INVESTIGATION INTO METHODS FOR THE DEVELOPMENT OF A PROTOCOL FOR QUANTITATIVE ASSESSMENT OF INDUSTRIAL EFFLUENTS FOR PERMITTING OF DISCHARGE TO SEWER

An eThekwini Case Study

Report to the

WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

Introduction

The major elements that the local authority has for managing industrial wastewater are its wastewater treatment plants for remediation, discharge permits for placing limits on what may be discharged, and a discharge tariff for financing the treatment and for providing a set of incentives and penalties to influence users of the system. An optimal management strategy will use all these elements in the proper relation to one another. However, the relationships are complex and poorly understood because of the complex and variable nature of both the multitude of effluents discharged from industries, and the response of the biological processes to them.

An effluent discharge permit consequently is a crucial interface between the local authority and an industry, and the permit system has to carefully balance protection of the general public and the environment against the rights of those working in industry and the promotion of economic activity.

The principle of administrative justice implies that the process of issuing a permit requires reasons for decisions taken. The White Paper on Integrated Pollution Control and Waste Management, 2000 requires all activities to control pollution to relate source control strategies and regulation directly to the resource it serves.

The activated sludge process is the most common form of treatment for municipal wastewater in South Africa. Industrial effluent can often be accommodated up to a point without compromising the quality of the treated water. The broad objective of this project was to develop a methodology for predicting this point with sufficient reliability to be useful in setting discharge limits for industrial effluents.

Respirometry is widely used for characterising the response of biological systems to biodegradable matter. However, it measures the aggregated oxygen uptake for all oxidative reactions occurring simultaneously, and one cannot directly measure the contribution of a particular reaction. This has to be inferred by manipulating experimental conditions, and comparing measurements made under different conditions. Since respirometry involves essentially a small scale replica of the treatment process, it can be adapted to investigate a variety of issues affecting the process.

The modelling of biological wastewater treatment systems has become widely accepted for design, monitoring and optimisation. The IAWPRC, later IAWQ and now IWA (International Water Association) task Group (Henze et al., 1987, 2000) has introduced an activated sludge model suit, which provides researchers and practitioners with a standard set of basic models for biological wastewater treatment processes.

The conceptual basis of this project was to develop a protocol, involving a combination of laboratory testing and process modelling, which would be able to predict the effect of a range of loads of factory effluent on the operation of the treatment plant receiving its effluent, to inform the process of granting a discharge permit. Because of the sustained high impact of textile effluents on several WWTWs in eThekwini, textile effluents were chosen as the subject of all the investigations.

Overall course of the project

The project started in 2007 and was originally planned to end in 2010, but was twice extended in 2011 and 2012. 2007 was used to conduct a survey of South African municipal systems for regulating the discharge of industrial effluent to sewers. The results of this survey were presented at a workshop for municipal wastewater treatment officers in November 2007. One of the outcomes of the workshop was to establish support for the methodology proposed for the rest of the project.

The broad conceptual outline of the methodology was:

- To use textile effluents discharged to wastewater treatment plants (WWTWs) in eThekwini as case studies.
- To develop laboratory techniques for characterizing effluents in terms of their impact of wastewater treatment processes.
- To set up simulation models of the wastewater treatment processes which are capable of assessing the risk of accepting an industrial effluent for treatment.
- To test the applicability model based risk assessment by participating in a permit evaluation process conducted by the eThekwini Pollution and Environment Department.

According to this concept, a *baseline model* of the WWTW would be set up and calibrated to represent the average conditions of the sewer catchment. This obviously involved characterisation of the average wastewater received by the WWTW. Factory effluent would be characterised in a similar way. The risk assessment would then consist of simulating WWTW operation for combinations of the factory effluent and the average wastewater, and predicting the quality of the treated wastewater.

The WWTW initially selected for the study was the Mariannridge plant, which in 2008 experienced significant problems with textile effluent from the Dyefin factory. A baseline for the Mariannridge WWTW was set up and calibrated in the MScEng project of Farai Mhlanga. However, in 2009 the Dyefin factory closed down and relocated to another catchment, which removed the textile effluent from the wastewater treated at Mariannridge.

Meanwhile, laboratory methods for characterising textile effluents were being investigated in the laboratory. The three key problematic constituents that were identified were residual dyes (colour), dissolved salts (conductivity) and surfactants (biodegradable COD and foaming). Of these, conductivity is not treated at all in biological processes, and can only be controlled within the textile factory. Dyes are also resistant to biodegradation; however they are partially removed by adsorption onto the activated sludge biomass. Surfactants used in textile processing are generally almost completely biodegradable, but their degradation rates may be different to normal sewage components.

In 2008, a study was undertaken by David Mzulwini, an eThekwini process engineer who registered for an MScEng, on the effectiveness of the municipality’s permitting system. Unfortunately he took ill and passed away before completing his degree, but he had come to the conclusion that the effluent discharge permits were not protecting the WWTWs as they should, not because of the way they were framed, but because their provisions were not being adequately enforced.

Since the Dyefin / Mariannridge WWTW system was no longer available for study, it was decided in 2009 to turn to the JMV Textiles / Verulam WWTW system. A new treatment plant at Verulam was commissioned towards the end of 2009, which had been provided with a much more comprehensive instrumentation and control system that is much more advanced than most other WWTWs in South Africa. A study at JMV Textiles in 2009 resulted in a mass-balance model of the factory which predicted the quantity and composition of effluent from their production schedule.

The development of a baseline model for the Verulam WWTW was hampered by major difficulties in characterising the wastewater that it receives. The MScEng student who was investigating the use of respirometry for characterising the biogradable fractions left the programme without completing. The first extension of the project, at the end of 2010, was requested to allow more time to solve the measurement problems. There were indications that the presence of some industrial components might be interfering with the measurements, but, without a student devoted to the topic, it was not easy to establish exactly where the problem lay.

It was anticipated that the JMV effluent discharge permit application would be processed during 2011, however personnel capacity constraints in the EWS Pollution and Environment department prevented them from undertaking it. The project was therefore extended once again for 2012. An EWS engineer, Avesh Ramburan was allocated to the task, and registered as a part-time MScEng student. Unfortunately for the project, he accepted a more remunerative job, and left EWS before completing the investigation as envisaged in his MScEng project. However, because his leaving would once again leave JMV Textiles with their permit application unprocessed, the permit was granted without engaging fully with the quantitative risk assessment protocol that was the topic of this research project.

Meanwhile, the modelling of the Verulam WWTW also ran into serious difficulties. It was also proposed as part part-time MScEng project for another EWS engineer, Akash Singh, and significant progress was made with setting up the simulation model and gathering and interpreting plant data. However, a satisfactory and consistent characterisation of the incoming wastewater could not be achieved. There appeared to be two main reasons for this. The first was that the composition of the Verulam wastewater was extremely variable: no two samples appeared to resemble each other. The second was that it appears that measurement of oxygen utilisation rate on the respirometry apparatus that we were using, which was our main characterisation tool, is seriously affected by some constituents of the wastewater. These two issues constituted a serious setback to the conceptual and experimental basis of our research methodology.

South African industrial effluent permit systems

A comparison of the permitting systems administered by SA municipalities was undertaken in 2007. A questionnaire was sent to 37 municipalities requesting some basic information about their industrial effluent permit systems. Replies were received from 12 (32%, excluding eThekwini). Those that have sent replies include all the larger industrial centres.

The replies to the questionnaire were analysed in terms of the experience of dealing with industrial effluents that existed in each municipality, and the sophistication of the permit system which had been developed in response. According to these scores, eThekwini appeared to have the most sophisticated system, based on the most experience of dealing with industrial effluents, followed by Ekurhuleni, then Nelson Mandela, Buffalo and Uthukela. There were some surprises in the ranking of municipalities according to these scores, with some larger municipalities ranking lower than one might have guessed (for instance Johannesburg and Tshwane). However, these municipalities indicated that their WWTWs experience few problems associated with industrial effluents, which suggests that the more sophisticated permit systems have evolved in response to more problematic effluents.

Baseline wastewater treatment models

Most wastewater treatment plants were originally designed for the treatment of domestic wastewater. The presence of industrial wastewater introduces various difficulties in the treatment process due to the complex and varying nature of the industrial wastewater.

Developing a simulation model for a wastewater treatment plant and calibrating it against plant operating data should allow the response of the wastewater treatment plant to a particular wastewater to be evaluated. For this application, the model needs to be able represent the performance of the WWTP while treating the combined influent received from its catchment.

Baseline models were developed for two WWTPs in the eThekwini municipality: Mariannridge and Verulam. Both were selected because they received a significant proportion (approximately 30% by volume) of industrial effluent, and because they experienced significant problems associated with textile effluent, primarily high colour and conductivity.

For Mariannridge, characterisation of the incoming wastewater was accomplished largely through the use respirometry (oxygen utilisation rate) measurements to fractionate the incoming COD into the categories required for modelling. However, in the case of Verulam it was found that substances present in the wastewater (presumably of industrial origin) interfered with the functioning of the respirometer, and invalidated the measurements. Consequently, a method was developed to estimate the wastewater characteristics based on the flow balance on the WWTPs catchment, using data on the major industrial sources drawn from records kept as part of the municipality's permit system.

Laboratory methods for WWTP feed characterisation

The objective of influent wastewater characterisation is to determine the volumes and concentration of the carbon, nitrogen, phosphorus and other constituents present in the wastewater entering the WWTP. Characterisation of the effluent leaving the wastewater treatment plant provides a way to assess the extent to which transformations of the wastewater constituents occur, in relation to achieving the required effluent standards. The measurements required to support WWTP modelling are much more intensive than those generally used to monitor their operation.

The combination of respirometry and COD measurements was the main focus of the laboratory work in this project. For most of the other measurements, such as ADMI colour, conductivity and metal determinations, results from the municipal analytical service were used. The respirometry apparatus that was used was the one developed by the University of Cape Town, which has been used extensively by the UCT Water Research Group, and is generally considered to give reliable results. However, the experience of this project was that it was not possible to obtain consistent and reliable results. The investigation into biodegradability of surfactants suggested that the problem was interference with the DO electrode by concentrations of surfactants encountered in the wastewater which had high proportions of textile effluent. Unfortunately the realisation of the problem came too late for a different system to be tried. There are respirometers that used a closed reactor, and measure the oxygen concentration in the gas phase rather than the aqueous phase, which would not be subject to this kind of interference.

Attempts to transfer the OUR measurement techniques to municipal staff met with very little success. Obviously this was partly due to the problems with the reliability of the technique, but it also had a lot to do with the unavailability of technical staff with the required level of skill, patience and time to devote to such a time-consuming measurement.

Laboratory testing of textile effluents

Effluent from textile wet finishing operations typically has BOD and COD values that are above generally accepted levels for discharge to sewer, with significant contributions from detergents and softeners Textile wastewater composition varies frequently and markedly. It has been observed that a change in the surfactant content of such wastewater can affect the COD removal efficiency.

SAlkyl-phenol oxylates (non-ionic surfactacts commonly used in textile processing) have intermediate degradation products with an aromatic group that is more difficult to bio-degrade. Consequently, textile effluent COD may be more slightly difficult to treat than normal sewage, not necessarily in terms of ultimate biodegradability, but in terms of the rate at which degradation takes place.

Several series of tests were carried out to establish a methodology for assessing the biodegradability of surfactants using the OUR apparatus available to us, but these failed to provide consistent and reliable results. It appeared that the surfactant interfered with the response of the dissolved oxygen electrode, causing it to give incorrect oxygen utilisation rate results.

The interference by surfactants in textile effluents in the oxygen utilisation rate measurement also prevented us from obtaining reliable indicators of whether textile effluents inhibit the activated sludge process. However no indications have been found in the literature of such inhibition.

Textile effluents contain a variety of highly coloured components, depending on the combination of processes that give rise to them. From a WWTP point of view, these can be divided into two broad classes, particulate and soluble. Two laboratory studies on the removal of representative particulate and soluble dyes by activated sludge were carried out in order to provide a basis for a model of colour removal in a WWTP.

The activated sludge process removes azo dyes from wastewater to a small extent. The mechanism for this appears to be physical adsorption onto the sludge, with the adsorptive capacity of actively growing sludge a little higher than for inactive sludge. The adsorption rates are such that equilibrium is attained within approximately 1 hour, which is substantially faster than other processes in the activated sludge process. Consequently an accurate kinetic model of the adsorption process is not necessary.

The integrated effluent evaluation protocol

The project plan envisaged that the entire protocol would be tested in a case study which would be undertaken as part of the process of granting an actual effluent discharge permit to a textile factory. However, for reasons that were not all within the control of the research project the case study could not be completed. The factory that was originally chose (Dyefin in Westmead) closed down. JMV Textiles in Verulam was then chosen as a substitute, but because the pollution officer assigned to the permit investigation left the employ of the municipality, the permit was granted hurriedly, without involving the proposed protocol. So this report is only able to present the preliminary investigations that were part of the envisaged protocol

A spreadsheet model of the process was developed which could be used to predict the quantity and composition of textile effluent from the factory's production schedule, based on dyeing 'recipes' provided by the factory. The model predictions have been partially validated by comparing the predicted and measured cumulative frequency distributions of conductivity in the factory effluent.

Discussion

The principal reasons for not completing the main objective of achieving a fully tested evaluation protocol were:

1. The closure of Dyefin, the first factory selected, which discharged to the Mariannridge WWTP. This meant that the baseline model developed for Mariannridge could not be used, and a new one developed from Verulam.
2. The problems encountered with the unreliability of the respirometry measurements on wastewater entering the Verulam plant. The impact of this factor on the overall project was aggravated because it was only realized so late, because the MSc project to establish the technique had not progressed.
3. The problems with personnel capacity at the municipality, which caused long delays in undertaking a permit evaluation on the JMV Textiles factory, and then its abrupt termination.

The positive developments that were achieved during the project were:

1. A much deeper understanding of the complex issues surrounding the treatment of industrial wastewater in conventional municipal WWTPs.
2. A body of experience in the modelling of WWTPs, although not complete, particular in relation to treating industrial effluents.
3. A body of experience, similarly incomplete, in respirometry and other laboratory techniques for characterising industrial wastewater for modelling purposes.
4. A production based model of effluent generation in a textile factory.
5. A promising, material balance approach to characterizing wastewater in an industrial catchment, which appears to provide a much more effective alternative to the laboratory based approach which was pursued for most of the project.

6. A greater appreciations on the part of the municipality of the potential, the limitations and the resource requirements of WWTP modelling.

Conclusions and recommendations

The potential advantages of modelling for design, optimisation and control of WWTPS are well documented. However, to realise these requires a critical mass of expertise, in both the computational and analytical aspects. It is clear that these requirements were seriously underestimated, firstly in the matter of the research project, but perhaps more critically in terms of what municipalities are able to devote to the technology. Their ability to attract and retain sufficient staff with the requisite skills is severely limited, and those they have are needed for more immediate urgent responsibilities. On the other hand, there is a perception within the municipality that they need to develop in-house modelling competency to meet their future needs. This project has turned out to be too ambitious, with too many aspects that needed to be developed simultaneously.

Although the project was motivated by a perceived need of the municipality to develop a more scientifically defensible basis for setting permit limits, there seems little chance that they would be able to implement such a complex protocol in-house in the near future. The obvious alternative would be to set up a specialist consultant service, with integrated laboratory and computational capabilities. This possibility has been discussed with the municipality, and there is a proposal to establish a laboratory service along these lines as part of the MOU between the municipality and the university.

A follow-up project (WRC K5/2221) has just started, which will provide a vehicle for continuing the development of WWTW modelling. How it is conducted will be informed by the experiences gained in this project. The proposed methodology and deliverables are formulated in sufficiently broad terms that they do not need to be re-formulated, but the following issues should be emphasised:

Research issues

1. Investigation of more robust and reliable laboratory methods for wastewater characterisation.
2. The further development of influent wastewater characterisation using a combination of catchment balance and laboratory measurements.

Technology transfer issues

3. Training of municipal staff in setting up and using WWTW models.
4. Establishing a sustainable system for providing modelling services to municipalities.
5. Establishing a sustainable system for providing the supporting laboratory investigations.

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Mr P Gaydon	Umgeni Water
Mr R McInerney	Durban Chamber of Business
Mr D Louw	Erwat
Mr J Mnisi	Johannesburg Water (Pty) Ltd
Mr A Van Rooyen	Johannesburg Water (Pty) Ltd
Mr C Fennemore	eThekwini Water and Sanitation
Mr LR Gravelet-Blondin	Department of Water Affairs and Forestry
Dr K J Riedel	Sasol Technology (Pty) Ltd

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PUBLICATIONS

Conference presentations

MHLANGA FT, BROUCKAERT CJ, FOXON KM, FENNEMORE C, MZULWINI D, and BUCKLEY CA (2008). Development of a simulation model to assess the performance of a wastewater treatment plant. *WISA 2008 Sun City, May 18-22, 2008*

MZULWINI D, BROUCKAERT CJ, FENNEMORE C and BUCKLEY CA (2008). A critical evaluation of the industrial effluent system used by the eThekwini municipality. *WISA 2008 Sun City, May 18-22, 2008*

BROUCKAERT CJ, MHLANGA FT and BUCKLEY CA (2010). A protocol for the quantitative assessment of industrial effluents for discharge permitting. *South African Industrial Water Division of WISA Conference, 3 – 4 November 2010, Maccauvlei, Vereeniging*.

MHLANGA FT, BROUCKAERT CJ, FENNEMORE C, and BUCKLEY CA (2012). Influent characterisation of wastewater from wastewater treatment plants receiving industrial effluent. *WISA 2012 Cape Town, May 5-9, 2012*

Journal publications

MHLANGA FT, BROUCKAERT CJ, FOXON KM, FENNEMORE C, MZULWINI D, and BUCKLEY CA (2009). Simulation of a wastewater treatment plant receiving industrial effluents. *Water SA* **35**(4) 447-454

BROUCKAERT CJ, MHLANGA FT, FOXON KM, FENNEMORE C, MZULWINI D, and BUCKLEY CA. (2009) A protocol to assess the impact of industrial effluents on wastewater treatment plants. *Chemical Technology, October 2009.*

MHLANGA FT, and BROUCKAERT CJ (2013). Characterisation of wastewater for modelling of wastewater treatment plants receiving industrial effluent. *WaterSA, in press.*

CAPACITY BUILDING

Students

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First name: Farai	**Surname:** Mhlanga
ID or Passport Number:	
Country of origin: Zimbabwe	**Citizenship:** Zimbabwe
Gender: Male	**Race:** Black
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First name: Farai	**Surname:** Mhlanga
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First name: Arnold	**Surname:** Mashava
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Gender: Male	**Race:** Black
Institution: University of KwaZulu-Natal	**Degree:** MScEng

2007-2008

First name: David	**Surname:** Mzulwini
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Country of origin: South Africa	**Citizenship:** South African
Gender: Male	**Race:** Black
Institution: University of KwaZulu-Natal	**Degree:** MScEng

2007-2008

First name: Kavisha	**Surname:** Nandhlal
ID or Passport Number:	
Country of origin: South Africa	**Citizenship:** South African
Gender: Female	**Race:** Indian
Institution: University of KwaZulu-Natal	**Degree:** BScEng (Chemical)

Technology transfer initiatives

1. **Workshop** on "Standard setting in Municipalities", Paradise Valley, Westville, 29-30 November 2007.

   The workshop drew 17 delegates from municipalities around South Africa.

2. **Oxygen utilisation rate measurement**: training for eThekwini and Umgeni Water laboratory staff.

3. **WEST modelling**: training for eThekwini and Umgeni Water staff.

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ACRONYMS

ADMI	American Dye Manufacturers Institute (colour unit).
ASM1, ASM3	IWA Activated sludge models No. 1 and No. 3.
COD	Chemical oxygen demand.
DO	Dissolved oxygen.
EWS	eThekwini Water and Sanitation.
IWA	International Water Association.
OUR	Oxygen utilisation rate.
TSS	Total suspended solids.
VSS	Volatile suspended solids.
WEST	Worldwide engine for simulation and training.
WWTP / WWTW	Wastewater treatment plant / works.

1 INTRODUCTION AND OBJECTIVES

The major elements that the local authority has for managing industrial wastewater are its wastewater treatment plants for remediation, discharge permits for placing limits on what may be discharged, and a discharge tariff for financing the treatment and for providing a set of incentives and penalties to influence users of the system. An optimal management strategy will use all these elements in the proper relation to one another. However, the relationships are complex and poorly understood because of the complex and variable nature of both the multitude of effluents discharged from industries, and the response of the biological processes to them.

An effluent discharge permit consequently is a crucial interface between the local authority and an industry, and the permit system has to carefully balance protection of the general public and the environment against the rights of those working in industry and the promotion of economic activity.

The Constitution of the Republic of South Africa No. 108 of 1996 has through section 33 of the Bill of Rights strived to ensure efficient administration. It guarantees that everyone has a right to administrative action that is lawful, reasonable and procedurally fair. The Promotion of Administrative Justice Act 2000 was enacted to give clearer legislative power to ensure this Constitutional right. While the Act refers to several aspects of administrative justice it is specifically the sections dealing with the duty of any organ of state in control of an administrative action to give reasons (Section 5) and the remedies in proceedings for judicial review (Section 8) where orders to give reasons may be given, which is applicable to the standards setting process for industrial discharges to sewer.

