BIOLOGICAL DECOLOURISATION OF TEXTILE EFFLUENT IN A NUTRIENT REMOVAL SYSTEM

An Investigation into the Performance of a 5-Stage Bardenpho Nutrient Removal System for the Removal of Colour

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Abstract

The Hammarsdale Wastewater Treatment Plant (HWWTP) 5-stage Bardenpho nutrient removal reactors were assessed to determine their decolourising performance and to determine methods of improving this performance. The assessment incorporated both full-scale and laboratory experimentation.

The decolourisation of a C.I. Reactive Red 141, an azo reactive dye, was studied in a series of laboratory experiments. The inoculum used was obtained from the HWWTP return activated sludge pumps. The results demonstrated that the dye would be decolourised by approximately 92 % within 4.5 h if the system was strictly anaerobic. Based on these results and previous research, it was concluded that the oxidation reduction potential (ORP) of the system affected the rate of decolourisation. Measurement of the ORP of the HWWTP sludge showed that decolourisation of C.I. Reactive Red 141 was taking place at a higher ORP than that recommended by other researchers. It was concluded that the discrepancy in the results was due to the difference between the inoculum and feed substrates used in these experiments and those used by other researchers.

The full-scale experiments were required to determine the performance of the HWWTP reactors, in terms of colour removal, at normal operating conditions. It was determined that the majority of the decolourisation of the influent to the reactors was occurring in the anaerobic zone of the Bardenpho reactors and that a layer of scum on the surface of this zone appeared to increase the decolourisation. The ORP of the bulk sludge in the anaerobic zone was determined to be approximately -120 to -140 mV, which was lower than the ORP required for the decolourisation of C.I. Reactive Red 141 as indicated by the laboratory experiments. A residence time distribution (RTD) model of the anaerobic zone was developed to determine the flow characteristics within this zone. The RTD demonstrated that the residence time in the anaerobic zone, approximately 57 min, was insufficient for effective decolourisation of C.I. Reactive Red 141. The RTD model was complimented by a simultaneous computational fluid dynamics (CFD) study which modelled the flow vectors of each inlet fluid.

It was concluded that decolourisation of azo dyes was feasible in the anaerobic zone of the HWWTP reactors, but that the residence time in this zone was insufficient for effective decolourisation.

Declaration of Candidate

I, Connel Bruce Bell, declare that unless indicated, this dissertation is my own work and that it has not been submitted for a degree at another University or Institution.

Connel Bruce Bell

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Glossary

Term	Description
Acclimation	The adaptation of a microbial community to degrade a previously recalcitrant compound, though prior exposure t that compound
Activated sludge	A mixed population of prokaryotic and eukaryotic microorganisms, which aerobically decompose waste in an aerated treatment system
Adsorption	Binding of dye compounds to surfaces such as microbial cells or activated carbon, usually through electrostatic interaction between the charged support and the charged cell.
Aerobic	The condition of living or acting only in the presence of molecular oxygen.
Anaerobic digestion	The microbial degradation of an organic compound in the absence of oxygen.
Anoxic	An environment where oxygen is present in the form of compounds such as nitrate or sulphate.
Anthraquinone dyes	Dyes based on the structure of 9,10-anthraquinone, with powerful electron donor groups in one or more of the four alpha positions.
Azo	Nitrogen-nitrogen double bond (-N=N-)
Bardenpho	5-stage nutrient removal system incorporating anaerobic, anoxic and aerobic treatment
Biodegradation	The microbial degradation of organic compounds to inorganic molecules
Carcinogenic	Cancer causing
Catabolism	The dissimilation of complex organic molecules, generally for the purpose of obtaining energy or simple compounds needed for synthesis of other organic matter.
Chemical oxygen demand (COD)	A measure of the total amount of organic material in the waste stream.
Chromophore	Colour causing component of dyes
Colourant	Organic chemical used for colouring fabrics or food products and includes dyes and pigments
Decolourisation	The removal of colour from solution by destruction of the

Term	Description
	chromophore
Denitrification	Microbial reduction of nitrates to free nitrogen, commonly observed with certain types of organisms utilising anaerobic respiration.
Dyeing auxillaries	Chemicals used in the dyeing process to aid the dyeing of the cloth/yarn.
Effluent	A stream flowing from a sewage tank or industrial process.
Electron transport chain	A chain of carrier molecules with fixed orientation in the cell membrane, through which electrons are transported and ATP generated.
Enrichment	Selection of microorganisms with certain characteristics, from a mixed culture, through manipulation of culture conditions.
Facultative anaerobe	An organism capable of either aerobic or anaerobic respiration.
Head space	The volume in a sealed vessel not occupied by the liquid phase.
Inhibition	An impairment of bacterial function.
Intermediates (dye)	The compounds used to synthesise dyes.
Labile	Readily degradable.
Medium	Mixture of nutrient substances required by cells for growth and metabolism.
Metabolism	The physicochemical transformations through foodstuffs are synthesised into complex elements, complex substances are rendered into simple ones and energy is made available for use by the organism.
Metabolites	Intermediate compounds formed during dye catabolism.
Mineralisation	Microbial decomposition of an organic compound into inorganic constituents such as carbon dioxide, methane and water.
Mixed culture	Culture consisting of two or more types of microorganisms.
Nutrient	Nitrogen or phosphorus
Pigment	A chemical used to impart colour on a substrate. Pigments tend to be particulate and insoluble.
Pollution	An adverse alteration of the environment.
Reactive dyes	Coloured components capable of forming a covalent bond between the dye molecule and the fibre.

Term	Description
Recalcitrant	Resistant to microbial degradation.
Redox potential	The potential produced between two electrodes in a solution referenced to a standard electrode such as hydrogen or calomel.
Residence time distribution (RTD)	The distribution of ages of liquid elements in a vessel.
Respiration	The oxidative breakdown and release of energy from nutrient molecules by reactions with molecular oxygen (aerobic respiration) or inorganic molecules such as nitrate (anaerobic respiration).
Scum	Layers of fats and oils which float on a liquid surface.
Sludge	The general term applied to the solid and liquid phases, in wastewater, as a whole.
Volatile fatty acid (VFA)	Short-chain organic acid formed by the anaerobic digestion process.
Wastewater	Liquid effluent discharged to a sewage treatment facility

Table of Contents

List of Figures

Figure No.	Description	Page
	6 were at a depth of 1.5 m and points 7 to 12 at 3.0 m.	

List of Tables

Chapter One

Introduction

1.1 WATER QUALITY IN SOUTH AFRICA

In South Africa, the increasing demand for water arising from the growth of the population and the economy has to be met from limited resources (Department of Water Affairs and Forestry, 1986). South Africa is a water deficient country, with an average rainfall of ca. 500 mm, compared to the world average of 860 mm (Department of Water Affairs and Forestry, 1986). Water is a public commodity and the actions of users and polluters generally affect others.

Although industry accounts for only ca. 16 % of South Africa's direct water use, its impact is much higher because effluents often contain toxic pollutants. Industrial water use includes process use, evaporation losses, product content and losses such as leakage. The textile industry in South Africa is both a major water user and polluter.

In coastal areas, the biggest problem with industrial water users is the amount of fresh water lost to the sea; the water should be treated and returned to the rivers for reuse. The strict effluent discharge regulations promulgated in terms of the Water Act of 1956 resulted in the construction of wastewater purification plants which discharge highly treated effluents. The reuse of effluent as a source of water will assume increasing importance in many areas of the country, particularly in areas of urban and industrial growth (Department of Water Affairs and Forestry, 1986).

1.2 THE HAMMARSDALE REGION

The Hammarsdale region was initially zoned for industrial development. Although the development never reached the expected target, the region has become the centre of the textile dyeing and yarn industry in KwaZulu-Natal. The area is primarily industrial, with approximately nine textile industries, two chicken processing plants and a number of smaller industries. The wastewater in the region, as a result, is highly coloured and of a complex nature. The Hammarsdale Wastewater Treatment Plant (HWWTP) receives approximately 65 % of its flow from textile industries. Of the balance, 25 % is from the chicken abattoirs and 10 % from domestic sources. The effluent from the HWWTP is discharged to the Sterkspruit river which feeds the Shongweni impoundment. The use of the Shongweni impoundment for large scale water supply was discontinued in 1992 (Umgeni Water, 1994) and, together with the parts of the Sterkspruit river, is regarded

as an important recreational asset to the area. Due to the industrial nature of the influent to the works, the works has experienced difficulties in the past in complying with the General Effluent Standard and the Special Phosphate Standard.

In 1994 a *Receiving Water Quality Objectives Study* (Umgeni Water, 1994) was performed to assess the Sterkspruit/Shongweni catchment system and the impact of the Hammarsdale WWTP effluent on this catchment. It was concluded that conductivity and colour impacted significantly on the Sterkspruit river (receiving water body). The colour results from unexhausted dyes which are discharged to sewer. The majority of the organic load to the works (approximately 70 %) is from the chicken processing plants while the textile industries contribute a high concentration of dissolved salts and soluble and insoluble organic compounds such as the complex textile dyes, size and natural cotton impurities.

1.3 THE SOUTH AFRICAN TEXTILE INDUSTRY

The South African textile industry was established in the first half of this century, and by 1939, was providing 3 500 jobs (Gilfillan, 1997). Major expansion took place within the industry and by 1996, there were approximately 70 textile factories registered with the Textile Federation. The Textile Federation plays an active role in negotiating with labour, monitoring the effect of international trade on South Africa, as well as producing statistics and market economics on the current state of the industry.

1.3.1 The Problem of Colour

Colour in textile effluent arises from the dyeing and printing processes, with the degree of colouration being dependent on the colour, or shade, dyed and the type of dye used. Colour is noticeable at dye concentrations of 1 mg/ℓ, thus textile dyehouse effluent is highly visual even when diluted. Colour is a surrogate property and generally indicates the presence of other chemicals or pollutants. The concentration and volume of dyehouse effluent discharged from textile industries often exceeds the assimilative capacity of the receiving water body, resulting in visible colour in the effluent. The result is aesthetic problems which initiates public concern and, moreover, restricts downstream usage of the water. The latter is most serious in water-restricted countries such as South Africa where the extensive recycling of water is relied upon to fulfil the ever increasing demand for water by the agricultural, industrial and domestic sectors (Carliell, 1993).

Cleaner production is the continuous application of an integrated preventative environmental strategy, applied to processes, products and services to increase eco-efficiency and to reduce risks for humans and the environment. In the textile industry, the concentration and volume of dye-containing effluent could be reduced by the recycling some of the dyes, auxiliaries and water and also reducing the overall chemical consumption. However, not all classes of dyes can be reused and, furthermore, dye lots can use up to four

different dyes to obtain the required hue making colour matching using the recycled stream difficult. Waste treatment involves the ultimate disposal of compounds that cannot be reused.

Waste treatment (with respect to the decolourisation of dye-containing effluent) can be achieved by chemical or biological processes. Chemical treatment processes usually consist of oxidative techniques such as ozonation which cleaves the conjugated bridges of the dyes, and ultraviolet irradiation combined with hydrogen peroxide, which cleaves the azo groups of azo dyes. In general, commercial dyes are resistant to mild to strong oxidising conditions, e.g. household bleach.

Options for the biological treatment of textile dyeing effluent may be single-phase aerobic or anaerobic processes, or multi-phase systems combining both aerobic and anaerobic processes. Decolouristaion in aerobic systems has been limited (Meyer, 1981). By contrast, anaerobic biological systems have shown considerable potential for non-specific decolourisation (Carliell, 1993; Carliell, 1994; Knapp, 1995; Seshadri, 1994; Zaoyan, 1992).

1.4 LEGISLATION

In light of the steady deterioration of water quality in rivers, the Department of Water Affairs and Forestry adopted a pollution prevention approach to control hazardous pollutants and a receiving water quality approach to control non-hazardous pollutants.

1.4.1 The South African Water Act

Before the advent of the Water Act of 1956, there was no statutory provision for State control over the purification and disposal of effluent, except that the discharge of sewage into public streams was prohibited (Department of Water Affairs, 1986). The Water Act of 1956, in anticipation of water shortages, made provision for the compulsory purification of effluent by the user to specified standards and its subsequent disposal in a manner that would make it available for reuse. The Act provided for control over the use of water for industrial purposes as well as for control over and the prevention of water pollution.

An intensive review of the 1956 Water Law was conducted in 1997 by the Department of Water Affairs and Forestry. The review was motivated by the need for preparation for new legislation that would reflect democratic principles and equitable access to the resource by all; symbolised by the slogan *some for all, forever* (Department of Water Affairs and Forestry, 1997). While management's goal is to ensure all water users will benefit from access to the water resource, ecological integrity provides a good indication of sustainability in the use of the resource. The proposed policy (Department of Water Affairs and Forestry, 1997) integrated resource-directed measures for protection, such as resource quality objectives, with source-directed measures, such as effluent standards.

The source-directed measures included the use of discharge or impact standards. These standards should be stringent enough to protect the specific water resource affected. The development of new standards, which should be more flexible and may be more strict than existing standards, was proposed. Development of a successful source-based classification system for emission standards requires that stakeholders, who are interested and affected by waste discharge, participate in the development of the standards. With the adoption of the White Paper (Department of Water Affairs and Forestry, 1997), a new process of consultation will begin in support of the development of a new National Water Bill and regulations for implementation of the policy. Participation will include communities, water users, academic institutions, scientific councils, and Government at national, provincial, and local levels. The Water Bill will provide the basis from which to ensure that all South Africans are able to satisfy their basic needs for water supply and sanitation with dignity and equity. Unless measures are taken to cherish and maintain the scarce water resources on which these services depend, these efforts will come to nothing (Department of Water Affairs and Forestry, 1997).

