.89 ± 0.10	11	May 16	5	2855	86	56.2
B-01	2.89 ± 0.10	11	May 16	5	2792	69	60.3
B-01	2.71 ± 0.17	12	May 29	5	2495	67	76.5

3.2.4 Bleaching (B-01)

Sludge	ML VSS (g/l)	Exp.	Date	Sample (ml)	BOD (mg/l)	Length (min)	Height (r)
B-01	2.82 ± 0.07	14	June 4	5	1959	98	22.1
B-01	2.82 ± 0.07	14	June 4	10	2168	121	38.0
B-01	2.18 ± 0.05	15	June 7	5	2407	75	29.0

3.2.5 Light Reactive Dyeing (I-06)

Sludge	ML VSS (g/l)	Exp.	Date	Sample (ml)	BOD (mg/l)	Length (min)	Height (r)
Livescia	4.25 ± 0.06	16	June 12	50	104	50	9.2
Livescia	3.19 ± 0.06	17	June 17	50	142	84	10.3
Livescia	3.19 ± 0.06	17	June 17	100	157	112	14.7
B-01	-	20	June 24	20	32	27	1.5
B-01	-	20	June 24	50	12	29	2.4

3.2.6 Double Scouring Bath 1 (I-06)

Sludge	ML VSS (g/l)	Exp.	Date	Sample (ml)	BOD (mg/l)	Length (min)	Height (r)
Livescia	2.79 ± 0.08	18	June 18	50	107	119	6.1
Livescia	2.79 ± 0.08	18	June 18	100	63	83	10.0
B-01	-	20	June 24	50	18	38	4.0

3.2.7 Double Scouring Bath 2 (I-06)

Sludge	ML VSS (g/l)	Exp.	Date	Sample (ml)	BOD (mg/l)	Length (min)	Height (r)
Livescia	4.25 ± 0.06	16	June 12	50	309	85	15.7
Livescia	3.03 ± 0.04	19	June 19	50	122	92	7.3
B-01	-	20	June 24	20	14	64	4.3

3.2.8 Degumming (I-09)

Sludge	ML VSS (g/l)	Exp.	Date	Sample (ml)	BOD (mg/l)	Length (min)	Height (r)
Alto Seveso	-	21	June 27	5	610	24	19.1
Alto Seveso	4.52 ± 0.05	22	July 1	10	716	47	24.3
Alto Seveso	4.52 ± 0.05	22	July 1	20	685	49	32.8
Alto Seveso	-	25	July 4	50	745	181	29.4
Alto Sev. +ATU	2.73 ± 0.04	26	July 8	10	477	62	9.4
Alto Sev. +ATU	2.73 ± 0.04	26	July 8	20	457	100	12.6
Alto Sev. +ATU	2.69 ± 0.46	27	July 9	10	75	21	6.0

3.2.9 Dark Acid Dyeing (I-09)

Sludge	ML VSS (g/l)	Exp.	Date	Sample (ml)	BOD (mg/l)	Length (min)	Height (r)
Alto Seveso	-	21	June 27	10	629	26	26.0
Alto Seveso	3.94 ± 0.02	24	July 3	10	791	59	19.3
Alto Seveso	3.94 ± 0.02	24	July 3	20	787	69	26.2
Alto Seveso	-	25	July 4	50	650	159	28.3
Alto Sev. +ATU	2.73 ± 0.04	26	July 8	10	549	96	10.6
Alto Sev. +ATU	2.69 ± 0.46	27	July 9	10	642	80	13.0

3.2.10 Dark Reactive Dyeing (I-09)

Sludge	ML VSS (g/l)	Exp.	Date	Sample (ml)	BOD (mg/l)	Length (min)	Height (r)
Alto Seveso	-	21	June 27	10	372	29	13.3
Alto Seveso	2.65 ± 0.22	23	July 2	10	389	39	12.4
Alto Seveso	2.65 ± 0.22	23	July 2	20	400	49	23.1
Alto Seveso	2.65 ± 0.22	23	July 2	50	359	69	41.8
Alto Sev. +ATU	2.69 ± 0.46	27	July 9	10	589	87	10.0

3.3 SEPARATE RESPIROGRAMS B-01 SLUDGE

From the results presented in section 3.1 the particular shape of the responses of the sludge to the different wastewaters is not always very clear. In this section representative isolated responses are shown for the tested wastewaters.

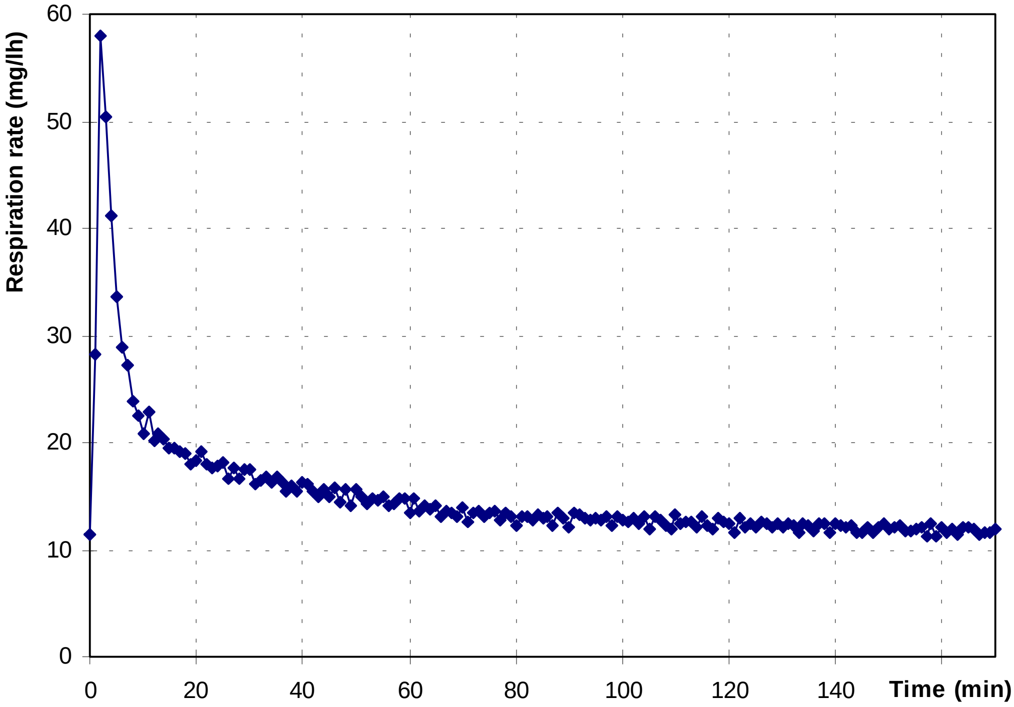


Figure 11, Respirogram of 5 ml Scouring wastewater (B-01 sludge)

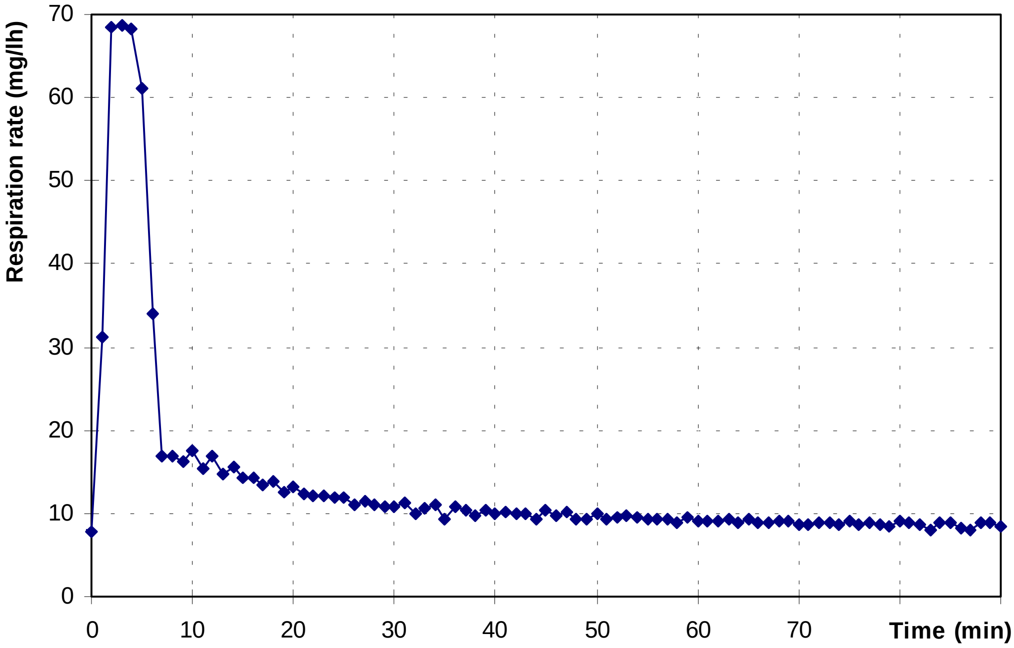


Figure 12, Respirogram of 5 ml Black sulphur dye wastewater (B-01 sludge)

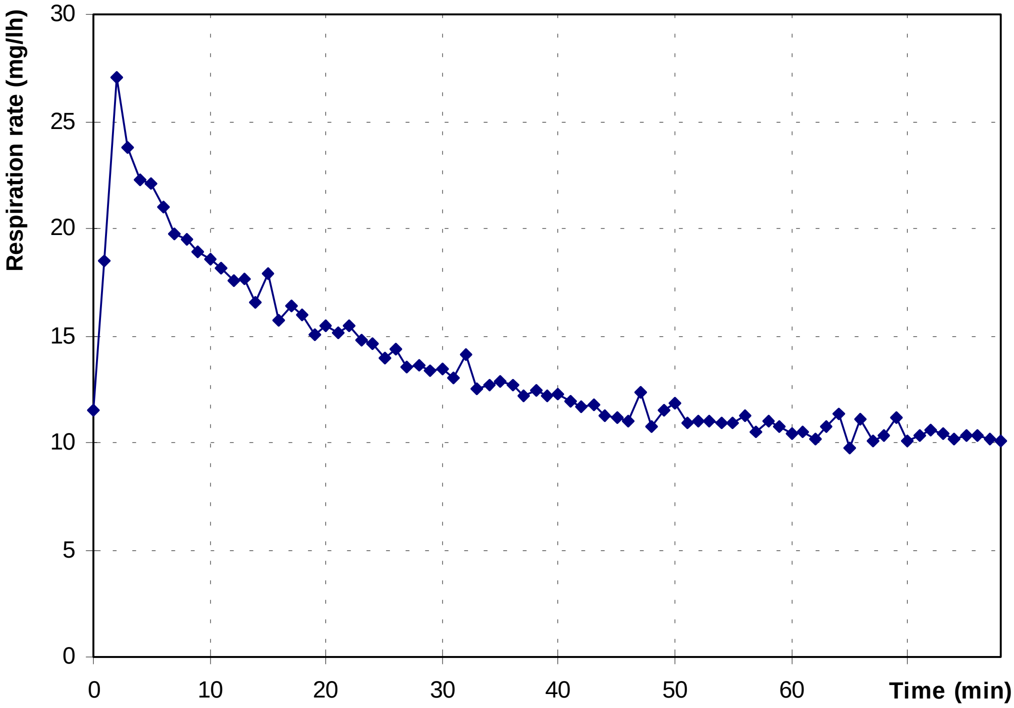


Figure 13, Respirogram of 2.5 ml Sizing liquid (B-01 sludge)

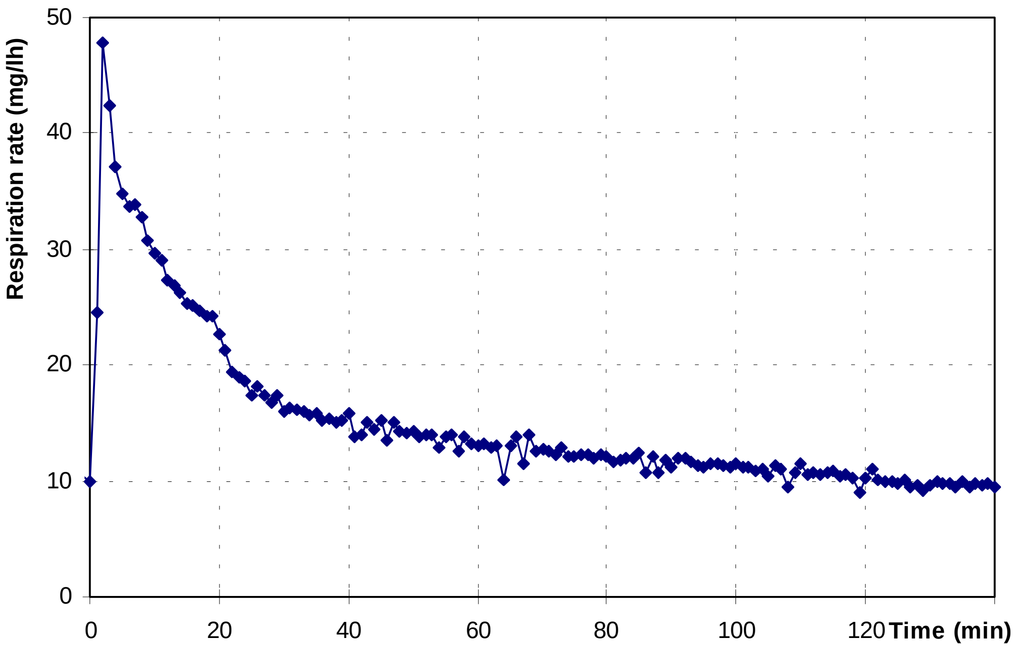


Figure 14, Respirogram of 10 ml Bleaching wastewater (B-01 sludge)