All municipal Bylaws in South Africa need to be codified as per requirements of the Local Government: Municipal Structures Act, 1998 and the Local Government: Municipal Systems Act, 2000. Any new legislation must be incorporated into Municipal Bylaws to ensure that these are compliant with national legislation. As such the eThekwini Municipality has embarked on the codification of its Bylaws, which are currently in draft form for comment. However important to note is the golden thread of administrative justice which is now embodied in all actions of municipal officials, for example permitting of industries to discharge industrial effluent. Therefore the due process to issue a permit includes very strongly the giving of reasons for decisions taken. The White Paper on Integrated Pollution Control and Waste Management, 2000 requires all activities to control pollution to relate source control strategies and regulation directly to the resource it serves.

The activated sludge process is the most common form of treatment for municipal wastewater in South Africa. Because biomass is retained in the process, it evolves a population of microorganisms which are specifically adapted to degrading the substrates that are presented to it by the local sources of wastewater. This means that industrial effluent can often be accommodated up to a point without compromising the quality of the treated water. The broad objective of this project was to develop a methodology for predicting this point with sufficient reliability to be useful in setting discharge limits for industrial effluents.

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2 SOUTH AFRICAN INDUSTRIAL EFFLUENT PERMIT SYSTEMS

This chapter consists chiefly of a description of the eThekwini Industrial Effluent permitting system, but includes a brief comparison with a sample of other South African municipalities. A comparison of the permitting systems administered by SA municipalities was undertaken in 2007. A questionnaire was sent to a 37 municipalities requesting some basic information about their industrial effluent permit systems. Replies were received from 12 (32%, excluding eThekwini). Those that have sent replies include all the larger industrial centres.

2.1 The eThekwini permit system

The target outcomes to be achieved through the permitting process are:

- A clean and safe and sustainable environment
- Each person is treated in a fair and transparent manner.
- Environmental impacts are identified, prevented or steadily reduced.
- The cost or remedying or preventing or reducing an environmental impact is paid by the person causing it.

eThekwini has, in effect, a dual system. A new and very comprehensive system was introduced in 2004, but has been introduced gradually to larger industrial effluent producers. For smaller water users, an older and less elaborate system is applied.

2.1.1 The permit system for smaller users

The municipal area is divided into 3 zones (North, West and South), with 14 sub-zones each with a Water Quality Officer (WQO). The areas are adjusted according to the factories within them, to achieve approximately equal workloads for the WQOs. Each sub-zone is inspected regularly (approximately once a week) for new water using industries.

Once such a new water user has been identified, a formal procedure is initiated that leads to the issuing of a discharge permit.

The user completes a questionnaire giving company details and water and electricity account numbers (part 1), and a water balance, excluding domestic use (part 2).

1. The municipality undertakes a programme of compliance sampling to measure Chemical Oxygen Demand (COD), settleable solids (SS), pH and other restricted determinands as set out in the municipal bylaws.
2. If the user’s effluent is found to be non-compliant, a notification is issued, which must indicate the probable cause of the non-compliance and suggest appropriate corrective measures.
3. The notification initiates a permit negotiation process between the user and the municipality. The goal of this negotiation is agreement on a programme, which is primarily set by the company, which will lead to compliance. The programme is required to set out the measures that are required, and the timeframe for implementation.
4. To allow the company to operate during the implementation of the programme, there is a conditional legalisation of the effluent discharge. This specifies the applicable relaxations of the bylaws, which are conditional on movement towards compliance, which is monitored by monthly sampling and reports on out-of-limit incidents.
5. Once compliance is achieved, the permit is issued, which may specify limits on volume and concentrations or loads of specific restricted pollutants, and in certain cases relaxations of the

bylaws. Where it is deemed necessary, the permit may specify that compliance reports must be submitted.

6. The effluent is monitored by regular sampling carried out by municipal inspectors, and analytic results are stored on a Laboratory Information Management System (LIMS) which allow the history of any factory effluent to be examined.

2.1.2 The permit system for larger users

For large and other high-risk industries, a new five-year permitting system was introduced in December 2004 with the aid of the Norwegian Pollution Control Authority (Statens Forurensningstilsyn). It requires that the industry implements elements of an environmental management system. As such, the industry must identify and prioritise its risks, and compile a five-year improvement program to address these risks. The municipality will then assess the program against recognised international benchmarks and incorporate it into the permit. The company's performance will then be measured through reporting mechanisms, compliance monitoring and annual audits.

2.1.2.1 Sections of the permit

The permit has 7 sections:

2.1.2.1.1 General conditions

- The authority under which the permit is issued – normally the local sewage disposal bylaws.
- The legal sanctions for non-compliance.
- Buildings, processes and plant may not be changed without approval.
- Discharges to sewer, stormwater or groundwater must be controlled.
- Emission Limit Values (ELVs) are set in consultation with the company.
- There is a requirement to establish an Environmental Management System with a 5 year improvement plan.
- Annual performance review meetings must be held.
- Change of ownership or decommissioning must be managed to prevent adverse environmental impacts.

2.1.2.1.2 Production and chemicals used

- Maximum permitted production capacity is specified.
- Registers of substances used and Material Safety Data Sheets (MSDSs) must be maintained.
- Substances must be evaluated for harmful effects, and continuous improvement must be demonstrated.
- Cleaner Production (CP) principles must be followed and reported at the annual meeting. CP projects must be included in the 5 year plan.
- Energy Conservation. The permit holder shall evaluate its activities in order to improve energy utilisation and efficiency.

2.1.2.1.3 Discharges to Sewer: Permitting the Quality and Quantity.

This section is specific to the company concerned and must provide:

- Discharge limit values with respect to quantity and quality.

- Specific improvement targets required for the factory in order to reduce its impact.

2.1.2.1.4 Objectionable Discharges to Stormwater or Groundwater.

Generic requirements include:

- Compliance with national and local legislation.
- All borehole or river water used, excepting that supplied by the local authority must be registered with the Department of Water Affairs and Forestry (DWAF)
- The company has the duty to educate and inform employees about the environmental risks of their work and to take reasonable action to evaluate and reduce impacts,
- Separation of Stormwater and trade effluent
- Initiating a 5 year improvement plan to improve quality of storm-water.

2.1.2.1.5 Waste

- An annual waste study must be conducted and the report submitted together with the Annual Report, covering both solid and liquid wastes,
- Waste Storage and Transport. An adequately designed waste storage facility must be provided.
- Transporters must have legal permits.

2.1.2.1.6 Emergency Response and Contingency Plan

Following any emergency incident involving a major emission potentially leading to serious pollution, a permit holder must:

- immediately report the incident, including the risks and steps taken to minimise the effects.
- conduct an assessment of the actual impacts.

2.1.2.1.7 Annual Reporting

The permit holder must submit an annual report to the Authority detailing:

- Trade Effluent: volumes, analysis and compliance.
- Stormwater and Groundwater: all objectionable discharges, together with incident reports.
- Waste Audits
- The 5 year Environmental Plan and progress reports, detailing Cleaner Production initiatives.

2.1.2.2 The permitting process

Permits are either issued for a one year period or a five year period. A one year period is allocated for the complete permitting process, for both the new applicants and renewals. The process essentially involves the company submitting an application, which initiates a negotiation, to set the permit conditions and discharge standards. It can be broken down into the following steps:

1. The application has 11 modules, and up to 5 months are allocated to completing it, with the assistance of the municipality.

2. The municipality reviews the application, and may request additional information (up to 3 months).

3. The application is then assessed in the following terms:

- impact on the receiving environment;

- a Best Available Technology (BAT) review;
- identifying key pollutants;
- conducting a site inspection;
- setting targets for improvement;
- setting emission limit values (ELVs) in consultation with the company ;
- setting a monitoring programme.

4. The permit is then issued.

2.1.2.3 Annual Performance Review

The Annual Performance Review Meeting (APR) is a requirement of the permit issued to a company. Information required of the company to present at the APR meeting is pre-specified in a letter, and failure to submit the required information for the APR could result in suspension of the permit. The APR addresses the generic permit outcomes of continuous improvement, the responsibility of the local authority to ensure a clean, safe and sustainable environment, and for the requirement that the polluter pays.

- The APR serves as an annual check upon the company's compliance with all aspects of the permit.
- Changes in tariffs or permit conditions are discussed at the APR meeting.
- A Permit Inspection Report is provided by the Inspecting Official. The scope of the report includes the relevant site conditions referred to in the permit, such as the stormwater drainage, the process and process areas, the raw material, chemicals and product storage areas, together with the effluent conditions, waste minimisation status, and the environmental management systems.

2.1.2.4 Inspections and audits

In inspection involves a site visit, whereas and audit concerns only documentation. These are carried out once a year or when a special need arises.

2.2 Comparisons between municipalities

A questionnaire was sent to a 37 municipalities requesting some basic information about their industrial effluent permit systems. Replies were received from 12 (32%, excluding eThekwini). Those that have sent replies include most of the larger industrial centres.

Table 2.1 represents a simple analysis of the replies received. In Table 2.1, the first 2 rows present the numbers of wastewater treatment works in the respective municipalities and the number that receive industrial effluent. All the other entries represent the presence or absence of a particular feature in the permitting system, with 1 signifying that the feature is present, 0 that it is absent, and 0.5 that it is present with some qualification; for example, in the row for ‘Regular permit reviews’, 0.5 means that the permits of certain companies within the municipality are reviewed regularly, but others are not.

The last two rows present aggregated scores for each municipality. “Sophistication’ is just the total of the entries representing features of the permit system, and ‘Experience’ is the sophistication score multiplied by the number of WWTPs that receive industrial effluents. According to these scores, eThekwini appears to have the most sophisticated system, based on the most experience of dealing with industrial effluents, followed by Ekurhuleni. There are some surprises in the ranking of municipalities according to these scores, with some larger municipalities ranking lower than one might have guessed (for instance Johannesburg and Tshwane). However, these municipalities indicated that their WWTPs experience few problems associated with industrial effluents, which suggests that the more sophisticated permit systems have evolved in response to more problematic effluents.

The last two columns are aggregated scores for each feature. Thus, for example, 100% of the responding municipalities have laboratories supporting pollution monitoring, and 27% provide training for their staff in administration of their permit systems.

Table 2.1: Comparison of South African municipal effluent discharge permitting systems.

	eThekwini	Ekurhuleni	Nelson Mandela	Buffalo	Cape Town	Jo'burg	Uthukela	Tshwane	Umsunduzi	George	Drakenstein	Mhlatuze	Total	%
No of WWTPs	30	9	6	12	22	6	18	9	2	4	6	4	128	
No WWTPs receiving IE	10	9	5	5	5	6	4	5	2	2	2	2	57	
IE problems	1	1	0.5	1	1	0.5	0.5	0	1	0.5	0	0.5	7.5	64
Laboratory	1	1	1	1	1	1	1	1	1	1	1	1	12	100
LIMS	1	1	1	0.5	1	1	1	0	1	0	0	0	7.5	68
Inspectors	1	1	1	1	1	1	1	1	1	0	1	0	10	91
Factory inspections	1	1	1	1	1	1	1	1	1	1	0	0	10	91
Pollution investigations	1	1	1	1	1	0.5	1	1	1	1	1	0	10.5	95
Permit system	1	1	1	1	1	1	1	0	1	1	1	1	11	91
Negotiatied permits	1	1	1	0.5	0.5	0	1	0	1	0	0	1	7	55
Regular permit reviews	1	1	1	1	0.5	0	1	0	1	0	0	0	6.5	59
Volumetric limits	1	1	1	0	0	0	0.5	0	1	1	0	1	6.5	50
Pollutant limits	1	1	1	1	1	1	1	1	1	0	1	1	11	91
Limits according to WWTP	0.5	0	1	0	0	0	0	0	1	0	0	0	2.5	23
EMS required	0.5	0	0	0	0	0	0	0	0	0	0	0	0.5	5
Continuing improvement	0.5	1	0	0.5	0.5	0	1	0	1	1	0	0	5.5	50
Compliance assistance	1	1	0.5	1	1	0	1	1	1	1	1	0	9.5	86
Permit system training	1	0	0	1	0	0	0	1	0	0	0	0	3	27
Permit system documentation	1	0.5	0	1	0	1	0	0	1	0	0	0	4.5	41
Sophistication	14.5	12.5	11.5	11.5	9.5	7.5	11.5	7	14	7	6	5		
Experience	145	112.5	57.5	57.5	47.5	45	46	35	28	14	12	10		

3 BASELINE WASTEWATER TREATMENT MODEL

One of the consequences industrialisation is the generation of industrial wastewater which requires treatment before being released into the natural aquatic environment. Most wastewater treatment plants were originally designed for the treatment of domestic wastewater. The presence of industrial wastewater introduces various difficulties in the treatment process due to the complex and varying nature of the industrial wastewater.

A method needs to be developed that will allow the municipality to evaluate if a wastewater treatment plant can adequately treat a particular composition or type of wastewater to a quality suitable for release to the environment. Developing a simulation model for a wastewater treatment plant and calibrating it against plant operating data should allow the response of the wastewater treatment plant to a particular wastewater to be evaluated.

For this application, the model needs to be able represent the performance of the WWTP while treating the combined influent received from its catchment. Typically this will include domestic sewage together with the industrial effluent generated by all the factories in the catchment. To avoid having to individually characterise effluents from all the other factories in order to evaluate the effect of the one of interest, the *baseline model* is based on experimental characterisation of the combined feed to the WWTP.

The modelling of biological wastewater treatment systems has developed from fundamental concepts to mathematical models. The IAWPRC, later IAWQ and now IWA (International Water Association) task Group (Henze et al., 1987, 2000) has introduced an activated sludge model suit, which provides researchers and practitioners with a standard set of basic models for biological wastewater treatment processes. The first model developed for municipal activated sludge WWTPs was the Activated Sludge Model No. 1 (ASM1) (Henze et al., 1987). It describes the removal of organic carbon compounds and ammonia-nitrogen, with facultative consumption of oxygen or nitrate as the electron acceptor, depending on the conditions in the activated sludge system. Other models, ASM2 (Henze et al., 1995) and ASM2d (Henze et al., 1999), which include chemical precipitation processes and phosphorus removal, have also been developed. To correct a number of shortcomings of the ASM1 model, the ASM3 model (Gujer et al., 1999) was developed based on the ASM1 model. ASM3 was used to model the Mariannridge WWTP.

3.1 The Mariannridge WWTP

The Mariannridge WWTP has a sister plant on the same site called Shallcross WWTP. These two parallel plants make up what is known as the Umhlatuzana Works. Mariannridge receives an average of 8 000 m^3/d wastewater of which about 30% is industrial and 70% domestic, while Shallcross receives an average of 2 000 m^3/d which is entirely domestic wastewater. The layout of Mariannridge WWTP is shown in Figure 3.1.

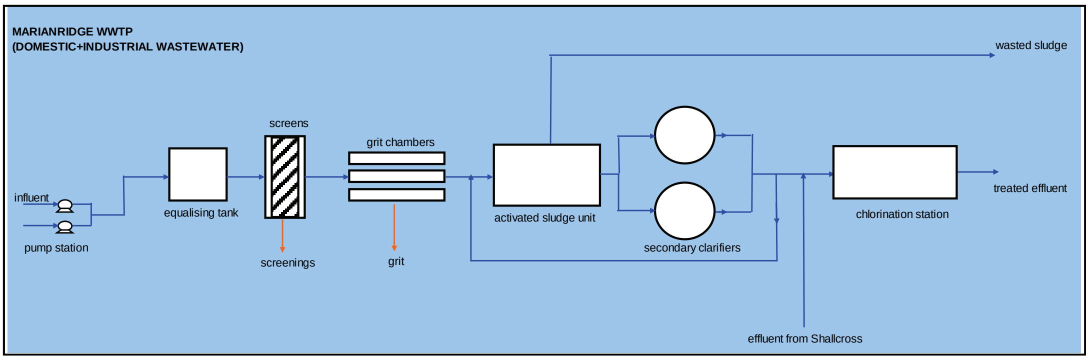

Figure 3.1: Flow diagram of the Mariannridge WWTP

3.1.1 Site description and layout

Influent is pumped into an equalisation tank, and then screened before going through the grit chambers. From the grit chambers the flow rate is measured before the biological reactor (an extended aeration basin), which is followed by secondary clarification in settling tanks. The effluent from the Mariannridge WWTP is combined with the effluent from Shallcross WWTP and dosed with chlorine before releasing it to the Umhlatuzana River.

3.1.2 Influent characterisation

The mathematical models developed for the simulation of the activated sludge unit of the WWTP are based on the division of wastewater into various fractions (Sperandio et al., 2000). The carbonaceous fraction of wastewater is determined by the COD test. In the ASM3 model the total influent COD of municipal wastewater is divided into seven fractions, as shown in Table 3.1.

Table 3.1: Influent COD fractionation according to ASM3 (for no biological phosphorus removal)

Symbol	Component
S_S	Readily biodegradable substrate
S_I	Soluble inert organics
X_I	Inert, particulate organics
X_S	Slowly biodegradable substrate
X_H	Heterotrophic biomass
X_A	Autotrophic, nitrifying biomass
X_{STO}	Organics stored by heterotrophs

Table 3.2: Historical data of the influent composition - Mariannridge WWTP (NB: This plant does not include biological phosphorus removal)

Component	Average	Minimum	Maximum	Units	No. of samples
Total COD	774	105	2 700	mg O_2/L	291
Total Kjeldahl nitrogen	55	11	80	mg N/L	15
Free ammonia ǂ	25	1	82	mg N/L	325
Nitrate	0.8	0.4	1.6	mg N/L	15
Total phosphate	8	1	15	mg P/L	113
Orthophosphateǂ	9	6	12	mg P/L	15
Settleable solids	18	2	100	mg /L	81
Suspended solids	300	21	1 592	mg /L	62
Total dissolved solids	570	212	934	mg /L	19
Total solidsǂ	1 095	320	2 426	mg/L	48

ǂ Inconsistencies in phosphate and solids statistics reflect inconsistencies in the measurements.

In activated sludge models the division of the influent COD in municipal wastewater is based on biological response in which the response of activated sludge to wastewater is monitored, rather than the difference in molecular size hence the use of a batch respirometric test in this study to determine the readily biodegradable substrate S_S and heterotrophic biomass X_H in the influent wastewater using batch respirometric experiments outlined by Wentzel et al. (1995).

3.1.3 Modelling the WWTP

The scope of the modelling included the activated sludge unit and the secondary settlers. Model simulations were performed using the software package WEST.

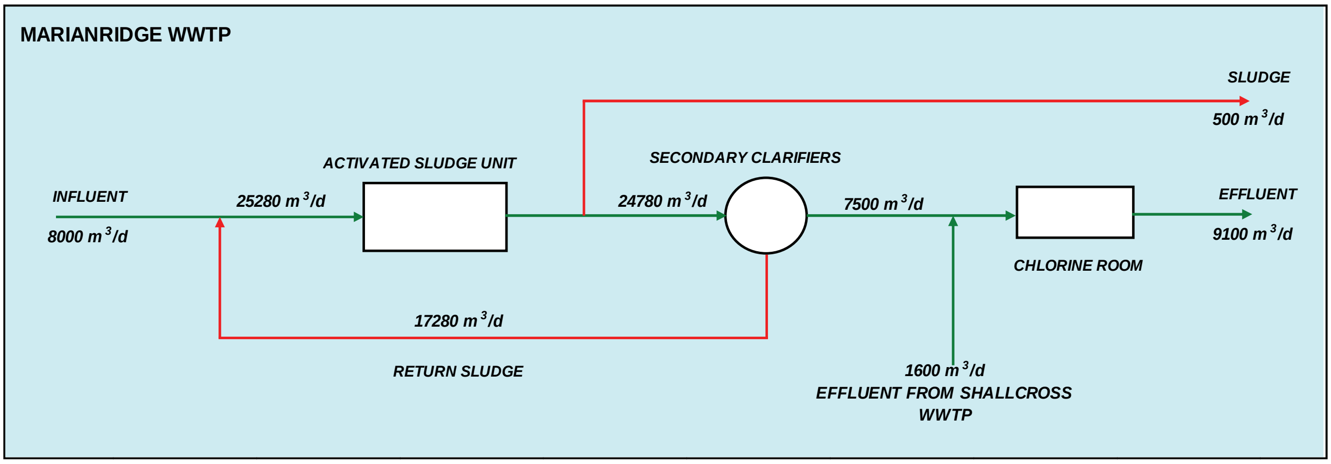

Figure 3.2: Flow balance of the Mariannridge WWTP

Design and operational data were obtained from the plant records of the Mariannridge Plant. The flow balance of the Mariannridge WWTP based on the average influent of 8 000 m^3/d at the head of the works and a recycle stream of 17 280 m^3/d is shown in Fig. 3. The effluent from Mariannridge WWTP is combined with 1 600 m^3/d effluent coming from the Shallcross WWTP. The volume of the activated sludge unit is 13 600 m^3 and it contains 8 aerators each of which deliver 100 kg O_2/h. Only 4 aerators run at a time. The volume of the two secondary clarifiers is 2 037 m^3.