1.4.2 Legislation for Discharge of Textile Effluent

Increasingly strict environmental legislation has led to textile finishing industries being labelled high priority industries with respect to pollution (Licis et al., 1991). In South Africa, the following priority ranking is given to textile effluent characteristics (Carliell, 1993):

(i) Colouration of the effluent;
(ii) Salt content; and
(iii) Effluent toxicity.

Thus, effluent colouration is of priority status. Legislation in South Africa states that discharged effluent must adhere to a general standard of zero colour, however, in practice the measurement of colour is complicated by inadequate analytical methods as well as natural colouration and suspended solids in receiving water bodies. In addition, when colour is undesirable for aesthetic reasons it is difficult to correlate analytical colour measurements with colour perception by the human eye. Therefore, in practice, the zero colour standard may be modified so that the impact of the coloured effluent on the receiving water body is such that the total colour in the water is acceptable to all existing and potential downstream users. The chosen method of colour measurement at the HWWTP is based on the traditional platinum-cobalt (Hazen) measurement first introduced by Hazen (1892; cited in Davies-Colley et al., 1993) whereby the yellowness of the water sample is compared to that of a standard solution of chloroplatinate ion ($PtCl_6^{-2}$) tinted with cobalt and 1 °H (degrees Hazen) is equivalent to 1 mg Pt/ℓ of the chloroplatinate ion. This method is described in *Standard Methods* (1989).

The HWWTP was granted a relaxation to 75 °H in 1989 (Umgeni Water, 1994) and the Hammarsdale works has achieved a maximum of 90 % compliance (1992) and a minimum of 63 % compliance (1994). Since 1994 the effluent colour has been consistently below the colour limit of 75 °H largely due to the efficient operation

of the biological reactors and due to some decolourisation of the effluent by the addition of aluminium sulphate to the process.

1.5 PROJECT OUTLINE

The objective of this research project was to assess the HWWTP process to determine the performance of the biological reactors in decolourising textile dyes. The following aspects were investigated :

(i) The ability of the sludge (mainly biomass and aluminium hydroxide flocculant) to decolourise textile dyes.
(ii) The mechanisms for decolourisation (anaerobic, aerobic or adsorption to the sludge).
(iii) The rate controlling factors.
(iv) The possible methods for improving the performance of the HWWTP biological reactors in terms of colour removal.

The first phase of the project involved a review of the current and retrospective literature relevant to the decolourisation of textile dyes. The literature review covered topics such as dyes and dye chemistry, various methods and mechanisms of decolourisation with emphasis on biological decolourisation, the fate of dyes and dye metabolites in biological treatment systems and the biology of and the continuous operation of nutrient removal processes.

The literature review identified some criteria that had to be met in order to achieve biological decolourisation of textile dyes. These were :

(i) The system should be anaerobic.
(ii) An additional source of carbon should be available for metabolism.
(iii) There should be an absence of competitive electron acceptors like nitrate or oxygen.
(iv) Reducing conditions and, thus, a low oxidation reduction potentials, were favourable.
(v) Sufficient residence time in the biological system was required.

To determine whether these criteria were being met at the HWWTP, laboratory and full-scale experiments were made. It was decided to use one target dye for the laboratory experiments. The target dye was required to be representative of a dye class that was known to be problematic in wastewater systems. The dye chosen was C.I. Reactive Red 141, an azo reactive dye. Reactive dyes are hydrophilic and thus difficult to treat by adsorption techniques in activated sludge systems. Furthermore, azo dyes account for approximately 70 % of all dyestuffs and are the most important chromophore in reactive dyes. Finally, the red colour was chosen because it is known to give rise to aesthetic problems even at very low concentrations. The red colour would also make it possible to monitor the progress of the decolourisation experiments by visual inspection.

The laboratory experiments were required to elucidate the dominant mechanism of decolourisation in the HWWTP sludge. The mechanisms investigated were anaerobic decolourisation, aerobic decolourisation and colour removal by adsorption of the dye molecules to the sludge. Anaerobic serum bottle experiments were conducted using an inoculum from the HWWTP reactors to which a defined nutrient medium, the dye and a glucose solution, as the source of carbon, were added. Later, the experiments were conducted using only HWWTP inoculum, the dye and raw sewage as the source of carbon. The aerobic and adsorption experiments were conducted simultaneously and showed very little decolourisation of C.I. Reactive Red 141. The focus of the project was, thus, shifted to the anaerobic sections of the HWWTP reactors.

In determining whether the HWWTP reactors were meeting the criteria for decolourisation at the current operating conditions it was necessary to become familiar with the HWWTP nutrient removal process. A review of the literature pertaining to Bardenpho processes and similar nutrient removal processes was performed. Historical data from the plant were compiled and reviewed to assess the operation of the plant and some preliminary tests were conducted to determine the areas in the HWWTP reactors where decolourisation was most prevalent. These preliminary investigations confirmed the results found in the laboratory experiments and showed that the anaerobic zone was responsible for the majority of the decolourisation occurring in the HWWTP reactors.

Carliell (1993), Mphephu (1995) and Naidoo (1995) demonstrated that azo dyes would be decolourised by cleavage of the azo bond in strongly reducing environments. This led to the conclusion that oxidation reduction potential (ORP) may be used to determine whether a particular solution or sludge is capable of decolourising textile dyes. For this reason a detailed study of the ORP of the sludge in the anaerobic zone of the HWWTP reactors was performed. The intention was to develop a relationship between ORP and colour removal.

A tracer test was performed on the anaerobic zone to determine the residence time distribution (RTD) and develop a model of the flow patterns within this zone. This residence time was then compared with the required time for decolourisation as determined from the laboratory experiments. In a parallel study a model of the flow patterns in the anaerobic zone was developed using computational fluid dynamics (CFD) techniques and a computer program called FLUENT. The results of the CFD model were then compared to that of the RTD model

Finally, the results of the full-scale experimentation were compared with those of the laboratory experiments to determine the efficiency of the HWWTP process in terms of decolourisation. Modifications to the reactors, in order to improve decolourisation, were recommended based on the results from the full-scale and laboratory experiments.

1.6 THESIS OUTLINE

The thesis begins with a review of current and retrospective literature on the subject of dyes and the treatment of dye containing effluents which is presented in **Chapter 2**. **Chapter 3** is a review of the Hammarsdale Wastewater Treatment Plant with a description of the process and a review of the current performance of the plant. Since the project involved a wide range of experimental and modelling techniques it was decided to discuss the background and theory for each technique prior to presenting the results of the experiments. The laboratory experiments, including a brief literature review of current experimental techniques, are discussed in **Chapter 4**. **Chapter 5** presents the results of the full-scale experimental work including the measurement of the ORP of the sludge in the anaerobic zone, the residence time distribution test, a dye tracer test and a computational fluid dynamics study of the anaerobic zone. The laboratory and full-scale results are discussed and compared in **Chapter 6** and recommendations for further research and modifications to the HWWTP reactors are made in **Chapter 7**.

Chapter Two

Literature Review

Decolourisation of textile dyes is a complex and diverse topic due to the wide variety of commercial dyes available. Knowledge of the dyes and their chemistry, as well as the techniques involved in treating them, is necessary to reduce potential environmental impact of the dyes. This chapter presents a review of current and retrospective literature on the topic of decolourisation. A description of the diversity of dyes and pigments is given in **Section 2.1**, with an indication of the variability in the chemical structures and application. **Section 2.2** outlines potential treatment options for coloured effluents, with emphasis on biological treatment. This is expanded in **Section 2.3** with an explanation of the fates of dyes in biological treatment systems. The efficiency of nutrient removal systems for decolourisation is assessed in **Section 2.4**.

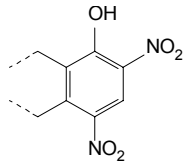
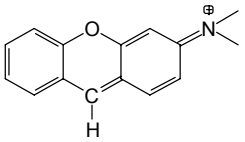
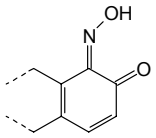
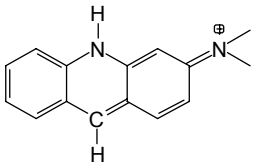
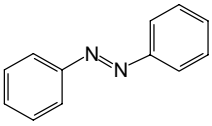
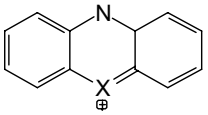
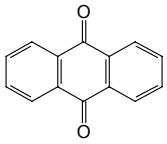
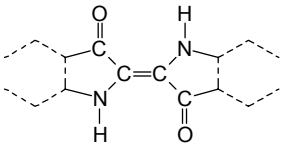
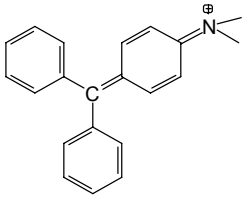
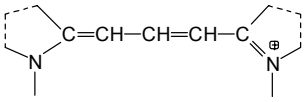
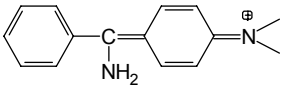
2.1 ORGANIC COLOURANTS

The introduction of synthetic organic colourants (dyes and pigments) has provided the colourant user with the ability to dye, print or pigment virtually any colour to a variety of substrates, natural or synthetic (Shore, 1990).

The structure and variety of dyes and pigments is such that they cannot be classified under a particular heading. Perhaps the only common characteristic is that they all absorb light in the visible region. This is due to the colour component of the dye called the chromophore. If one classifies colourants according to chromophores, ten to twenty classes are obtained (Meyer, 1981). The structural variety of organic colourants is best expressed by the number of dyes listed in the *Colour Index* (1976). The third edition listed over 40 000 dyes and pigments which consist of over 7 000 different chemical structures (Meyer, 1981). Most of the dyes and pigments in the *Colour Index* are placed in one of the 25 structural classes according to their chemical type (where it is known). The largest class, azo colourants, is subdivided into sections depending on the number of azo groups in the molecule, i.e. monoazo, disazo, etc. Excluding the colourant precursors, such as azoic components and oxidation bases, as well as sulphur dyes of intermediate constitution, azo dyes make up approximately two thirds of all organic colourants in the *Colour Index*. The next largest chemical class is the anthraquinones (15 % of the total), followed by triarylmethanes (3 %) and phthalocyanines (2 %) (Shore, 1990).

An illustration of this diversity of colourants is given in **Table 2.1** where eleven different chromophores are shown.

Table 2.1 : An illustration of the classification of organic colourants by chromophore.

Chromophore	Dye Class	Chromophore	Dye Class
	Nitro		Xanthenes
	Nitroso		Acridines
	Azo		Quinoneimines
	Anthraquinones		Indigoids
	Triphenylmethanes		Cyanines
	Diphenylmethanes		

In general, dyes consist of two basic components : the chromogen (electron acceptor) and the auxochrome (electron donor) which regulates solubility and dyeing (Carliell, 1993). The *chromogen* is an aromatic body containing a colour giving group called a *chromophore*. **Azo** colourants are characterised by the azo (–N=N–) chromophore and may contain one (monoazo), two (disazo), three (trisazo) or more (polyazo) azo

bonds. At least half of all commercial dyes belong to the monoazo subclass (Shore, 1990). The azo group is attached to two radicals of which at least one, but usually both, are aromatic, i.e. A–N=N–E. In monoazo dyes, the A radical contains electron accepting groups and the E radical contains electron-donating groups, particularly hydroxy and amino groups.

Dyes in the **anathraquinone** dye class (**Table 2.1**) are often termed anthraquinoids to include other polycyclic quinone structures (Shore, 1990). These are often synthesised from anthraquinone derivatives and most of them are strongly coloured even in the absence of auxochromes. The majority of anthraquinone dyes are either vat or disperse dyes.

Substituted derivatives of metal-free **phthalocyanine** (C.I. Pigment Blue 16) and a series of metal complexes, notably copper phthalocyanine (C.I. Pigment Blue 15), contribute brilliant blue and green colours to several application ranges. Pigments and reactive dyes are especially dependent on this chemical class, but examples exist in all the important ranges except disperse dyes.

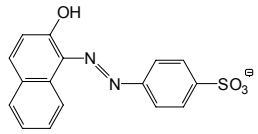
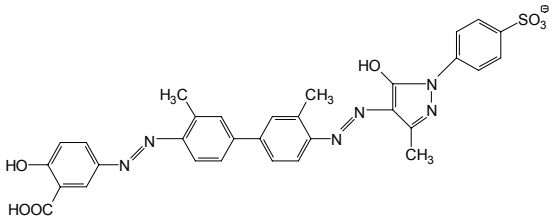
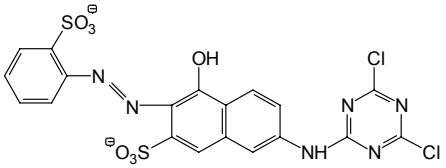
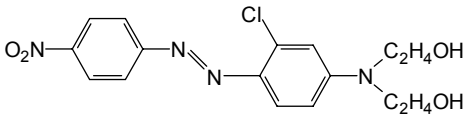
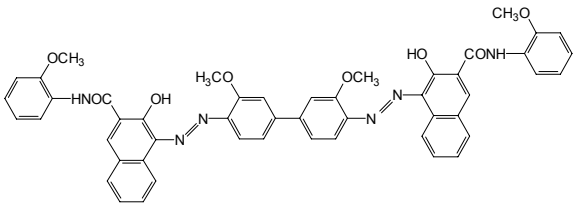
The chromophore may not necessarily determine whether the dye will be subject to microbial attack. Therefore, in terms of biodegradation, it may be useful to classify dyes according to other properties like solubility, ionic character or the various chemical substituents; a classification based on application. To further illustrate the great structural variety of dyes a classification, based on application of the azo dyes, is shown in **Table 2.2**.