3.4 SEPARATE RESPIROGRAMS ALTO SEVESO SLUDGE

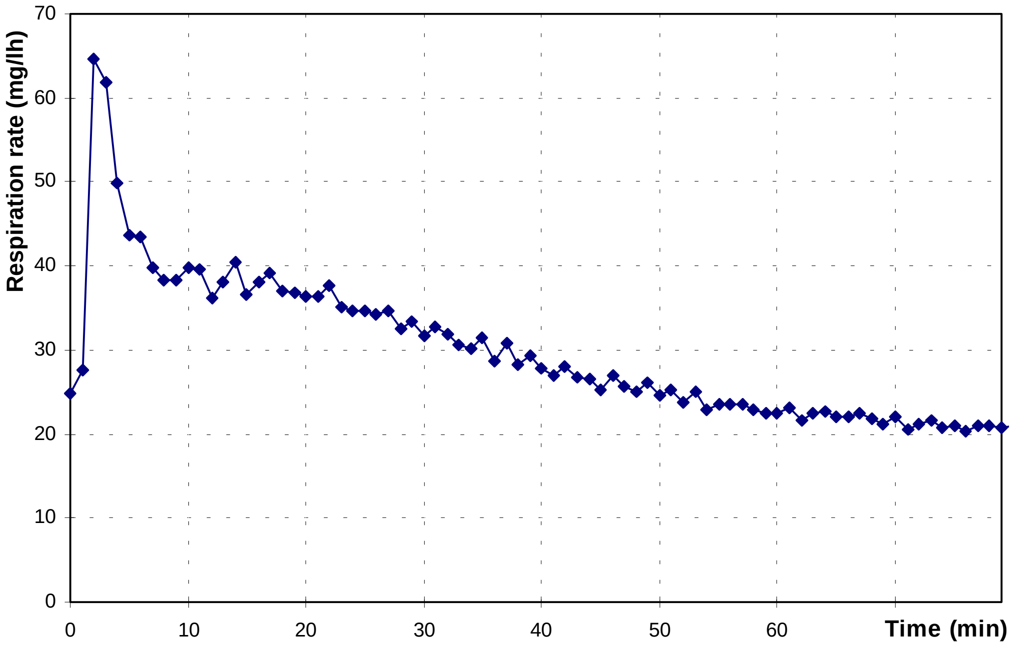


Figure 15, Respirogram of 50 ml Dark reactive dyeing wastewater (Alto Seveso sludge)

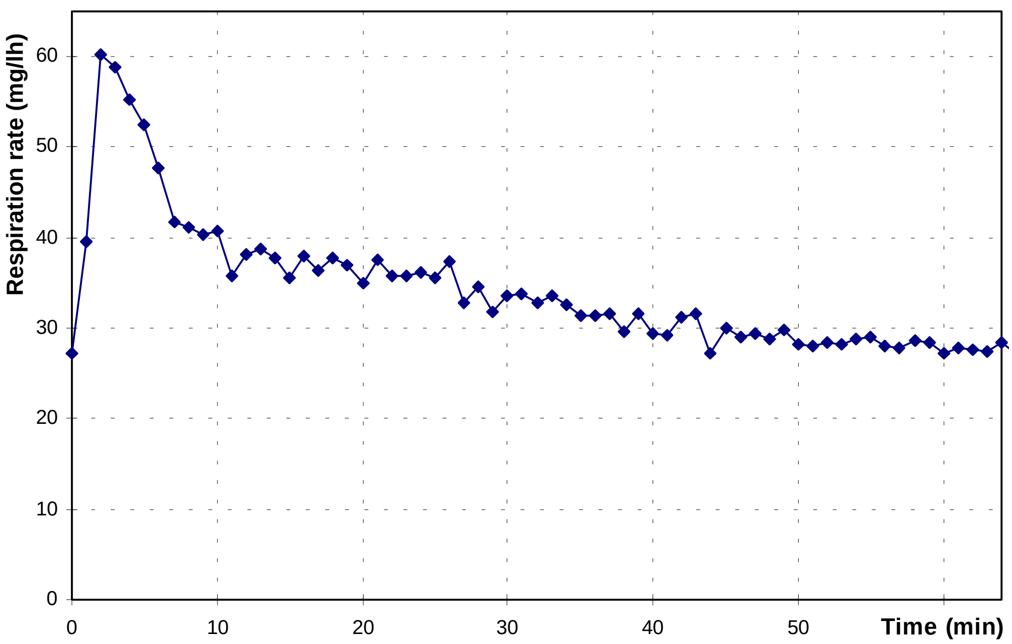


Figure 16, Respirogram of 20 ml Degumming wastewater (Alto Seveso sludge)

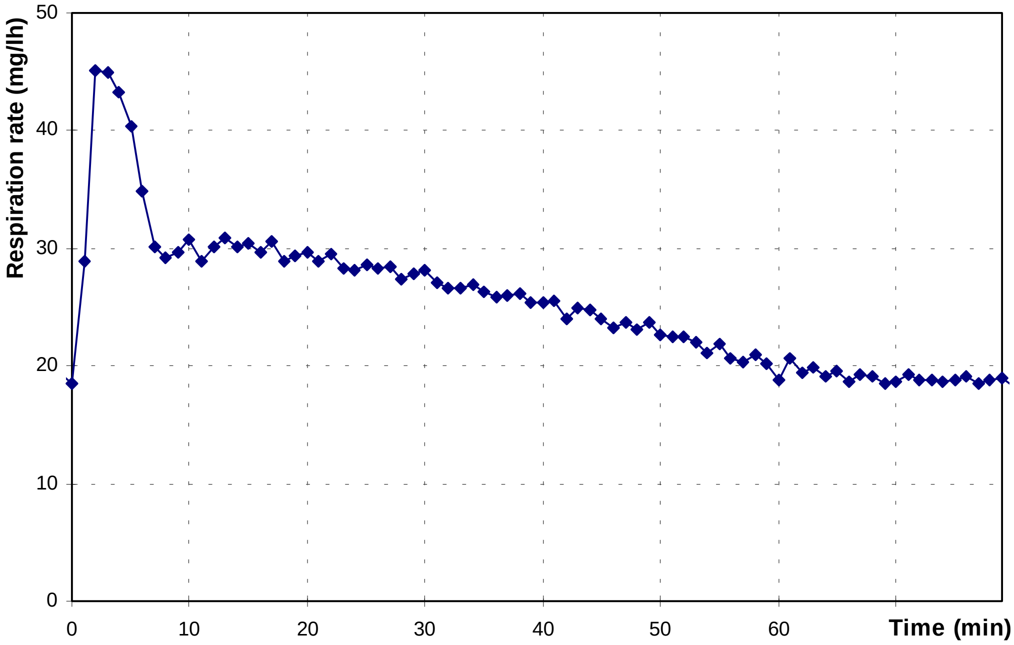
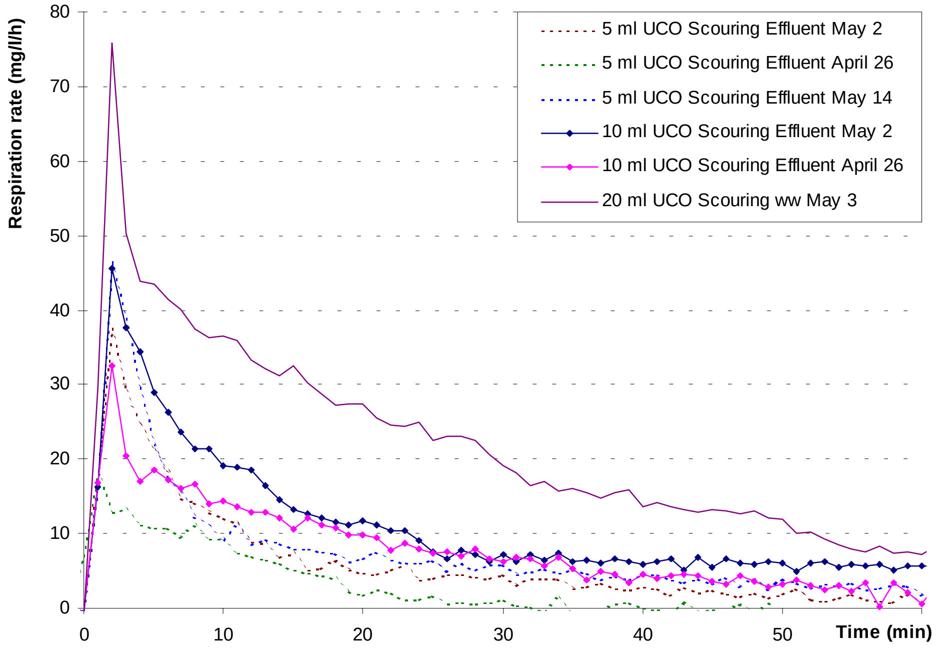


Figure 17, Respirogram of 20 ml Dark acid dyeing wastewater (Alto Seveso sludge)

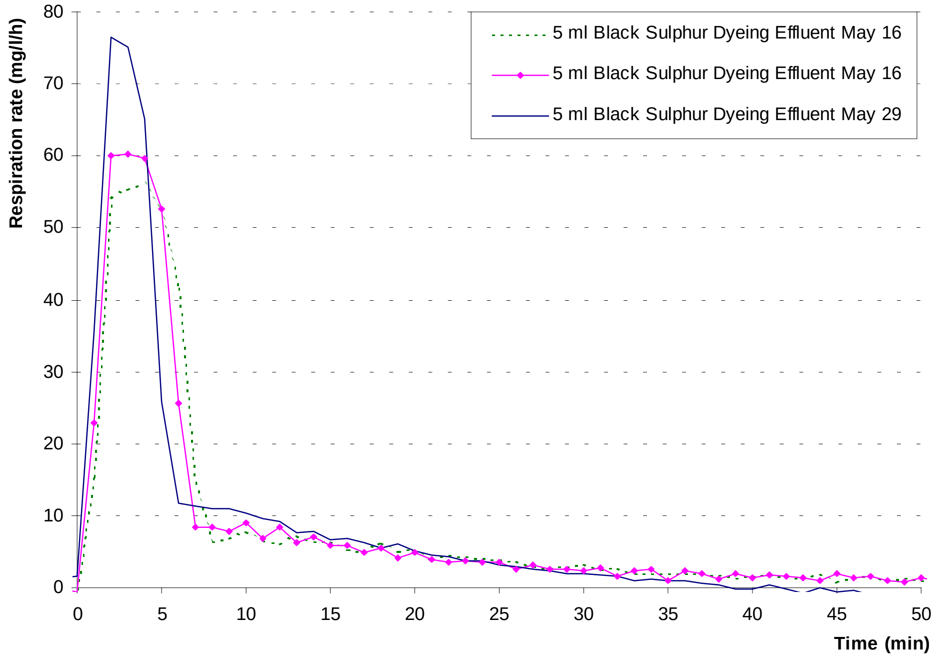
3.5 GRAPHS OF DIFFERENT RESPIROGRAMS OF THE SAME WASTEWATER

In this section the response of sludge to different amounts of wastewater are compared.