For the characterisation of the setter model, measurements of the total suspended solids (TSS) were available for the final combined effluent from both Mariannridge and Shallcross, not for the individual effluents. Therefore the TSS in the Mariannridge effluent stream was estimated by assuming that Mariannridge contribute twice as much suspended solids as the Shallcross Plant, to the final combined effluent. This estimate was based on spot measurements and the greater volumetric loading of the Mariannridge Plant.

The characterisation for the activated sludge biological model combined some values from literature, historical plant operating data and information from laboratory scale experiments carried out on samples of wastewater and activated sludge.

3.1.4 Kinetic and stoichiometric parameters

The sources of the values of reaction kinetic and stoichiometric parameters were literature (Gujer et al., 1999) and laboratory experiments. Batch respirometric experiments were carried out on wastewater and activated sludge samples to determine some of the kinetic and stoichiometric parameters of the model and COD fractions.

3.1.5 Modelling strategy

The modelling of the WWTP was carried out in four steps:

1. creating a configuration for the WWTP in WEST

   running simulations using the default values and experimentally determined model parameters and evaluating the predictions of the model against measured historical data

   calibrating the model by systematically adjusting selected model parameters validation of the model using measured historical data which was not used for model calibration

3.1.6 Results

The results for the COD fractionation of the influent from the Mariannridge WWTP are compared against the typical fractions of South African wastewater by Wentzel and Ekama (2006), in Table 3.3.

The biodegradable COD fractions for the Mariannridge influent are lower than typical values for South African wastewater of domestic origin, as might be expected because of the significant proportion of industrial effluent. The difference between the experimental results and the literature values confirms the need for plant-specific influent characterisation.

Table 3.3: COD fractions of the Mariannridge influent wastewater compared to typical South African wastewater

Symbol	Description	% of Total COD in influent wastewater	
		Mariannridge	SA wastewater
S_I	Soluble inert organics	7.5	7
S_S	Readily biodegradable substrate	18.1	20
X_S	Slowly biodegradable substrate	44.2	60
X_I	Inert particulate organics	15.6	13
X_H	Heterotrophic biomass	14.6	*

**In the guide on the typical South African wastewater by Wentzel and Ekama (2006) the presence of heterotrophic biomass is considered negligible and is ignored because the greater portion of the micro organisms develop in the biological reactor*

3.1.7 The WEST model configuration

The WEST configuration for the Mariannridge WWTP is shown in Figure 3.3.

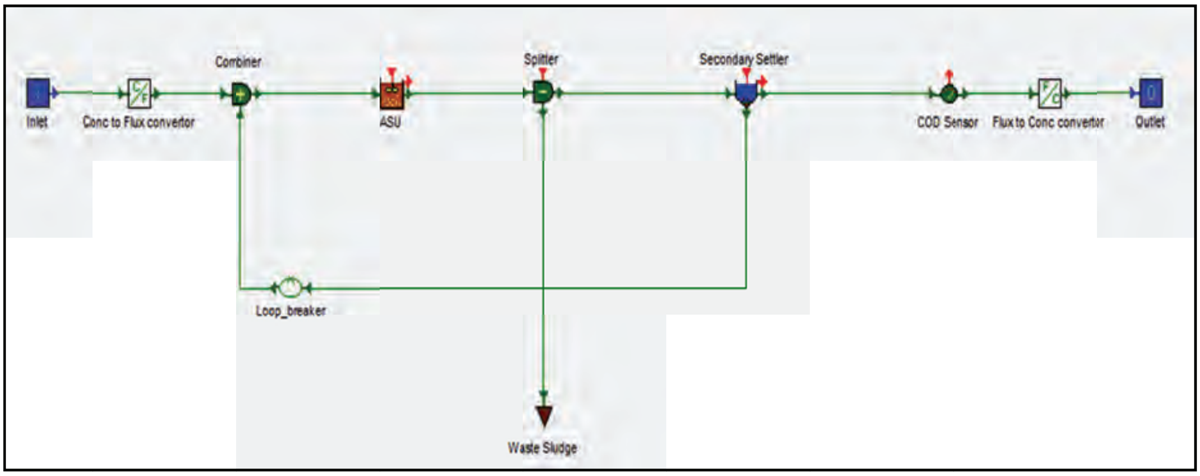

Figure 3.3: The WEST configuration for the Mariannridge WWTP

The configuration consists of the major units of the WWTP, the activated sludge unit (ASU) and the two secondary settlers. The secondary settlers are configured as one unit since it is assumed that they operate in the same way. Combiners and splitters have been added to combine and split flows, respectively. A COD sensor has been added to the outlet stream, to measure the COD concentration of the treated effluent. Convectors in the configuration are used to convert concentrations of constituents in the wastewater to flux values, and flux to concentration values, as required by the following sub-models.

3.1.8 Model calibration

A major difficulty encountered in calibration of activated sludge models is the lack of identifiability of the model parameters, which is the ability to obtain a unique combination of parameters that fit the calibration data (Petersen et al., 2002). More than one combination of influent characterisation and model parameters can give a description of the available data of similar quality (Gernaey et al., 2004) Due to the identifiability problem a stepwise procedure was used, where just a few parameters are changed at a time instead of applying an automatic mathematical optimisation routine. A steady-state calibration was done followed by a dynamic calibration.

3.1.9 Steady state calibration

During the steady-state calibration the model parameters responsible for the long-term behaviour of the activated sludge were adjusted to fit the collected plant data for the sludge total suspended solids concentration. Based on the earlier mentioned assumption that the Mariannridge effluent contributes twice as much suspended solids as the Shallcross WWTP, to the final combined effluent TSS concentration. The non settleable fraction of suspended solids f_{ns} was determined from mass balance of suspended solids across the secondary clarifier. The calculated value was 0.0052.

The measured value of the waste sludge total suspended solids was 456 gSS/m^3. The experimentally determined decay rate constant b_H was adjusted from 0.03/d determined from the laboratory batch tests to 0.27/d (a value close to the default ASM3 value of 0.2 d^{-1}), for the model to be able to match the waste sludge total suspended solids concentration.

3.1.10 Dynamic calibration

During dynamic calibration, selected saturation coefficients and kinetic parameters were adjusted to improve the prediction of effluent total COD and free ammonia concentration in the activated sludge unit. Before adjusting the selected saturation coefficients and kinetic parameters, a sensitivity analysis was done to establish the most sensitive kinetic or model parameters, which have the most significant impact on the chosen variables of concern, the predicted value of the effluent COD or free ammonia in this study.

The simulated effluent COD for the year 2006 after adjusting the model parameters is shown in Fig. 3.4.

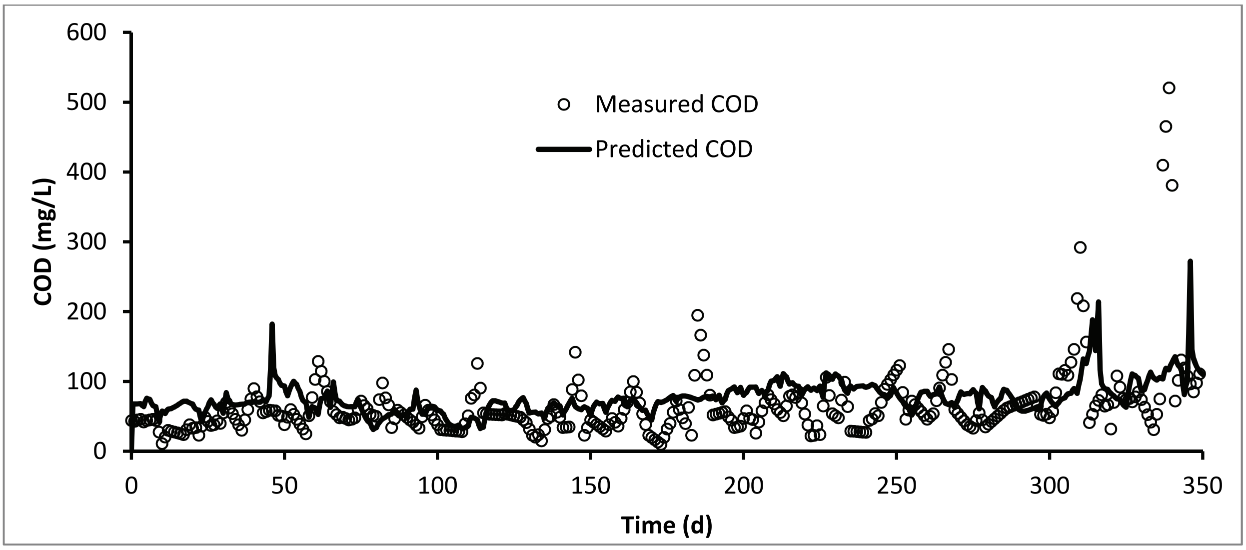

Figure 3.4: Simulation of Effluent COD for the year 2006

The model for the Mariannridge WWTP predicts trends of the effluent COD and the concentration, however it does not follow all the sharp fluctuations that occur in the measured variables. However since the data were taken from routine plant records, it is not known how accurate the extreme values may be. Gaps in the measured data also affect the comparison.

3.1.11 Model validation

After dynamic calibration, validation of the model was carried out using historical data for the year 2007. Validation gives an indication of how well the model can simulate the treatment plant after the calibration effort. Figure 3.5 shows that the calibrated model can simulate the trend and fluctuations of the effluent COD concentration.

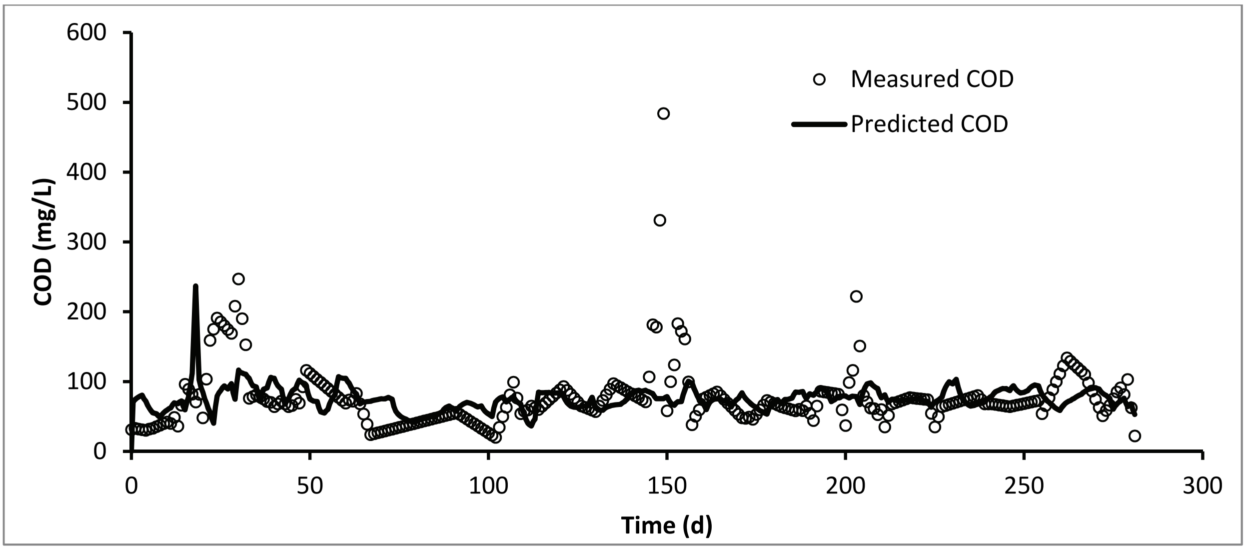

Figure 3.5: Effluent COD simulation after calibration for the year 2007

At the early stages of the simulation, the model indicates a noticeable high peak far from the measured value. This peak is due to a high COD value in the input file based on the measured influent COD. There is no way of being certain whether such individual discrepancies are due to problems with sampling and measurement, or with shortcomings in the model The measured effluent COD does not indicate the peak, only the model shows how the high influent COD reflects in the effluent COD. For the rest of the simulation the model estimates the trends satisfactorily though the peaks during fluctuations turn out to be higher.

3.1.12 Conclusions

The conclusion of this study was focused on two key points:

1. The adequacy of the available data for the modelling of Mariannridge WWTP:

There is need for more reliable and complete plant data with fewer gaps in order to avoid loss of vital information especially for dynamic simulations in the study. Daily measurements of the average total suspended solids concentration leaving with the settler over-flow for a period of 1 year would allow model parameters for the settler model to be determined more accurately which will allow sufficient dynamic calibration to be done on the secondary settler.

The modelling results of the study also indicated that determining the model parameters only for heterotrophic biomass is not sufficient. There is need to carry out experiments to determine model parameters related to the activity of autotrophic biomass.

2. The transferability of experimentally determined model parameters to the model:

The COD fractionation of the influent wastewater based on the OUR measurements, flocculation filtration, and simulation of the batch experiment, on the wastewater, is assessed to be satisfactory for modelling, because of the modelling response achieved even before calibration. Reliable values of the maximum yield of heterotrophic biomass YH, and the maximum specific growth rate for heterotrophic biomass µH, for ASM3 modelling, were determined from the respirometric batch test on composite samples of the influent wastewater. The value of the decay constant of the heterotrophic biomass bH in the activated sludge, determined by monitoring the endogenous respiration of the biomass turned out to be lower than expected suggesting that there was need to repeat the procedure or modify the experimental procedure used. Since it is difficult to determining values of half saturation coefficients from laboratory experiments which are transferable to the model representing the full scale system, the approach of tuning the values of these coefficients during model calibration can be used. If an attempt is made to determine the values of half saturation coefficients using laboratory experiments, the values obtained from the experiments can be used as initial estimates during the calibration procedure.

3.2 The Verulam WWTP

Verulam WWTP is located in Verulam which lies about 40 km north of the Durban. The estimated population of Verulam is over 63,000 (Wikipedia). The town contains densely populated residential and industrial areas. Large farming areas, several built-up townships, and rural townships can be found at the outskirts of Verulam. There are 6 major companies discharging industrial wastewater to Verulam WWTP. The location of the companies relative to the WWTP is shown in Figure 3.6. The list of companies and their core business is presented in Table 3.4

Figure 3.6: Location of the companies discharging industrial effluent to Verulam WWTP

Table 3.4: List of companies and their core business in the catchment area for Verulam WWTP

Company Name	**Core business**
JMV Textiles	Weaving and finishing textiles
Colgate Palm olive	Soap, tooth paste manufacturers
Budget Soap	Soap and detergent manufacturer
Packo	Food products
Nampak Tissue	Hygiene services- tissue paper production
Frimax Foods	Food products, chips

3.2.1 Influent characterisation

The methodology followed during the Mariannridge case study was unsuccessful for the Verulam WWTP. The laboratory investigations failed to produce a consistent characterisation of the influent wastewater, partly because the samples taken showed very different characteristics from each other, and partly because the measurements themselves could not be made consistent. Consequently a different approach was tried, which involved modelling the wastewater generation in the WWTPs catchment, using data from the permit system records maintained by the municipality. The incomplete nature of this data meant that a number of modelling assumptions needed to be made. The calibration of the catchment model and the WWTP model then had to be carried out simultaneously, as the outputs from the WWTP model depended on both its own parameters and those of the catchment model.

3.2.1.1 Trade effluent volumes

Wastewater characteristics depend on the sources within the catchment served by a particular WWTP. The presence of industrial effluents can cause the wastewater to be significantly different from purely domestic effluent. The monthly trade effluent volumes of the major factories in the Verulam catchment show that JMV textiles discharges the most trade effluent volumes of up to 20 000 kL/month followed by Nampak Tissue, Frimax, Packo and Budget Soap. The monthly trade effluent volumes from the Verulam catchment for 2010 and 2011 are presented in Figures 3.7 and 3.8.

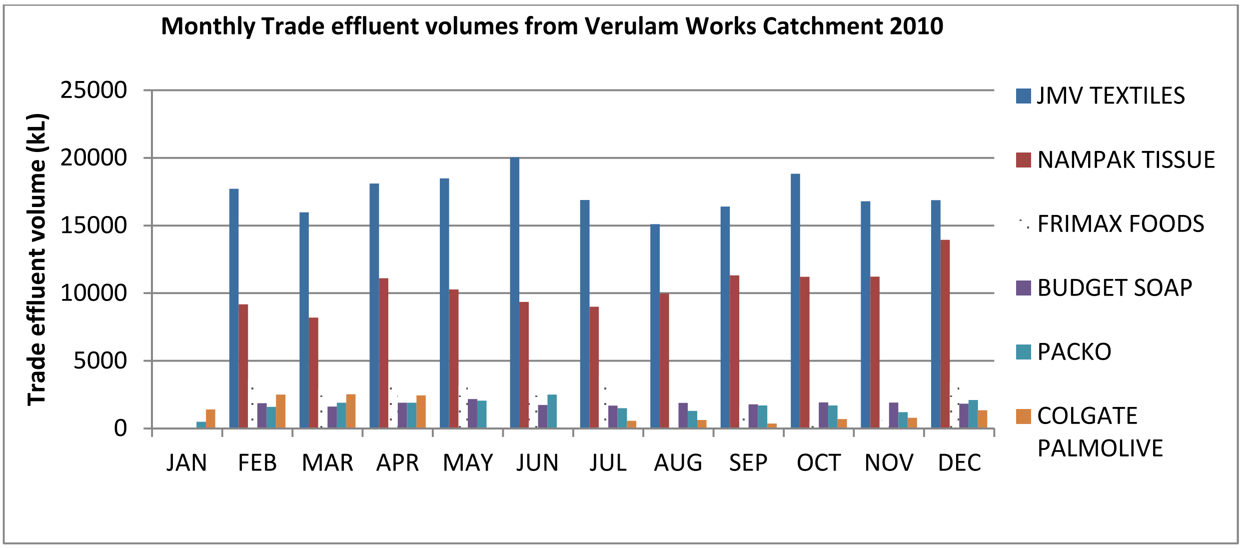

Figure 3.7: Monthly trade effluent volumes from Verulam Works catchment for 2010

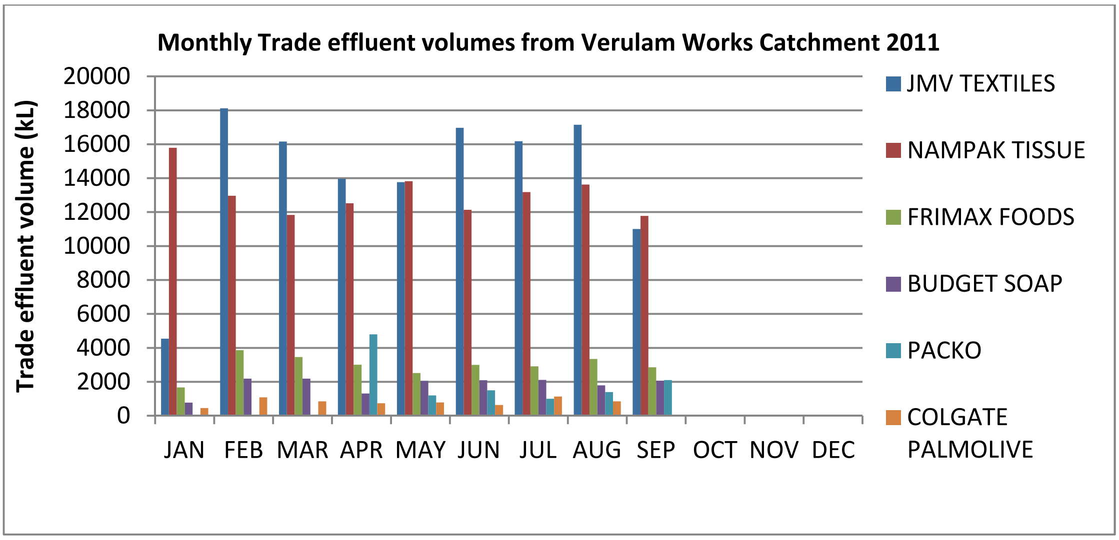

Figure 3.8: Monthly trade effluent volumes from Verulam Works catchment for 2011

3.2.2 Composition of grab samples

The Pollution Division of eThekwini Municipality collects grab samples from the factories as part of regular monitoring of the wastewater produced by each factory in the catchment area. The grab samples are collected and tested for colour (ADMI), COD, conductivity, settleable solids, sulphates, sulphites, sugar, vegetable oils and pH. The JMV textile factory is the only one which is tested for colour since the factory uses dyes in the manufacturing process. The test results obtained from grab samples collected from the JMV factory are presented in Figure 3.9.