Reactive dyes (**Table 2.2**) are coloured components capable of forming a covalent bond between the dye molecule and the fibre (Godefroy, 1993). The characteristic structural feature is thus the possession of one or more reactive groupings of various kinds, the most important being vinylsulphone and several halotriazine and halopyrimidine systems. Unsaturated groups such as acrylamide or vinylsulphone react with cellulose by addition to the double bond, whereas the dyes with an activated halogen substituent (Cl or F) undergo a nucleophilic substitution reaction (Shore, 1990). Reactive dyeing requires auxiliary chemicals during the dyeing process such as sodium chloride, sodium hydroxide and ethylene diamine. These chemicals are present in the waste stream together with the unexhausted dye.

A **vat** dye (**Table 2.2**) is a water insoluble colourant containing one or more keto groups. It can thus be brought into aqueous solution by a reduction process (vatting), which converts the vat dye into its alkali-soluble enolic (leuco) form. In its soluble sodium enolate form the leuco vat dye has substantivity for cellulose. The vat dyeing process thus proceeds in four stages : (i) reduction and dissolution, (ii) absorption by cellulose, (iii) re-oxidation and (iv) association of the vat dye molecules within the fibre. Vat dyes are used in both cellulosic and polyester applications and represent hues from yellows to blues to black (Shore, 1990). Auxiliaries associated with vat dyeing include sodium hydroxide, sodium hydrosulphite and other salts and surfactants.

Direct dyes (**Table 2.2**) can dye cotton (cellulosic) and viscose rayon (polyester) directly from a neutral dyebath containing sodium chloride, which decreases the solubility of the dyes. Direct dyes are relatively inexpensive and provide a wide range of hues, however, they are characterised by poor fastness. Auxiliaries associated with direct dyes are sodium salts, fixing agents and metal salts (copper or chromates).

Table 2.2 : An illustration of the classification of organic azo colourants by properties (application).

Azo Dye	Dye Class and Substrate	Dominant Mechanism of Binding
	Anionic Dye for Wool	Electrostatic
	Direct Dye for Cotton	Van der Waal
	Reactive dye for Cotton	Chemical Reaction
	Disperse Dye for Polyester	Solubility
	Pigment Dye for various Substrates	Insoluble with Resin Binder

Azo dyes are of concern because some of the dyes, dye precursors and/or their degradation products such as aromatic amines (which are also dye precursors) have been, or are suspected to be, carcinogenic (Shaul et. al., 1988). It has also been reported that most decolourisation in activated sludge systems is achieved by adsorption of the dye compounds to the sludge (Shaul et al., 1986). Therefore, treatment problems will arise when dyes that are highly soluble in water are introduced to the system. Reactive dyes are hydrophilic and,

therefore, have a low affinity for the biological sludge, remaining in solution and causing the treated effluent to be coloured (Carliell, 1993).

The structural variety and complexity of commercial dyes and pigments has motivated the need for versatile, non-specific treatment processes to eliminate colour from wastewater such that there is no impact on the environment. Unfortunately, the variety of dyes has also necessitated a variety of treatment processes making the effluent treatment task that much more difficult and costly.

2.2 TREATABILITY OF TEXTILE DYES

Over the past two decades, manufacturers and users of synthetic dyes (both local and international) have faced increasingly stringent regulations promulgated by agencies established to safeguard human health and the environment. This has meant that much of the emerging technology in these two areas arose from the need to comply with the regulations enacted. A significant proportion of this technology has been designed, specifically, to analyse for and remove colour and other priority pollutants from wastewater effluents and to circumvent pollution problems by elimination at their source (Reife and Freeman, 1996). Dyes can be removed from wastewaters by chemical, physical and biological treatment methods. Some examples of these methods are presented in this section.

2.2.1 Chemical Treatment

Chemical treatment of dyes involves subjecting the test dye or wastewater to strong reducing or oxidising agents. Naidoo (1995) found that refluxing azo reactive dyes with stannous chloride resulted in cleavage of the azo bond and thus decolourisation. The degradation products were identified and were found to be consistent with azo reduction.

Technologies using borohydride (BH_4^-) reduction are being applied to water soluble dyes containing azo or other reducible groups (Reife and Freeman, 1996). The process is generally catalysed by the presence of bisulphite and is implemented by first adjusting the pH value, then adding the bisulphite and the borohydride solution until the redox potential of the solution is between -500 and -600 mV. This then provides a reducing environment sufficient to degrade the dye. The final steps of the process involves addition of a coagulant (polyamine or aluminium based) to precipitate solids followed by either adsorption, oxidation or biological post-treatment.

Industrial dye wastewaters treated by the bisulphite catalysed borohydride reduction method showed colour removal of greater than 99 % in some instances and a minimum colour removal of 93 %. The required borohydride dosage varied between 12 and 30 mg/ℓ $NaBH_4$.

Ozone is one of the most active oxidants and exhibits strong toxicity toward animals. It is detectable as a pungent odour at levels of 0.01 to 0.02 ppm. Ozone fading of dyes occurs by the oxidative cleavage of the conjugated system of the molecule. In particular the reactivity of an azo linkage with ozone is very low compared to an olefinic or azomethine group. Although no practical commercial work method for the ozone treatment of dye wastewater has been reported, there have been interesting results from pilot-plant studies. A study in Bisai, Aichi, Japan in 1992 used a pilot plant to treat 100 t/d of the local wastewater; 95 % of which is dye wastewater. The treatment was successful at ozone concentrations up to 9.2 mg/ℓ, however the cost of treatment was more than double that of activated sludge treatment; ca. $1,57/t as opposed to $0,72/t, respectively (Reife and Freeman, 1996).

Treatment of textile effluents with hydrogen peroxide results in decolourisation, but not substantial COD removal and further treatment is often required (Naidoo, 1995). Chlorine in the form of a liquid or gas, chlorine water or hypochlorite is often used to decolourise wastewater (Reife and Freeman, 1996). This is also generally used as a pre-treatment prior to activated sludge treatment, however there is the potential for generating chlorinated organics that may be carcinogenic.

Chemical treatment of wastewaters is effective in removing the colour and, in some cases, degrading the dye compounds completely, but stabilisation of the wastewater is the ultimate goal in wastewater treatment; reduction of the organic load or COD is required. For this reason, chemical treatment is generally used as a specialised form of pre-treatment to remove a particular component (e.g. dyes), prior to the traditional activated sludge treatment.

2.2.2 Physical Methods of Decolourisation

Physical treatment methods are designed to remove the colour from the wastewater prior to discharge to an aerobic biological treatment system. Pre-treatment with flocculation compounds such as lime, alum, ferric salts or polyelectrolytes, followed by sedimentation, can remove dyes, pigments and other compounds that may be resistant to biodegradation. The disadvantage of flocculation is the production of a large amount of sludge that needs disposal (Reife and Freeman, 1996). Some treatment facilities require the addition of chemicals to reduce the level of phosphorus. Sometimes this has a two fold effect in that it removes some types of dyes from the wastewater (DeHaas, 1993) either by chemical reaction with the chromophore or by flocculation.

Membrane plants are generally used in waste minimisation and waste reduction practices to recycle some of the dyes, auxiliaries and water back into the process. Membrane plants are very effective in removing chemicals of particular molecular weights from effluent streams, however, the concentrate still requires some type of treatment or disposal. Nanofiltration and reverse osmosis have proved to be the most effective

filtration processes for removing colour and recovering water and electrolytes (Barclay, 1996, WRC No. 456).

2.2.3 Electrochemical Treatment

Electrochemical ion generation is a superior technology for the physical treatment of dyes, including metal complex dyes. This technology is also capable of removing BOD, COD, total organic carbon (TOC), total dissolved solids (TDS), total suspended solids (TSS) and heavy metals such as chromium, copper, molybdenum and zinc. The system most commonly uses an electrochemical cell to generate ferrous hydroxide directly from steel or aluminium electrodes. The wastewater is passed over the electrodes, degassed and then passed to a clarifier to settle out the newly formed solids. Typically a polymer is added to aid the flocculation of the solids. In a batch of six case studies performed in 1992 (Reife and Freeman, 1996) electrochemical iron dosages ranged from 25 to 400 mg/ℓ depending on the chemistry and concentration of the wastewaters tested. Colour removal efficiencies of up to 96 % were reported along with similar reductions in TDS and TSS and the treatment costs ranged from \$0,14 to \$0,56/m³.

Mphephu (1996) demonstrated that Reactive Red 2, an azo reactive dye, was decolourised by bulk electrolysis at a pH of 7.06. A solution of Reactive Red 2 was exposed to a potential of -715 mV (SHE) and the UV-vis spectrum of the solution was monitored with time. The absorbance of the solution between 511 and 540 nm, the range of wavelengths of the maximum absorbance of the dye, was observed to decrease with time which demonstrated that the dye was decolourised due to reduction of the azo chromophore. Isolation and identification of aniline in the completely electrolysed solution, by nucleo-magnetic resonance (NMR), proved that the dye was electro-degraded into the corresponding aromatic amines.

2.2.4 Biological Treatment

Biological treatment offers a successful and cost effective method of treating textile industry wastewaters. Biological treatment may be either aerobic, anaerobic or a combination of both. Experience has shown that the primary removal mechanism in aerobic systems is adsorption to the sludge (Reife and Freeman, 1996; Hitz, 1978; El-Geundi, 1990) whereas anaerobic bacteria have shown the potential for non-specific biodegradation of a number of commercial dyes (Zaoyan, 1992; Carliell, 1993; Carliell, 1994; Seshadri, 1994; Knapp, 1995).

2.2.4.1 Aerobic Biological Treatment

An important quality of textile dyes is that it should be resistant to oxidation. Garments and fabrics are constantly being exposed to moisture and perspiration which provides an excellent medium for bacterial growth. Only chemicals that are resistant to oxidation under these conditions are acceptable as stable dyes (Straley, 1984). An extensive study by Pagga and Brown (1986) assessed the degradability of 87 different

commercial dyes and selected five, which showed the potential to be degraded under aerobic conditions, for further investigations. Their investigations found that the five dyes contained some degradable component, but that this was not the chromophore responsible for the colour and that the colour removal was due to sorption mechanisms. Pagga and Brown (1986) concluded that short term biodegradation in activated sludge tests was unlikely and that specialised (acclimated) bacteria would be required to degrade commercial dyes aerobically.

Shaul et al. (1986) investigated the degradation of seven acid azo dyes in three pilot scale activated sludge processes. No overall conclusions were made about the fate of the azo dyes since each dye demonstrated different characteristics in the activated sludge, however C.I. Acid Orange 7 and C.I. Acid Red 88 demonstrated good removal, 87 to 99 %, by moderate adsorption and significant biodegradation. As part of a study by the United States Environmental Protection Agency (USEPA) entitled the *Fate of Water Soluble Azo Dyes in the Activated Sludge Process*, Shaul et al. (1988) investigated all possible removal mechanisms including adsorption, biodegradation, air stripping, photo degradation and chemical transformation and eliminated all possibilities except adsorption and biodegradation.

From the literature presented it was concluded that although dyes may cause some concern in conventional sewage treatment processes due to colour, they do not present any threat of toxicity.

It therefore follows that, with a few exceptions, the majority of commercial textiles dyes will pass through a conventional activated sludge treatment process. This is especially true for the hydrophilic dyes (e.g. reactive) which are not settled out in the traditional sedimentation processes (Barclay, 1996).

2.2.4.2 Anaerobic Biological Treatment

Anaerobic treatment is relatively easy to achieve and is accomplished by a number of microorganisms with rather non-specific enzymes. Anaerobic treatment has also shown the potential to degrade a number of recalcitrant and even toxic substances. Carliell (1993) demonstrated that C.I. Reactive Red 141 would be decolourised in an anaerobic system provided a source of labile carbon was available, the redox potential was below -450 mV and if there were no competitive electron acceptors present. The decolourisation was found to be first order with respect to dye concentration and the degradation occurred through the reduction of the azo bond. In this study, a series of serum bottle tests and a laboratory scale (2 ℓ) anaerobic digester were used to determine the rate of decolourisation and the factors that may influence the process. An enrichment program preceded these experiments in order to investigate the efficiency of acclimated biomass compared to biomass with no previous exposure to C.I. Reactive Red 141. The result was that previous exposure showed little improvement in rate of decolourisation i.e. 0.289/h to 0.310/h (Carliell, 1993). A period of acclimatisation is usually only required when dealing with aerobic bacteria (Kulla, 1981; Meyer, 1981; Pagga and Brown, 1986).

Metabolic pathways and a correlation between degradability and chemical structure was sought in an investigation by Meyer (1981). A reductive fission of the azo group was found to be the first step in the degradation of 14 azo dyes tested. The microorganism used was a strain of *Bacillus cereus* isolated from soil suspensions. After azo reduction no further decomposition was observed. It was concluded that for effective wastewater treatment, oxygen would have to be introduced after the first stage of the degradation to reduce the organic load, measured as the chemical oxygen demand (COD), and to fully degrade the aromatic amines formed from dye degradation. This conclusion is in agreement with the results found by Malaney (1960) and Dagley (1975) (cited in Meyer, 1981) where it was found that simple aromatic amines could be degraded under aerobic conditions via hydroxylation and ring opening.