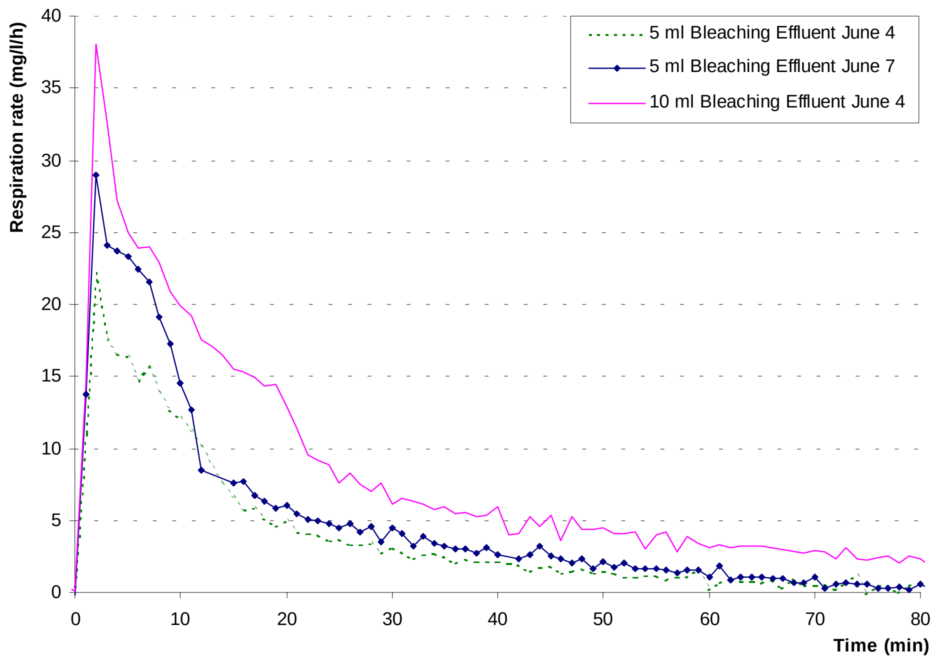
3.5.1 Scouring wastewater from indigo dyed fabric – Factory B-01



3.5.2 Black Sulphur Dye wastewater –Factory B-01

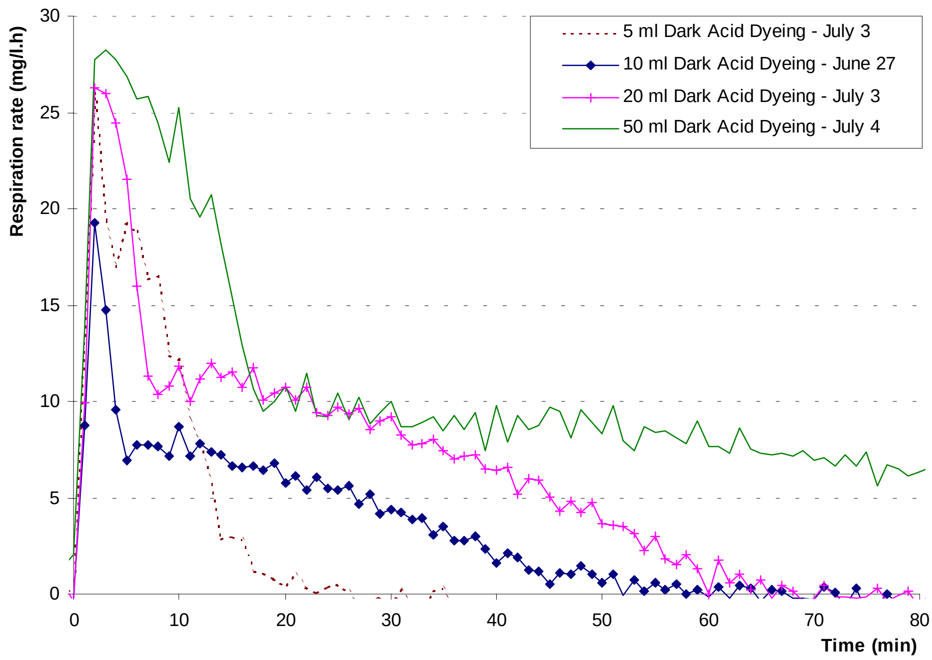


3.5.3 Bleaching wastewater –Factory B-01

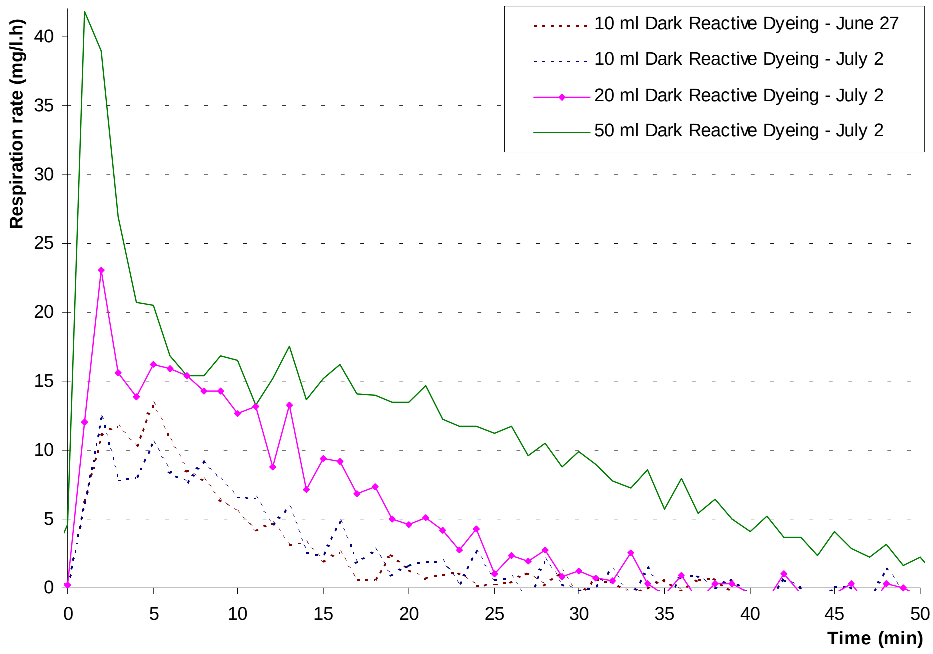


3.5.4 Sizing Liquid – Factory B-02

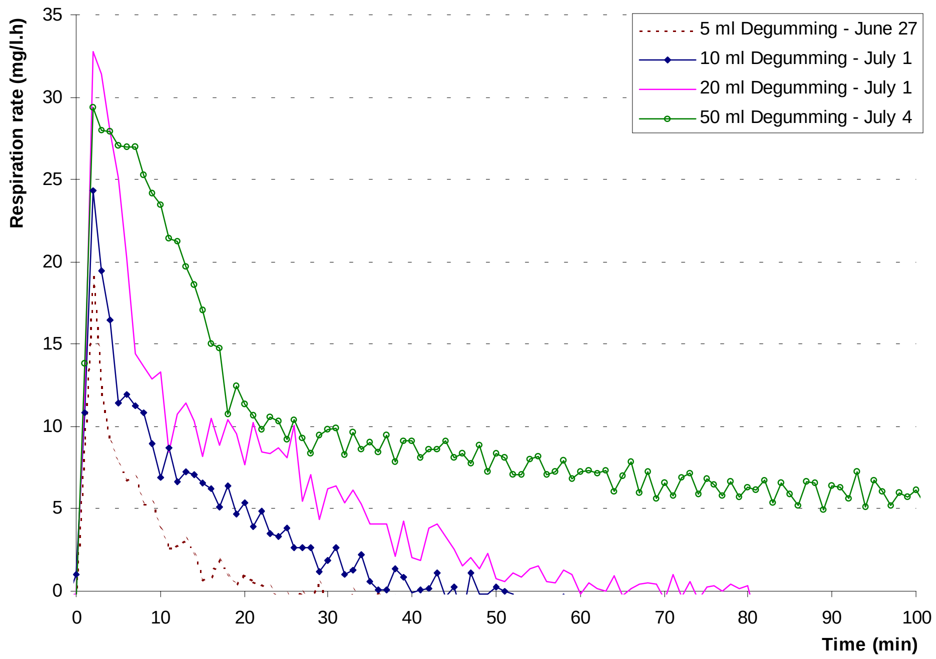
3.5.5 Dark Acid Dyeing wastewater – I09 factory



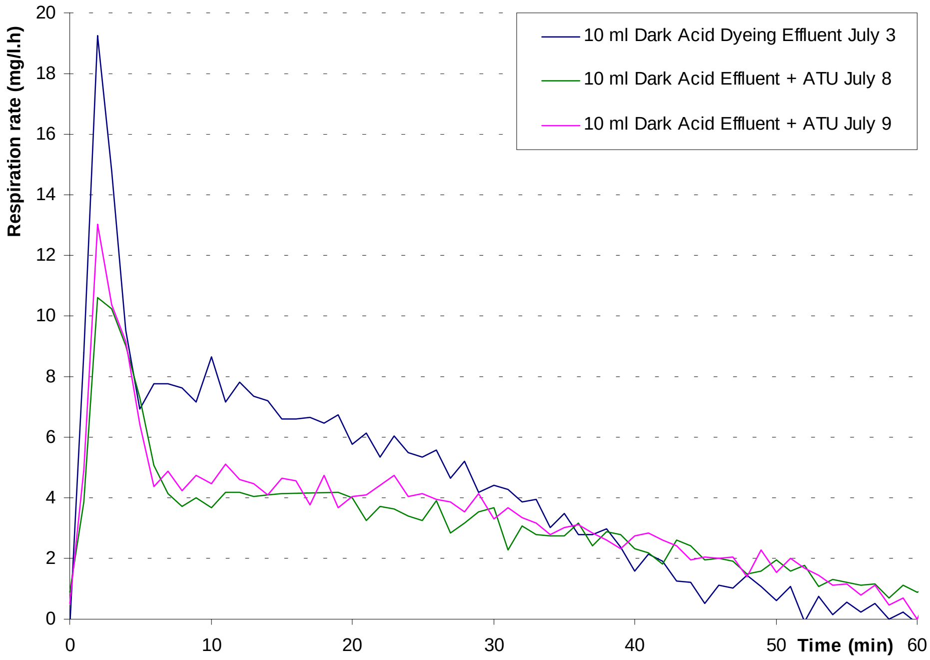
3.5.6 Dark Reactive Dyeing wastewater – I09 factory



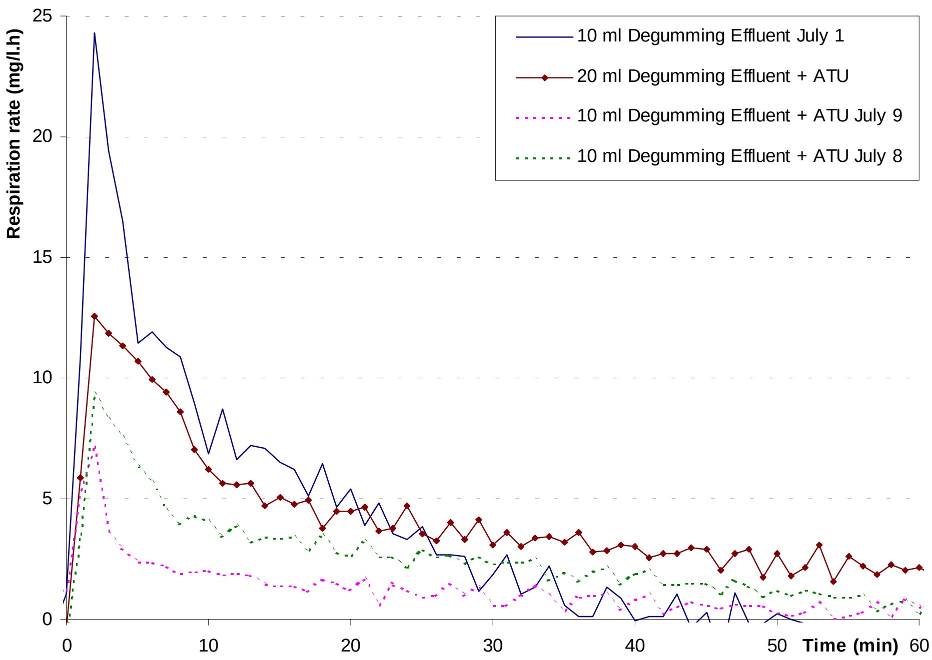
3.5.7 Degumming Wastewater – I09 factory



3.5.8 Dark Acid Dyeing wastewater – I09 factory – Using ATU



3.5.9 Degumming wastewater – I09 factory – Using ATU



3.6 YIELD AND O/N VALUES

Yield and O/N ratio are characteristics of the sludge. This is a summary of the results presented in section 3.1

Table 36, Yield on acetate (g COD/g COD). Multiple Y values indicate multiple additions.

Experiment	Date	Sludge	VSS (g/l)	Sample (ml)	Y (g COD / g COD)
1	February 8	Alto Seveso	3.77 ± 0.34	5 10 15 20	0.76, 0.78 0.79 0.79 0.80
2	February 15	Alto Seveso	4.61 ± 0.12	25 40	0.80, 0.80 0.81
3	February 25	Alto Seveso	4.45 ± 0.14	20 10	0.77, 0.79, 0.80 0.80
4	March 8	Alto Seveso	5.95 ± 0.11	10 20 40	0.83 0.79, 0.80, 0.80, 0.81 0.80
5	March 15	Bennekom	-	20 10	0.82 0.77, 0.79, 0.83, 0.84
6	April 25	B-01	-	5 10 25	0.77 0.74, 0.74 0.67
7	April 26	B-01	-	5 10	0.76 0.73, 0.79, 0.79
8	May 2	B-01	2.54 ± 0.03	10	0.71, 0.78
9	May 3	B-01	-	10	0.75
10	May 14	B-01	2.87 ± 0.13	10 20	0.64, 0.65, 0.68 0.67
11	May 16	B-01	2.89 ± 0.10	5 10 20	0.59 0.56, 0.57 0.57
12	May 29	B-01	2.71 ± 0.17	10 20	0.60 0.56, 0.61, 0.63
13	May 30	B-01	2.29 ± 0.05	10 20	0.68 0.58, 0.60
14	June 4	B-01	2.82 ± 0.07	10 20	0.55 0.57, 0.60
15	June 7	B-01	2.18 ± 0.05	10 20	0.47 0.50, 0.51
16	June 12	Livescia	4.25 ± 0.06	20	0.71
17	June 17	Livescia	3.19 ± 0.06	10	0.69, 0.72
18	June 18	Livescia	2.79 ± 0.08	10	0.64
19	June 19	Livescia	3.03 ± 0.04	20	0.72
20	June 24	B-01	-	10	0.71, 0.71
21	June 27	Alto Seveso	-	10 20	0.81, 0.82 0.77
22	July 1	Alto Seveso	4.52 ± 0.05	10 20	0.80 0.70
23	July 2	Alto Seveso	3.65 ± 0.22	10	0.70
24	July 3	Alto Seveso	3.94 ± 0.02	20	0.69, 0.69
25	July 4	Alto Seveso	-	20	0.68
26	July 8	Alto Seveso	2.73 ± 0.04	20	0.68

27	July 9	Alto Seveso	2.69 ± 0.46	20	0.66

Table 37, Oxygen/Nitrogen values listed for each expiriment with nitrifying sludge.