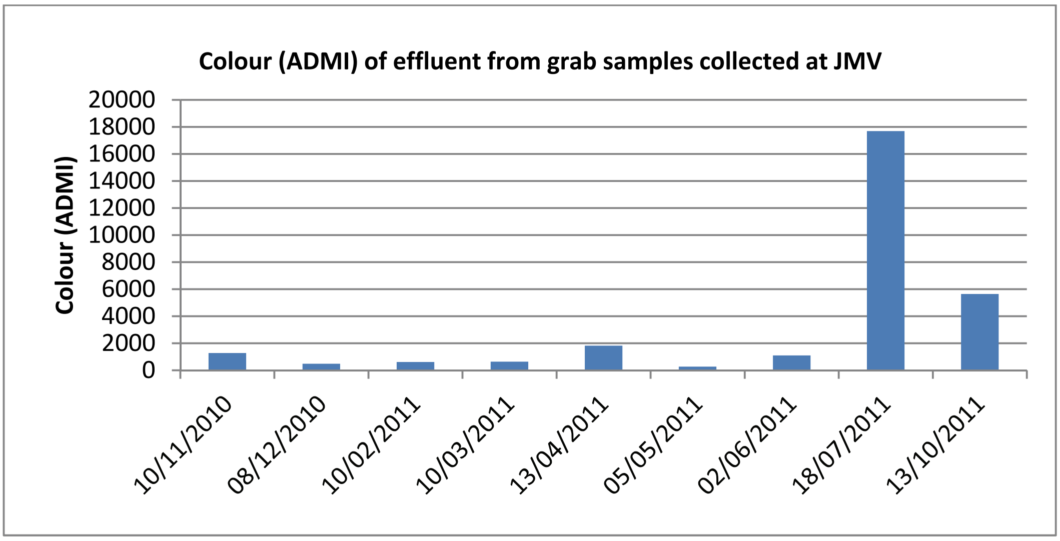

Figure 3.9: Wastewater colour in ADMI of grab samples collected at JMV 2010/2011

Seven out of nine grab samples show that the colour of the wastewater from JMV below 2000 ADMI. Two grab samples out of nine show colours of more than 2000 ADMI.

The total COD and conductivity of the effluent from the factories is also important. The significance of the contribution of COD and conductivity by each factory to the combined wastewater stream going into the WWTP can be quantified by comparing volumes produced and the corresponding concentrations.

The COD and conductivity test results of grab samples collected from factories in Verulam are presented in Figure 3.10 and 3.11. Gaps in the graphs are due to missing data.

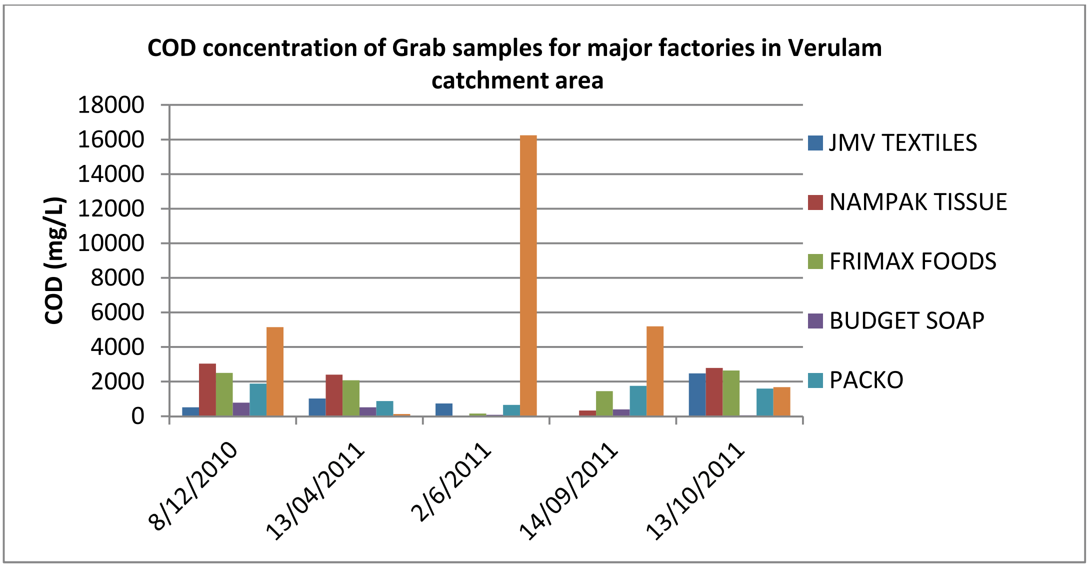

Figure 3.10: COD of wastewater grab samples collected from Verulam Works catchment

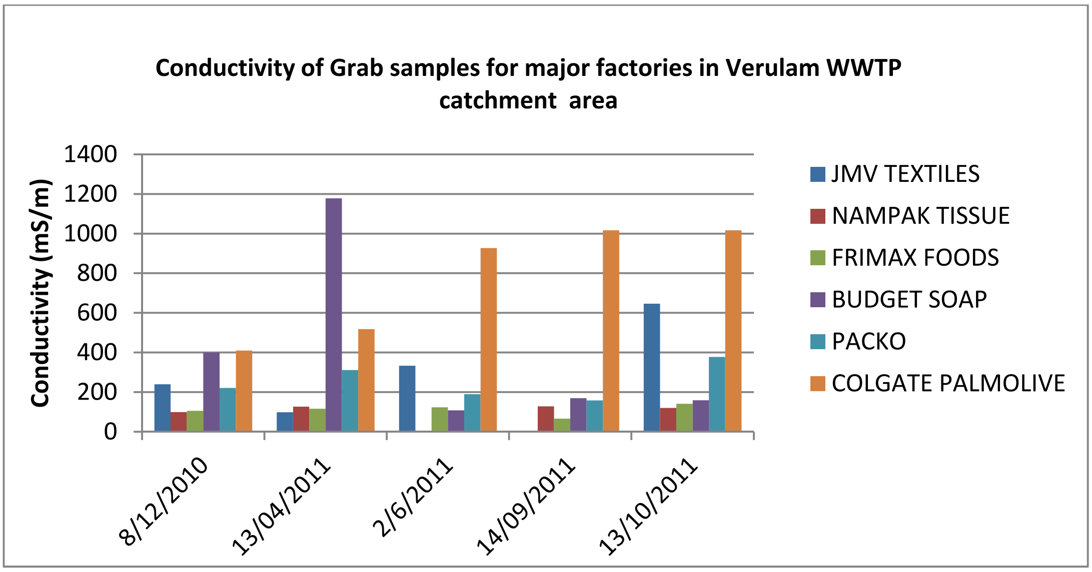

Figure 3.11: Conductivity of wastewater grab samples from Verulam Works catchment

Colgate Palm Olive produces the highest concentration of COD and conductivity but less volume than the bigger factories such JMV and Nampak Tissue. The true COD or conductivity load contributed to the WWTP load is determined from the trade effluent volume and concentration of the wastewater.

3.2.2.1 Attempted Influent characterisation from laboratory measurements

In order to determine the amount of readily biodegradable fraction S_S and heterotrophic active biomass X_H, the batch test procedure outlined in Wentzel et al. (1995) was followed. 1.5 L of wastewater collected from WWTP was poured into a bioreactor. The stirrer was switched on before an aliquot of the uniformly mixed wastewater was drawn to determine the initial total COD. The total COD of wastewater was determined using the standard test presented in Standards Method (1995). The bioreactor used had a cooling jacket which kept the contents of the reactor at 20 ± 1 °C during the course of the experiment. Agitation was provided by a magnetic stirrer and the contents of the beaker were assumed to be completely mixed. The sample was aerated intermittently using an air pump and an aeration stone. The pH in the respirometer was maintained at 7.0 ± 0.2 by addition of hydrochloric acid and sodium hydroxide. The dissolved oxygen concentration (DO) was measured with an oxygen sensor (YSI DO probe) connected to the UCT OUR meter. The oxygen uptake rate (OUR) was calculated and stored inside the UCT OUR meter which also controlled the aeration in the bioreactor. The aeration intervals were set at 4.5 to 6 mg O_2/L. Surface aeration of the contents of the bioreactor was prevented by introducing a predetermined nitrogen and air mixture on the surface of the contents of the bioreactor. A simplified version of the UCT Model (Dold et al., 1991) was used to interpret the respirogram.

The inert soluble substrate, S_I was determined by a flocculation-filtration procedure on the wastewater collected at the end of the batch respirometric test (Wentzel et al., 1999). After running the batch test for 24 h or more, the only soluble COD remaining should be non-biodegradable soluble COD (Wentzel et al., 1999). Therefore, at the end of the batch test, 1 L of the bio reactor contents was drawn as sample, flocculated and filtered using a 0.45 µm filter. The COD of the filtrate gives the inert soluble fraction of the total COD of the wastewater.

3.2.2.2 Respirometry measurements

The batch test results of the industrial effluent from Verulam WWTP confirm the complexity of industrial effluent and its significant variation when compared to domestic effluent. Figure 3.12 shows the OUR profile obtained from a batch test on raw domestic effluent. Figure 3.13 to 3.15 show some of the OUR profiles obtained from the aerobic batch test for Verulam wastewater water samples.

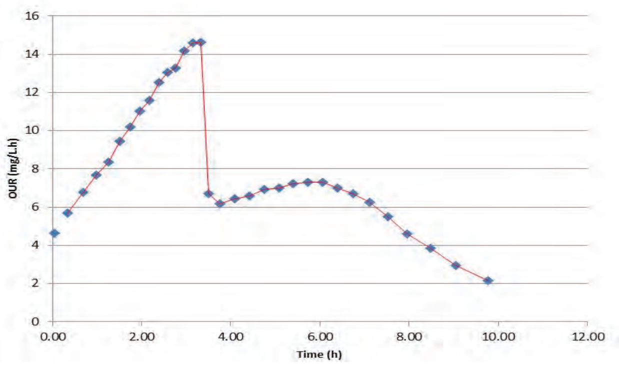

Figure 3.12: OUR response with time from the batch test on raw domestic effluent from Shallcross WWTP (24 July 2012)

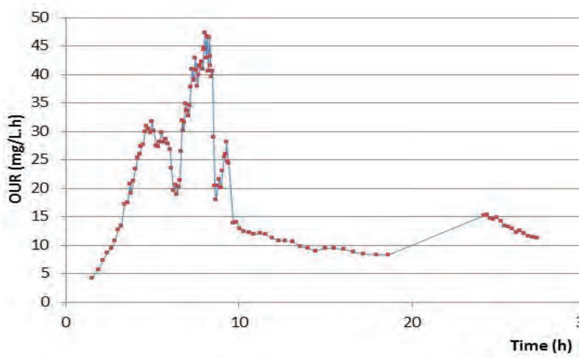

Figure 3.13: OUR response with time from the batch test on industrial effluent from Verulam WWTP (26 July 2012)

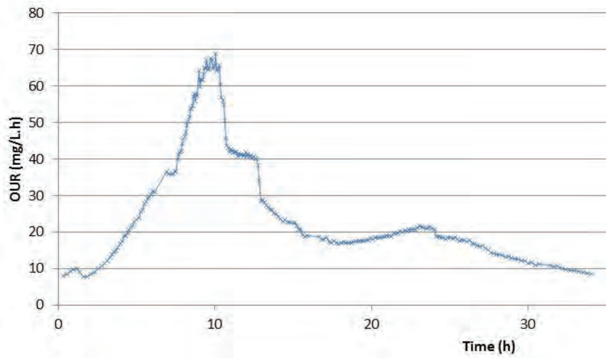

Figure 3.14: OUR response with time from the batch test on industrial effluent from Verulam WWTP (27July 2012)

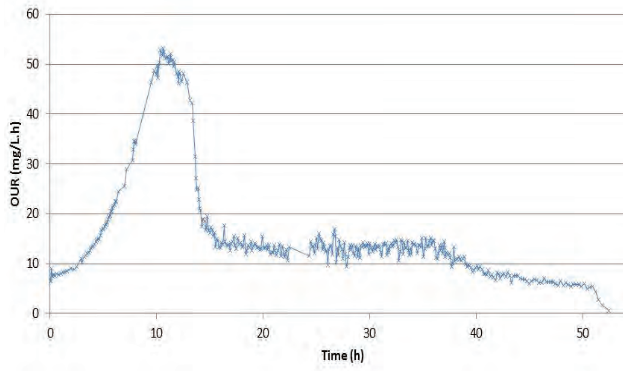

Figure 3.15: OUR response with time from the batch test on industrial effluent from Verulam WWTP (28 June 2012)

The respirograms for the wastewater received by the Verulam WWTP showed characteristics very different from the (typical) respirogram of domestic wastewater from the Shallcross WWTP. Furthermore, samples taken on different days differed markedly from each other. In trying to understand the inconsistencies in the measurements, an investigation was done where CODs of samples were measured before and after the respirometry tests, since the total oxygen absorbed should balance the difference in before and after COD values. However the balance gave errors of 80 to 90%. The problem appeared to be interference with the dissolved oxygen electrode by surfactants present in the wastewater (see sections 5.1 and 5.4).

3.2.3 The catchment balance approach

The principle behind this approach was to review the present knowledge or measured data with respect to the characteristics and volumes of the wastewater released by the major contributors to the WWTP catchment and then come up with a reasonable estimate of the composition of the combined wastewater stream received by the WWTP with special focus on the COD fractionation.

As the information is limited, the methodology includes estimates. The information that is needed for estimation of the characteristics of each wastewater source stream was obtained from combining the data available from measurements made during the time to time monitoring of individual factory effluent quality done by municipal inspectors and a qualitative assessment of wastewater aimed at estimating the chemical and physical properties that theoretically could be expected to be present based on the knowledge of the factory's core business. The list of the major contributors (factories and households) and their core business in the catchment area for Verulam WWTP is presented in Table 3.5. The proportions of the wastewater types contributed to Verulam WWTP are presented in Table 3.6. The physical and chemical properties measured on the different contributing wastewater streams are presented in Table 3.7. The flow weighted COD contributions of the major contributors in the Verulam catchment are presented in Table 3.8.

Table 3.5: Trade effluent volumes from major factories in the catchment for Verulam WWTP for 2010

Source	**Core business**	**Trade effluent 2010 (m^3/y)**	**% Contribution to total**
JMV	Weaving and finishing textiles	176630	8.5
Colgate Palmolive	Soap, tooth paste manufacturers	86391	4.2
Budget Soap	Soap and detergent manufacturer	29594	1.4
Packo	Food products	1201	0.1
Nampak tissue	Hygiene services- tissue paper production	19949	1.0
Frimax Foods	Food products, chips	16362	0.8
Domestic house holds	Production domestic wastewater	1740445	84
Total		**2070572**	**100**

Table 3.6: Industrial and domestic wastewater fractions in the catchment for Verulam WWTP for 2010

Wastewater type	**Trade effluent 2010 (m^3/y)**	**Trade effluent 2010 (m^3/d)**	**% Contribution to total**
Industrial	330 127	904	16
Domestic	1 740 444	4 768	84
Total	2 070 571	5 673	100

The information presented in Tables 3.5 to 3.8 shows that 16 % of the total wastewater received at Verulam WWTP is industrial wastewater. JMV Textiles contributes more that 50 % of the industrial effluent in the catchment area. 84 % of the total wastewater in the catchment area is domestic effluent from households in the Verulam community. Nampak Tissue and JMV Textiles contribute the highest proportion of COD per day among the factories in the catchment, 7.23 and 6.32 % respectively. The rest of the industrial COD comes from the smaller factories, Frimax Foods, Budget Soap, Colgate Palm Olive and Packo. Households in the Verulam area contribute 81 % of the total COD received at the WWTP. From the assessment of contributors of wastewater in the catchment area it can be seen that most of the COD received at the WWTP comes from the domestic wastewater from households.

Table 3.7: Characteristics of the wastewater streams in the catchment for Verulam WWTP for 2010

	JMV Textiles	Colgate Palmolive	Budget Soap	Packo	Nampak Tissue	Frimax Foods
Average flow (m^3/d)	484	45	3	55	237	81
Physical properties						
No of samples	9	10	11	7	9	11
Settleable Solids (mL/L)	0.4	1.9	0.2	1.2	1.6	42
Suspended solids	-	-	-	-	173	-
Vegetable oils (mg/L)	-	65.3	6.5	163.3	-	123
Conductivity (mS/m)	525	814	525	251	122	104
pH	8.0	7.4	7.9	7.1	7.6	9.6
Chemical properties						
COD (mg/L)	941	4166	267	1203	2200	1378
Sugar (mg/L)	-	-	-	35.6	-	84
Sulphate (mg/L)	2092	-	-	15	35	24.7
Sulphide mg/L)	198	-	-	6.6	120	-

- No measurements available

Table 3.8: Flow weighted COD contributions of major factories in the catchment for Verulam WWTP for the year 2010/11

Source	**Trade effluent 2010(m3/d)**	**Average COD (g/m^3)**	**Flow × COD (g/d)**	**% Contribution**
JMV	484	941	45 544	6.32
Nampak Tissue	237	2200	521 400	7.23
Frimax Foods	81	1378	111 618	1.55
Budget Soap	3	268	804	0.01
Packo	55	1203	66 165	0.92
Colgate Palmolive	45	4166	187 470	2.60
Domestic Households	4768	1230	5 864 640	81.37
Total Q_T	5673	1270	7 207 541	100.0

Average COD received at WWTP (mg/L) 2010/11 was 1270 mg/L

The information presented in the Tables 3.5 to 3.8 is not enough to establish the COD fractionation of the influent wastewater at the inlet of Verulam WWTP, but it provides a measure of proportions of industrial and domestic effluent present, which in turn determines the COD fractionations present in the wastewater.

3.2.3.1 ASM 1 COD fractionation

Since the simulations of the WWTP model will be based on the ASM1 model, the influent characteristics for the plant model needs to represent 13 components specified in the ASM1 model. In addition to the COD fractions, components representing the nitrogenous content of the wastewater, alkalinity and dissolved concentrations need to be specified. Table 3.9 identifies the components in the input file and gives information on how each component was estimated to represent the influent characteristics of the influent into Verulam WWTP.

Table 3.9: ASM1 effluent characterisation for Verulam WWTP

Symbol	Component	Source of values
S_{S1}	Readily biodegradable COD	Method presented in Table 3.10
S_{I1}	Soluble inert COD	Method presented in Table 3.10
X_{I1}	Inert particulate COD	Method presented in Table 3.10
X_{S1}	Slowly biodegradable COD	Method presented in Table 3.10
X_{BH}	Heterotrophic biomass	Assume that concentration is negligible
X_{BA}	Autotrophic biomass	Assume that concentration is negligible
X_P	Particulate products arising from biomass decay	Assume that concentration is negligible
$C_{TCOD} = S_{S1} + X_{S1} + X_{I1} + S_{I1}$		
X_{ND}	Particulate biodegradable nitrogen	Method presented in Table 3.10
S_O	Dissolve oxygen concentration	Estimated, since no measurements available.
S_{ALK}	Alkalinity	Estimated, since no measurements available.
S_{NO1}	Soluble nitrate nitrogen concentration	Assume that concentration is negligible
S_{NH1}	Soluble ammonia nitrogen concentration	FSA is measured (historical data)
S_{ND1}	Soluble biodegradable organic nitrogen from hydrolysis of particulate organic nitrogen	Estimated, since no measurements available.

Table 3.10 presents the methods and corresponding references of the methods used to estimate the components of the influent wastewater.

Table 3.10: Estimation of COD fractions of the combined influent from measurements in the influent and effluent

COD fractions	Method of estimation	Reference
S_S	$S_S = COD_{TOTAL} - S_I - X_I - X_S$	
S_I	Assumed to be equal to the final **filtered** measured effluent COD Assumptions: sludge age > 3days for all the biodegradable COD to be removed, steady state system, No generation of S_I in activated sludge unit Points to consider: With higher strength industrial wastewaters, residual microbial products may constitute a significant part of the effluent soluble COD.	Marais and Ekama , 1976
X_I	Assumption: Most of the particulate COD comes from the domestic effluent generated in the catchment area. hence X_I will be estimated from characteristics of South Africa domestic effluent as shown below: X_I (in domestic wastewater) = $f_{XI} \times COD_{TOTAL,\ DOMESTIC\ WW}$ Assume that $f_{XI} = 0.15$ for raw domestic wastewater X_I (in combined influent in wastewater) $= (f_{XI} \times COD_{TOTAL,\ DOMESTIC\ WW} \times Q_{DOMESTIC\ WW})/Q_{COMBINED\ WW}$	Henze et al., 2008
X_S	Assumption: Most of the suspended solids come from the domestic effluent generated in the catchment area. Frimax foods also generates the most significant concentration of suspended solids For domestic wastewater : VSS/TSS =0.8 VSS=0.8×TSS TSS is measured in the influent Particulate COD ($X_I + X_S$) =1.48×VSS = 1.48×0.8×TSS Therefore; X_S = (1.48×VSS = 1.48×0.8×TSS)- X_I	Henze et al., 2008
X_{ND}	Estimated from elemental formula for biodegradable particulate and soluble organics from literature.	Ikumi et al.,2011, Sötemann et al., 2005a

3.2.3.2 Calibration strategy

Model calibration is the adaptation of the model to fit a certain set of information obtained from the full-scale wastewater treatment plant under study (Petersen et al, 2002). The purpose of the model determines how to approach the calibration, as well as the quality and quantity of information required to achieve the calibration, hence the challenge in generalising the procedure of model calibration (Henze et al, 1995). Successful calibration of activated sludge models involves collecting information for model calibration, parameter estimation and adopting a stepwise calibration procedure in which different parts of the model are calibrated in each stage (Petersen, 2002).

The purpose of the model determines to a certain level the information required for calibration. For general purposes where a model does not have to describe a real existing plant, such as the use of a model for educational purposes, or comparison of design alternatives of non-existent plants, default (ASM) parameters for typical municipal sewage maybe sufficient (Henze et al., 1999). However when a plant-specific model has to be set up, a more accurate model calibration procedure is necessary to fine tune the default parameters. To achieve successful calibration in such a situation will require more plant specific information.