In most cases the rate limiting step in anaerobic decolourisation is permeation through the cell wall (Meschner and Wuhrman, 1982; Yatome et al., 1991). One of the problems in determining poor biodegradability is determining whether the substance is failing to enter the cell or whether true metabolic recalcitrance exists due to the lack of enzymes controlling the metabolism of the compound. This can be overcome by investigating assays with cell free extracts. Yatome et al. (1991) found that unsulphonated azo dyes were readily decolourised by growing cells of *P. stutzeri*, but that sulphonated dyes were scarcely reduced after 8 h of incubation. However, both were readily degraded in the corresponding cell free extract indicating that the $-SO_3H$ group hindered the passage of the dye molecule through the cell membrane and thus limited the decolourisation. There is evidence (Meschner and Wuhrman, 1982) that these permeability barriers can be weakened, with toluene, to further the decolourisation process.

Carliell (1994) investigated the primary biodegradability (decolourisation) of seventeen reactive dyes associated with both dyeing and printing of cellulosic fibres. The seventeen dyes were made up of eleven azo dyes, three phthalocyanine, one anthraquinone and two metal complex azo dyes. The results were in agreement with those reported by the Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD), where Brown and Labourer (1983) found that the structure of the dye chromophore was more important than the dye class in determining the ease of decolourisation, with azo dyes generally showing substantial colour removal under anaerobic conditions. The azo dyes (with the exception of C.I. Reactive Yellow 95) showed decolourisation in excess of 70 % under anaerobic test conditions similar to Carliell (1993). The anthraquinone dye investigated (C.I. Reactive Blue 49) showed no substantial degradation. Brown and Labourer (1983) reported a variation in the results for these dyes ranging from no degradation to substantial degradation. The phthalocyanine dyes also showed a variation of results under anaerobic conditions.

2.3 FATE OF DYE DEGRADATION PRODUCTS

Complete mineralisation of the dye (e.g. to methane and carbon dioxide) can be achieved in anaerobic environments provided a well acclimatised bacterial population is used. Terzis (1997) investigated the

degradability of Acid Blue 113, a disazo dye. The bacterial population was acclimated over a period of 125 d and the final dye concentration was 100 mg/ℓ. The acclimation proved to be successful and an anaerobic biodegradation pathway for Acid Blue 113 was proposed (**Figure 2.1**).

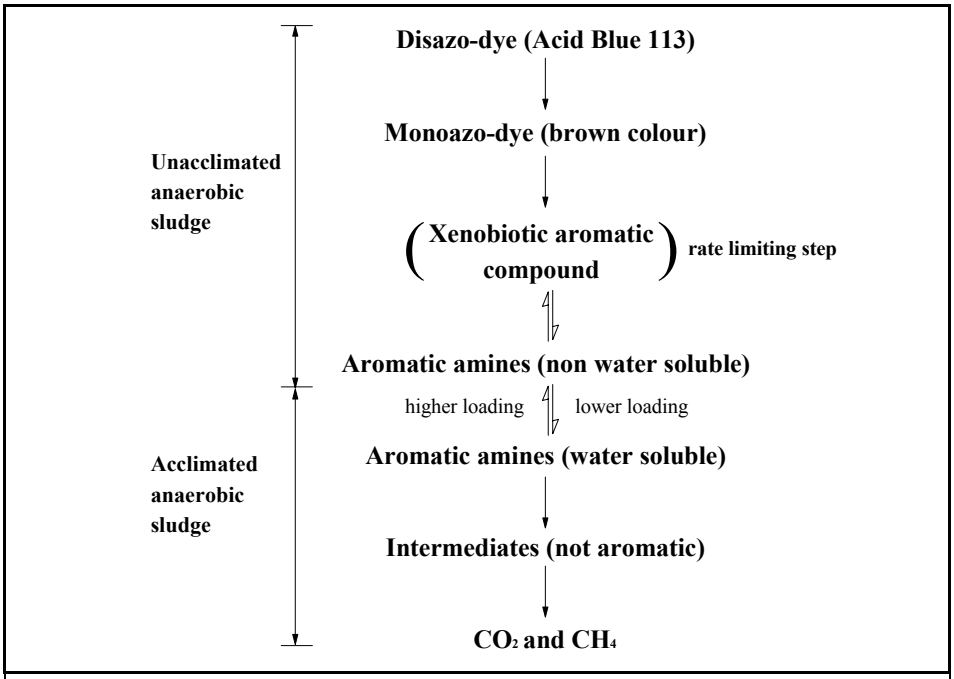


Figure 2.1 : Proposed pathway for the anaerobic biodegradation of Acid Blue 113 (Terzis, 1997).

Further serum bottle tests with the acclimated sludge revealed that an additional carbon source (glucose in this test) was required to achieve successful degradation of the dye. The decolourisation of the dye was found to be a relatively short process in the total degradability of the dye.

In the first stage of decolourisation, the colour is removed by destruction of the colour component, the chromophore; a relatively fast stage. Decolourisation of dyes by reductive cleavage represents a primary degradation step in anaerobic and some other systems. However, if the bacterial population is not acclimated or specific to the dye, this involves no elimination of chemicals from the wastewater and results in the production of aromatic amine metabolites. Environmental protection requires the mineralisation of waste compounds, therefore, if decolourisation is to be achieved in an anaerobic digester then some form of secondary treatment for the aromatic amines must be sought.

The study performed by the ETAD to investigate the primary degradability of dyes was extended to investigate the biodegradabilty of some aromatic amines suspected to be produced during primary dye degradation. Brown and Labourer (1983) investigated the degradability of the following aromatic amines :

aniline, *o*-toluidine, *p*-anisidine, *p*-phenetidine, *o*-dianisidine and 3,3'-dichlorobenzidine. The test concentration was 20 mg/ℓ dissolved organic carbon (DOC) and the inoculum was obtained from a domestic sewage works. The reference substance was aniline and the criterion for validity of the test specified that *the level of aniline degradation must be 70 % by day 14*. Both DOC and more specific (gas chromotography) analyses were used to determine the degree of biodegradation.

The results showed that aniline, *o*-toluidine, *p*-anisidine and *p*-phenetidine were degraded in aerobic environments. There was reasonably good agreement between the non-specific DOC and the specific chromatography analysis results indicating that when these substances do degrade they do so completely and do not give rise to stable metabolites.

Another observation from the experiments showed that the presence of a degradable organic source, yeast extract in this case, enhanced the biodegradation of the aromatic amines. It was not determined whether the yeast extract was (i) providing specific growth factors necessary for the breakdown of these amines, or, (ii) merely acting as a readily biodegradable food source and building up a large concentration of active bacteria which were able to mineralise the amines.

2.4 NUTRIENT REMOVAL PROCESSES

Clearly it would be advantageous to combine the anaerobic and aerobic processes to achieve both colour removal and mineralisation of the degradation products. Biological nutrient removal processes use both aerobic and anoxic/anaerobic processes to achieve removal of nitrogen and phosphorus (N and P).

2.4.1 Introduction and Background

Biological nutrient removal refers to the removal of **nitrogen** and **phosphorus** (Bailey and Ollis, 1986; Metcalf and Eddy 1991). Nutrient removal is accomplished by manipulating the activated sludge configuration to create environmental conditions in the activated sludge system that are conducive to the optimal growth and action of organisms that naturally perform the biological reactions necessary to treat the wastewater - aerobic zones for nitrification, anoxic zones for denitrification and anaerobic/aerobic sequence of zones for biological excess phosphorus removal (Wentzel and Ekama, 1996). The biological processes that take place in nutrient removal processes are discussed in the following sections.

2.4.2 Microbiology of Nutrient Removal

The highly diverse mixed cultures that develop in these activated sludge systems are responsible for the removal of carbon (C), nitrogen (N) and phosphorus (P) from the influent wastewater. These mixed cultures generally work in sequences to remove different components at different stages of the process, i.e. some lie

dormant while others are actively metabolising. The principle organism groups, their functions and the zones in which these functions are performed are summarised in **Table 2.3**.

Table 2.3 : Principle organism groups in nutrient removal systems, their function and the zones in which these functions are performed (Wentzel and Ekama, 1996).

ORGANISM	BIOLOGICAL PROCESS	ZONE
Ordinary heterotrophs (unable to accumulate poly-P)	COD removal (organic degradation; DO uptake)	Aerobic
	Ammonification (organicN $\rightarrow$ NH_4^+)	Aerobic
	Denitrification (organic degradation; $NO_3^- \rightarrow NO_2^- \rightarrow N_2$)	Anoxic
	Fermentation (F-RBCOD $\rightarrow$ VFA)	Anaerobic
Poly-Phosphate heterotrophs (accumulate poly-P)	P release (VFA uptake; PHA storage)	Anaerobic
	P release (VFA uptake; PHA storage)	Anoxic
	P uptake (PHA degradation)	Anoxic
	P uptake; P removal (PHA degradation; DO uptake)	Aerobic
Autotrophs (nitrifiers)	Nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$; DO uptake)	Aerobic

F-RBCOD = Fraction of Readily Biodegradable COD
VFA = Volatile Fatty Acid
PHA = Polyhydroxyacetate
DO = Dissolved Oxygen

2.4.2.1 Nitrogen Removal

Nitrification may be described as the oxidation of reduced nitrogen compoundssuch as proteins. These partial oxidations yield ammonia which must further be oxidised to nitrite then nitrate in order to yield a final effluent of sufficiently low oxygen demand. Two microbial species are responsible for these conversions, *Nitrosomonas* and *Nitrobacter*. This process is shown in **Equations 2.1** and **2.2**.

$$\textit{Nitrosomonas} \ : \ NH_3 + CO_2 + O_2 \rightarrow \text{cells} + NO_2^- \qquad [2.1]$$

$$\textit{Nitrobacter} \ : \ NO_2^- + CO_2 + O_2 \rightarrow \text{cells} + NO_3^- \qquad [2.2]$$

Nitrification is performed by autotrophic and heterotrophic nitrifiers. In autotrophic nitrification the bacteria derive energy for growth from the oxidation of ammonia to nitrite and nitrite to nitrate and use CO_2 as the carbon source. In the process one NADPH, a reductive cofactor (electron carrier), is consumed and two energy rich adenosine triphosphate (ATP) molecules are formed. Heterotrophic nitrifiers only oxidise

reduced nitrogen compounds if supplied with an external, organic substrate, and have not been shown to gain any energy from the reaction (Jetten, 1997).

Biological **denitrification** only takes place under anoxic conditions where no dissolved oxygen is present, but oxygen is available as part of the nitrate ion, NO_3^- (Cooper et al., 1994). Denitrification is at its most efficient under anaerobic conditions, but many bacteria can denitrify at significant oxygen concentrations (Jetten, 1997), and the entire pathway is not always shut down at a particular critical oxygen concentration, i.e. anoxic conditions can be visualised to exist between anaerobic and aerobic conditions with ideal conditions tending towards anaerobic.

The facultative bacteria that use this oxygen require a readily biodegradable source of carbon during the process (Dold et al., 1991; Cooper et al., 1994). Therefore, the anoxic zone is usually at the beginning of the activated sludge process, preceding the aerobic zone, where the concentration of readily biodegradable COD is high.

2.4.2.2 Phosphorus Removal

Phosphorus (P) appears in wastewater as orthophosphate (PO_4^{3-}), polyphosphate (P_2O_7), and organically bound phosphorus. The latter two compounds make up approximately 70 % of the influent phosphorus. Microbes use the phosphorus for cell synthesis and energy transport. As a result, 10 to 30 % of the influent phosphorus is removed during secondary biological treatment. Additional uptake beyond that required for normal cell maintenance and synthesis is required to achieve low effluent concentration levels (Metcalf and Eddy, 1991). Biological excess phosphorus removal is achieved by incorporating the orthophosphate, polyphosphate and organically bound phosphorus into cell tissue by stimulating the growth of polyphosphate (polyP) accumulating bacteria, of which *Acinetobacter* is the most common (Wentzel, 1990). The total amount of phosphorus removed then depends on the net solids (new cells) produced.

To stimulate the growth of polyP bacteria in activated sludge systems two conditions are required :

(i) An anaerobic/aerobic sequence of reactors.
(ii) Presence of volatile fatty acids (VFA's) in the anaerobic zone.

In the anaerobic reactor the VFA's are taken up from the liquid by the polyP organisms and stored internally as polyhydroxybutyrate (PHB). To convert the VFA's to PHB requires energy. The energy is obtained by breaking down the energy-rich polyP to orthophosphate. The orthophosphate is released to the bulk solution increasing the soluble P concentration in the anaerobic zone. This is termed P-release or sequestration (Wentzel, 1990).

In the subsequent aerobic reactor the polyP organisms use the stored PHB as a carbon and energy source for cell function and for growth of new cells. The organisms also use the PHB as an energy source to take up P

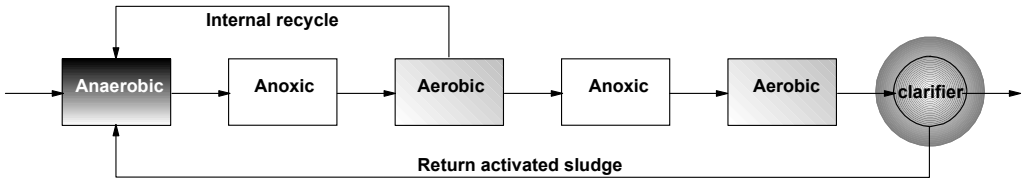
from the bulk solution to re-manufacture the polyP broken down in the anaerobic reactor, and to make new polyP in the new cells that are generated. This process is termed P-removal. Due to the new cells produced, more P is taken up in the aerobic zone than was released in the anaerobic zone which results in a net removal of P from the liquid phase in the activated sludge system.