Experiment	Date	Sludge	VSS (g/l)	Sample (ml)	O/N
1	February 8	Alto Seveso	3.77 ± 0.34	5 10	4.68, 4.41 4.46
2	February 15	Alto Seveso	4.61 ± 0.12	10 20	2.84 2.92
3	February 25	Alto Seveso	4.45 ± 0.14	20 10	2.68 2.78
4	March 8	Alto Seveso	5.95 ± 0.11	20 10	2.23 2.10
5	March 15	Bennekom	-	10 5	2.09 2.36
16	June 12	Livescia	4.25 ± 0.06	5	3.44
17	June 17	Livescia	3.19 ± 0.06	10	4.23
18	June 18	Livescia	2.79 ± 0.08	5	4.51
19	June 19	Livescia	3.03 ± 0.04	5	4.02
20	June 24	B-01	-		
21	June 27	Alto Seveso	-	10	3.29
22	July 1	Alto Seveso	4.52 ± 0.05	5 10	4.22 4.13
23	July 2	Alto Seveso	3.65 ± 0.22	10	4.40
24	July 3	Alto Seveso	3.94 ± 0.02	5	4.52
25	July 4	Alto Seveso	-	5	4.31

4 RESULTS OF NNW AUTOMATIC END-POINT DETECTION

The presented results of the calculations with the neural network are a selection of representative results obtained after many trials with different configurations and datasets (=matrix of training and validation data). For each dataset different approaches were tried:

- different numbers of input neurons
- applying noise to the simulated training set or not
- putting a training goal of 0.01 or not (without a set goal, the goal of the NNW is 0)

In the following paragraph the most illustrative results are presented in tables, and the conclusion for each result can be seen in the last column, the relative difference based on BOD_{ST}. What matters is in fact not the end-point identified by the neural net, but the BOD_{ST} calculated with that end-point. Differences are given in percentages (NNW-BOD_{ST} / Manual-BOD_{ST}*100). Values that are within a 5% difference are put in bold.

4.1 TRAINING WITH SIMULATED RESPIROGRAMS – VALIDATION WITH REAL RESPIROGRAMS

With this approach reasonable results are found only for the real respirograms that resemble the simulated data most. Best results were obtained when 4 neurons were used, and noise was added to the simulated data (noise = 0.1 mg/l.h). See Table 38 for the outcome.

Table 38, 4-neuron NNW, trained with simulated respirograms, noise = 0.1 (data lined up on last row)

Respirogram	End point			BOD_{st} (mg/l)		
	Manual	NNW	Δ	Manual	NNW	%
Acid dyeing 52	98	98	0	184	184	**100**
Acid dyeing 203	95	95	0	340	340	**100**
Acid dyeing C	106	105	1	334	336	**101**
Acid dyeing 106	68	85	-17	222	229	**103**
Indigo cotton scouring	95	71	24	1950	1597	82
Black sulphur dyeing	85	70	15	2528	2383	94
Bleaching	100	70	30	2407	1944	81
Size	106	70	36	2805	2251	80
Light reactive dyeing	101	70	31	154	130	84
Silk degumming	89	105	-16	685	714	**104**
Silk degumming 2	91	105	-14	788	838	106
Dark acid dyeing	90	94	-4	792	792	**100**
Dark acid dyeing 2	100	98	2	787	786	**100**
Dark reactive dyeing	92	103	-11	359	347	**97**

For the next calculation, respirograms were lined up on the first row, to make sure that this time all points of sample addition were the same. They were filled at the back with the last value until reaching the length of the longest one. Due to this change in position the number corresponding to the end point changed. See Table 39 for results.

Table 39, 5-neuron NNW, trained with simulated respirograms, noise=0.1 (data lined up on first row)

Respirogram	End point			BOD_{st} (mg/l)		
	Manual	NNW	Δ	Manual	NNW	%
Acid dyeing 52	54	52	2.1	184	186	**101**
Acid dyeing 203	94	92	2.2	340	340	**100**
Acid dyeing C	80	68	11.7	334	319	**96**
Acid dyeing 106	50	65	14.8	222	227	**102**
Indigo cotton scouring	73	82	9.2	1950	2035	**104**
Black sulphur dyeing	57	78	21.3	2528	2490	**98**
Bleaching	85	84	0.8	2407	2403	**100**
Size	84	85	1.0	2805	2822	**101**
Light reactive dyeing	101	86	14.5	154	145	94
Silk degumming	70	66	3.9	685	666	**97**
Silk degumming 2	70	66	3.9	788	720	91
Dark acid dyeing	68	62	6.5	792	763	**96**
Dark acid dyeing 2	79	77	2.4	787	786	**100**
Dark reactive dyeing	81	74	6.6	359	345	**96**

This approach clearly improved the performance of the neural network when comparing the results for the calculation with the respirograms lined up on the last row (Table 38). However, the result presented in this table is the best one of a series of repeated running of the NNW with the same settings. Every repetition the outcome was different, which means that obtaining an improved performance can be a stroke of luck (see appendix 4).

4.2 TRAINING WITH REAL RESPIROGRAMS – VALIDATION WITH REAL RESPIROGRAMS

In this attempt half of the respirograms was used for training, and half for validation. This meant that only a small number could be used for each step, as the total number of real respirograms was 14. The choice for which data were used for training was made by just taking the order as they appeared in the excel file (which was random) and indicate in the NNW file that the first seven were for training. Table 40 gives the result of the trial with the data lined up on the last row, while Table 41 shows the results of the trial with the data lined up on the first row.

Table 40, 5-neuron NNW, trained with real respirograms, (data lined up on last row)

Respirogram	End point			BOD_{st} (mg/l)		
	Manual	NNW	Δ	Manual	NNW	%
Acid dyeing 52	98	training	-	184	training	-
Acid dyeing 203	95	training	-	340	training	-
Acid dyeing C	106	training	-	334	training	-
Bleaching	68	training	-	2407	training	-
Size	106	training	-	2866	training	-
Light reactive dyeing	101	training	-	157	training	-
Silk degumming	89	training	-	685	training	-
Acid dyeing 106	68	90	-22	222	230	**104**
Indigo cotton scouring	95	103	-8	1950	2014	**103**
Black sulphur dyeing	85	108	-23	2528	2469	**98**
Silk degumming 2	91	93	-2	788	782	**99**

Dark acid dyeing	90	97	-7	792	815	**103**
Dark acid dyeing 2	100	100	0	787	787	**100**
Dark reactive dyeing	92	94	-2	359	361	**101**

Table 41, 5-neuron NNW, trained with real respirograms, (data lined up on first row)

Respirogram	End point			BOD_{st} (mg/l)		
	Manual	NNW	Δ	Manual	NNW	%
Acid dyeing 52	55	training	-	184	training	-
Acid dyeing 203	95	training	-	340	training	-
Acid dyeing C	81	training	-	334	training	-
Bleaching	86	training	-	2407	training	-
Size	85	training	-	2866	training	-
Light reactive dyeing	106	training	-	157	training	-
Silk degumming	71	training	-	685	training	-
Acid dyeing 106	51	65	-14	222	227	**102**
Indigo cotton scouring	74	78	-4	1950	1982	**102**
Black sulphur dyeing	58	80	-22	2528	2457	**97**
Silk degumming 2	71	61	10	788	741	94
Dark acid dyeing	69	68	1	792	790	**100**
Dark acid dyeing 2	80	89	-9	787	814	**103**
Dark reactive dyeing	82	89	-7	359	349	**97**

4.3 TRAINING WITH SIMULATED RESPIROGRAMS – VALIDATION WITH SIMULATED RESPIROGRAMS

The simulated respirograms were based on a model calibrated using real respirograms. For the respirograms 106, 203 and 52 (see section 2.5.3) a fit was found with ASM1. Then the amount of readily biodegradable material was varied (-50%, -20%, -10%, +10%, +20% and +50%) and with those values new respirograms were calculated. For training the ones of 10% and 50% were used, and for validation the ones of 20% and the "original" simulated one (the fit for the real respirogram). A 7-neuron network gave the best results, even with an applied 0.1 noise. In Table 42 the results are shown for the top-filled matrix, in Table 43 for the bottom-filled matrix.

Table 42, 7-neuron NNW, trained with part of the simulated respirograms, (data lined up on last row)

Respirogram	End point			BOD_{st} (mg/l)		
	Manual	NNW	Δ	Manual	NNW	%
Sim Acid Dyeing 106 –20%	84	84	0.2	124	124	**100**
Sim Acid Dyeing 106	86	86	0.0	169	169	**100**
Sim Acid Dyeing 106 +20%	89	89	0.5	220	220	**100**
Sim Acid Dyeing 203 –20%	79	79	0.2	153	153	**100**
Sim Acid Dyeing 203	83	84	0.8	212	212	**100**
Sim Acid Dyeing 203 +20%	87	86	0.7	277	277	**100**
Sim Acid Dyeing 52 –20%	94	94	0.2	92	92	**100**
Sim Acid Dyeing 52	100	100	0.4	128	128	**100**
Sim Acid Dyeing 52 +20%	103	104	0.8	170	171	**101**

Not surprisingly, this approach gave the best results until now, because training data and validation data have close resemblance, which is basically a prerequisite for the functioning of a neural network.

Table 43, 7-neuron NNW, trained with part of the simulated respirograms, (data lined up on first row)

Respirogram	End point			BOD_{st} (mg/l)		
	Manual	NNW	Δ	Manual	NNW	%
Sim Acid Dyeing 106 –20%	64	65	0.5	124	124	**100**
Sim Acid Dyeing 106	66	66	0.2	169	169	**100**
Sim Acid Dyeing 106 +20%	69	68	1.1	220	219	**100**
Sim Acid Dyeing 203 –20%	79	79	0.2	153	153	**100**
Sim Acid Dyeing 203	83	83	0.2	212	212	**100**
Sim Acid Dyeing 203 +20%	87	87	0.2	277	277	**100**
Sim Acid Dyeing 52 –20%	49	50	0.6	92	95	**103**
Sim Acid Dyeing 52	55	54	0.7	128	132	**103**
Sim Acid Dyeing 52 +20%	58	58	0.2	170	170	**100**

4.4 TRAINING WITH MODIFIED REAL RESPIROGRAMS – VALIDATION WITH REAL RESPIROGRAMS

To simulate the effect of really similar data for training and validation with real respirograms, all respirograms were multiplied with a random number. The resulting modified respirograms were used for calibration of the neural network, and the original data were used for validation. Results are presented in Table 44 and Table 45.

Table 44, 6-neuron NNW, trained with modified real respirograms, (data lined up on last row)

Respirogram	End point			BOD_{st} (mg/l)		
	Manual	NNW	Δ	Manual	NNW	%
Acid dyeing 52 × 1.15	98	97	0.6	184	185	**101**
Acid dyeing 203 × 1.23	95	86	8.9	340	324	**95**
Acid dyeing C × 0.98	106	106	0.1	334	334	**100**
Acid dyeing 106 × 1.07	68	68	0.3	222	222	**100**
Indigo cotton scouring × 0.86	95	89	6.1	1950	1890	**97**
Black sulphur dyeing × 1.13	85	91	5.5	2528	2522	**100**
Bleaching × 1.22	100	103	2.5	2407	2441	**101**
Size × 1.76	106	101	5.4	2805	2783	**99**
Light reactive dyeing × 1.11	101	102	0.8	154	153	**99**
Silk degumming × 0.83	89	90	1.0	685	686	**100**
Silk degumming 2 × 1.05	91	91	0.4	788	788	**100**
Dark acid dyeing × 0.97	90	94	4.0	792	792	**100**
Dark acid dyeing 2 × 0.91	100	105	5.1	787	786	**100**
Dark reactive dyeing × 1.17	92	94	1.7	359	361	**101**

Table 45, 6-neuron NNW, trained with modified real respirograms, (data lined up on first row)

Respirogram	End point			BOD_{st} (mg/l)		
	Manual	NNW	Δ	Manual	NNW	%
Acid dyeing 52 × 1.15	50	47	3.0	184	185	**101**
Acid dyeing 203 × 1.23	90	90	0.0	340	340	**100**
Acid dyeing C × 0.98	76	76	0.2	334	334	**100**
Acid dyeing 106 × 1.07	46	47	1.0	222	220	**99**
Indigo cotton scouring × 0.86	69	74	4.9	1950	2024	**104**
Black sulphur dyeing × 1.13	53	53	0.2	2528	2528	**100**
Bleaching × 1.22	81	71	10.2	2407	2262	94
Size × 1.76	80	68	11.7	2805	2589	92
Light reactive dyeing × 1.11	101	96	5.4	154	151	**98**
Silk degumming × 0.83	66	70	3.8	685	689	**101**
Silk degumming 2 × 1.05	66	64	1.7	788	756	**96**
Dark acid dyeing × 0.97	64	65	0.7	792	791	**100**
Dark acid dyeing 2 × 0.91	75	74	1.5	787	789	**100**
Dark reactive dyeing × 1.17	77	78	0.6	359	359	**100**

4.5 SENSITIVITY ANALYSIS

The simulated respirograms were generated from the activated sludge model No. 1 (ASM1; Henze et al., 1999). This model was first calibrated with a number of measured respirograms. Subsequently, by setting various combinations of values of three selected parameters, the calibrated model was used to generate respirograms for training the NNW. For these respirograms, the end-point of exogenous respiration will depend on the values of the model parameters and initial values of the state variables. Factorial sensitivity analysis was carried out to investigate how the output of the NNW depends upon the most significant parameters used in the simulation model: $X_s(0)$, K_S and μ_m. For this purpose a normalised second order composite design around a reference parameter vector was used. Parameters were normalised according to a cubic/spherical parameter space as indicated in Table 46.