The strategy employed in this case was largely driven by the information available. This consisted of:

1. Daily measured flowrates for received wastewater.
2. Daily rainfall measurements.
3. COD and ammonia measurements in the received wastewater, at approximately 3 day intervals.
4. COD and suspended solids measurements in the treated wastewater at approximately weekly intervals.
5. COD measurements on samples taken from the major factories in the catchment, at approximately monthly intervals.
6. The annual total volume of effluent produced by each factory.

Different methods were used on the various information streams to bring them to a common daily basis.

1. For the plant measurements (items 3 and 4) the measured values were assumed to hold until the next measurement.
2. For the factory data, the intervals between measurement were clearly too long to use this strategy, so a Monte Carlo approach was used. The measurements were assumed to come from a random sample, and a probability distribution was fitted to them. Unfortunately, the number of measurements for each factory (between 9 and 11) was too small for the estimated probability distributions to be reliable. Synthetic daily factory effluent streams were generated using random number generators following the fitted probability distributions. For organic nitrogen, the two food processing factories (Frimax and Packo) were assumed to have similar contents to kitchen waste (Henze et al., 2008), and the others zero.
3. Modelling the effect of rainwater infiltration involved a more complex strategy. A clear correlation was established between the measured wastewater flows and rainfall. The received water flowrate was therefore modelled as a combination of *user generated* flow and rainwater infiltration. To establish the user generated component, the measurements were selected where there had been no rain for the previous 3 days. This series of values was subjected to a 7 day moving average smoothing. The differences between these smoothed values and the daily total flows were then attributed to rainwater infiltration. The attributed rainwater infiltration was then fitted to a linear function the actual rainfall measurements, with a coefficient for each of the rainfall values recorded for the day and for the previous 4 days. The flow predicted by this linear function was then taken as that of rainwater infiltration. The COD and organic content were estimated from literature (Langeveld et al., 2012)
4. The contribution of domestic sewage to the total flow was modelled as the difference between the total measured flowrate and the sum of the modelled factory contributions plus the rainwater contribution. The COD and organic nitrogen content of domestic sewage were estimated from literature (Henze et al., 2008); however the COD adjusted to match the average received wastewater COD. The organic nitrogen content was not adjusted, because no measurements were available.

The fractionation of the various contributing streams into the fractions presented in table 3.10 was then estimated from literature sources. The domestic sewage fraction was taken from Henze et al. (2008), rainwater infiltration from Langeveld et al. (2012), JMV effluent from Orhon and Çokgör (1997).

From the above, it can be seen that the apparent 'input data' to the process model was itself the outcome of a modelling exercise, which involved a large number of assumptions and considerable uncertainty. This provided no basis for calibrating the kinetic and stoichiometric parameters of the process model, so these were left at their default values. However there was one process model aspect which had a significant effect on the treated effluent quality, and that was the efficiency of the final clarifiers, since any suspended solids in the final effluent contribute directly to the COD. The only measured data available that provided any information about this were the measured effluent suspended solids. To represent this effect, the secondary clarifier model was modified to accept a specified value the clarified effluent TSS, so that it could be made to match the measured values.

Finally, since the catchment balance and the wastewater treatment process model, taken together, form a probabilistic model, its evaluation was carried out on a statistical basis by comparing its outputs with measurements on a cumulative probability basis, rather than a day-by-day basis. This is consistent with the envisaged use of the model, which would be to predict the probable cumulative impact of a factory's effluent on the quality of treated wastewater being returned to the environment.

3.2.3.3 Modelling Verulam WWTP

Verulam WWTP uses a modified Bardenpho process, which has a multi-stage biological reactor. The Verulam configuration differs from the standard Bardenpho configuration. Nitrate rich mixed liquor from the first aerobic cell is not recycled to the head of the process.

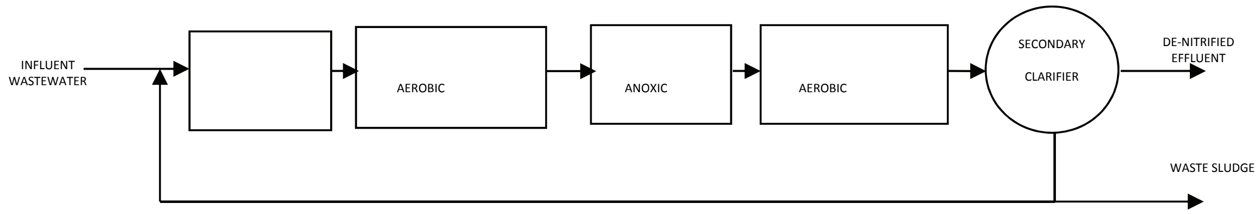

Figure 3.16: Configuration of the activated sludge process at Verulam WWTP.

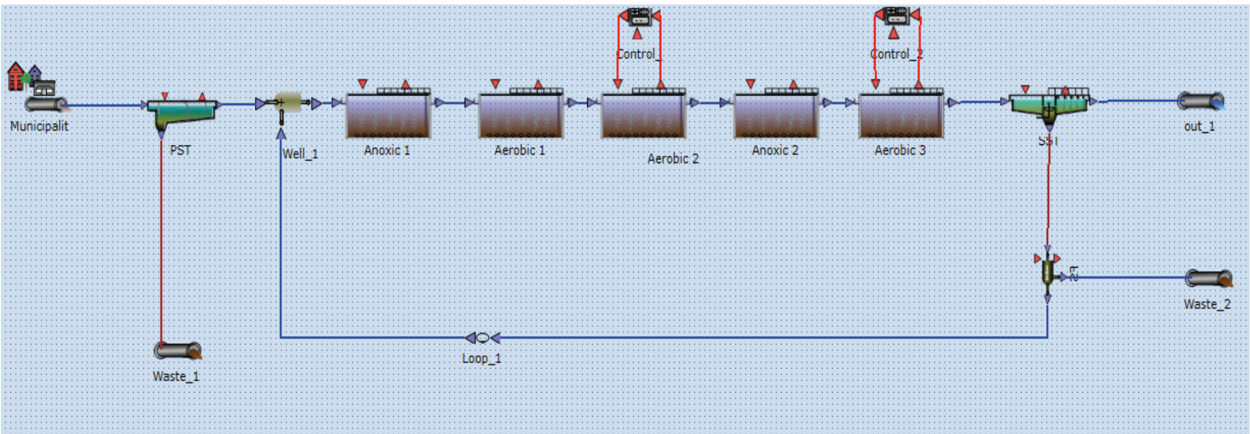

Figure 3.17: WEST configuration of Verulam WWTP

3.2.3.4 Simulations and Model calibration in WEST

Figure 3.18 shows the comparison between 200 days of model predictions and measured values of COD in the final treated effluent from the Verulam WWTW. The COD agreement is good, apart from the very high predicted values at around 100 days. There were due to a high measured value of the suspended solids. As explained in section 3.2.3.2, the secondary clarifier model follows the measured values exactly. There is clearly an inconsistency between the reported COD and TSS values at this point, a high TSS in the clarifier overflow must be accompanied by a high COD in reality.

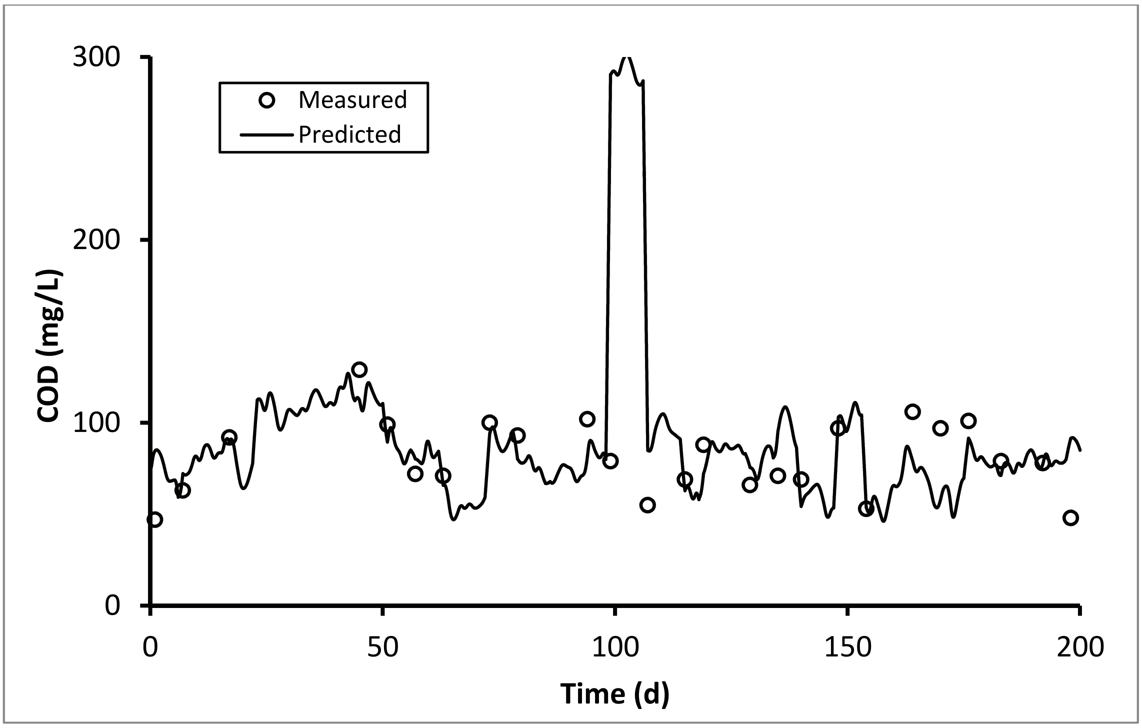

Figure 3.18: Measured and predicted final effluent CODs for the Verulam WWTP.

Figure 3.18 is a similar plot for ammonia. The agreement here is less good, however the measurements appear to mostly be at the lower detection limit of the method, and it is not clear how to assess their significance.

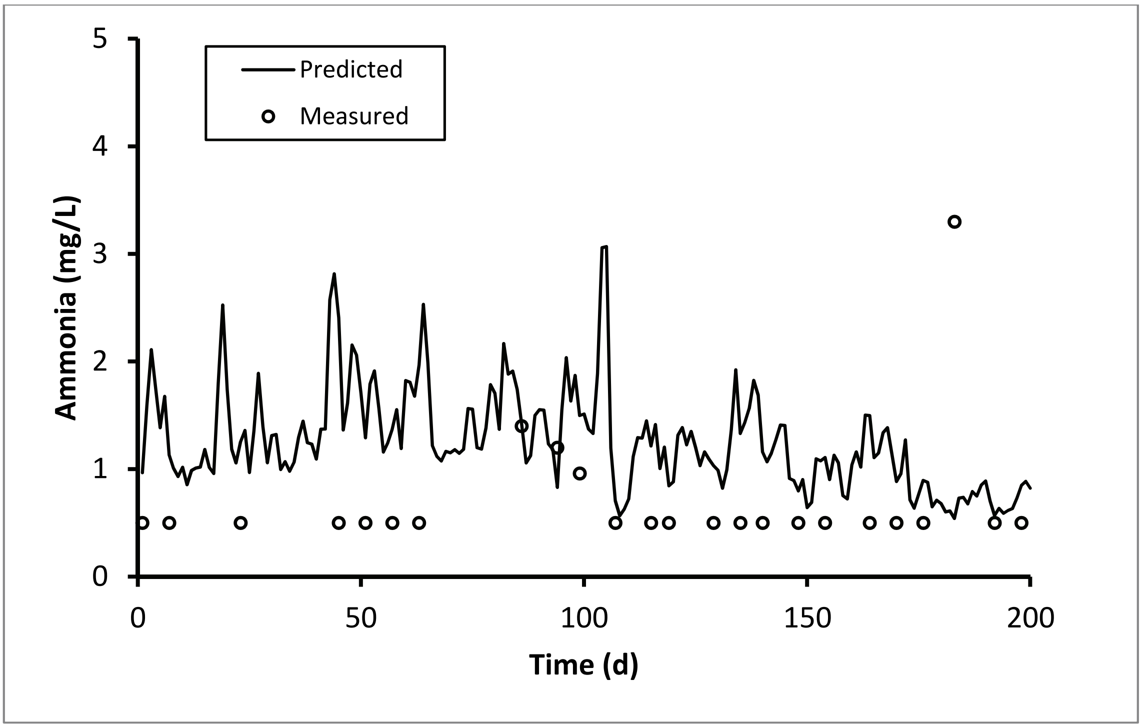

Figure 3.19: Measured and predicted final effluent ammonia for the Verulam WWTP.

Figure 3.20 presents the COD comparison on a cumulative frequency basis. The agreement is very good up to the 95% level, and the discrepancy thereafter is largely a result of the almost certainly incorrect measurement previously noted.

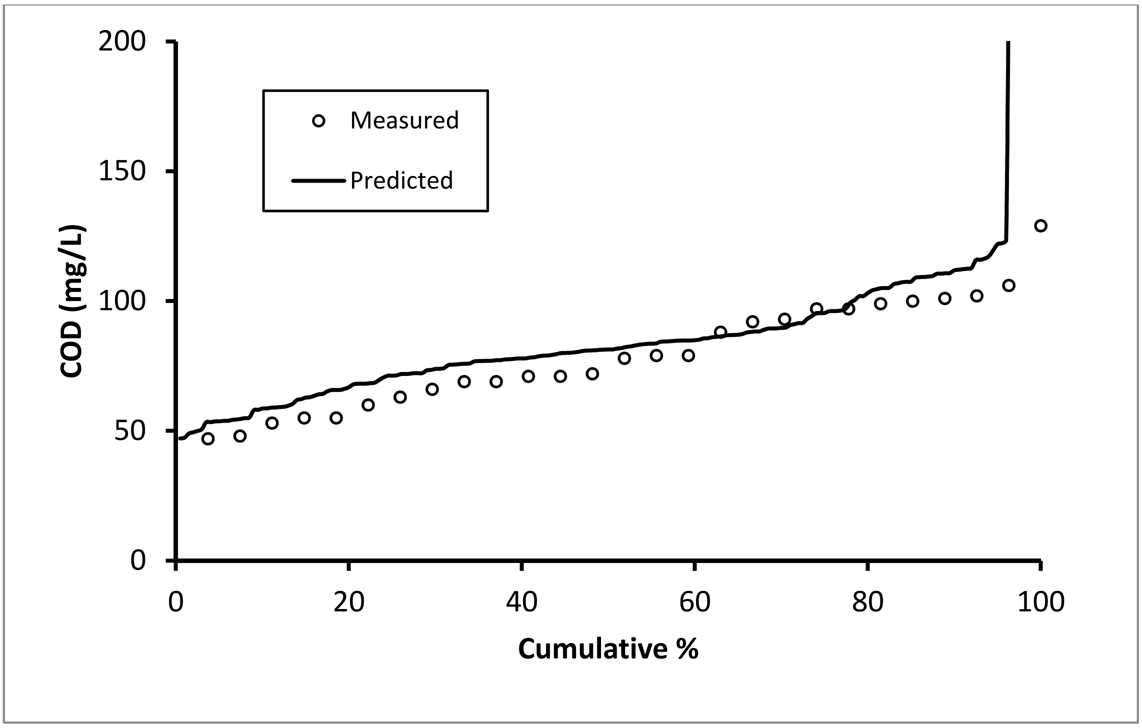

Figure 3.20: Measured and predicted final effluent ammonia for the Verulam WWTP.

3.2.4 Conclusions

To obtain a representative influent COD fractionation using direct measurement techniques is a complex and time consuming process, and a fully satisfactory result was never achieved during the project. Our experiences indicate that the problem even more difficult in the case of a WWTW that receives a large proportion of industrial effluent. There also seems to be a problem of consistency, in that the OUR protocol was reasonably successful for characterising the Mariannridge wastewater, but unsuccessful in the case of Verulam. It is clearly important for the protocol to be reliable.

The catchment balance approach was attempted only at the end of the project, in a bid to overcome the impasse which the failure of the direct approach had created. It's evident success has far exceeded any expectations, and points to a substantially different approach that should have been followed in the project. Unfortunately this result was only achieved during the last phase of completing this project report.

This methodology that suggests itself would be to start with a catchment balance characterisation along the lines of the one presented here. The role of laboratory investigations would then be to investigate and specific issues for which the catchment balance failed to resolve. For example, a special investigation might be undertaken if it was considered that the ammonia predictions shown in Figure 3.18 were a cause for concern.

This does not mean that the need for the laboratory techniques falls away, just that they should be applied more selectively than was originally envisaged. After all, the estimated fractionations that were used in the catchment balance were all based on literature reports of laboratory studies. It should also be noted that the good agreement was demonstrated for only the basic monitoring measurements of effluent COD and ammonia. Further investigation would be required to assess the model's predictions of the process performance in other areas, such as power consumption and sludge production.

A significant feature of the catchment balance methodology is that the influence of each factory is already represented in the wastewater characterisation, albeit in a very approximate form. The evaluation of the factory effluent for the purpose of setting the permit conditions thus becomes just a special case of the process of improving the model to represent specific issues in the catchment, rather than a separate modelling process as envisaged in the original project proposal.

4 LABORATORY METHODS FOR WWTP FEED CHARACTERISATION

The objective of influent wastewater characterisation is to determine the volumes and concentration of the carbon, nitrogen, phosphorus and other constituents present in the wastewater. Characterisation of the effluent leaving the wastewater treatment plant provides a way to assess the extent to which transformations of the wastewater constituents occur, in relation to achieving the required effluent standards.

Wastewater characterisation is crucial in process modelling. Wastewater characteristics have a significant impact on the performance of the activated sludge unit, particularly for nutrient removal systems (Melcer, 2003). A single characteristic may have such impact as determining whether or not a system designed for excess phosphorus removal will in fact remove phosphorus (Melcer et al., 2003). Hence a detailed knowledge of the composition of influent going into the wastewater treatment system is essential for the development of a model which will be able to predict the performance of the WWTP.

The quality of the model predictions depends on the wastewater characterisation (Henze et al., 1995). Characterization of wastewater for a given WWTP can be done by a very detailed or a less detailed procedure depending on the intended use of the process model. A more detailed procedure will give more reliable results.

In the context of treatment plant simulation, wastewater characteristics not only are important for activated sludge system modelling; simulating the performance of other unit operations also depends on appropriate wastewater characterisation (Melcer et al., 2003).

The methods for determination of wastewater characteristics can be divided into two main categories:

Direct methods-the methods include characteristics that can be inferred from direct measurements using standard methods and analytical techniques. Examples include total COD, total suspended solids (TSS) and volatile suspended solids (VSS)

Bioassay methods-information is derived from the observation of biological system such as a batch or sequencing batch reactor activated sludge systems. An example of such a method is the estimation of readily biodegradable COD fraction from oxygen utilization rate in a bioreactor.

4.1 Sampling

The quality of the data generated in the laboratory for analysing the collected samples of wastewater, depends on the integrity of the samples that are brought to the laboratory. The aim of wastewater sampling is to obtain a sample that will provide the required information for the model. It is important to sample at the correct location and to prevent deterioration and contamination of the samples before analysis.

Weighted composite sampling will be done since municipal wastewater systems receive influent over a 24 h period during which the volume and strength characteristics of the wastewater vary throughout the day. This variation causes fluctuations in the biological treatment systems. Composite samples collected and analysed over an extended period (about 30days) will provide verifiable indication of the characteristics of the influent wastewater.

Precautions will be taken to prevent sample contamination and deterioration. Samples should be preserved and transported to the laboratory for analysis within 24 h

4.1.1 Parameters to be measured

The parameters to be measured in the composite wastewater sample are listed in Table4.1.

Table 4:1 Parameters to be measured on the composite wastewater sample

Type of fraction of influent	Parameter to be determined
Organic	Total COD
	Readily biodegradable COD S_S
	Soluble inert COD S_I
	Particulate inert COD X_I
	Slowly biodegradable COD X_S
	Heterotrophic active biomass X_H
Nitrogenous	TKN
	Free and saline ammonia
	Nitrate/nitrite
Phosphorus	Total phosphorus
	Ortho phosphorus
Others	Total solids TS, total suspended solids TSS, volatile suspended solids VSS

4.1.2 COD fractionation procedure

The COD of municipal wastewater is divided into three main fractions, non-biodegradable, biodegradable and active biomass. The non-biodegradable COD has two fractions, the non-biodegradable particulate (X_I) and non- biodegradable soluble (S_I). The biodegradable COD also has two fractions, the slowly biodegradable (X_S) and readily biodegradable (S_S) fractions. The active biomass consists of heterotrophic X_H and autotrophic organisms X_{AUT} (Wentzel et al, 1995). The concentration of autotrophic biomass X_{AUT} in the influent is negligible hence the total COD can be expressed ad the sum of five fractions.

$$C_{TCOD} = S_I + S_S + X_I + X_S + X_H$$

4.1.2.1 Determination of readily biodegradable fraction S_S - Aerobic batch method

Three experimental methods for estimating the readily biodegradable fraction S_S in influent wastewater are outlined in Ekama et al., 1986. Among these methods the aerobic batch method appears to be the most practical since it requires the least amount of analytical and laboratory facilities (Melcer et al., 2003). A measured volume of wastewater of known total COD is combined with a measured volume of activated sludge mixed liquor in a batch bioreactor. The contents of the bio reactor are maintained well mixed throughout the test. The OUR in the bioreactor is measured and plotted against time to give an OUR profile.