For this process to be performed, it is critical that VFA is present in the anaerobic zone. However, very little VFA exists in municipal sewage yet biological excess phosphorus removal is obtained with these influents. Research has shown that the P-release can be related to the readily biodegradable fraction of influent COD (RBCOD) (Wentzel et al., 1985). This sewage fraction consists of simple molecules that can be rapidly metabolised by microorganisms and usually makes up about 24 % of the biodegradable fraction of COD or 20 % of the total COD (Dold et al., 1980). The polyP organisms are able to use this COD fraction in preference to the non-polyP organisms because of the lack of oxygen and/or nitrate in the anaerobic zone which the latter organisms require for normal metabolism, i.e. the non-polyP organisms remain dormant in the anaerobic section of the nutrient removal process. To provide the polyP organisms with the required RBCOD it is therefore necessary to place the anaerobic zone at the beginning of the nutrient removal process.

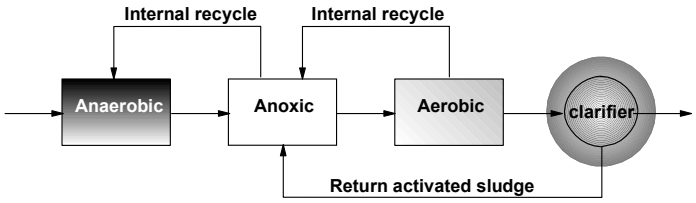
2.4.2.3 Continuous Nutrient Removal Processes

As was previously stated, nutrient removal systems were initially incorporated into existing activated sludge systems as legislation was introduced and the effluent standards amended. The first denitrification system in the UK was built in 1973-76 (Cooper et al., 1995). Today, anoxic sections are regarded as standard in activated sludge plants and biological P-removal is being favoured over chemical methods. In some cases, however, the chemical dosing is required in addition to BEPR.

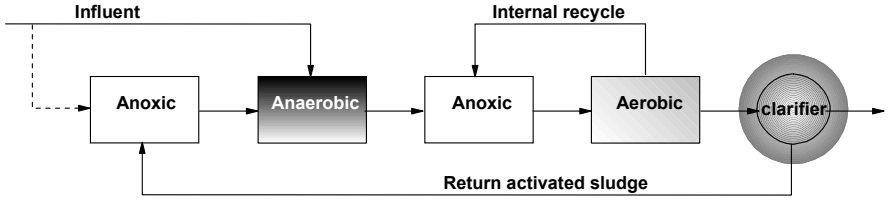
There are many variations on the anaerobic/anoxic/aerobic combination processes, e.g. 5 and 4-stage Bardenpho process (DeHaas, 1990; Metcalf and Eddy, 1991; Cooper et al., 1994; Cooper et al., 1995; Wu et al., 1995), UCT process (Walker and Gingell, 1971; Pagga and Brown, 1986; Tratnyek and Wolfe, 1990; Dold et al., 1991; Cooper et al., 1994; Mizuno et al., 1994), Biodenpho process (Metcalf and Eddy, 1991; Cooper et al., 1994). Some typical nutrient removal processes are shown in **Figure 2.1**.



(a) 5-Stage Bardenpho process



(b) University of Cape Town (UCT) process



(c) Johannesburg process

Figure 2.2 : Configuration of typical nutrient removal processes (Reardon, 1993)

The **Bardenpho** process was derived from a pilot denitrification plant which showed excellent P-removal. This led to the first biological nitrogen and phosphorus removal plant in South Africa. This process had two anoxic and two aerobic zones and a recycle of nitrified sludge from the first aerobic zone to the first anoxic zone (Cooper et al., 1994). Denitrification in the second anoxic zone was low due to the lack of biodegradable material. The five-stage Bardenpho process (**Figure 2.2a**) was aimed at enhanced P-removal by the addition of an anaerobic zone for the production of VFA's. The anaerobic zone is created by mixing the return activated sludge (RAS) with the feed sewage. The main weakness to this process was that the recycle of RAS may have contained nitrate and/or dissolved oxygen which could have lead to the anaerobic zone not being truly anaerobic. The presence of oxygen in the anaerobic zone would result in the non-polyP organisms metabolising the RBCOD in the feed sewage and thus deprive the polyP organisms of a food source and ultimately reduce the efficiency of the BEPR process (Wentzel and Ekama, 1996).

This was overcome by the **UCT** (University of Cape Town) process (**Figure 2.2b**) whereby return sludge is passed to the anoxic zone to enhance denitrification. The denitrified mixed liquor is then passed back to the anaerobic zone where P-release can occur.

Another method of protecting the anaerobic zone is the **JHB** (Johannesburg) process (**Figure 2.2c**) where the return sludge is denitrified in an extra anoxic zone prior to being sent to the anaerobic zone. The requirement of a biodegradable carbon source is sometimes met by feeding a small fraction of the raw sewage to the extra anoxic zone.

Biological nutrient removal is often supplemented by addition of an alternative carbon source (Metcalf and Eddy, 1991; Wu et al., 1995). Experimentation into N and P removal by addition of either acetate or hydrolysate was done by Isaacs et al. (1995). It was found that the denitrification rate could be instantaneously increased through the addition of either acetate or hydrolysate to the anoxic zone. The nitrogen removal capacity was approximately 7 mg COD/mg N.

2.4.3 Nutrient Removal and Decolourisation of Textile Dyes

From the literature presented previously (**Section 2.2.4** and **Section 2.3**), nutrient removal systems would possibly be suitable not only for decolourisation of textile dyes but for mineralisation of the resulting degradation products as well. Anaerobic decolourisation of dyes would take place in the anaerobic zone of the Bardenpho, UCT and JHB processes provided the conditions were sufficiently anaerobic. According to Carliell (1993) and Mphephu (1996) most azo dyes would undergo cleavage of the azo bond and become decolourised if the reducing conditions created by the anaerobic bacteria were sufficiently low (-200 to -500 mV). Therefore degradation of the dyes would depend on the levels of DO and nitrate in the return sludge and on the concentration of RBCOD in the feed sewage.

The Hammarsdale Wastewater Treatment Plant consists of six annular 5-stage Bardenpho nutrient removal reactors. Colour removal at the Hammarsdale Wastewater Treatment Plant (HWWTP) is discussed in **Chapter 3**.

2.5 CONCLUSIONS

A review of the literature on dyes, treatment of dyes and the facilities suitable for the treatment of dye containing effluents lead to the following conclusions.

- ➢ The variety and complexity of dyes in use has motivated a number of treatment processes.
- ➢ Biological treatment offers a feasible and economic method of treatment for dye containing effluents.
- ➢ Anaerobic treatment has proved more successful in the primary degradation of dyes.
- ➢ Aerobic treatment has shown the potential to degrade a number of aromatic amines which may be either toxic or carcinogenic.

- ➢ Combined anaerobic and aerobic treatment would provide the necessary environments for both primary degradation of the dyes (decolourisation) and mineralisation of the degradation products.
- ➢ Nutrient removal processes could serve as an effective form of treatment for dye containing effluents.
- ➢ The Hammarsdale Wastewater Treatment Plant has the potential to effectively treat the highly coloured wastewater produced in the region.

Chapter Three

The Hammarsdale Wastewater Treatment Plant

The Hammarsdale Wastewater Treatment Plant (HWWTP) was the focus of this research project. The treatment plant receives a large proportion of its effluent from a number of textile industries in the area and is thus required to treat a wastewater that contains a relatively high concentration of commercial dyes. The HWWTP is discussed in the following sections. **Section 3.1** gives a background to the Hammarsdale region and the HWWTP. A process description is given in **Section 3.2** and **Section 3.3** discusses the quality of the influent to the HWWTP. **Section 3.4** describes the effluent quality and the removal efficiency of the process and **Section 3.5** discusses the quality and disposal of the final effluent.

3.1 INTRODUCTION

Hammarsdale was intended to be a region of industrial development advocated by the Government decentralisation policy in the 1960's and 1970's. The ultimate daily wastewater flow for the fully developed area was estimated to reach 27 Mℓ/d (Shand & Partners, 1974; cited in DeHaas, 1990) by October 1985.

The large quantity and industrial nature of the sewage produced in this area, the high cost of chemicals and the projected growth in the area, pointed towards biological treatment of the wastewater. The most feasible option was an activated sludge process.

In 1981 an activated sludge plant in the form of a 5-stage Bardenpho annular reactor was commissioned and built. Six reactors were constructed, as opposed to two or three large ones, due to the steepness of the slope at the particular site. The result is that all the mechanical and civil structures have been reproduced six times which is a disadvantage in the operation of the plant.

3.2 PROCESS DESCRIPTION

3.2.1 Screening and Detritus Removal

The raw, unsettled sewage enters the works below the maturation river (**Figure 3.1**) where it is screened before it flows into the raw sewage sump. The flow is measured hourly by an ultrasonic flow meter. The raw sewage is pumped to the top of the works by three lift pumps (18 Mℓ/d capacity each) which are level

controlled by sensors in the raw sewage sump. Fibre and feathers are removed using 8 mm fine mesh (hydrosieve) screens. They are cleaned by hot water sprays to remove fatty deposits and prevent clogging of the sieves. The residue is disposed to landfill. Grit channels have been installed at the head of the works to reduce wear on the lift pumps. The entire plant is supported by a diesel powered generator in case of power failure.

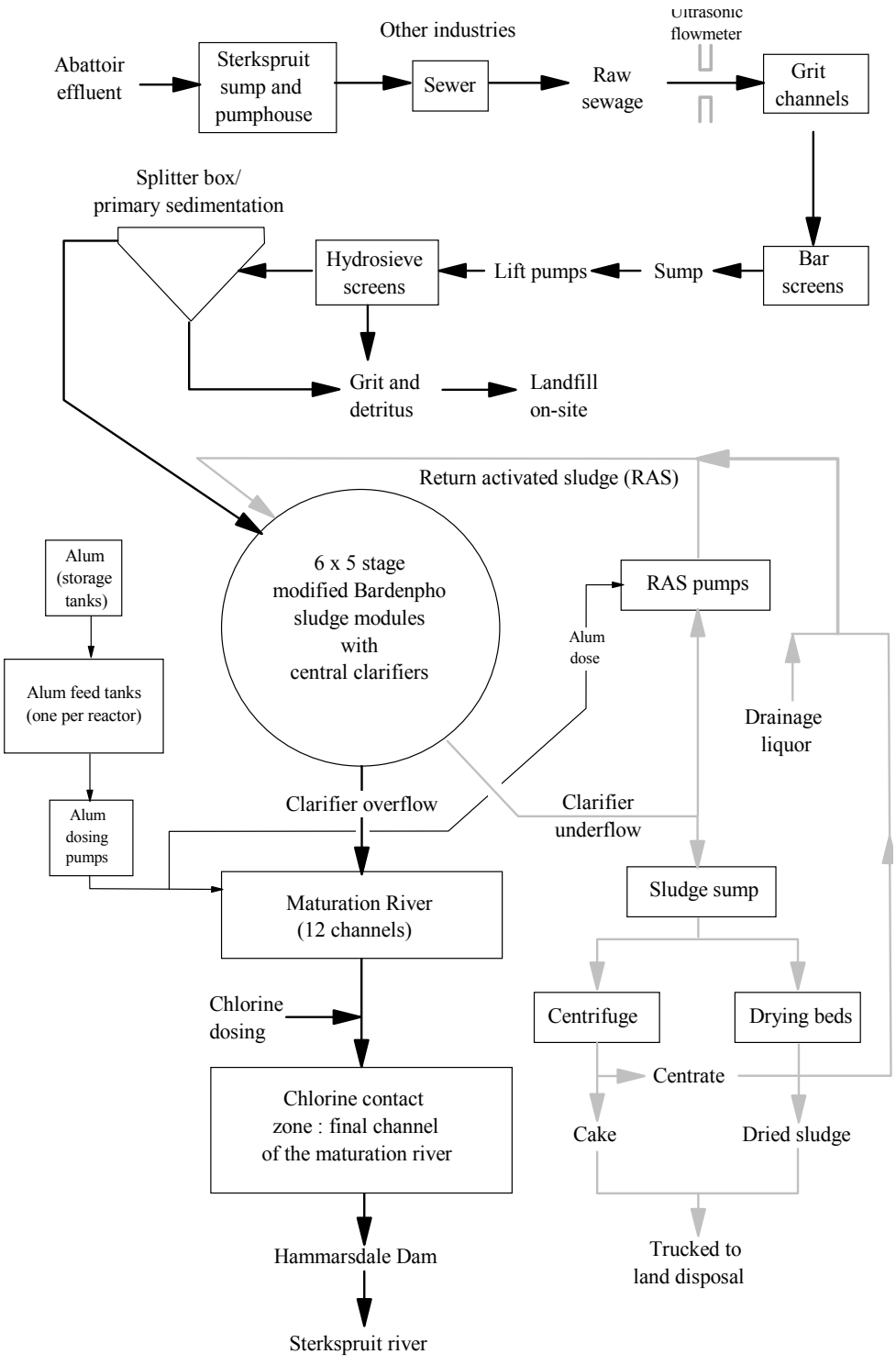


Figure 3.1 : Overview of the HWWTP process from influent to effluent. The thick, dark arrows indicate the major sludge and effluent flows, the lighter arrows indicate the solids and sludge underflows and the small arrows show dosing of chemicals.

The screened, raw influent (raw feed) then flows to the primary sedimentation tank. Due to the industrial nature of the raw feed, primary sedimentation is generally not required. This tank, therefore, serves primarily as a flow distribution box (splitter box).