Table 46, Coded levels of most sensitive parameters

	Coded levels, x_i					In terms of variables
	$x = -\sqrt{3}$	$x = -1$	$x = 0$	$x = 1$	$x = \sqrt{3}$	
$X_s(0)$	25.6	40	60	80	94.6	x1=(Xs-60)/20
K_s	1.34	5	10	15	18.66	x2=(Ks-10)/5
μ_m	0.17	2	4.5	7	8.83	x3=(μ_m –4.5)/2.5

Based on this design 15 parameter combinations (2^3=8 for the cube, plus 3×2=6 for the sphere and one for the centre point) can be defined. This results in the following matrix:

$$x_{i,j} = \begin{bmatrix} -1 & -1 & -1 \\ 1 & -1 & -1 \\ -1 & 1 & -1 \\ 1 & 1 & -1 \\ -1 & -1 & 1 \\ 1 & -1 & 1 \\ -1 & 1 & 1 \\ 1 & 1 & 1 \\ -\sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 \\ 0 & -\sqrt{3} & 0 \\ 0 & \sqrt{3} & 0 \\ 0 & 0 & -\sqrt{3} \\ 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 \end{bmatrix}$$

Where $x_{i,j}$ denotes the j^{th} combination of parameter i. Main and interaction effects of the parameters were analysed by using the following second-order regression (meta) model:

$$k_j^* = a_0 + a_1 x_{1j} + a_2 x_{2j} + a_3 x_{3j} + a_{11} x_{1j}^2 + a_{22} x_{2j}^2 + a_{33} x_{3j}^2 + a_{12} x_{1j} x_{2j} + a_{13} x_{1j} x_{3j} + a_{23} x_{2j} x_{3j}$$

where k^*_j denotes the end point of exogenous respiration assessed from the respirogram simulated with the j^{th} parameter combination. The coefficients a_i and a_{ij} represent the sensitivities and are found by regression of the meta model.

The above procedure was used to generate 15 respirograms. Subsequently, from these respirograms the exogenous end point was determined by means of visual (expert) inspection. In addition, the end point was assessed by identifying from the simulation data the time instant where quasi steady-state for the readily biodegradable substrate (S_S) is reached (Keesman and Spanjers 2000). This calculated end point can be considered as the exact time instant where exogenous substrate is exhausted. Figure 18 shows that there is a good agreement between the two methods, indicating that the visual identification of the exogenous end point is fairly reliable.

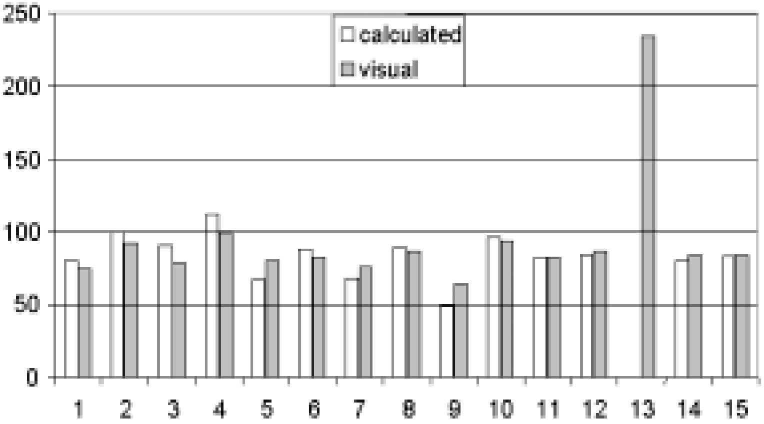


Figure 18, End point of exogenous respiration for 15 respirograms simulated on the basis of 15 parameter combinations. Two methods were used: visual inspection by expert and calculated and by identifying the time instant where quasi steady state is reached. The number on the Y-axis indicates the position of the end point (index number sampled respiration rate)

The visual end points k_j^* were used to estimate the coefficients in the meta model, and the results are depicted in Table 47. It is concluded that μ_m, the maximum growth rate of heterotrophic bacteria, is the most sensitive parameter with respect to the visually determined end point of exogenous respiration, followed by $X_S(0)$, the initial concentration of slowly biodegradable matter. The half saturation coefficient for heterotrophic growth, K_S, is the less sensitive. The sensitivity of the model parameters has to be taken into account when using simulated respirograms to train the NNW.

Table 47, Parameter sensitivities normalized meta model

Coefficient	Parameter	Value
a_0		85.0048
a_1	$X_S(0)$	7.2830
a_2	K_S	1.6186
a_3	μ_m	-19.7196
a_{11}	$X_S(0)^2$	1.2500
a_{22}	K_S^2	-3.2500
a_{33}	μ_m^2	-1.2500
a_{12}	$X_S(0)K_S$	-6.5578
a_{13}	$X_S(0)\mu_m$	-4.7243
a_{23}	$K_S\mu_m$	20.2771

5 RESULTS OF INFRARED SPECTROMETRY COD METHOD

5.1 RESULTS FOR THE FIRST SET OF TEXTILE WASTEWATER SAMPLES

The first samples were sent by mail to INRA for analysis. These were samples from different textile processes, to try if infrared spectra could be recorded for a wide range of textile wastewaters. For samples 1 – 6, the company that took the samples provided COD and pH values, but when analysing some of the samples at LeAF the values were found to be different. Therefore measurements were repeated at INRA. Differences between analysis might be caused by changes in composition during transport, or by the usage of different sample preparation or measurement techniques.

Table 48, Analysis data of the tested wastewater samples. Values in mg/l.

(1) = Data provided with wastewater, (2) = analysis in LeAF-lab, (3) = analysis at INRA.

Sample		COD (1)	COD (2)	COD (3)	pH (1)	pH (2)	pH (3)	VFA (3)
1.	Light reactive dyeing	750	675	1290	7.4	10.5	10.71	0
2.	Double scouring 1st bath	2650	445	47	9.8	6.3	7.23	0
3.	Double scouring 2nd bath	5250	6500	6550	9.05	6.4	7.53	0
4.	Silk degumming	3220	3400	2100	6.95	6.4	6.73	0
5.	Dark reactive dyeing	2264	3900*	2680	7.96	9.0	9.26	0
6.	Dark acid dyeing	2070	2300	2300	4.96	6.5	7.52	0
7.	Scouring dyed fabric	-	11574	7220	-	5.5	5.52	620
8.	Bleaching	-	13012	10800	-	10.5	11.7	1100
9.	Black sulphur dyeing	-	6027	6170	-	4.6	4.5	5000
10.	Sizing liquid	-		65210	-		5.1	9500

* Wastewater gave precipitation problems when analysing COD, result not reliable.

5.1.1 Spectra of the first set of textile wastewater samples

These results were used to make a calibration, but not all of the samples were useful. Samples 2, 3 and 4 resulted in spectra that were not much different from a water spectrum (despite their high COD's) and they were ignored in calibration. The biggest problem is the large differences between spectra of samples used for calibration, which makes the result of the calibration unreliable. Because the samples contained solids, they were centrifuged before IR analysis. Spectra of the samples are given in Figure 19, numbers for wavelengths and optic density are removed as this is confidential information. In sample 1 a big peak can be seen, this is sulphate (known from ingredients and checked with spectrum library). Samples 7 – 10 are less diluted and look more interesting, but no list of ingredients has been provided by the factories. When it is known which compounds may be present in the sample, spectra libraries can be used to check for the spectra of these compounds. If only separate compounds are measured infrared spectrometry is a very accurate technique.

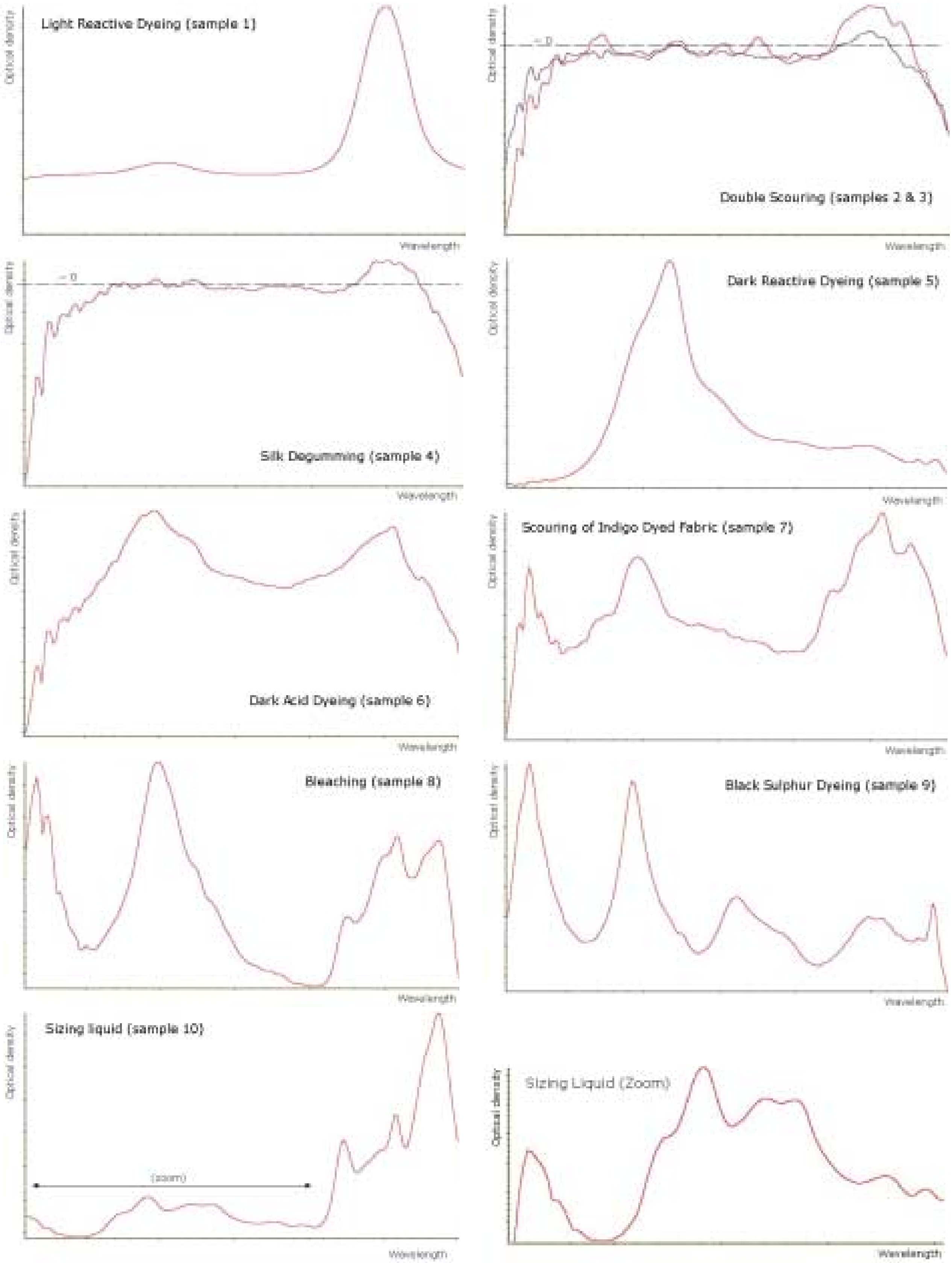


Figure 19, Spectra for the first ten textile wastewater samples

5.1.2 Attempted calibration with different textile wastewater spectra

With seven of the samples (number 2, 3, 4, 7, 8, 9, 10) calibration lines for COD and VFA were made. Figure 20 and Figure 21 are screenshots of calibration lines made with those samples.