4.1.2.2 Determination of the inert soluble COD fraction, SI

The inert soluble substrate, S_I in wastewater can be determined by a flocculation-filtration procedure on the wastewater collected at the end of the batch respirometric test on composite wastewater. After running the batch test for 24 h, the only soluble COD remaining should be non-biodegradable soluble COD. Therefore, at the end of the batch test, 1 L of the batch reactor contents is drawn as sample to determine the inert soluble substrate. The sample is dosed with 10 mL of aluminium sulphate with a concentration of 50 g/L. The mixture is stirred rapidly for 2 min and then poured slowly into a Perspex cylinder (settling column) equipped with a magnetic stirrer. The content of the column are then stirred slowly for 30 min (flocculation phase). During the flocculation phase the flocs settle and leave a clear liquid zone. A 50 mL sample is drawn from the clear liquid zone and filtered through a glass fibre filter (Whatman GF/C) and the COD of the filtrate determined. The COD of the filtrate gives the amount of the inert soluble substrate, S_I.

4.1.2.3 Determination of active biomass X_H

To determine the quantity of heterotrophic active biomass in wastewater the procedure outlined by Wentzel et al. (1995) is useful. A volume of influent of known COD concentration is mixed and aerated while the oxygen uptake rate is measured continually for a period of up 20 h.

The amount of heterotrophic active biomass X_H is estimated from the OUR response using an appropriate activated sludge model such as the ASM-type or the UCT model (Dold et al., 1980).

4.1.2.4 Determination of the inert particulate COD fraction XI

The procedures for determining the concentration of particulate inert organics involves the kinetic analysis of a laboratory scale completely mixed activated sludge unit operated at steady-state with a sludge age longer that 5 d (Orhon et al., 1996). Ekama et al. (1986) proposed a calculation of the concentration of X_I which involves comparing the measured mixed liquor volatile suspended solids (MLVSS) concentration with the calculated value on the basis of calculated kinetics. The IAWPRC Task Group (Henze et al., 1987) recommends a similar approach based upon the comparison of observed and calculated sludge production (Orhon et al., 1996). For these procedures, the heterotrophic yield, Y_H the endogenous decay rate, b_H and the inert fraction of biomass must be correctly determined by independent experiments.

4.1.2.5 Determination of slowly biodegradable fraction X_S

The slowly biodegradable fraction X_S is obtained by difference from the measured total COD and the previously estimated COD fractions as shown in the equation below.

$$X_S = C_{TCOD} - (S_I + S_S + X_I + X_H)$$

4.1.2.6 Determining the nitrogenous fraction in wastewater

The nitrogenous fraction in the wastewater is determined by measuring the total TKN and the nitrate/nitrite concentration. Ammonia accounts for the major portion of the total TKN in municipal wastewaters and the remaining portion is organic nitrogen, which is less critical for modelling purposes in some cases (Melcer et al., 2003). The fraction of the total TKN that is free and saline ammonia f_{SNH} is determined by direct analysis. A sample of the wastewater is taken and a portion filtered through a 0.45 µm membrane filter to remove particulate material. The unfiltered sample is analysed using standard methods (1995) to determine the concentration of TKN and the filtrate analysed for ammonia concentration. The ammonia concentration will be the same in the filtered and unfiltered sample. The fraction of the total influent TKN that is free and saline ammonia is calculated as follows:

$$f_{SNH} = \frac{InfluentNH_3 - N}{InfluentUnfilteredTKN}$$

The standard tests for the determination of total TKN, nitrates/nitrites and free and saline ammonia can be found in Standard Methods (1997).

4.1.2.7 Determining the phosphorus fraction in wastewater

The phosphorus fraction in wastewater is determined using Standard methods (1997).

4.1.2.8 Other tests carried out

Other tests that can be carried out on the wastewater samples include influent solids characterisation (total solids TS, total suspended solids TSS and volatile suspended solids VSS. These tests can be carried out using standard methods outlined in Standard methods (1997).

4.1.2.9 Modelling and interpretation

Modelling of the respirometric tests can be used to either check the results of the COD fractionation, or in fact provide an alternative method for determining some of the parameters. The respirometric test depends on the biodegradable substrate and biomass concentrations present in the reactor, and parameter regression can be used to characterise these constituents. This method is useful for distinguishing between readily- and slowly-biodegradable substrates, and it describes them in terms which are directly applicable to the simulation model.

A typical OUR-curve plotted from the data obtained from OUR measurements on a composite sample of wastewater with addition of sodium acetate is shown in Figure 4.

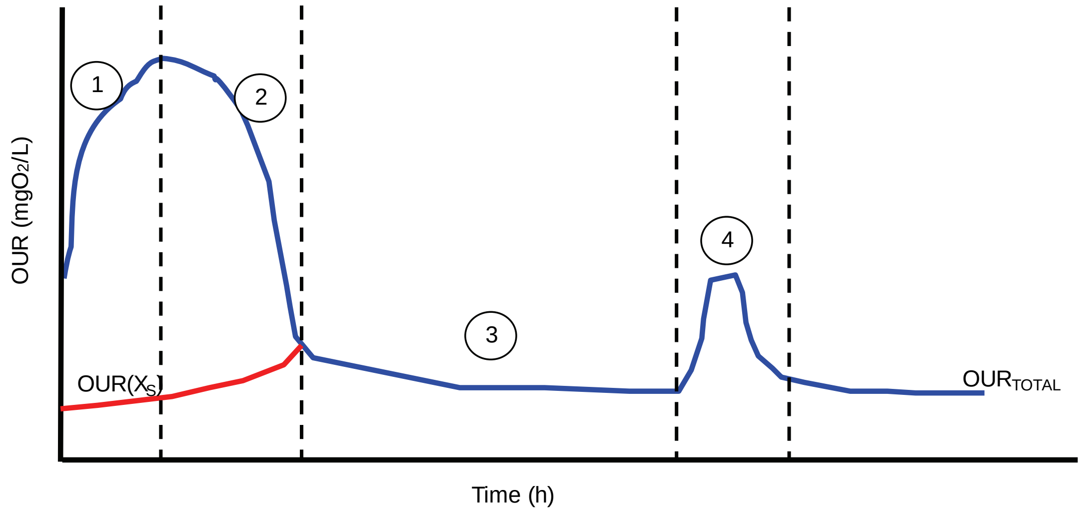

Figure 4.1: A typical OUR-curve on raw incoming sewage with addition of readily biodegradable substrate (Hvitved-Jacobsen et al., 2002)

The curve labelled OUR (X_S) shows the oxygen uptake rate due to the utilisation of slowly biodegradable substrate while the curve labelled OUR_{TOTAL} shows the total oxygen utilisation rate due to utilisation of both slowly biodegradable substrate and readily biodegradable substrate. The area above the curve which shows the OUR due to utilisation of slowly biodegradable substrate, OUR (X_S), is a result of utilisation of readily biodegradable substrate by the micro-organisms and the area below is as a result of the utilisation of slowly biodegradable substrate.

The OUR curve is divided into four regions based on the substrate concentrations in the wastewater sample as shown in Figure 4.1

1) Substrate non-limited condition.

2) Substrate non-limited condition is being terminated.

3) Substrate limited condition.

4) Addition of readily biodegradable substrate (sodium acetate)

The figure shows that during region 1 the amount of readily biodegradable substrate present in the beginning is not limiting the growth of biomass. The amount of biomass increases in region 1 and the OUR also increases. This is followed by a sharp decrease in OUR, when the readily biodegradable substrate is depleted in region 2. After this period (region 3) the readily biodegradable substrate is only available due to the hydrolysis of slowly biodegradable substrate. When the production of readily biodegradable substrate by hydrolysis corresponds to the required maintenance energy for biomass, i.e. the when the OUR is stable, an aliquot of readily biodegradable substrate is added. This addition results in immediate growth of the biomass under substrate non-limited conditions, where the OUR increases, followed by a rapid decrease to the maintenance value as seen in region 4.

The purpose of addition of readily biodegradable substrate after region 3 (the substrate limited conditions) in the experiment is to let the biomass growth rate change from zero to its maximum value. The experiment is then interpreted using a model which represents the processes which are occurring in the batch reactor.

4.1.2.9.1 Interpreting the experiment using the UCT and IWA models

The data from the first stage of the batch test before the addition of sodium acetate, (zone 1, 2, and 3) can be interpreted in terms of the UCT (Dold et al., 1980; 1991) and IWA model. Both the UCT model and the IWA model used by Hvitved-Jacobsen (2002) were used to interpret the results.

UCT model

For interpretation using the UCT model, the model was simplified by recognising the following specific conditions:

- the batch test is done under aerobic conditions so de-nitrification processes need not be included,
- a nitrification inhibitor was added therefore, nitrification processes need not be included,
- excess ammonia is present in the wastewater so nitrite as an N-source for growth need not be considered and also transformations from organic to ammonium nitrogen does not need to be included.

IWA model

For interpreting using the IWA model, the original model-matrix in Hvitved-Jacobsen (2002) is modified to suit, the COD fractions needed for this particular model. The modification means, that the originally two fractions of hydrolysable substrate are combined to one fraction of slowly biodegradable substrate.
Check of COD recovery

A mass balance of oxygen shows whether the data from the OUR measurements are acceptable. Before and after the experiment a sample was drawn to obtain the initial COD and end COD, also taking into account the readily biodegradable substrate added. A mass balance constructed, yields equation 4.1.

$$\%\ COD\,recovery = \frac{COD_{t=T} + \int_{t=0}^{t=T} OUR \cdot dt}{COD_{t=0}} \cdot 100 \qquad [4.1]$$

Where:

t = Time (h)

T = Time used at the end of the experiment (h)

$COD_{t=T}$ = Total COD concentration at the end of experiment (mg COD/L)

$COD_{t=0}$ = Total COD concentration at the beginning of experiment (mg COD/L)

A COD recovery in the range of 95 to 105 % indicates that the OUR measurements are reliable (Wentzel et al., 1995). COD recoveries of 95 to 97% were achieved in this study indicating that the experimental results were reliable.

4.2 Model parameter estimation

4.2.1 Determination of inert soluble substrate, S_I

The inert soluble substrate, S_I in wastewater was determined by a flocculation-filtration procedure on the wastewater collected at the end of the batch respirometric test on composite wastewater described in section 4.2.1.9. After running the batch test for 24 h, the only soluble COD remaining should be non-biodegradable soluble COD. Therefore, at the end of the batch test, 1 L of the batch reactor contents was drawn as sample to determine the inert soluble substrate. The sample was dosed with 10 mL of aluminium sulphate with a concentration of 50 g/L. The mixture was stirred rapidly for 2 min and then poured slowly into a Perspex cylinder (settling column) equipped with a magnetic stirrer. The contents of the column were then stirred slowly for 30 min (flocculation phase). During the flocculation phase the, flocs coalesce and settled out to leave a clear liquid zone. A 50 mL sample was drawn from the clear liquid zone and filtered through a glass fibre filter (Whatman GF/C) and the COD of the filtrate was determined. The COD of the filtrate gives the amount of the inert soluble substrate, S_I.

4.2.2 Inert particulate substrate X_I, and slowly biodegradable substrate X_S

From the batch OUR test, it is impossible to differentiate between inert particulate substrate and slowly biodegradable substrate. Furthermore, physical separation technique, such as flocculation-filtration can not separate the two COD fractions, since both are particulate. The inert particulate substrate, X_I is determined from the simulation model of the batch respirometric experiment. With four COD fractions known, the slowly biodegradable substrate X_S is determined from equation 4.2.

$$C_{TCOD} = S_I + S_S + X_I + X_S + X_H \qquad [4.2]$$

4.2.3 Determination of kinetic and stoichiometric parameters

The determination of kinetic and stoichiometric parameters for the model is discussed in the following sections.

4.2.3.1 Aerobic yield of heterotrophic biomass, Y_H

The aerobic yield of heterotrophic biomass, Y_H was determined from the OUR curve results obtained in the batch respirometric experiment outlined in section 4.2.1.9**Error! Reference source not found.**.

4.2.3.2 Heterotrophic maximum growth rate μ_H

The heterotrophic maximum growth rate, μ_H is determined from the same OUR experiment where the aerobic yield of heterotrophic biomass, Y_H is determined.

4.2.3.3 Decay rate constant, b_H

To determine the decay constant of the biomass in the activated sludge, an activated sludge sample is put in a batch reactor where the endogenous respiration rate is measured by measuring the oxygen uptake rate of the biomass over a period of 24 h or several days. Nitrification is inhibited during the test by addition of 20mg/L of thiourea. Since the endogenous respiration is proportional to the active biomass concentration, a plot of the natural logarithm of the endogenous respiration as a function of time describes the exponential biomass decrease as a straight line with slope b'_H which refers to the traditional decay coefficient described by Henze et al (1987).

In this study a sludge sample was taken from the outlet of the activated sludge unit and kept cool and anaerobic, to prevent significant transformation of the organic matter in the sample during the period of transportation and storing. OUR measurements were performed on the sample in the 2 L continuously stirred batch reactor, the upper set point of the dissolved oxygen was 6 mg O_2/L and the lower set point was 4 mg O_2/L. The OUR measured was done over a period of 24 h. Nitration was inhibited during the test by addition of 20 mg/L of thiourea.

The plot of the natural logarithm of the recorded OUR values versus time showed the expected exponential decrease of the biomass as a straight line with the slope, b'_H. However when determining the model specific decay coefficient activated sludge models which use the death regeneration model concept to describe the decay of biomass, like ASM1, the value of b'_H obtained from the experiment needs to be adjusted to get the model specific parameter b_H.

To obtain the model specific parameter, b_H, b'_H must be adjusted according to the values of the yield coefficient for heterotrophic biomass, Y_H, and the fraction of inert particulate biomass, f_p, as shown in equation 4.3 (Henze *et al.,* 1987).

$$b_H = \frac{b'_H}{1 - Y_H \cdot (1 - f_P)} \quad [4.3]$$

The change in ASM3 to the traditional endogenous respiration decay rate concept makes it more straight forward to determine the decay rate of the model from the experiment. There is no need to adjust the decay coefficient obtained from the plot of the natural logarithm of the recorded OUR values versus time.

4.2.3.4 The hydrolysis constant, k_h

Attempts have been made to analyse hydrolysis in laboratory-scale experiments (Petersen et al., 2002) in order to try and determine the hydrolysis constant, k_h. However the real enzymatic hydrolysis is not the same as the hydrolysis process in the model. The hydrolysis process in the model might also include consumption of storage polymer, hydrolysis of decayed biomass and other processes. Hence it remains difficult to design an experiment that is representative of both the model concept and the hydrolysis process as it takes place in the full-scale plant. Therefore in practice the value of the hydrolysis constant may have to be tuned during the model calibration (Petersen et al., 2002). In this study k_h, was estimated by fitting the OUR results predicted by the simulation model of the batch experiment, to the OUR results which were recorded in the batch experiment that was carried out on influent wastewater. The estimated value would further be adjusted during calibration if necessary.

4.2.3.5 Half saturation coefficients, K_S and K_X

In pure cultures the half saturation coefficients can be regarded as pure biological parameters that give measures of the affinity of the biomass for substrates (Petersen et al., 2002). In activated sludge models where the biological meaning of the model half saturation coefficient is mixed with the hydraulics of the system, it becomes difficult to get values of half saturation coefficients from laboratory-scale experiments which are representative of the full-scale system. If a very detailed model is available to describe the hydraulics of system accurately it might be possible to separate the effects of biomass affinity for substrate and the hydraulic effects. The lumping of the biomass affinity for substrate and the hydraulics of the system means that processes such as mixing will affect the value of the coefficient. The different mixing characteristics of the laboratory-scale and full-scale system make it difficult to transfer the laboratory-scale observation to the full scale system. The coefficients may be estimated by laboratory-scale experiments but the values may not be very representative. Therefore in practice these values may have to be tuned during the model calibration (Petersen et al., 2002).

In this study the saturation coefficient for readily biodegradable substrate, K_S, and the saturation coefficient for particulate COD, K_X, are estimated by fitting the OUR results predicted by the simulation model of the batch experiment, to the OUR results which were obtained from the batch experiment that was carried out on wastewater. The curve fitting was done up to the point just before the addition of readily biodegradable substrate. The curve fitting is done by use of numerical techniques, during a trajectory optimisation run in the WEST software. The values would further be adjusted during calibration if necessary.

4.3 General conclusions

The measurements required to support WWTP modelling are in themselves much more intensive than those generally used to monitor their operation, although the catchment balance approach (section 3.2.3) indicated that they can be applied quite selectively, thereby reducing their overall burden.

The combination of respirometry and COD measurements was the main focus of the laboratory work in this project. For most of the other measurements, such as ADMI colour, conductivity and metal determinations, results from the municipal analytical service were used. The respirometry apparatus that was used was the one developed by the University of Cape Town, which has been used extensively by the UCT Water Research Group, and is generally considered to give reliable results. However, the experience of this project was that it was not possible to obtain consistent and reliable results. The investigation into biodegradability of surfactants suggested that the problem was interference with the DO electrode by concentrations of surfactants encountered in the wastewater which had high proportions of textile effluent. Unfortunately the realisation of the problem came too late for a different system to be tried. There are respirometers that used a closed reactor, and measure the oxygen concentration in the gas phase rather than the aqueous phase, which would not be subject to this kind of interference.

In hindsight, given the difficulties involved in applying these techniques, it may have been more effective to have employed simpler, but more robust measurements such as filtration methods for fractionating the COD.

4.3.1 Technology transfer issues

Attempts to transfer the OUR measurement techniques to municipal staff met with very little success. Obviously this was partly due to the problems with the reliability of the technique, but it also had a lot to do with the unavailability of technical staff with the required level of skill, patience and time to devote to such a time-consuming measurement. For much of the time the OUR apparatus that was used actually belonged to the municipal laboratory. It was lent to the project when the university's unit developed a fault, because it was not in use. The understanding was that we would repay the loan by providing training to the municipal laboratory staff in its use. However, apart from a brief session in which we simply demonstrated its use, an effective training course never materialised. This was because the laboratory was unable to allocate time to appropriate staff to be trained. Part of the problem was that, while the discussions around this were under way, the laboratory was damaged by a fire which destroyed much of their equipment. This placed their normal operations under severe pressure for more than a year. By the time we eventually raised the issue again, the person who had been interested in the OUR had retired.

If wastewater treatment modelling is to become an established practice, it will be necessary to have the capability in place for the supporting laboratory measurements. It now seems unlikely that municipalities will be able to do this in-house, given their problems with attracting and retaining skilled technical personnel, and an alternate model needs to be found for providing such a service.

5 LABORATORY TESTING OF TEXTILE EFFLUENTS

5.1 Biodegradability

Effluent from textile wet finishing operations typically has BOD and COD values that are above generally accepted levels for discharge to sewer, with significant contributions from detergents and softeners. Textile wastewater composition varies frequently and markedly. It has been observed that a change in the surfactant content of such wastewater can affect the COD removal efficiency (Carvalho et al., 2000).

Carvalho et al. (2000) evaluated the oxygen uptake response of activated sludge to the presence of non-ionic synthetic surfactants using closed respirometry techniques which were complemented with titrimetric surfactant measurements and Total Organic Carbon (TOC) experiments to assess the primary and ultimate biodegradation of the surfactant. Though non-acclimatized sludge was apparently not inhibited by the surfactant products, total degradation took at least 20 hours. Respirograms showed several peaks, suggesting stepwise degradation of the surfactant molecules. Alkyl-phenol oxylates (non-ionic surfactacts commonly used in textile processing) have intermediate degradation products with an aromatic group that is more difficult to bio-degrade.

From the above, that textile effluent COD may be more slightly difficult to treat that normal sewage, not necessarily in terms of ultimate biodegradability, but in terms of the rate at which degradation takes place.

Several series of tests were carried out to establish a methodology for assessing the biodegradability of surfactants using the OUR apparatus available to us, but these failed to provide consistent and reliable results. It appears that the surfactant interfered with the responsiveness of the dissolved oxygen electrode, causing it to give incorrect oxygen utilisation rate results. A remark in Carvalho et al. (2000) suggests that they had encountered similar problems, which prompted them to use a closed respirometer, with oxygen concentration measured in the gas phase rather than the liquid phase.

5.2 Inhibition of biodegradation

The interference by surfactants in textile effluents in the oxygen utilisation rate measurement has also prevented us from obtaining reliable indicators of whether textile effluents inhibit the activated sludge process. However no indications have been found in the literature of such inhibition. Calvalho et al. (2004) have shown that sludge which has not been acclimated to surfactants is initially slow to break down the intermediate degradation products, but acclimated sludge deals with them satisfactorily.

5.3 Colour and decolourisation

Textile effluents contain a variety of highly coloured components, depending on the combination of processes that give rise to them. From a WWTP point of view, these can be divided into two broad classes, particulate and soluble. Two laboratory studies on the removal of representative particulate and soluble dyes by activated sludge were carried out in order to provide a basis for a model of colour removal in a WWTP.