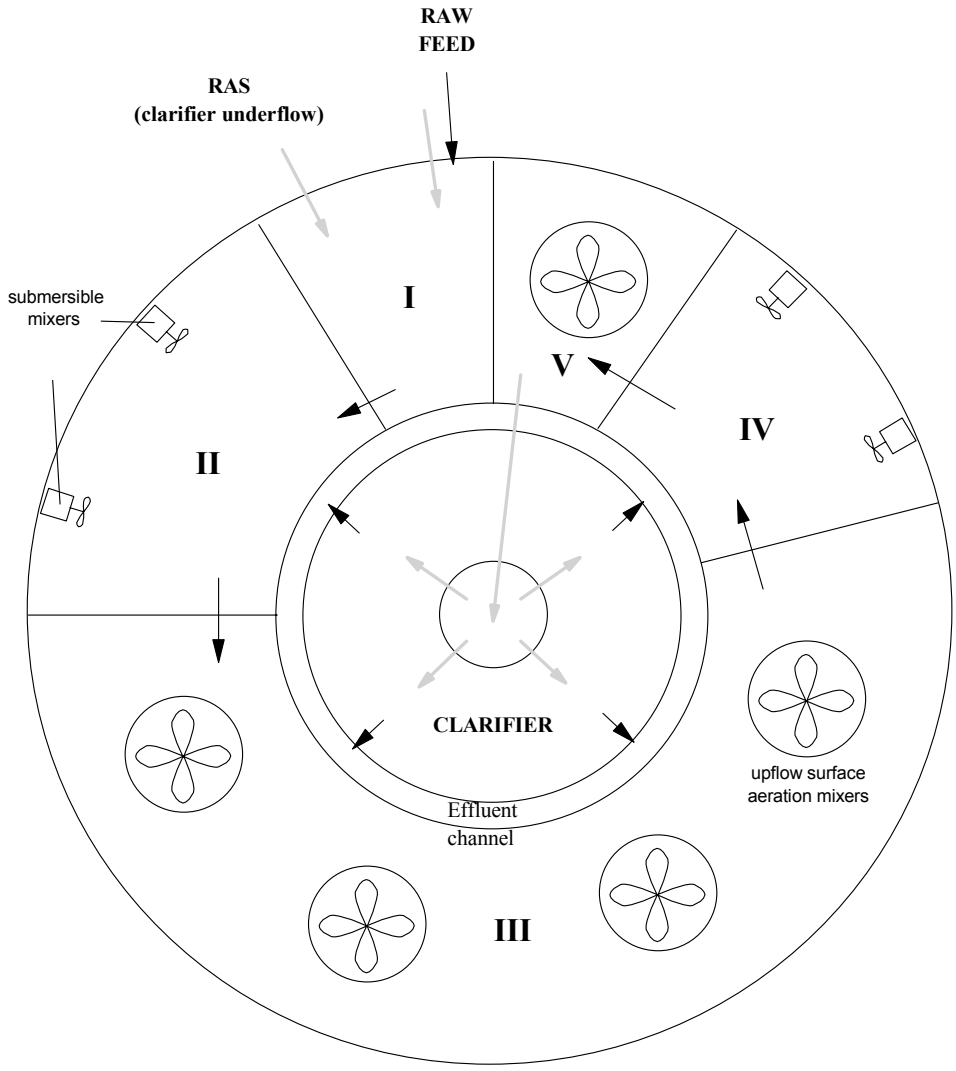
The splitter box evenly distributes the raw feed to the six Bardenpho reactors. The design capacity of the plant is ca. 32 Mℓ/d, but the flow into the plant almost never exceeds ca. 15 Mℓ/d. Therefore, it is not required to run all six reactors simultaneously and the plant has the advantage of being able to rotate reactors if required, i.e. for maintenance purposes. Generally, five reactors are operational at one time.

The operation of the Bardenpho reactors is discussed in the following section.

3.2.2 The Bardenpho Reactors

The Bardenpho system is a nutrient removal system which incorporates anaerobic, anoxic and aerobic treatment processes. The process is essentially an extended aeration system, i.e. an activated sludge system with additional modules for the removal of nitrogen and phosphorus. **Figure 3.2** shows the annular construction of one of the Bardenpho reactors at the HWWTP. Photographs of the Bardenpho reactor and the anaerobic and primary anoxic zones are shown in **Section A.7** of **Appendix A**.

The first zone in the Bardenpho reactor is the anaerobic zone (I) where the raw feed from the splitter box is mixed with the return activated sludge (RAS) from the clarifier. The anaerobic zone is not heated and is exposed to the atmosphere. The three inlet streams (one raw feed and two RAS inlets) are positioned to attain maximum contact between the raw feed and the biomass in the RAS. Nozzles have been fitted to the RAS inlets to throttle the flow and thus achieve maximum agitation in the anaerobic zone. In the anaerobic zone, the long chain organics are converted, or broken down, to volatile fatty acids (VFA's) by interacting microbial populations. The VFA's are necessary for the metabolism of the polyphosphate accumulating bacteria, the most common being *Acinetobacter*. Phosphate is released from the cell biomass in the anaerobic stage and then taken up in the aerobic stage. The release of phosphate is achieved by the taking up of the VFA's and the subsequent consumption of energy which is derived by the hydrolysis of polyphosphates stored within the cell. When these bacteria reach the aerobic stage, they become saturated with phosphates which are stored as polyphosphate. The anaerobic stage is vital to this process and acts as a selector which causes the selection of bacteria favouring phosphorus uptake (Cooper et al., 1995).



	Compartment/Zone	Angle subtended	Approximate volume (m³)
I	Anaerobic	19	290
II	Primary Anoxic	62	947
III	Primary Aerobic	205	3 133
IV	Secondary Anoxic	55	840
V	Secondary Aerobic	19	290

Figure 3.2 : Plan view of the 5-stage Bardenpho nutrient removal process. The dark arrows indicate the major fluid flows whereas the lighter arrows indicate the sludge underflow.

The anaerobic zone (I) is followed by the primary anoxic zone (II) (**Figure 3.2**). The organic and inorganic nitrogen in the feed is converted to nitrates under aerobic conditions (III); a process called nitrification. When nitrification is followed by anaerobic conditions, the bacteria begin to use the nitrates in the sludge as a source of oxygen and thus reduce the nitrates to nitrogen (called denitrification) resulting in a reduction of nitrogen in the wastewater; this is termed *anoxic conditions*. This sequence of processes (aerobic followed by anoxic) is achieved in the Bardenpho process by recycling part of the mixed liquor from the aerobic zone (III)

to the primary anoxic zone (II). This recycle used to be relatively high at 5:1, but is no longer used since the ammonia levels in the raw feed sewage are relatively low, and significant denitrification occurs through the sludge underflow recycle to the anaerobic zone. Low nitrate levels are thus maintained by *fugitive denitrification*. One of the main reasons for reducing the internal recycle to the anoxic zone was to reduce nitrate feedback to the anoxic section, thus effectively creating a larger anaerobic zone. i.e. increasing the holding time of the RAS to allow the denitrification to occur. The greater anaerobic fraction also promotes further production of VFA's and is thus beneficial to the phosphorus removal (P-removal) process (Cooper et al., 1995; DeHaas, 1993).

Experience at other Bardenpho facilities has shown that there is little advantage to increasing the anaerobic fraction beyond 0.15 (0.05 at Hammarsdale). However, fermentation at the head of the works promotes VFA production which improves the biological P-removal. This is not possible at the HWWTP due to the large industrial component of the influent wastewater. Laboratory studies (Cooper, 1994; DeHaas, 1993) have shown that activated sludge samples fed synthetic sewage containing acetate show enhanced biological P-removal, but redesign of the plant would be extraneous and probably ineffective due to the nature of the influent wastewater. Chemical dosing for P-removal was accepted as the most cost effective alternative, particularly in view of its beneficial effects in terms of COD and colour removal. Another reason for choosing chemical dosing was the possibility of complexing metals, in the sludge, which may inhibit the biological P-removal mechanism.

With the internal recycle not in use, submersible jets were installed in the primary anoxic zones to keep the sludge fully mixed in those zones. Geustyn et al. (1975; cited in DeHaas, 1990) estimated 10 W/m^3 would produce adequate mixing, but this value proved to be liberal and a mixing energy density of ca. 4 W/m^3 was found to be more reasonable. The jets' purpose has since been replaced by submersible flat mixers suspended from the outer walls of the anoxic zones.

The aerobic zones in the Bardenpho reactors are aerated by five upflow mixers; four in the primary aerobic zone and one in the secondary. To avoid sludge bulking and to improve settleability in the clarifier, the upflow mixers near the end of the primary aerobic zone and in the secondary aerobic zone operate intermittently. All six reactors were originally aerated with diffused air blowers. These were problematic since they promoted foaming (this could also be attributed to non-biodegradable detergents) and had a tendency to become blocked. They were replaced by upflow mixers which aided in breaking up the thick scum layer on the surface and had a similar replacement cost.

The blowers had a warming effect on the sludge (the air reached the reactors at ca. 35 to 40^oC) and resulted in average temperatures of 24 to 31^oC in the Bardenpho modules (even in winter). This was beneficial to the biological activity, but was not necessary since the effluent was largely of an industrial nature. After the

removal of the diffused air blowers the only source of heat was that produced by biological activity. The reduction in heating has had a negligible effect on the overall process.

The function of the secondary anoxic and aerobic zones is to reduce the concentration of nitrate and phosphate, respectively, in the wastewater to acceptable levels. Further phosphorus released in the secondary anoxic zone is then taken up by the polyphosphate accumulating bacteria in the secondary aerobic zone. From the secondary aerobic zone the sludge flows into the central clarifier where the overflow gravitates to the maturation river and part of the underflow is recycled to the anaerobic zone. The rest is wasted to the drying beds or the centrifuge for dewatering.

The sludge underflow recycle was originally proposed to be 1:1, relative to raw influent sewage, however the installed pumps provide a approximately 1.5 : 1 ratio (return sludge to raw sewage).

The clarifiers, situated in the centre of the annular reactors (**Figure 3.2**), were proportioned neglecting the recycles. Geusteyn et al. (1975) assumed that, to achieve a maximum solids concentration of 30 mg/ℓ in the clarifier overflow, a maximum rise rate of 0.6 m/h would have to be maintained provided the dissolved sludge volume index (DSVI) of the sludge did not exceed 100 mg/ℓ and the mixed liquor suspended solids (MLSS) concentration was 5 g/ℓ. At a rate of 4.5 Mℓ/d they sized the clarifiers at 20 m diameter. If the total flow (peak) is 16 Mℓ/d (i.e. 2.7 Mℓ/d per reactor) the flow to the clarifier, including recycle, would be ca. 9 Mℓ/d. Since the solids concentration is normally near 30 mg/ℓ it would seem the clarifiers were adequately over-designed. The clarifiers at the HWWTP are, however, the bottleneck of the process due to the poor settlealibility of the solids in the works.

Concentrations of MLSS as high as 10 g/ℓ have been used at Hammarsdale WWTP due to long sludge ages. Effluent quality varies very little at sludge ages older than 20 days. The limiting factor for MLSS concentrations is the performance of the clarifier. Clearly it is advantageous to have the highest possible mixed liquor solids concentration for sludge disposal to drying beds (dewatering).

3.3 SEWAGE FLOWS AND SEWAGE QUALITY

The wastewater flow into the HWWTP is shown in **Figure 3.3**. Maximum flows are experienced midweek and generally midday. The average flow into the works is ca. 12 Mℓ/d, but this drops to ca. 4 to 5 Mℓ/d on weekends and public holidays.

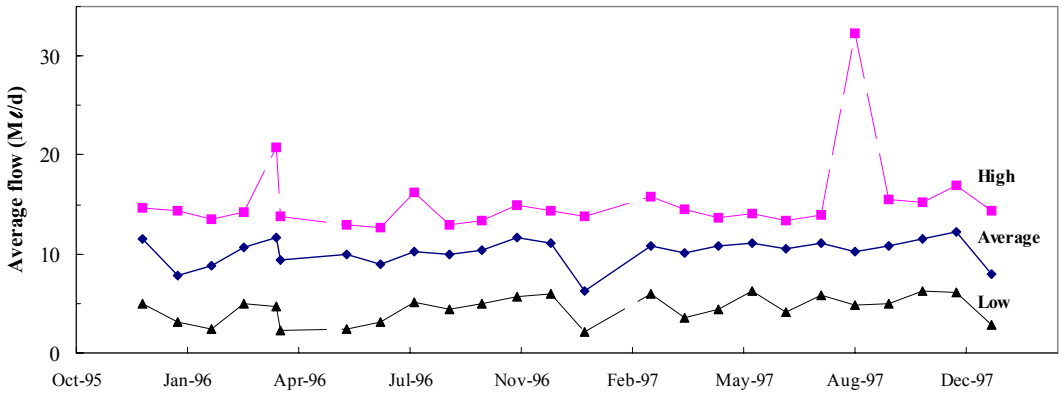


Figure 3.3 : Record of inflow into the HWWTP in the period November 1995 to December 1997

There is a relatively large industrial component to the HWWTP influent as is shown in **Figure 3.4**. Textile industries account for the majority of the flow (ca. 70 %) into the HWWTP with the remainder being supplied by a local chicken abattoir (28 %), a chemical manufacturer (0.12 %), other smaller industries and domestic sewage (2.39 %). Total flow data for the HWWTP is given in **Appendix A**.