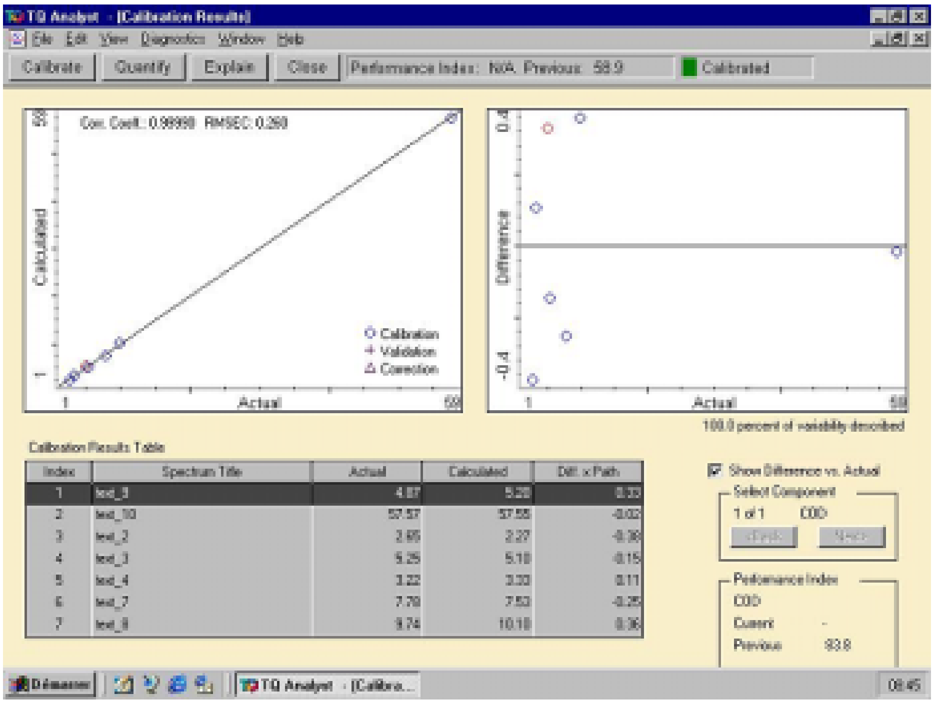


Figure 20, Screenshot of a calibration line for COD made with 7 of the textile wastewater samples

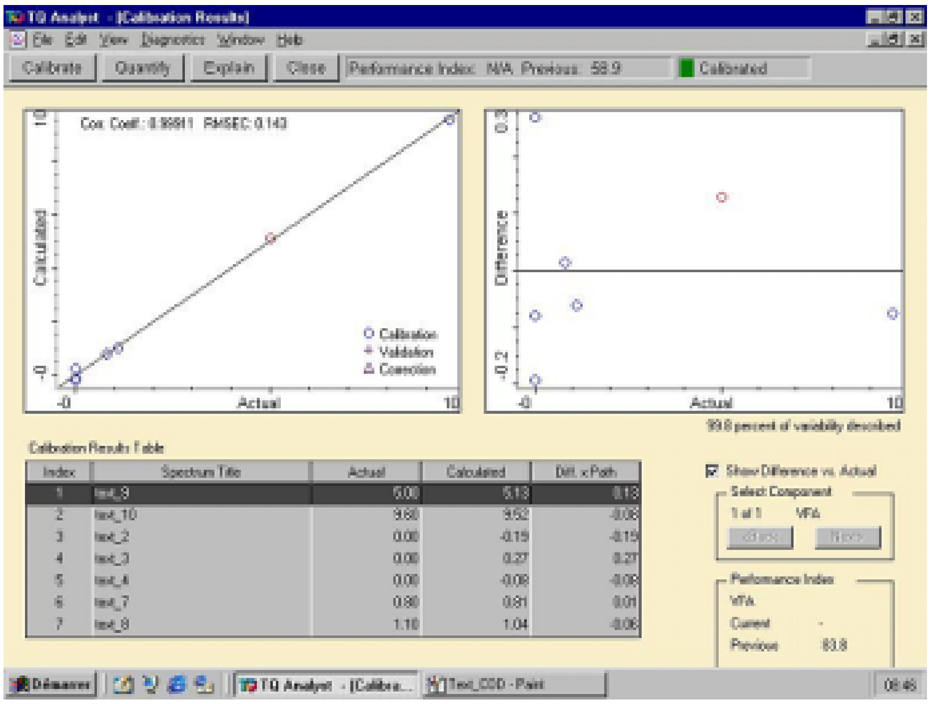


Figure 21, Screenshot of a calibration line for VFA made with 7 of the textile wastewater samples

Although the number of samples was very limited and the spectra are all completely different, the calibration lines are quite good. This is quite surprising, but nevertheless it looks promising for successful implementation. In paragraph 5.1.1 it was mentioned that samples 2, 3 and 4 were ignored for calibration, but in these pictures they are present in the list. According to the people in Narbonne, the 'water-like' spectra can be useful sometimes as a zero-point on the calibration curve, when used very carefully. Using too many of these spectra negatively affects the calibration. Figure 20 and Figure 21 were made when checking the influence of the samples on the calibration.

5.2 RESULTS FOR THE SECOND SET OF TEXTILE WASTEWATER SAMPLES

When the first results indicated that the recording of IR spectra was possible for different wastewater types a second set of samples was taken and brought to INRA for analysis. These samples concerned only four textile processes, but for each process samples were taken from the different process steps (initial processing bath and following rinsing steps). In this way samples with a similar composition but different concentrations could be compared. The results are presented in the following paragraphs, with "1" referring always to the initial bath and "2", "3", "4" or "5" to the step from which the sample was taken (e.g. dark acid dyeing 5 = 5th step of the process, meaning the 4th rinsing step).

5.2.1 Spectra of the second textile wastewater samples

Polymer Charge *(samples Polymer-1, -2, and -3)*

The main components of the polymer charge wastewater (methacrylamide and sulphate) could be clearly distinguished in the spectrum. With infrared spectrometry it is possible to make calibrations based on the various compounds and measure the concentrations of these compounds instead of COD. As can be seen in the picture on the left, the spectra of the three samples show a similar pattern. The lines are not depicted at the same optical density scale, because then sample *Polymer-3* would have been shown as a straight line without peaks. The picture on the right shows the spectrum of the polymer charge bath (sample *Polymer-1*) with the compounds indicated. The black band in figure 21B indicates which part of the spectrum belongs to methacrylamide.

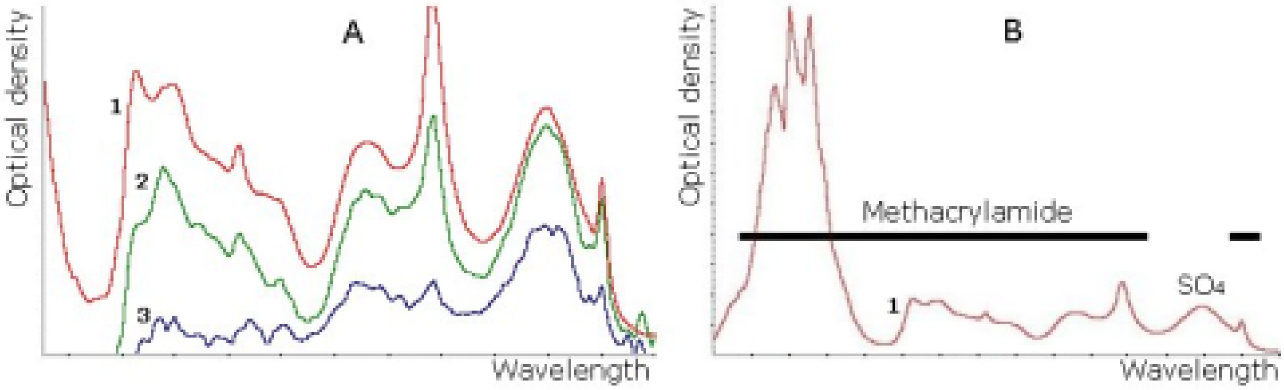


Figure 22, Spectra of all three polymer charge samples (A), and spectrum of sample Polymer-1, *with methylacrylamide and sulphate indicated (B). The "1" is situated in the same place in both figures.*

Silk degumming (samples Silk-1 and -2)

Figure 23 shows spectra of two silk degumming samples. For this wastewater the picture is less clear, because the samples were too diluted. Both spectra are depicted on the same scale, and they both are practically 0. Furthermore, hardly any similarity can be seen between the shapes of the two spectra.

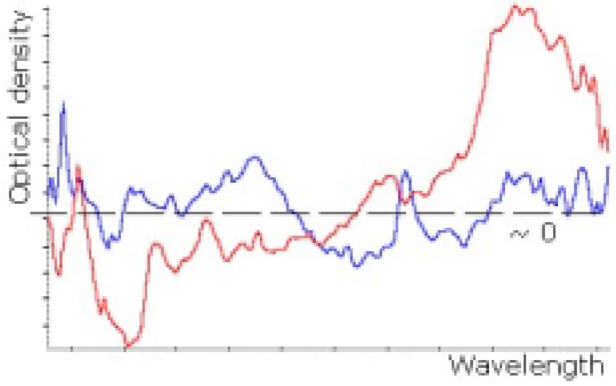


Figure 23, IR -spectra of silk degumming samples

Dark reactive dyeing
(samples Reactive-1, -2, -3, -4, -5)

The dark reactive dyeing spectra in Figure 24 are depicted on the same scale. As can be seen only the first three samples show a high enough optical density, the other samples of this process were too diluted.

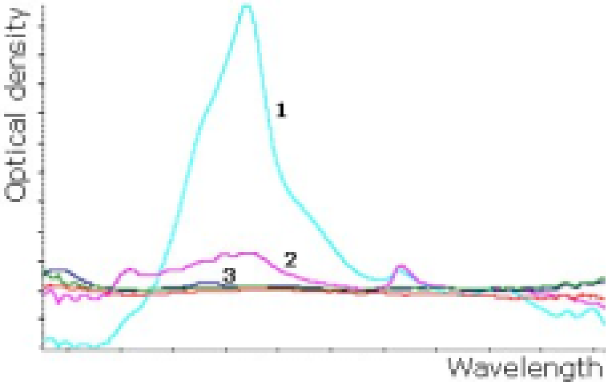


Figure 24, IR spectra of dark reactive dyeing samples

Dark acid dyeing
(Acid-1, -2, -3, -4 and –5)

The clear peak on the right that can be seen in the dark acid dyeing spectra Acid-1, Acid-2 and Acid-3 in Figure 25 is sulphate. Spectra are again on the same scale. Although sulphate has not been measured in the samples (for data see appendix B), it can be assumed that the concentration is lower after each wash-step. This is confirmed by the spectra, the sulphate peak is lower for each next sample.

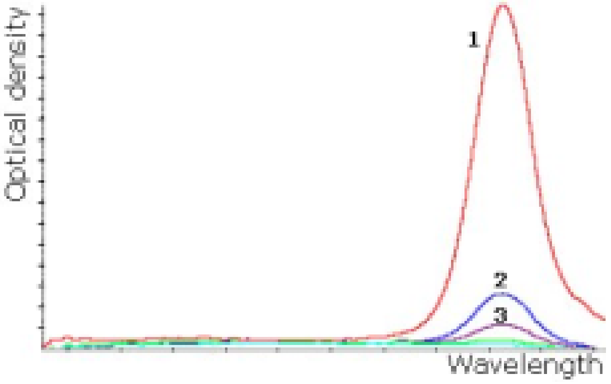


Figure 25, IR - spectra of dark acid dyeing samples

5.2.2 Interpretation of the second set of spectra

Most samples seem suitable for IR analysis, only the degumming wastewater is too diluted. For each textile process (except for the degumming process) a reasonable calibration line could be made, especially the groups of 5 samples were useful. The spectra show resemblance when compared per process and the samples with higher concentrations indeed show a higher optical density. An ideal calibration is made with many samples instead of just a few, but the result that could be obtained was promising. Infrared spectrometry can also recognise spectra as being of a certain type, and then use the right calibration for the type of sample. An attempt was made to see if the textile samples could also be distinguished in that way. The spectra of the samples were supplied to the software as belonging to spectra 'families': polymer charge family, reactive dyeing family, etc. Using the software, the computer was let to compare the spectra and determine which sample belonged to which family. In most of the cases the right family was assigned, showing that a certain process can give a very distinct type of spectrum.

5.3 RESULTS OF THE SAMPLES OF A REACTOR TREATING AZO DYE RR2

The objective of this experiment was to see whether the calibration used at INRA for the monitoring of an anaerobic reactor could be used for analysing samples from an aerobic reactor treating wastewater containing a textile dye. Samples were also analysed using the titrimetric sensor, to get values for VFA. Two different calibrations were used for calculation of the COD and VFA concentrations of the samples using the infrared method: the one developed for the reactor at INRA treating vinasses, and the calibration that was made with the first set of textile samples.

Reactors were fed with ~1370 mg COD/l, and in the effluent remains a concentration as low as ~184 mg/l. The influent consists of VFA, glucose and a textile dye. Reactor 1 is also fed an electron mediator (AQDS) to speed up the degradation of the dye, but further there are no differences between the reactors. The samples were shipped without cooling from Wageningen to Narbonne.

Table 49, Results for infrared analysis of effluent of anaerobic azo dye decolourising reactors

	Infrared		Titrimetric	Owner reactors
	"textile calibration"	Vinasses calibration		
Reactor 1 COD Reactor 2 COD	1170 1640	0 0	- -	185 183
Reactor 1 VFA Reactor 2 VFA	0 0	0.10 0.085	0.126 g/l 0.102 g/l	- -

No COD was found with the infrared method, when using the calibration for vinasses reactor effluent. When comparing the spectra of the two UASB reactor effluents to the spectrum of the anaerobic reactor effluent at INRA (see Figure 26), a clear difference can be seen. The signal of the vinasses effluent is much stronger than the signals of the reactors treating azo dye. Because of the low concentrations in the UASB effluent, it is difficult to make accurate measurements. So in fact the UASB effluent samples were not suitable to demonstrate the possibilities of the infrared technique. As can be seen in Table 49, the COD values resulting from both calibrations do not resemble the COD concentration measured using the traditional laboratory method. An explanation can be that neither one of the calibrations is really suitable for these samples.