5.3.1 Particulate colour

In the first study, a series of experiments were carried out in which different amounts of printing paste effluent, obtained from Ninian and Lester, were contacted with sludge taken from the activated sludge aeration basin at the Umbilo Wastewater Treatment Works in stirred and aerated vessels. Samples were withdrawn at intervals from the vessels for ADMI colour measurements. The mechanism appears to be adsorption of the coloured material onto the sludge. The results were consistent with an adsorption isotherm, where the amount of colour that the sludge adsorbs depends on the amount of colour remaining in the liquid.

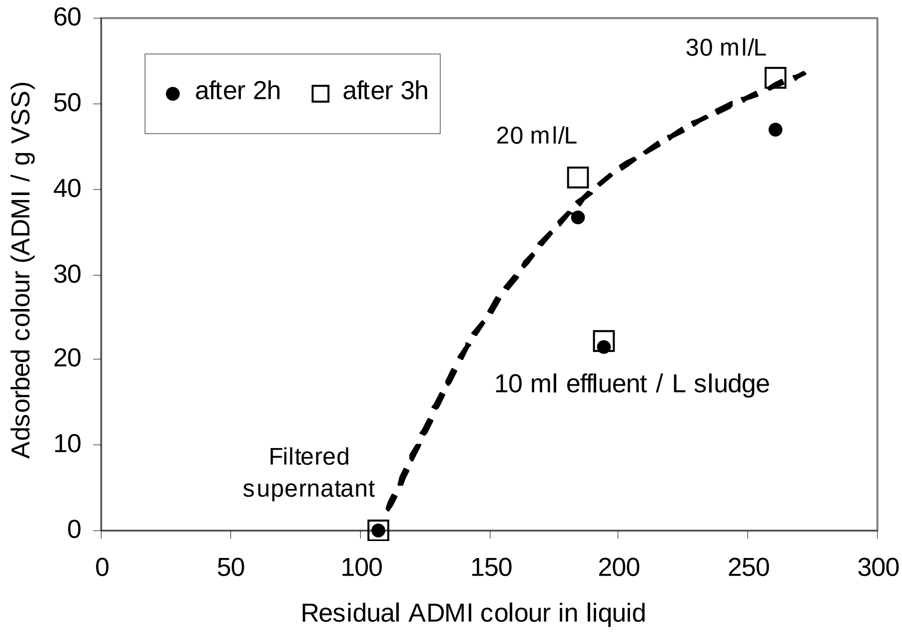

Figure 5.1: Adsorption isotherm for particulate colour onto activated sludge biomass (ADMI: American Dyestuff Manufacturer's Institute colour unit)

5.3.2 Soluble colour

The second study investigated the efficiency of the aerated batch bioreactor system as a means of decolourising a textile effluents containing Red H-E7B azo dye.

A dye solution of known concentration was contacted with activated sludge from the Mariannridge WWTP in various concentration ratios is an aerated vessel, to approximately simulate conditions in the WWTP Aeration basin. The residual dye concentration in filtered samples was measured using a UV/VIS spectrophotometer as function of the contact time.

Most of the tests were carried out under *endogenous respiration* conditions, i.e. with aeration but no biodegradable substrate addition. Under these conditions, the dye concentration in the liquid phase became constant after a contact time of about 1hour. This indicated that the removal mechanism was physical adsorption onto the sludge rather than biodegradation. Biodegradation is not expected for azo dyes under aerobic conditions.

However, when a biodegradable substrate (sodium acetate) was dosed into the vessel at a rate approximating the conditions at the WWTP, the dissolved colour did not become constant after 1 hour, but continued to decline gradually. The rate of this decline was too high to be attributed to purely the additional sludge growth generated from the acetate, indicating that the adsorptive capacity of the entire mass of sludge (old and new) had been enhanced. This indicates that the adsorptive capacity of sludge may influenced by its biological activity.

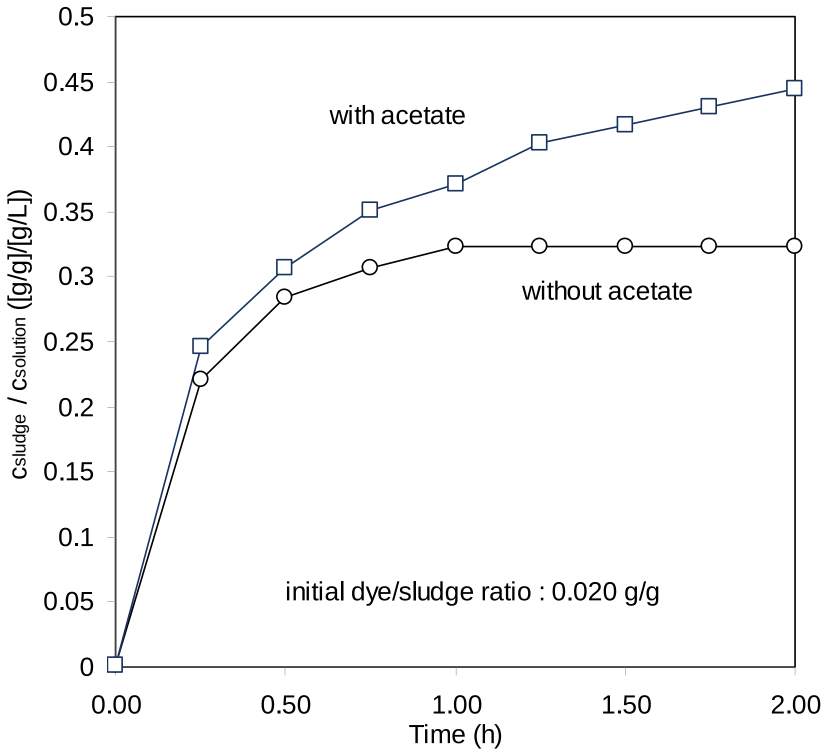

Figure 5.2: Adsorption isotherms for soluble colour onto activated sludge with and without acetate dosing.

5.3.3 Adsorption Kinetics

Rate controlled adsorption of the dye was observed during both sets of experiments. However, most import observation in this respect was that equilibrium was reached within 1 hour. If this is compared to a typical hydraulic retention time of a WWTP activated sludge unit of 6 hours, it is clear that colour removal in such a WWTP will not be rate limited. Consequently there is little motivation for a more detailed kinetic study.

5.3.4 Conclusions

The activated sludge process removes azo dyes from wastewater to a small extent. The mechanism for this appears to be physical adsorption onto the sludge, with the adsorptive capacity of actively growing sludge a little higher than for inactive sludge. The results of this investigation appear to be adequate to provide the basis of a reasonably accurate predictive model of colour removal in an activated sludge process.

The adsorption rates are such that equilibrium is attained within approximately 1 hour, which is substantially faster than other processes in the activated sludge process. Consequently an accurate kinetic model of the adsorption process is not necessary.

5.4 Oxygen transfer

Surfactants form a significant component of a textile effluent. It is known that they can reduce the oxygen mass-transfer coefficient in aeration basins, thereby affecting the efficiency of the treatment. The OUR test involves alternately aerating the bioreactor to raise the dissolved oxygen concentration and cutting off the aeration to measure OUR. It was postulated that the O_2 transfer coefficient (K_La) could be determined by analysing the O_2 concentration trajectory during the aeration phases.

However, the investigations only served to demonstrate that surfactant interference with the dissolved oxygen electrode invalidated the measurements of Kla with the apparatus that we had (Figures 5.3 and 5.4). The OUR apparatus switched aeration on at 2 mg O_2/L, and off at 6 mg O_2/L. It is notable how the DO trace overshot the limits with the surfactant present, indicating that the measurement was lagging behind the actual concentration. The impaired response of the electrode also appears to affect the OUR measurement.

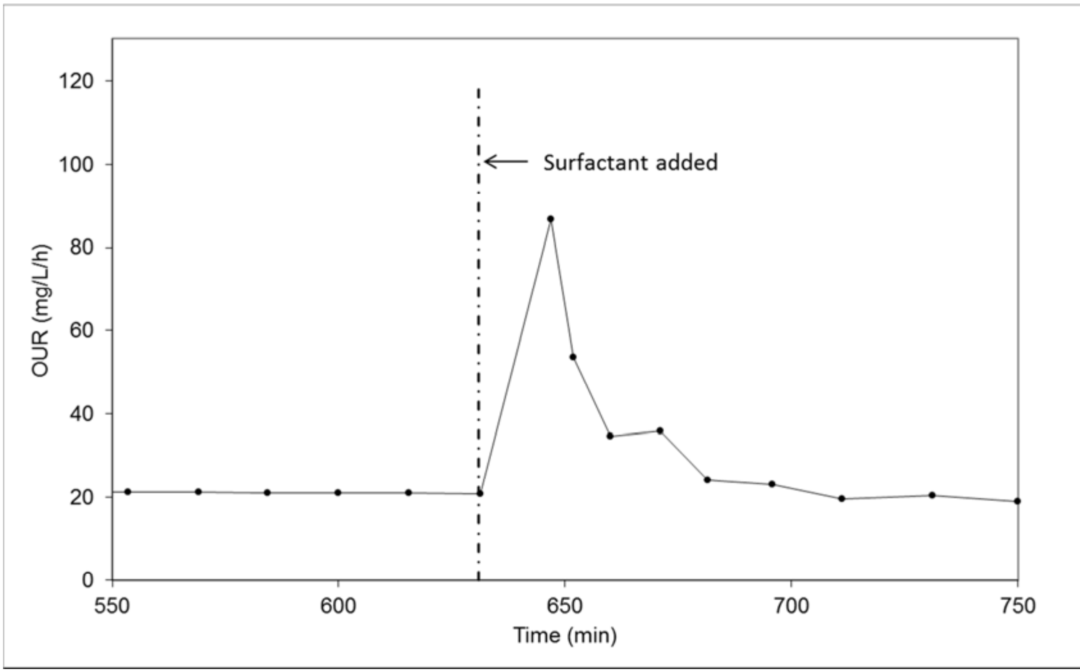

Figure 5.3: OUR trace with surfactant addition.

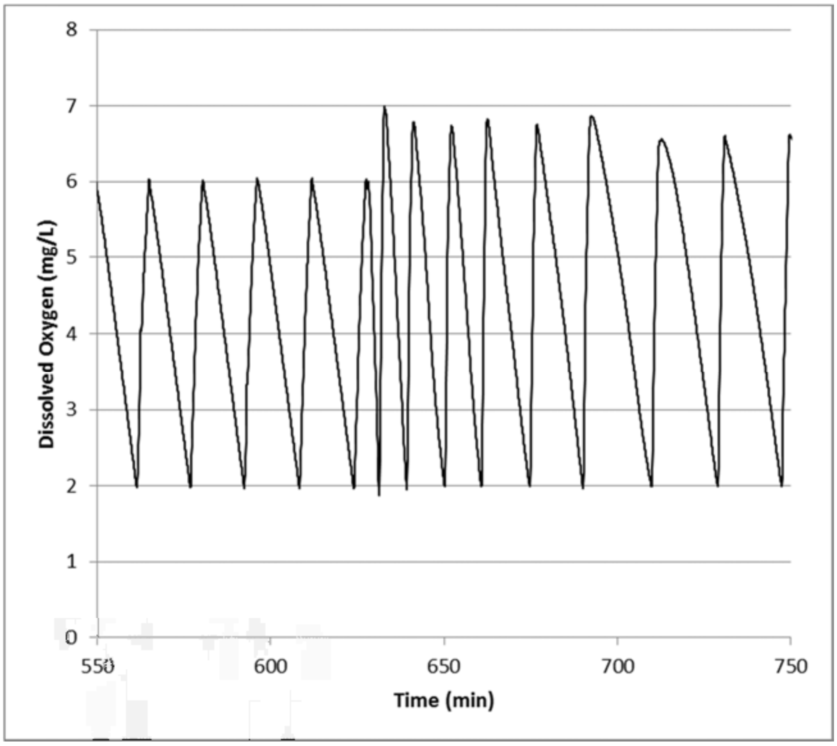

Figure 5.4: Dissolved oxygen trace with surfactant addition

5.5 Heavy metal adsorption

It should be noted that the investigation of heavy metals in this project was somewhat anomalous, since they are not associated with textile effluents. However, heavy metal contamination of wastewater is a problem commonly encountered in industrial areas, and Durban is no exception. For example, the Pinetown/New Germany area, which is served by the Umbilo Treatments Works has a number of metal fabrication and metal finishing industries, and the metal content of the sewage received by the Umbilo Works has been a concern for many years. Wastewater treatment processes are known to be reasonably effective in removing the metals from the treated water, however this results in the waste sludge being contaminated, which restricts the options for its disposal or beneficial use.

Bio-adsorption of heavy metals has been studied by many researchers, and there is broad consensus about the mechanisms involved. The limited purpose of this investigation was to set up a basis for model of these processes which can be incorporated into a model of the wastewater treatment process. Such a model should be capable of extrapolating the results of laboratory tests to predict the distribution of heavy metals in the WWTP effluents of treated water and waste sludge, as well as representing possible inhibition of the biological activity of activated sludge.

5.5.1 Laboratory measurements

The basic data required to predict the fate of heavy metals in a wastewater treatment process is the adsorption isotherm. Adsorption isotherms for sludge from the Umbilo WWTP were determined. The investigation focused on Zn and Cu, which are the main problems at the Umbilo WWTP, from which the sludge was obtained. Data from routine monitoring of the incoming sewage and outgoing effluent were also examined.

In the laboratory experiments, samples of effluent awaiting treatment before discharge to sewer were obtained from 2 metal finishing plants, and analysed for their Zn content. These were then blended and diluted to prepare a solution to be added to a sludge sample taken from the Umbilo WWTP. The resulting slurry was stirred, and samples withdrawn at 30 minute intervals for the 3 hours. The samples were centrifuged to separate the solids, and the supernatant liquid analysed for Zn by ICP. The solids content was determined by drying the sludge at 100°C. The amount of metal adsorbed onto the sludge was calculated from the difference in solution concentrations from the initial concentration, and then converted to a solids concentration by dividing by the concentration of dry solids. Since the sludge taken from the aeration basin at Umbilo would already have adsorbed some metals from the sewage, a sample was also analysed for the metal content of both the liquid and solid fractions.

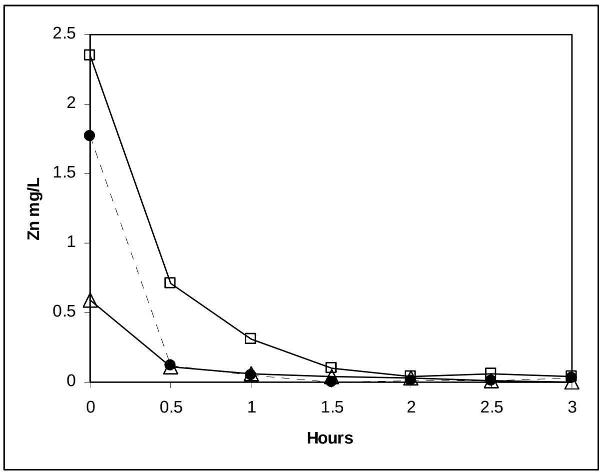

Figure 5.5: Liquid phase Zn concentration in sludge adsorption experiments.

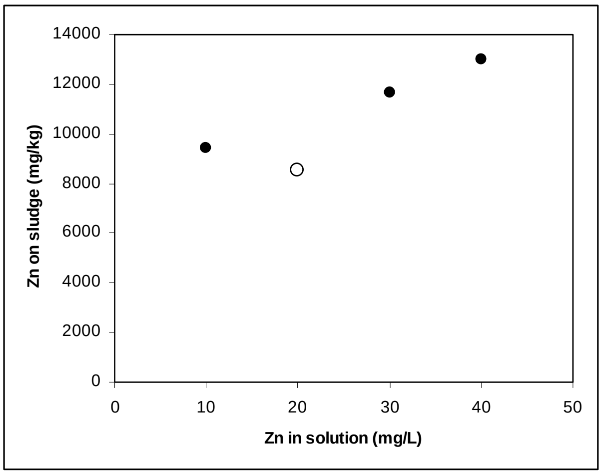

Figure 5.6: Apparent adsorption isotherm for Zn on activated sludge.

The "adsorbed" metal levels were even higher than those measured in dewatered waste sludge in 2007, and also considerably higher than those measured by Al-Qodah (2006). It therefore seems probable that the initial Zn content of the sludge did not reflect only metal adsorbed to the biomass, but also some contribution from an inorganic particulate fraction, which would also need to be accounted for in a model of the process. This idea also provides a possible explanation for the pattern of plant measurements. Whereas the metal content of the incoming sewage has wide variations, these show no correlation with the metal concentrations measured in the treated effluent, which remain within the same band of values, irrespective the trend of the influent values (Figure 5.7).

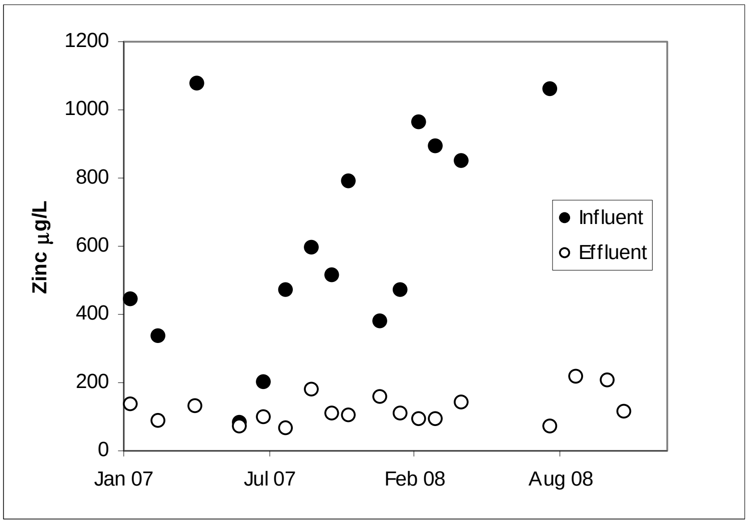

Figure 5.7: Influent and effluent Zn concentrations for the Umbilo WWTP.

This implies that the adsorbed metal concentrations on the sludge are also within a relatively narrow range, so that the observed variations must reflect a different capture mechanism. The most plausible possibility is entrapment of metal-containing particles in the sludge and subsequent settling.

5.5.2 Modelling implications

The practical measurements suggest that the mechanistic subtleties of an adsorption model along the lines suggested by Imai et al. (1988) would not be observable in practice, and that a simplified model of the adsorption of soluble metal per se would be appropriate. However, to this would be added a parallel process for capture of particulate metal. Thus, the model would consider 4 metal containing species: S_m (dissolved), X_m (free particulate), X_{ma} (adsorbed) and X_{mp} (particulate attached to sludge). These would have the very simple stoichiometry: $S_m \rightarrow X_{ma}$ and $X_m \rightarrow X_{mp}$. The rate expressions for these "reactions" would be of the form $d[S_m]/dt = k.([S_m] - [S_m]^e)$, where $[S_m]$ is the concentration of S_m, and $[S_m]^e$ is the equilibrium concentration calculated from the adsorption isotherm. As discussed above, the value of the rate constant k does not need to be accurately known, as the adsorption is significantly faster than other processes taking place, so all that matters is that a high enough value is chosen.

5.5.3 Laboratory measurement implications

The principal issues are to distinguish particulate metal from dissolved in the incoming sewage, and between metal adsorbed and metals in particles attached on the sludge. The former issue can be dealt with by determining both the total metal content, and the dissolved metal content (i.e. after filtration). The latter will probably have to be addressed by using isotherm data derived from tests on sludge from a WWTP that receives no heavy metals, and calculating the particulate fraction by difference.

5.5.4 Conclusions

Literature data and local measurements confirm that activated sludge is an efficient adsorbent for heavy metals in wastewater. The adsorption process is relatively rapid, and should approach equilibrium closely within an activated sludge aeration basin. A simple adsorption model should adequately describe the process for the purpose of setting permit levels, with the proviso that the inorganic particulate contribution to the heavy metal content of the raw sewage should be accounted for, both in the process model and in laboratory tests to characterise a factory effluent.

6 MODELLING ACTIVATED SLUDGE TREATMENT OF TEXTILE EFFLUENTS

The basis for a kinetic model was obtained from the literature, however implementing it as part of a wastewater treatment process model was not reached during the project, because the prior step of setting up a baseline model for the Verulam wastewater treatment process was completed too late.

6.1 Biodegradability

The main issue for the biodegradation of finishing effluent is the presence of surfactants. Other constituents such as sizes are like to be very readily biodegradable. Specific functions of surface active agents include removing soil (scouring), wetting, rewetting, softening, retarding dyeing rate, fixing dyes, making emulsions, stabilizing dispersions, coagulating suspended solids, making foams, preventing foam formation and defoaming liquids.