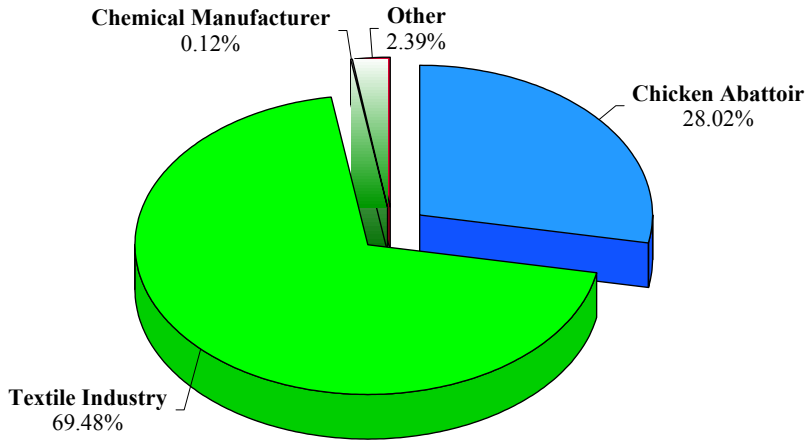


Figure 3.4 : Proportion of flows into the HWWTP according to source type

The fraction of readily biodegradable COD (RBCOD) supplied to the works is ca. 0.26 (as a fraction of biodegradable COD) which is higher than the value suggested for domestic sewage, 0.20. The RBCOD contribution to the works by the chicken abattoir is significant at 69 % of the total RBCOD. However it is similar to the total COD contribution by the chicken abattoir (61 %), which suggests that the biodegradable

content of the other industries is similar to that of the chicken abattoir. The total nitrogen (measured as TKN) contribution from the chicken abattoir is also relatively high at 77 % (DeHaas et. al, 1993).

The HWWTP site is on a steep slope which results in a wastewater of variable composition relative to domestic wastewater due to rapid gravitation, of the wastewater, to the raw sewage sump at the head of the works. The raw sewage sump offers little balancing capacity to the variable sewage feed. Although the composition of the raw feed varies during the day, the daily average composition remains relatively constant (**Table 3.1**).

Table 3.1 : Mean, minimum and maximum values measured in the raw feed during the period November 1995 to December 1997

		Mean	**Min**	**Max**	**Stdev.**
pH		7.4	6.7	8.2	0.3
Colour	°H	ND	ND	ND	ND
COD	mg/ℓ	2 375	1 888	3 015	316
Suspended Solids	mg/ℓ	541	350	965	154
Alkalinity	mg/ℓ	319	242	425	52
Nitrate	mg/ℓ	0.71	0.50	4.70	0.84
Conductivity	mS/m	258	168	900	143
Soluble Reactive P.	µg/ℓ	6 848	2 915	15 428	2 472
Permanganate Value	mg/ℓ	233	188	384	40

ND = Not Determined

The pH of the raw feed remains relatively constant at ca. 7.1 to 7.4 possibly due to the buffering capacity provided by the raw feed alkalinity. The high influent conductivity, due to the high concentration of dissolved salts contributed by some local industries, has always been problematic at the HWWTP. The activated sludge treatment system alone is not capable of reducing the conductivity and as a result these salts are released into the receiving water body.

The soluble reactive phosphate (SRP) concentration in the raw feed is relatively high and requires the addition of chemicals in the HWWTP process to reduce the levels to below the required standard. The raw feed COD is high, in comparison to domestic sewage, mainly due to the contribution by the local chicken abattoir. However, a high fraction of this COD is readily biodegradable and the process, along with alum dosing, is capable of maintaining sufficiently low effluent COD levels (**Table 3.2**). Nitrate levels in the influent are low enough to rely on fugitive denitrification to reduce the nitrate levels to below the standard.

The removal efficiency of the HWWTP process is summarised in **Table 3.2**.

Table 3.2 : Removal efficiency for the period November 1995 to December 1997

		Raw	Final	General standard [1]
pH		7.4	7.2	5.5 to 9.5
Colour	°H	ND	61	75 [2]
COD	mg/ℓ	2 375	58	75
Suspended Solids	mg/ℓ	541	15	25
Alkalinity	mg/ℓ	318	155	none
Nitrate	mg/ℓ	0.71	0.98	none
Conductivity	mS/m	258	234	85 [3]
Soluble Reactive P.	µg/ℓ	6 848	515	1 000
Permanganate Value	mg/ℓ	233	11	10

[1] Regulation No. 991, May 1994
[2] Relaxation granted by DWAF in 1995
[3] 75 mS/m + 10 mS/m form the raw water source (Midmar Impoundment)
ND = Not Determined

Data for the HWWTP effluent for the period November 1995 to December 1997 are given in **Appendix A**.

3.4 PROFILE OF REMOVALS AND FINAL EFFLUENT QUALITY

3.4.1 Colour and COD

Effective COD removal is being achieved in the HWWTP reactors (see **Table 3.3**). Due to difficulties associated with measuring the colour of the raw feed, the colour removal efficiency of the reactors cannot be determined in the HWWTP laboratory (discussed in **Chapter 5**). However the final effluent quality does meet the relaxation value, 75 °H, granted by the DWAF. Alum dosing contributes to the COD and biological colour removal by chemical degradation and flocculation of suspended or dispersed dyes (DeHaas, 1993). This is evident from the difference between the effluent quality from the clarifier and the final effluent from the maturation river (**Table 3.3**).

Table 3.3 : Colour and COD levels in the clarifier overflow and in the final effluent averaged for the period November 1995 to December 1997

	Raw	Clarifier overflows for reactors						Final
		R1	R2	R3	R4	R5	R6	
Colour (°H)	ND	80	84	80	80	84	97	61
COD (mg/ℓ)	2 375	84	85	88	87	87	112	58

3.4.2 Nitrogen and Alkalinity

Table 3.2 shows that nitrification is effectively achieved in the final effluent.

Denitrification was found to be more effective in the surface aerated reactors as opposed to the diffused aeration reactors. This may be due to the doughnut mixing pattern of the mixers which create small anoxic zones near the bottom of the aeration compartment. However, denitrification is mostly carried out in the anaerobic and anoxic sections where the concentration of readily biodegradable COD is higher.

The alkalinity in the raw wastewater is sufficient (see **Section 3.3**, **Table 3.2**) to support nitrification and provide safe levels (> 50 mg/ℓ as $CaCO_3$) in the effluent to protect the concrete structure.

3.4.3 Phosphate Removal and Alum Dosing

The biological phosphorus removal process is such that it has to supplemented by chemical dosing with alum ($Al_2(SO_4)_3$). Various techniques were tested at the Hammarsdale activated sludge plant, viz. pre-precipitation, post-precipitation and simultaneous precipitation with ferric chloride, lime and alum.

Simultaneous precipitation with alum was chosen as the most cost effective method of chemical dosing since the reactors would not have to be structurally modified other than to install alum dosing facilities.

Preliminary studies suggested that pH and alkalinity correction would not be required at doses up to 200 mg/ℓ alum, which should permit sufficient removal of COD, colour and phosphate. The average alum dosing concentration is ca. 170 mg/ℓ. The suspended solids increase, due to alum dosing, would not be problematic in sludge wasting, but would actually improve sludge settling.

Alum dosing occurs at the first channel of the maturation river via dosing pumps and to the anaerobic zones via the sludge underflow pumps (RAS pumps) from alum storage tanks. The dosing is based on a flow proportional system according to the number of lift pumps (at the head of the works) in operation, i.e. dosing is relative to the raw feed inflow.

Permanganate value (PV), also referred to as the oxygen absorbance (OA), and COD removal were optimal at 200 mg/ℓ alum dosing. However, dosing at this rate at sludge ages up to 60 to 65 days (as is sometimes required) resulted in loss of biological activity (it was assumed due to aluminium inhibition). The

concentration of aluminium in the mixed liquor solids is critical to operation. It is also interesting that surface aeration proved more effective than diffused air aeration with respect to P-removal. Alum dosing is presently the greatest expense at the Hammarsdale works.

3.5 FINAL EFFLUENT QUALITY

Although the chlorine levels were above the General Standard (0,1 mg/ℓ as Cl_2), *E.coli* counts were close to zero. This demonstrates that the final leg of the maturation river, the chlorine contact zone, was effective. The maturation river, on average, also reduces the suspended solids concentration to below the General Standard. Most of the solids generally settle out in the first leg of the maturation river.

Table 3.2 in **Section 3.3** showed that the conductivity of the effluent is high (2 to 3 times that of other works operated by Umgeni Water). This is attributable to the salt load reaching the works, principally from textile industries. A desalination plant or waste reduction/pollution prevention scheme at the factories would be required to decrease the conductivity to an acceptable level.

3.5.1 Toxic Metal Pollution

The removal of toxic heavy metals at the Hammarsdale works has always been a point of concern. **Table 3.4** shows the metal removal for a period of one month in 1986 and the Special Standards required.

Table 3.4 : Mean toxic metal influent and discharge at the HWWTP over a period of one month in 1986

Toxic Metal	Influent (µg/ℓ)	Final Effluent (µg/ℓ)	Special Standard (µg/ℓ)
Hg	43	2.4	20
Cd	1.6	1.5	50
Pb	10	3.3	100
Cr	47	30	50
Cu	160	38	20
Ni	62	59	none
Zn	593	73	300

3.5.2 Receiving Water Body

The Hammarsdale WWTP discharges effluent into the Sterkspruit river in the catchment area of the Shongweni impoundment.

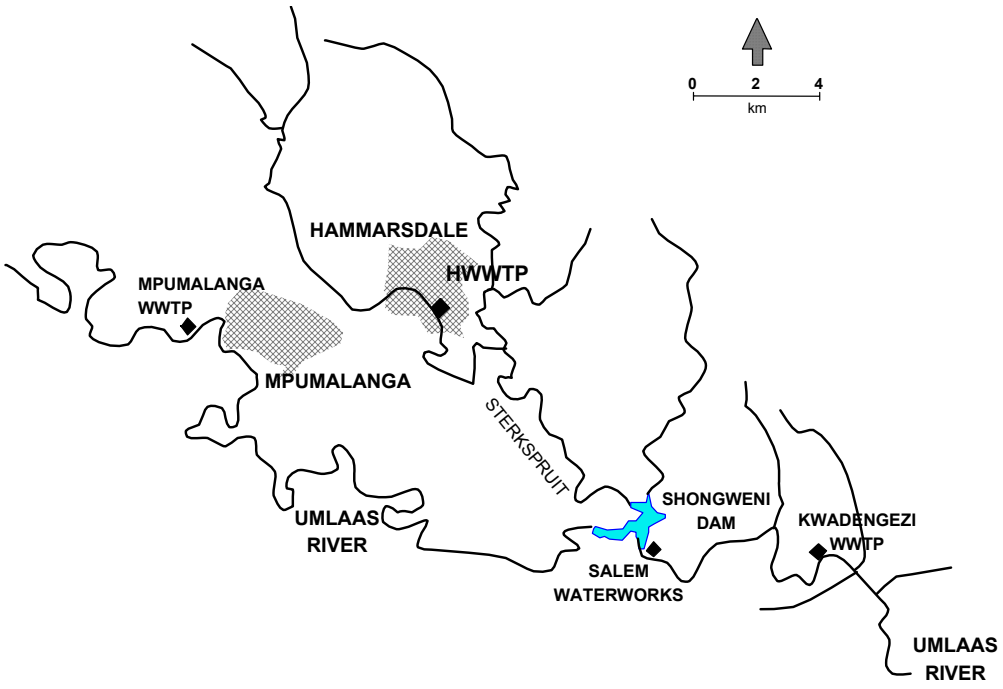


Figure 3.5 : The Sterkspruit and Umlaas catchment areas around the Shongweni impoundment.

The Sterkspruit river and the Shongweni impoundment are not used as potable water sources. Sections of the Sterkspruit river are, however, used for bathing, fishing and cattle watering. An important recreational use of the water derived from the river results from the Shongweni impoundment. Recreational activites around the impoundment include fishing, hiking, horse trails and limited boating. The impoundment is an important focus for integrating sustainable rural development and resource conservation and is likely to become an important recreational area for the Durban-Pietermaritzburg area (Umgeni Water, 1994).

The land-use between the HWWTP and the Shongweni impoundment is primarily animal grazing with limited agricultural activities due to the topography of the catchment area. The conductivity and sodium adsorption ratio of the HWWTP effluent renders the water generally unsuitable for irrigation. The colour of the HWWTP effluent due to the textile industries in the region impacts aesthetically on the receiving water body significantly in terms of the zero colour requirement of the Department of Water Affairs and Forestry (DWAF) for recreational waters.

A Receiving Water Quality Objectives Study performed by Umgeni Water in 1994, determined that colour and conductivity were the most significant impacts from the the HWWTP effluent. Relaxations on the General Standard for colour and conductivity to 75 °H and 212 mS/m, respectively, were requested and the works has complied with these standards for at least 95 % of the time since 1995 (see **Section A.5** in **Appendix A**).

3.5.3 Sludge Disposal

The detritus and grit is disposed of to landfill on-site. Part of the sludge return to the anaerobic zone is wasted to the drying beds. The longest possible sludge age is maintained in the Bardenpho modules to improve dewatering and to reduce the possibility of odours being produced in the drying beds. The 21 drying beds have a turn around period of ca. 4 days. When the weather is inclement or the drainage in the beds is insufficient, centrifuging is sometimes required and is provided by a Penwalt decanting type centrifuge.