When looking more closely at the spectra, a large peak can be seen at the wavelength where normally the VFA are detected (this is not shown in detail in Figure 26). It is known from tests that the presence of ammonia interferes with the VFA measurements, because nitrogen compounds are also detected in that area of the spectrum. As Reactive Red 2 contains nitrogen (azo bond), it is possible that nitrogen interference occurred. However, if the presence of ammonia is accounted for in the calibration, it is possible to determine the VFA without interference. A second problem is the low concentration of VFA (and therefore COD) in the samples. The amount of COD present in the effluent (~185 mg/l) is actually too low to be measured with the infrared method.

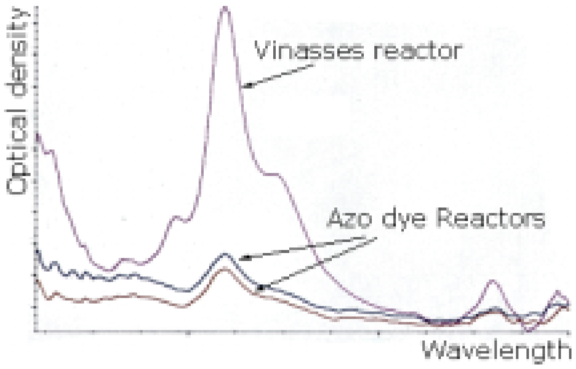


Figure 26, Representation of spectra of effluent from reactors treating azo dye RR2, and reactor at INRA treating vinasses.

5.4 RESULTS OF THE THIRD SET OF SAMPLES

The set of samples that had been used for NNW end-point detection (acid dyeing respirograms, see § 2.5.2) was also sent to the INRA in Narbonne for online COD analysis. The objective is to test the set-up for the on-line textile wastewater treatability measurement technique proposed in this document: COD values obtained with the on-line infrared measurement, BOD_{ST} values obtained from respirograms.

A good calibration was obtained for the samples, but due to the low number of samples the calibration could not be validated. Some of the samples were too diluted so in the end only 13 samples could be used. Twelve were used for calibration and only one for validation. However, as the calibration is the most important part of the infrared technique, obtaining a good calibration means that the samples are suitable for analysis. Figure 27 shows the calibration line obtained for the set of acid dyeing samples.

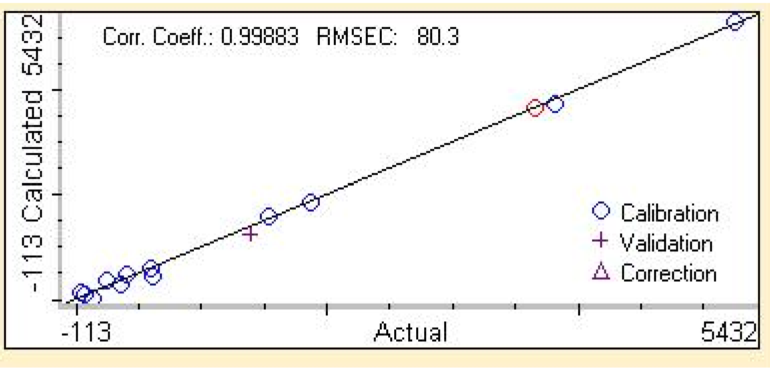


Figure 27, Calibration line for the online COD analysis of the set of acid dyeing samples

The line represents the relationship between the COD values as calculated by analysis of the infrared spectra and the COD values measured with a standard method ("Actual").

6 COMBINATION OF THE THREE METHODS TO FORM AN ON-LINE TREATABILITY MEASUREMENT TECHNIQUE

As explained in the introduction, the ultimate goal is the development of an on-line treatability analysis technique. In practice, both respirometric measurements and infrared spectrometry have been applied successfully online. Combination of these two techniques should therefore pose no problems. The difficult part is the analysis of the respirograms, and here the neural network approach seems to be a solution. Within this project it was not possible to test the proposed concept (Figure 1) in one experimental set-up in a textile factory. This would have to be tested in a follow-up project.

In Table 50 an example is given of the values that would result from the set-up. The values for treatability are just an indication, as the usage of the short-term BOD value is a new way of determining treatability.

Table 50, Treatability calculation using COD and short term BOD values.

Respirogram	BOD_{ST} (mg/l)	COD (mg/l)	BOD_{ST}/COD	Treatability
Acid dyeing 106	227	5244	0.04	- -
Indigo cotton scouring	1982	11574	0.17	-
Black sulphur dyeing	2457	6027	0.41	+ +
Silk degumming 2	741	3400	0.22	+
Dark acid dyeing	790	2300	0.34	+ +
Dark acid dyeing 2	814	2300	0.35	+ +
Dark reactive dyeing	349	2660	0.13	-

7 DISCUSSION AND CONCLUSION

7.1 TEXTILE WASTEWATER CHARACTERISATION USING RESPIROMETRY

Respirometry has been used already for a long time for the characterisation of wastewaters. The tests performed within this study confirm that respirometry can also be applied to textile wastewater. A possible drawback can be the phenomenon of foaming when scouring wastewaters containing detergents are tested, but the use of anti-foaming chemicals can solve this problem. When using these chemicals, one has to keep in mind that besides preventing foaming, they may also affect the aeration efficiency and may have an effect on biological activity.

For each wastewater stream the sample dose will have to be determined before beginning with the online measurement. Differences in concentration and potential toxicity can cause large differences between the results, when applying the same sample dose for all wastewaters.

The technology for on-line respirometry is commercially available. Application to a textile process would be a matter of direct implementation, possibly with some slight changes to the equipment to make it applicable in a textile factory.

Inherent to respirometry is that activated sludge is needed to characterise any wastewater. Generally, however, activated sludge is grown on mixed wastewater streams and thus not adapted to specific single streams that make up the mixed water. Therefore, care must be taken when extrapolating the results from single wastewater streams to the treatment of mixed streams. In any case, in an on-line measurement set-up for single wastewater streams the used activated sludge should preferably origin from the textile factory's own plant or, if not present, from the municipal wastewater treatment plant receiving the factory's wastewater.

7.2 APPLICATION OF NNW FOR END-POINT DETECTION

The results of this study are promising for the application of a neural network for the determination of the end point of exogenous respiration and hence the BOD_{st} of the wastewater sample. One of the most important results is the affirmation of the assumption that the network has to be trained with data that have a sufficiently close resemblance to the data it will have to deal with. For example when looking at the values presented in §4.1 (training with simulated data, validation with real data) the only good predictions were for respirograms that are either the original respirograms from which the simulations were generated, or ones that are similar. When training the network with part of the simulated data and validating it with the rest (§4.3) a very good result is obtained. Good results were also obtained in the trial described in §4.4 with the slightly modified respirograms for training and the original data for validation.
This was to be expected, as the simulated respirograms are noise-free and very similar. In cases when the resemblance is not very close, the neural network can make significant mistakes (see for instance §4.1). The mistakes the neural network makes, however, do not all have the same impact. A large difference between the end points does not necessarily mean a large difference in BOD_{ST}.

The conclusion is that a neural network can apparently be trained to identify the end-point of respirograms, when it is trained with data that are similar enough to the data it will have to analyse. The way a neural network calculates the outcome is completely unknown, which makes it impossible to find out why it makes mistakes and how these might be avoided. Proper training is the only way to make sure the outcome is reliable.

Due to the limited number of textile wastewater respirograms that were available for training and validation the outcome might be influenced by specific characteristics of the data. Almost all of the used respirograms had a gradual transition from exogenous to endogenous respiration, which reduces the effect of a non-precise prediction of the end point by the neural network. Repetition of this study with reprograms that have more abrupt endings would give valuable information about the applicability of this way of end-point detection.

When repeating an analysis of the same set of respirograms, the answer is never the same. Even for the trials where no random noise was added to the data, results changed every time. See appendix 4 for examples. The NNW seems to try something new every time, based on a random initialisation.

7.3 APPLICATION OF INFRARED SPECTROMETRY FOR COD MEASUREMENT IN TEXTILE WASTEWATER

Although based on only a few samples, the results of this experiment indicate the potential of using infrared spectroscopy for measurements of COD in wastewater. What is clear from these results is the large difference between spectra of samples of different textile processes. Therefore calibration should be done independently for each process. Making a generic textile wastewater calibration and using it for different processes would not lead to usable results.

When considering using this technique for a specific purpose, the first step is very important: determining the objective of the measurement. What kind of parameters have to be measured and in what concentrations? Is the objective to measure separate compounds (like normally is done with IR), or COD that is a multi-compound parameter? Also the range of the concentrations is important. As mentioned in the introduction, the more diluted the wastewater, the less reliable are the results for COD.

The first thing that has to be done to determine whether it makes sense to implement this technique in textile industry, is to determine the goal of the measurements. One can think of different implementations for an on-line COD monitoring system in a textile factory. In the textile industry there are several possible implementations:

1. Monitoring effluents of all steps of all different processes, to decide where to send the wastewater: to another process(step) or to a particular wastewater treatment

In this case problems can arise if the concentrations in the wastewater are lower than ~500 mg COD/l, as the IR method is not very suitable for low COD concentrations. Determining which streams have a low enough COD to be suitable for reuse is probably not possible, because many processes require water with a very low COD. The average value reported in the TOWEF0 report on textile wastewater characterisation is around 40 mg/l, which is much below 500 mg/l. However, if the concentrations do not need to be so low, the infrared method can be very interesting. When wanting to analyse a large number of streams, the 'family recognition' aspect that is mentioned in chapter 4 might be a practical thing to investigate further. Maybe one single spectrometer can be used to analyse various streams, recognising each different stream and using the right calibration for it. Of course this also depends on the desired sampling intervals. Something that has to be known to be able to determine where to send the wastewater is the COD concentration that is permitted in the process water. This can be different for each process.

2. Monitoring e streams that enter a biological treatment plant

Considering the potential for direct reuse of some hardly polluted streams, it is possible that in some factories only the more polluted streams will be sent to a treatment plant and that the almost clean streams are directly reused. In that case the infrared technique may be used to monitor the ingoing stream of the plant in order to control of the treatment process. Then the 500 mg COD/l limit will be no problem. Additionally, infrared spectrometry might be used for identification of certain known toxic compounds that can be present in the wastewater (the presence of certain compounds will probably be based on the process). Another use is the simultaneous assessment of a COD value by an infrared spectrometer and a BOD value by respirometry. Then the BOD/COD ratio can be calculated to determine whether the wastewater is biodegradable and can be send to a biological treatment facility.

3. Monitoring of the treated water, to decide whether the quality meets the effluent constraints

Here the same information is needed as for number 1: what concentrations are allowed to be present in the water? If these values are very low, the 500 mg/l limit will be a problem.

4. Measuring the concentrations of specific ingredients present in the used process baths

Measurement of specific ingredients can be useful to replenish the ingredients of a process step to their original concentration and reuse both the water and the chemicals that are still present. Whether this type of monitoring and replenishing would be feasible or not, depends on the type of chemicals and processes.

7.4 APPLICABILITY OF ONLINE TREATABILITY MEASUREMENTS IN THE TEXTILE INDUSTRY

All results indicate that the on-line treatability measurements involving on-line BOD_{ST} and on-line infrared COD analysis would be possible in practice. On-line respirometry is a well-established technology and on-line infrared COD measurements have been performed by the INRA already for a long period on pilot scale with good results. Automatic control of the whole on-line treatability measurement set-up, using neural networks for respirogram end-point detection, could still be a challenge. But until now, although the experiment was rather limited, also those results are promising. The application of on-line treatability measurements in the textile industry is feasible, and would facilitate a decision support system for the treatment and reuse of different wastewater streams.