The average surfactant concentration in domestic wastewater is from 10 to 20 mg/L, whereas in some industrial wastewater may reach even 300 mg/L (Shcherbakowa et al., 1999; Scott and Jones, 2000). Surfactants reveal strong adsorbing properties hence their molecules may adsorb onto the activated sludge. Due to adsorption and toxicity, surfactants may affect biological activity of microorganisms resulting in decreasing of wastewater treatment efficiency (Liwarska-Bizukojć and Bizukojć, 2005). Surfactants can also be biodegradable. The surfactant molecule can be broken down to substances that can be utilized by the biomass in the activated sludge process. However longer chain surfactants are more resistant to biodegradation (Carvalho et al., 2002).

6.1.1 Developing the model for surfactant biodegradation

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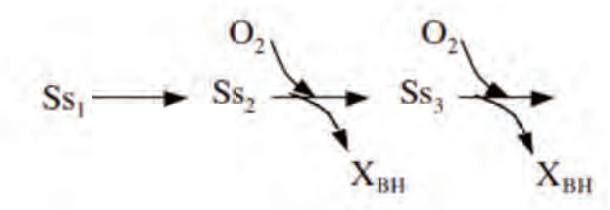
In the model developed by Carvalho (2004) degradation of the surfactant occurs in multiples steps. It is based on the assumption of three sequentially degraded COD fractions, where the second fraction is a metabolite of the original molecule and the third fraction is a more slowly biodegradable metabolite resulting from the secondary degradation. This is presented in the following scheme:



This dynamic model is referred to as the Fractionated Degradation Model (FDM) (Carvalho et al., 2001).

The original surfactant molecule and its successive metabolites can be regarded as different substrates which are degraded by different enzymes and bacterial consortia with different kinetic criteria (Carvalho et al., 2004).

Carvalho (2001, 2002, 2004) used respirometry for assessing the conditions and response of the activated sludge to surfactants.

6.1.2 The mathematical model

In the dynamic model the intact surfactant molecule was identified as a COD fraction S_1. The primary degradation of this molecule was considered to an enzymatic conversion with no growth associated to it (Carvalho et al., 2004). Michaelis-Menten kinetics was used to describe the first degradation step as shown in equation 2.1.

$$\frac{dS_1}{dt} = -k_h \cdot \frac{S_1 \cdot X_H}{K_{S_1} + S_1} \qquad [6.1]$$

Where:

t assay time after surfactant feed (min)

S_1 concentration of surfactant in its initial form (mg COD/L)

k_h hydrolysis rate constant for S_1(min^{-1})

X_H active heterotrophic biomass concentration (mg COD/L)

K_{S1} hydrolysis affinity constant for S_1 (mg COD/L)

It was assumed that the biomass growth due to a second COD fraction identified as S_2 followed Haldane inhibition kinetics represented by equation 2.2 and 2.4. The parameter Trans takes into account the initial start-up time required for solution homogenisation after substrate addition (Vanrolleghem et al., 1998).

$$\mu_{H_2} = Trans \cdot \mu_{\max H_2} \cdot \frac{S_2}{K_{S_2} + S_2 + S_2^2 / K_I} \qquad [6.2]$$

$$Trans = 1 - \beta \cdot e^{-t/\tau} \qquad [6.3]$$

$$\frac{dS_2}{dt} = \frac{\mu_{H_2} \cdot X_H}{Y_{H_2}} + k_h \cdot \frac{S_1 \cdot X_H}{K_{S_1} + S_1} \qquad [6.4]$$

Where:
μ_{H2} specific growth rates of heterotrophic biomass on S_2 (min^{-1})
μ_{maxH2} maximum specific growth rate on S_2 (min^{-1})
β transition parameter
τ transition time constant (min)
S_2 concentration of surfactant's metabolite (second COD fraction) (mgCOD/L)
K_{S2} hydrolysis affinity constant for S_2 (mgCOD/L)
K_I inhibition constant for S_2 (mgCOD/L)
The remaining COD fraction S_3 was assumed to follow first-order degradation kinetics represented by equation 2.5 and 2.6.

$$\mu_{H_3} = k_3 \cdot S_3 \qquad [6.5]$$

$$\frac{dS_3}{dt} = \frac{\mu_{H_3} \cdot X_H}{Y_{H_3}} + v_{S_3} \cdot \frac{\mu_{H_2} \cdot X_H}{Y_{H_2}} \qquad [6.6]$$

Where:
μ_{H3} specific growth rates of heterotrophic biomass on S_3 (min^{-1})
k_3 first-order constant for heterotrophic growth on S_3 (mg COD/L.min)
S_3 concentration of surfactant's metabolite (third COD fraction) (mg COD/L)
Y_{H2} yield of heterotrophic biomass for S_2 (mg COD/mg COD)
Y_{H3} yield of heterotrophic biomass for S_2 (mg COD/mg COD)
v_{S3} yield of conversion of S_2 into S_3 (mg COD/mg COD)

In summary, the proposed model is based on the sequential conversion of S_1 to S_2, the oxidation of S_2 to a third intermediate, S_3 and finally mineralised (Carvalho et al., 2001). The exogenous respiration rate (r_O) and the biomass growth were considered to be due to the consumption of S_2 and S_3 only.

$$r_O = \left[\frac{1-Y_{H_2}-v_{S_3}}{Y_{H2}} \cdot \mu_{H_2} + \frac{1-Y_{H3}}{Y_{H3}} \cdot \mu_{H_3} \right] \cdot X_H \qquad [6.7]$$

$$\frac{dX_H}{dt} = (\mu_{H_2} + \mu_{H_3} - b_H) \cdot X_H \qquad [6.8]$$

Taking the initial conditions (biomass concentration $X_H(0)$, surfactant concentration $S_2(0)$ and respiration and combining equations 2.2, 2.3 and 2.7 and assuming that S_3 is in negligible concentration at *t = 0*,

$$r_O = X_H(0) \cdot (1 - \beta \cdot e^{-t/\tau}) \cdot \mu_{\max H_2} \cdot \frac{S_2(0)}{K_{S_2} + S_2(0) + S_2(0)^2 / K_I} \cdot \frac{1-Y_{H_2}-v_{S_3}}{Y_{H_2}} \qquad [6.9]$$

Manipulating equation 2.9 gives equation 2.10.

$$\beta = 1 - \frac{K_{S2} + S_2(0) + S_2(0)^2 / K_I}{S_2(0) \cdot \mu_{\max H2}} \cdot \frac{r_O(0) \cdot Y_{H2}}{X_H(0) \cdot (1 - Y_{H2} - v_{S3})}$$

6.2 Inhibition of biodegradation

Inhibition of biodegradation can be measured as a drop in the oxygen utilisation rate (OUR) when an inhibitory substance is added to the biological reactor. This requires careful comparative tests, because the OUR depends on a number of factors which are often not directly measureable, such as the concentration of active biomass. Testing whether a mixed industrial effluent is inhibitory is further complicated by the presence of biodegradable components which increase the OUR.

The difficulties associated with the measurements were never fully resolved during the project, as has been described elsewhere in this report. Even so, in all the tests that were attempted, no inhibitory effect due to textile effluents were ever detected. This means that the biodegradability of the effluent is the only critical issue. In this case, the OUR test, with all its complexities and difficulty is not essential in practice, and could be replace by a less demanding and more robust measurement technique

7 THE INTEGRATED EFFLUENT EVALUATION PROTOCOL

The project plan envisaged that the entire protocol would be tested in a case study which would be undertaken as part of the process of granting an actual effluent discharge permit to a textile factory. However, for reasons that were not all within the control of the research project the case study could not be completed. The factory that was originally chose (Dyefin in Westmead) closed down. JMV Textiles in Verulam was then chosen as a substitute, but because the pollution officer assigned to the permit investigation left the employ of the municipality, the permit was granted hurriedly, without making use the proposed protocol. So this report is only able to present the preliminary investigations that were part of the envisaged protocol.

7.1 The JMV Textiles factory

JMV Textiles are manufacturers of knitted fabrics, rotary screen printers, dyers and finishers, based in Verulam near Durban. Effluent from the factory is treated at the Verulam WWTW, which is notable for having very recently had a new section added which is unusually highly instrumented in comparison with other South African wastewater treatment plants. The factory's effluent has a significant impact on the operation of the WWTW, which makes JMV a candidate for inclusion in eThekwini's new 5 year effluent discharge permit system. However, several attempts to implement the process of issuing the permit had stalled due to the relevant staff leaving the municipality's Pollution and Environment section at inopportune times. In conjunction with the Pollution and Environment section, was decided that situation presented by JMV Textiles and the Verulam WWTP would provide an ideal opportunity for testing the permitting protocol. A recent chemical engineering graduate, Avesh Ramburan, who is a pollution control technologist in the Verulam office, was identified as the person to drive the permitting process, with the possibility of using the project for an MScEng degree.

Four different textiles are manufactured processed at JMV Textiles, polycotton, cotton, polyester and nylon. JMV Textiles manufactured 50% cotton, 30% polyester and 20% polycotton. The plant used batch processing in order to carry out the procedure and reactive and disperse dyes are used in order to achieve successful dyeing of the fabrics. Acid dyes were used in dyeing the Nylon fabric; however, Nylon was rarely manufactured in the plant.

Wet processing consists of pre-treatment, dyeing and rinsing which produces a product ready to be sent for printing and finishing. The pre-treatment consists of removing contaminants from the fabric by using chemicals such as scouring agents as well as pre-bleaching the fabric in order to achieve successful dyeing. Dyeing consists of using different dyes in order to achieve a certain shade of colour and using chemicals in order to aid in the fixation and exhaustion of the dyes. Rinsing results in the excess chemicals and residues to be removed from the fabric so that the following stages can be carried out successfully.

The factors that needed to be addressed in order to attain the permit were the ADMI colour, Sulphate and sulphite concentrations as well as conductivity.

To support the process, an investigation to establish the water and effluent balance for the factory has been undertaken Ms. Sarah Westergreen. This led to a spreadsheet model of the process which could be used to predict the quantity and composition of textile effluent from the factory's production schedule, based on dyeing 'recipes' provided by the factory. The model predictions have been partially validated by comparing the predicted and measured cumulative frequency distributions of conductivity in the factory effluent. (Figure 7.1)

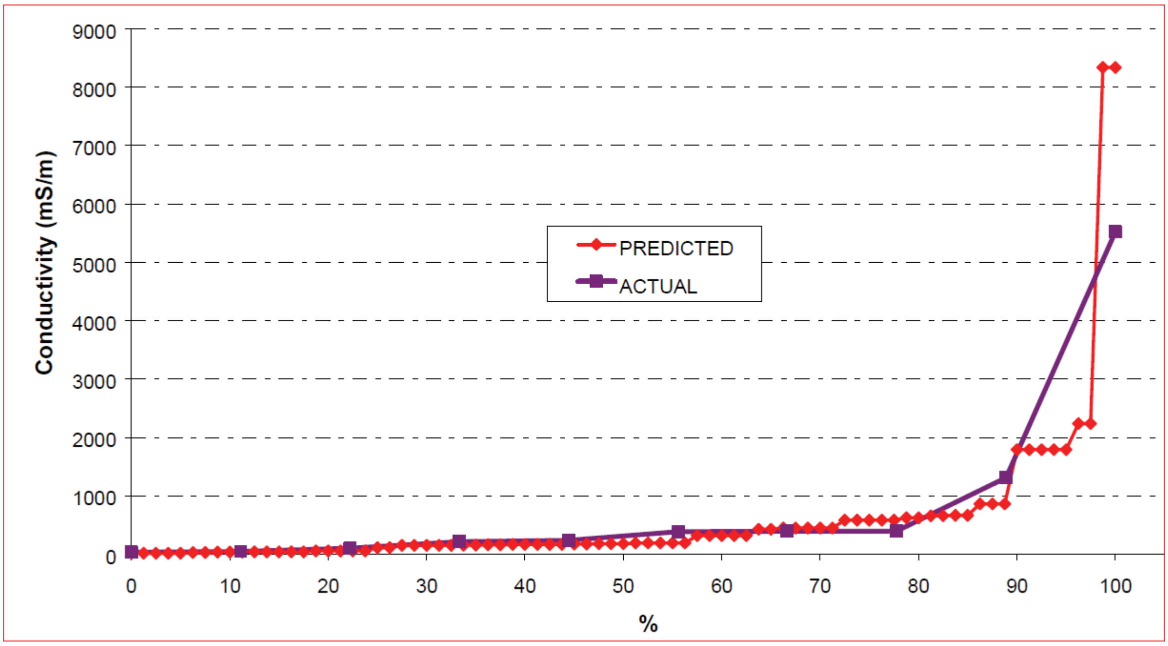


Figure 7.1: Predicted and measured cumulative frequency of JMV effluent sample conductivity

The prediction of conductivity is more straightforward than colour or surfactant concentration, because its interaction with cloth is minimal. For colour and surfactants the model requires some calibration using measured values.

7.2 The Verulam WWTP

The development of the baseline model for the Verulam WWTP is presented in section 3.2. This met two serious unexpected difficulties. The first was that the wastewater received by the WWTP was very variable in composition, presumably due to large variations in the industrial fraction. This undermined the very concept of a baseline model, which was based on the assumption that the characteristics of the average wastewater could be determined from respirometry measurements. Since these are time-consuming and labour intensive (a single test takes at least 24hours), it becomes impractical to do a large number of tests in order to establish a reliable average. The second was that the presence of some industrial components (probably surfactants) interfered with the dissolved oxygen measurements, and rendered the respirometry results unreliable.

A different approach was then tried, in which the average wastewater characteristics were estimated from a material balance on the sources of wastewater in the catchment (see section 3.2.3). This yielded very promising results, but these constituted the very last results of the project, and were achieved too late for the subsequent steps in the process to be completed.

8 GENERAL DISCUSSION

The principal reasons for not completing the main objective of achieving a fully tested evaluation protocol were:

1. The closure of Dyefin, the first factory selected, which discharged to the Mariannridge WWTP. This meant that the baseline model developed for Mariannridge could not be used, and a new one developed from Verulam.
2. The problems encountered with the unreliability of the respirometry measurements on wastewater entering the Verulam plant. The impact of this factor on the overall project was aggravated because it was only realized so late, because the MSc project to establish the technique had not progressed.
3. The problems with personnel capacity at the municipality, which caused long delays in undertaking a permit evaluation on the JMV Textiles factory, and then its abrupt termination.

The positive developments that were achieved during the project were:

1. A much deeper understanding of the complex issues surrounding the treatment of industrial wastewater in conventional municipal WWTPs.
2. A body of experience in the modelling of WWTPs, although not complete, particular in relation to treating industrial effluents.
3. A body of experience, similarly incomplete, in respirometry and other laboratory techniques for characterising industrial wastewater for modelling purposes.
4. A production based model of effluent generation in a textile factory.
5. A promising, material balance approach to characterizing wastewater in an industrial catchment, which appears to provide a much more effective alternative to the laboratory based approach which was pursued for most of the project.
6. A greater appreciations on the part of the municipality of the potential, the limitations and the resource requirements of WWTP modelling.

9 CONCLUSIONS AND RECOMMENDATIONS

The potential advantages of modelling for design, optimisation and control of WWTPS are well documented. However, to realise these requires a critical mass of expertise, in both the computational and analytical aspects. It is clear that these requirements were seriously underestimated, firstly in the matter of the research project, but perhaps more critically in terms of what municipalities are able to devote to the technology. Their ability to attract and retain sufficient staff with the requisite skills is severely limited, and those they have are needed for more immediate urgent responsibilities. On the other hand, there is a perception within the municipality that they need to develop in-house modelling competency to meet their future needs. This project has turned out to be too ambitious, with too many aspects that needed to be developed simultaneously.

Although the project was motivated by a perceived need of the municipality to develop a more scientifically defensible basis for setting permit limits, there seems little chance that they would be able to implement such a complex protocol in-house in the near future. The obvious alternative would be to set up a specialist consultant service, with integrated laboratory and computational capabilities. This possibility has been discussed with the municipality, and there is a proposal to establish a laboratory service along these lines as part of the MOU between the municipality and the university.

A follow-up project (WRC K5/2221) has just started, which will provide a vehicle for continuing the development of WWTW modelling. How it is conducted will be informed by the experiences gained in this project. The proposed methodology and deliverables are formulated in sufficiently broad terms that they do not need to be re-formulated, but the following issues should be emphasised:

Research issues

1. Investigation of more robust and reliable laboratory methods for wastewater characterisation.
2. The further development of influent wastewater characterisation using a combination of catchment balance and laboratory measurements.

Technology transfer issues

3. Training of municipal staff in setting up and using WWTW models.
4. Establishing a sustainable system for providing modelling services to municipalities.
5. Establishing a sustainable system for providing the supporting laboratory investigations.

10 REFERENCES

AL-QODAH Z (2006) Biosorption of heavy metal ions from aqueous solutions by activated sludge. Desalination 196 (2006) 164–176

CARVALHO G, NOPENS I, NOVAIS JM, VANROLLEGHEM PA and PINHEIRO HM (2001) Modelling of activated sludge acclimatisation to anon-ionic surfactant. *Water Sci. Technol.* **43** (7), 9–17.

CARVALHO G, NOVAIS JM, PINHERIO HM and VANROLLEGHEM PA (2004) Model development and application for surfactant biodegradation in an acclimatising activated sludge system. *Chemosphere* **54,** 1495-1502

DOLD, PL, WENTZEL, MC, BILLING AE, EKAMA, GA and MARAIS, GvR (1991) Activated sludge simulation programs. Water Research Commission, Pretoria, South Africa.

GUJER W, HENZE M, MINO T, and VAN LOOSDRECHT MCM (1999) Activated Sludge Model No. 3, IAWQ Technical Report, IAWQ, England.

HENZE, M, GUJER, W, MINO, T, MATSUO, T, WENZTEL, MC, MARAIS, GVR AND VAN LOOSDRECHT MCM (1999) Outline of Activated Sludge Model No. 2d. *Water Sci.Technol*. **39**(1) 165-182.

HENZE M, VAN LOOSDRECHT, EKAMA GA, and BRDJANOVIC D, (2008) *Biological Wastewater Treatment: Principles, Modelling and Design* IWA Publishing, London, UK ISBN:9781843391883

HENZE, M, GRADY, CPL, GUJER, W MARAIS, GvR and MATSUO T (1987) Activated Sludge Model No.1. IAWPRC Scientific and Technical Report No.1, IAWPRC, London.

HENZE, M, GUJER, W, MINO, T, MATSUO, T, WENTZEL, CM, and MARAIS, GvR (1995) Activated Sludge Model No.2, IAWQ Scientific and Technical Report No.3, IAWQ, England.

HENZE, M, GUJER, W, MINO, T, MATSUO, T, WENZTEL, MC, MARAIS, GvR and van Loosdrecht MCM (1999) Outline of Activated Sludge Model No. 2d. *Water Sci.Technol*. **39**(1) 165-182.

HENZE, M, GUJER, W, MINO, T, and VAN LOOSDRECHT MCM (2000) Activated Sludge Models ASM1, ASM2, ASM2d, and ASM3, IWA Scientific and Technical Report No. 9. IWA, UK.

IMAI A (1988) The behaviour of chromium in the activated sludge process. PhD Thesis, University of Texas at Austin, Austin, USA

HVITVED-JACOBSEN (2002) *Sewer processes-Microbial and chemical process engineering of sewer networks.* (1^{st} ed) CRC Press, USA

LANGEVELD JG, LIEFTING B and BOOGAARD FC (2012) Uncertainties of stormwater characteristics and removal rates of stormwater treatment facilities: Implications for stormwater handling. *Water Research* **46,** 6868-6880

MARAIS G.v.R and EKAMA G.A (1976) The activated sludge process part 1-Steady state behaviour. *Water SA* **2**(4), 163-200.

MELCER H (2003) Methods of wastewater characterization in activated sludge modelling. Report *Water Environment Research Foundation*

ORHON, D and ÇOKGÖR, EU (1996) COD fractionation in wastewater characterization: The state of the art. *Chem. Tech. Biotechnol*. **68**(1) 283-293.

PETERSEN B (2002) Calibration, identifiability and optimal experiential design of activated sludge models. Ph.D. Thesis. Ghent Univ. Belgium

PETERSEN, B, GERNAEY, K, HENZE, M, and VANROLLEGHEM, PA (2002) Evaluation of an ASM1 model calibration procedure on a municipal-industrial water treatment plant. *Res J. hydroinformatics.* **4**(1) 15-18.

SÖTEMANN SW, WENTZEL MC and EKAMA GA (2005) Towards developing a mass balance based wastewater treatment plant model. *WISA 2005*1

SPÉRANDIO M and PAUL E (2000) Estimation of wastewater biodegradable COD fractions by combining respirometric experiments in various So/Xo ratios. *Water Research.* **34** (4) 1233-1246

STANDARD METHODS (1995) *Standard methods for the examination of water and wastewater.* (19th edn) American Public Health Association, Washington DC, USA

SZYMAŃSKI A, WYRWAS B and LUKASZEWSKI Z (2003) Determination of non-ionic surfactants and their biotransformation by-products adsorbed on alive activated sludge. *Water Research* **37** 281-288

WENTZEL MC, MBEWE A and EKAMA GA (1995) Batch measurements of readily biodegradable COD and active organism concentration in municipal wastewater. *Water SA* **21**(2) 117-124.

WENTZEL MC and EKAMA GA (2006) Characterization of municipal wastewater. Dept Civil Eng, Univ. of Cape Town, South Africa.