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APPENDIX 1 - TRANSCRIPTION OF THE USED NEURAL NETWORK

```
% NN for detection of endogenous phase using Matlab Neural Network Toolbox
%% Author: Karel J. Keesman

close all;
clear;

Y=xlsread('datamatrix.xls');            % Reading input data
[M,N] = size(Y);                        % number of respirograms
Nt= 21;                                 % number of respirograms used for training, variable
l = 0.0;                                % noise level: set e.g. l=0 or 0.05
X = Y(1:M-1,:);                         % matrix of column-wise stored respiration rates
X = X+(l*(rand(M-1,N)-0.5));            % noise added
y = Y(M,:);                             % vector of switching indices

% Using Matlab's NEWFF
% Initialisation
%
[Xn,mX,stdX,yn,my,stdy]=prestd(X,y);
%[Xt,Phi]=prepca(Xn,0.02);              % Pre-Principal Component Analysis – not possible because
                                        # rows > # columns
Xt=Xn;
net = newff(minmax(Xt),[4 1],{'tansig' 'purelin'});     %number of input neurons [x 1] is variable
yhat= sim(net,Xt(:,1:Nt));
[Xp,yhatp] = poststd(Xt(:,1:Nt),mean(Xt')',std(Xt')',yhat,my,stdy);
%
subplot(211);                           % Plotting of prediction of untrained network
plot(y(1:Nt),'*'); hold on; plot(yhatp,'o'); hold off;
subplot(212)
plot(y(1:Nt)',yhatp,'+'); pause;
%return;
%
% Training                  % training of the network using the data selected previously (Nt)
%
net.trainParam.epochs = 50;
net.trainParam.goal = 0.01;             % when disabled, the NNW tries to go to difference=0
net = train(net,Xt(:,1:Nt),yn(1:Nt));
yhat= sim(net,Xt(:,1:Nt));
[Xp,yhatp] = poststd(Xt(:,1:Nt),mean(Xt')',std(Xt')',yhat,my,stdy);
%
subplot(211);                           % Plotting of training result
plot(y(1:Nt),'*'); hold on; plot(yhatp,'o'); hold off;
subplot(212)
plot(y(1:Nt)',yhatp,'+'); pause
%return;
%
% Validation           %validation of the network training using data it has not “seen” before
%
yval = sim(net,Xt(:,Nt+1:N));
[Xp,yvalp] = poststd(Xt(:,Nt+1:N),mean(Xt')',std(Xt')',yval,my,stdy);
%
figure
subplot(211);               % Plotting of validation result, this is the outcome of the exercise
plot(y(Nt+1:N),'*'); hold on; plot(yvalp,'o'); hold off;
subplot(212)
plot(y(Nt+1:N)',yvalp,'+'); pause;
```

APPENDIX 2 - EXAMPLES OF THE FIGURES PRESENTED BY MATLAB NNW (GOOD RESULT)

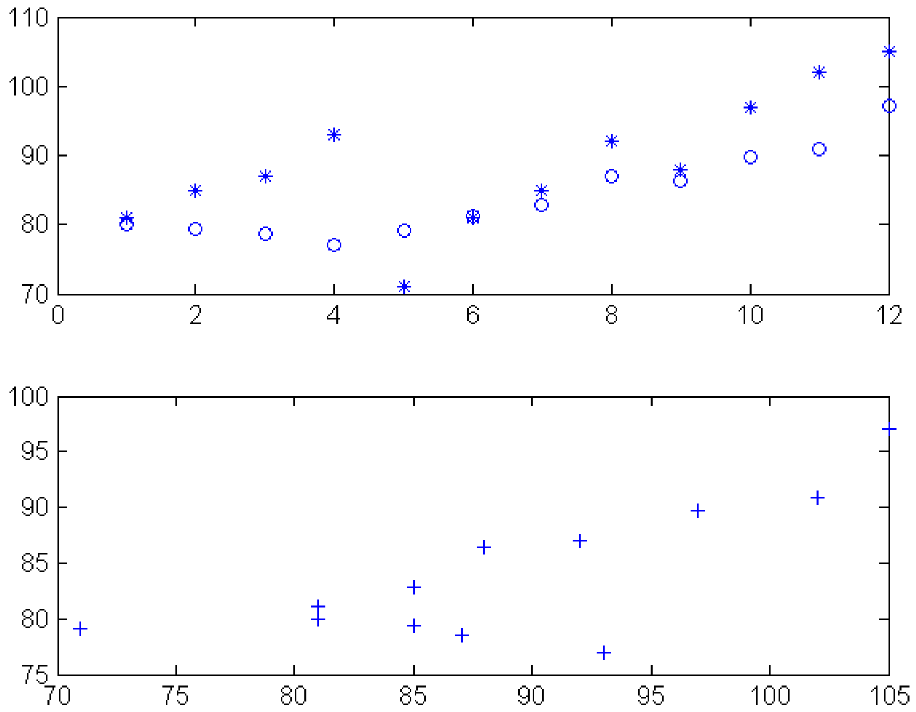

Figure 28, Simulation with the untrained neural network (from §4.3)

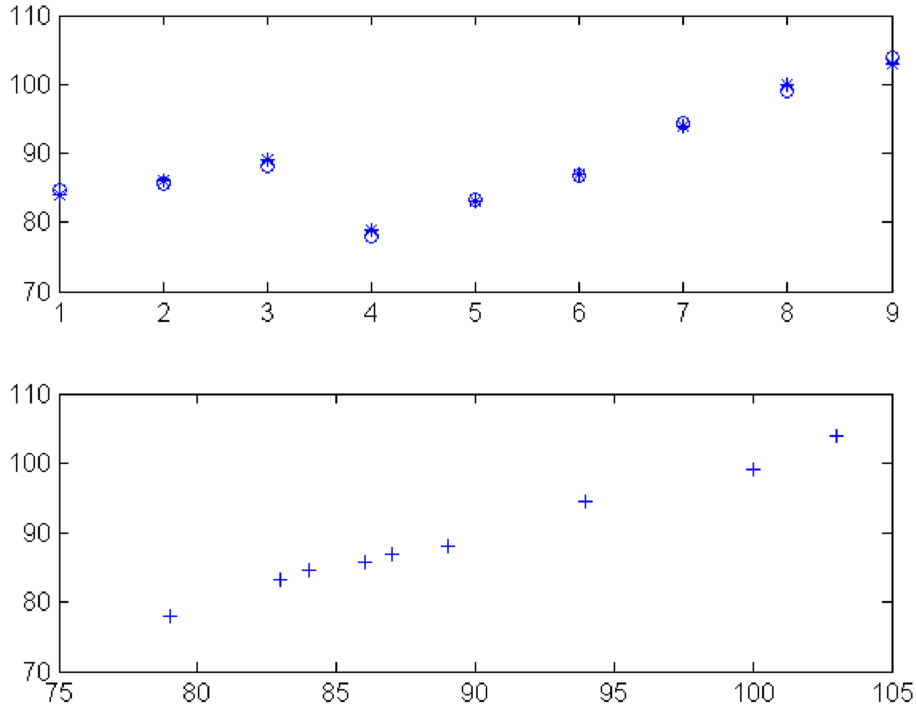

Figure 29, Outcome of the trained neural network (from §4.3)

APPENDIX 3 - EXAMPLES OF THE FIGURES PRESENTED BY MATLAB NNW (BAD RESULT)

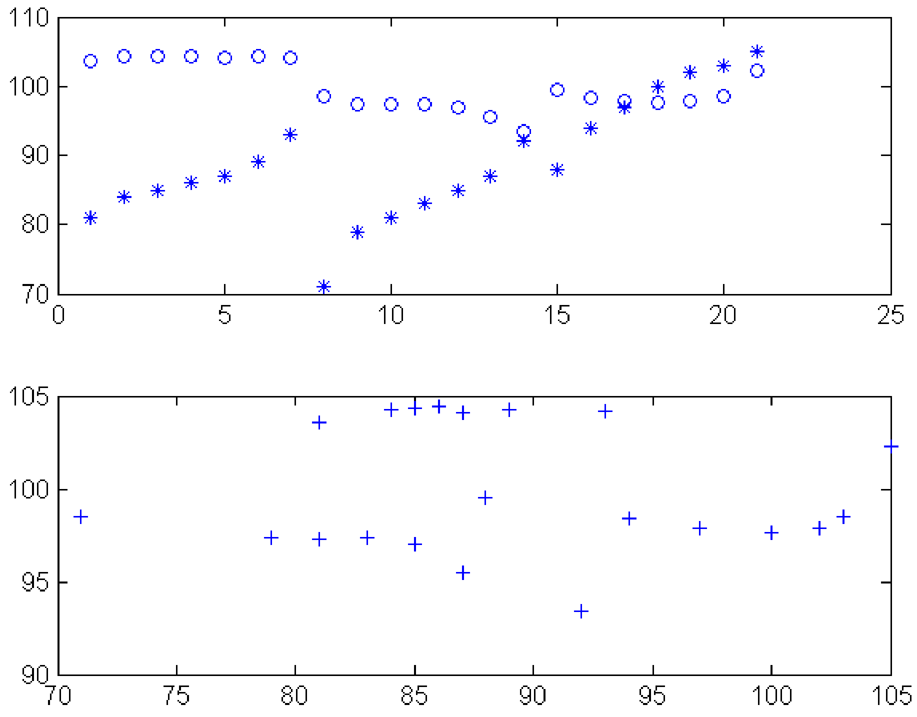

Figure 30, Simulation with the untrained neural network (from §4.1)

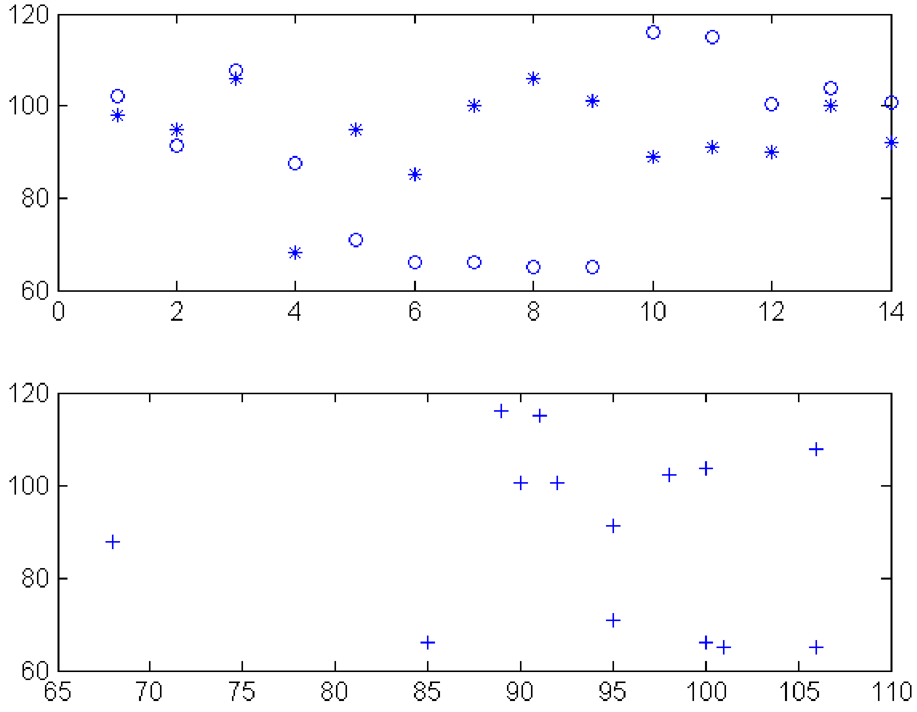

Figure 31, Outcome of the trained neural network (from §4.1)

APPENDIX 4 - REPEATED CALCULATIONS USING THE SAME SETTINGS

For a neural network of 6 neurons, using the data matrix reported in § 3.4 with no noise added.

Trials	106-20	106	106+20	203-20	203	203+20	52-20	52	52+20
1	84.03	85.89	88.90	77.69	83.28	86.55	93.97	99.48	103.19
2	84.56	85.61	88.04	77.05	82.36	84.13	93.70	99.86	102.81
3	84.38	85.96	89.14	77.57	83.56	86.81	94.17	99.96	103.35
4	84.12	85.94	87.90	78.32	83.03	86.98	94.27	99.52	103.39
5	84.36	86.17	89.33	77.94	83.34	86.03	95.10	99.92	104.21
6	84.29	85.81	88.80	78.08	83.35	86.23	94.26	99.49	103.49
7	84.31	86.28	88.95	78.50	82.83	86.46	94.48	99.56	103.08
8	84.80	86.41	87.81	77.19	83.47	86.34	94.36	99.70	103.62
9	83.73	86.08	88.54	78.54	83.11	86.84	94.03	99.65	103.19
10	84.59	85.69	88.15	78.04	83.31	86.84	94.39	99.07	103.99
STDEV	0.30	0.25	0.55	0.51	0.35	0.83	0.37	0.26	0.42
Taken out	78.90	88.50	86.74	77.60	83.51	92.17	93.11	100.20	112.14

For a neural network of 5 neurons, using the data matrix reported in § 3.2 with 0.1 noise added. On line 10 the outcome represented in table 4 in chapter 3.2 is given. By chance trial 4 gave the exact same values.

Trials	AD 52	AD 203	AD C	AD 106	ICS	BSD	B	Size	LRD	SD	SD 2	DAD	DAD 2	DRD
1	54.82	86.48	43.53	66.02	81.69	83.21	82.49	81.88	81.63	39.46	39.38	51.52	72.11	50.79
2	60.65	84.46	63.57	66.82	78.60	72.28	80.96	81.07	86.40	65.90	56.12	67.41	86.02	77.70
3	62.17	85.86	72.53	67.66	77.71	77.99	78.47	78.40	78.43	51.36	49.82	69.69	85.73	87.29
4	51.85	91.77	68.29	64.82	82.18	78.34	84.15	85.04	86.49	66.15	66.12	61.53	76.63	74.36
5	55.12	86.42	72.72	66.23	71.94	64.38	75.03	76.89	77.41	49.24	46.85	73.34	84.36	78.24
6	60.80	86.80	68.09	66.08	74.71	70.78	73.78	75.25	89.46	67.70	65.65	68.17	78.72	68.45
7	52.20	88.07	52.36	63.76	87.25	91.08	86.49	82.58	85.70	47.85	46.78	55.16	85.88	54.87
8	57.68	86.39	62.82	69.56	85.63	85.75	84.06	83.52	87.83	53.54	45.89	59.46	80.98	67.45
9	48.39	91.40	56.69	61.72	98.99	96.85	95.71	95.29	94.63	48.12	47.22	66.08	84.66	54.86
10	51.85	91.77	68.29	64.82	82.18	78.34	84.15	85.04	86.49	66.15	66.12	61.53	76.63	74.36
STDEV	4.62	2.71	9.43	2.15	7.56	9.71	6.23	5.59	5.14	10.08	9.83	6.80	4.92	11.96
Taken out	55.46	96.46	56.97	69.43	109.20	111.57	112.95	113.60	113.61	48.17	43.68	54.43	83.78	68.44

(D)AD = (dark) acid dyeing, ICS = Indigo cotton scouring, BSD = Black sulphur dyeing, B = Bleaching, LRD = Light reactive dyeing, SD = Silk degumming, DRD = Dark reactive dyeing