3.6 DISCUSSION AND CONCLUSIONS

The Hammarsdale WWTP is a nutrient removal system using five-stage Bardenpho annular reactors. The system is required to remove nitrogen and phosphorus from the influent wastewater and the reactors incorporate both aerobic and anaerobic biological treatments. The HWWTP influent wastewater contains a high concentration of textile dyes and dissolved salts due to the number of textile industries in the region discharging to the works. The dissolved salts are not removed in the biological system, but there is the potential to remove the majority (possibly all) of the influent colour, due to the dyes, by biological degradation in the anaerobic sections of the Bardenpho reactors. Unfortunately, in the past, it has not been possible to determine the extent of the colour removal of the Bardenpho reactors due to difficulties associated with measuring the raw feed colour. However, the effluent colour has complied with the 75 °H requirement since 1995 (**Appendix A**) and alum dosing has increased this removal efficiency.

The degradation of commercial dyes generally occurs in anaerobic environments (**Chapter 2**). The Bardenpho system is essentially an aerated system with small anaerobic sections which makes it non-ideal for colour removal. Alternatively, the aerobic sections of the Bardenpho reactor offer the advantage of completely degrading the dye molecules and thus reducing the risk of releasing possibly carcinogenic chemicals into the receiving water body. Therefore, the HWWTP system offers the an economical and potentially ideal environment for complete degradation of commercial dyestuffs.

Chapter Four

Laboratory Experiments

Laboratory experiments were made to determine the decolourisation of C.I. Reactive Red 141 in the Hammarsdale Wastewater Treatment Plant (HWWTP) sludge. The extent of and factors influencing decolourisation were investigated in a series of experiments. The methods of investigating microbial degradation had to be investigated to find the most suitable methods. A background to these methods is given in **Section 4.1**. **Section 4.2** discusses the laboratory experiments used to determine the rate of decolourisation of C.I. Reactive Red 141 in HWWTP sludge under anaerobic and aerobic conditions. Adsorption of the dye to the sludge is also discussed. Previous research determined that C.I. Reactive Red 141 was decolourised in reducing environments brought about by anaerobic conditions and it was concluded that the redox potential of the system was important. **Section 4.3** provides a background to the measurement and application of redox potential to aquatic environments and discusses the experiments used to determine the effect of redox potential on the decolourisation of C.I. Reactive Red 141. The laboratory experiments and their significance to the HWWTP process are discussed in **Section 4.4**.

4.1 INTRODUCTION

A literature review on microbial degradation was performed to become familiar with the methods used to determine the degradation of various organic compounds. These methods are discussed in the following sections.

4.1.1 Analytical Methods for Microbial Degradation

A simple and inexpensive method is needed to monitor the relative biodegradability and possible toxicity of constituents in feed sources to microbiological treatment processes. Owen et al. (1979) developed a batch bioassay technique to determine Biochemical Methane Potential (BMP) and Anaerobic Toxicity Assay (ATA) of anaerobic treatment processes. BMP is a measure of the substrate biodegradability determined by monitoring the cumulative methane production from a sample which is anaerobically incubated in a chemically defined medium (see **Appendix D**). ATA measured the adverse effect of a compound on the rate of total gas production, i.e. the toxicity or toxic strength of a compound. This method thus eliminated the necessity for time consuming and expensive analyses during the progress of the experiment to determine the reduction in substrate strength and enabled the determination of the biodegradability of complex organic substrates.

The BMP method uses anaerobic serum bottles containing samples (substrate), defined medium and seed inoculum. The bottles are incubated at the desired temperature and the respective gas productions monitored, volumetrically, using a syringe method described by Nottingham and Hungate (1969; cited in Owen et al., 1979). The withdrawn gas is analysed for methane content. The BMP can be referenced to either volume (m^3 CH_4/m^3 sample), mass (m^3 CH_4/kg sample) or sample organic content (m^3 CH_4/kg COD). The ATA method involves exposing the anaerobic seed inoculum to increasing concentrations of the test substance and then monitoring the microbial activity (BMP). The toxic strength is determined by the concentration that results in little or no microbial activity.

The Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) developed *A Screening Test Method for Assessing the Primary Anaerobic Biodegradability of Water Soluble Dyestuffs* (Ecological Method No. 105). The method was not developed to determine the possible toxic effects of dyes on the anaerobic digestion process. The purpose of this screening test was to identify those dyes with the potential to be degraded in an existing anaerobic treatment process, domestic or industrial. Serum bottles containing anaerobic seed sludge, preferably from a nearby sewage works, and defined media (similar to Owen et al., 1979) are spiked with a known concentration of the test dye at Day 0. The sampling and analysis is then performed as follows :

Day 0 : Samples are withdrawn and diluted with distilled water. The absorbance spectrum is determined and the wavelength of the maximum absorbance and the value of the absorbance recorded.

Day 14 : The serum bottles are gently stirred and the dissolved oxygen (DO) measured to determine whether the sludge is anaerobic (DO < 1 mg/ℓ). Samples are withdrawn and analysed as on Day 0.

Day 28 and 42 : Repeat the procedure as on Day 14. The experiment may continue to Day 42 unless the decolourisation, with respect to Day 0, exceeds 80 %.

The control for the experiment was chosen as Direct Red 7, a dye which is known to be decolourised by anaerobic sludge. The validation criteria was that the Direct Red 7 should be 70 % decolourised at the Day 14 sample. The results are reported as a percentage decolourisation with respect to the absorbance of the sample measured on Day 0.

The screening test would also identify whether the dye was removed by a mechanism other than anaerobic degradation. Adsorption to the biomass would be identified by significant decolourisation on Day 0. Unstable dyes would show decolourisation in the sample bottles not inoculated with anaerobic seed sludge and reversible decolourisation would be identified by samples increasing in colour when exposed to oxygen (during sampling or analysis).

Carliell (1993) followed the methods prescribed by Owen et al. (1979) and the ETAD (Method No. 105) for the measurement of the degradability of C.I. Reactive Red 141, an azo reactive dye. The methods were modified to suit individual experiments and the standard assay condition for the dye was chosen as 100 mg/ℓ since lower concentrations made determination of the rate difficult. Although precautions were taken to minimise oxygen contamination during preparation of the sample bottles, it was difficult to exclude all oxygen from the system. This resulted in a lag phase of approximately 15 h prior to the onset of decolourisation. To minimise the lag phase, the sample bottles were pre-incubated overnight (18 h) in the presence of glucose prior to dosing with the test dye.

The experimental conditions required to determine the decolourisation of dyes in aerobic environments are less rigorous in comparison to anaerobic methods because air does not have to be excluded from the system. Sampling and analysis is performed in the same manner as anaerobic systems, however, biological activity is monitored by the oxygen uptake rate (OUR) of the aerobic bacteria as opposed to monitoring gas production rates.

The laboratory methods used to determine the decolourisation potential of the HWWTP sludge were similar to those in the ETAD Method No. 105 in terms of the sample preparation. To simulate the Hammarsdale works process (open reactors) it was initially decided to measure the microbial degradation of the HWWTP sludge under *uncontrolled* anaerobic conditions, i.e. the samples were sealed to reduce the effect of oxygen inhibition, but they were occasionally exposed to air (during sampling). Later, due to the inconsistency of these initial tests, it was decided to perform the tests under more controlled anaerobic conditions, i.e. DO < 1 mg/ℓ. The feed substrate to the bacteria used in the experiments was also important. The experiments were performed in a defined nutrient medium which was prepared as described in Owen et al. (1979) with some modifications (**Appendix D**). Raw feed, from the HWWTP, and a glucose solution were used as the feed substrate and later the experiments were performed using only raw feed and the HWWTP sludge as inoculum. Samples were withdrawn as frequently as possible and the experiments generally ran for approximately 8 h. The method of pre-incubation (Carliell, 1993) was used to reduce the lag phase prior to decolourisation of the test dye.

As mentioned in **Chapter 1**, the test dye chosen was C.I. Reactive Red 141, an azo reactive dye. This dye was determined to be representative of a dye class that was known to be problematic with respect to treatability in conventional sewage treatment systems. Reactive dyes are hydrophilic and, therefore, have little affinity to absorb to biomass and generally pass through activated sludge systems. Azo dyes account for approximately 60 to 70 % of all dyestuffs and are the most common chromophore for reactive dyes. Lastly, the red dye was chosen since this hue is known to give rise to aesthetic problems at relatively low concentrations and the red colour would make visual inspections of the progress of the experiments simple.

4.1.2 Determination of Colour in Water and Wastewater

The most representative method of determining the colour of water or wastewater is the American Dye Manufacturers Institute (ADMI) Method (Standard Methods, 1989). The method is applicable to any hue and is sensitive to small changes in colour. The method is, however, complex and requires a spectrophotometer with the ability to scan over a range of wavelengths. The process can be automated and the results logged to a computer, but this requires a dedicated spectrophotometer.

A second method, which is used at the HWWTP, determines the colour of the solution based on the spectrophotometric measurement of the liquid at a single wavelength, 400 nm, and reports the value in degrees Hazen (°H). The single wavelength method is based on potassium chloroplatinate standards (Standard Methods, 1989) where 1 °H is equivalent to 1 mg Pt/ℓ of the chloroplatinate ion. This method is less complex compared to the ADMI method, but is not sensitive to hue. Measurement of the absorbance at 400 nm is generally more specific to the range of hues from brown to yellow.

It was decided to measure colour (where necessary) on the Hazen scale in order to compare the results obtained in the laboratory experiments to those obtained at the HWWTP.

4.2 DECOLOURISATION OF C.I. REACTIVE RED 141

To determine the potential of the HWWTP sludge for colour removal, laboratory-scale experiments were conducted using C.I. Reactive Red 141. Complete evaluation of the Hammarsdale process for colour removal involved investigation of the rate, mechanism and factors affecting colour removal under both anaerobic and aerobic conditions. Adsorption of the dye to biomass was investigated as part of the aerobic degradation assay.

4.2.1 Decolourisation Screening Tests

The objective of these tests was to determine whether biological degradation of the textile dyes by the HWWTP sludge was occurring. These tests served as screening tests and were required to provide insight into the biological processes taking place in the HWWTP sludge and to provide information necessary for further detailed analysis.

4.2.1.1 Method

The tests were performed in the laboratory at the HWWTP. Samples of the raw feed and return activated sludge (RAS) were collected from the splitter box and the RAS pumps, respectively. The raw feed and the RAS were added to five 2 ℓ plastic bottles with a raw feed to RAS ratio of 1:4. This ratio was based on the flow information at the time of the test. The bottles were sealed and incubated under ambient conditions (24

°C), for approximately 12 h. The head space was estimated to be ca. 200 mℓ. Four of the bottles were then dosed with C.I. Reactive Red 141. The dye test concentrations were 50 and 100 mg/ℓ. Dye was not added to the control. To assess the effect of mixing on decolourisation, two of the dosed bottles and the control were vigorously shaken every 5 min for the first 30 min and then prior to withdrawing a sample. The remaining two sample bottles were not shaken.

Samples (25 mℓ) were withdrawn by pipette every 15 min for the first hour after dosing and then every hour thereafter. The samples were filtered (Whatman 45 µm) and the colour of the filtrate determined on the Hazen scale by absorbance measurement at 400 nm. The sample bottles were allowed to stand for a total of 5 d to determine whether there would be any long term effects on the sample colour.

4.2.1.2 Results and Discussion

The results (**Figure 4.1**) indicated active decolourisation. In the plot, the symbols represent the results of the mixed and unmixed duplicate bottles and the lines are the linear regression through the average of each duplicate set.

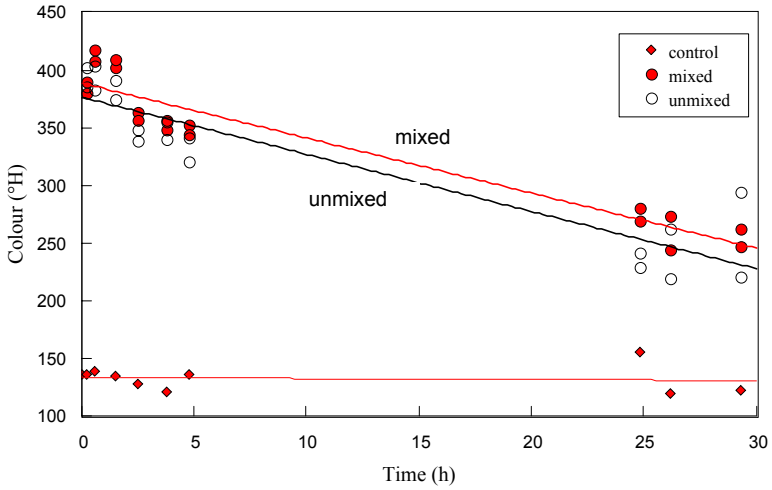


Figure 4.1 : Decolourisation of C.I. Reactive Red 141 for the degradation screening tests.

The results showed decolourisation in both the mixed and the unmixed samples with respect to time, with little difference being observed between the mixed and unmixed bottles. The colour decreased from an initial value of 400 °H to 250 °H in approximately 24 h. The change in the colour of the solutions after 5 d was negligible in comparison to the change after ca. 29 h. To better illustrate the initial degradation, the long term data are not shown in **Figure 4.1**.

The control functioned to differentiate between the residual colour in the sludge/raw feed mixture and the colour due to the test dye, C.I. Reactive Red 141. The colour in the control, largely due to the colour of the raw feed, was initially ca. 140 °H and decreased to 102 °H after 5 d.

The background colour in the samples was assumed to be equal to the residual colour in the control. The colour removal of the test samples was then ca. 60 % after 29 h. However, the colour in the test samples was still 100 °H greater than that of the control, i.e. all of the added colour was not removed. A visual observation of the samples showed that the colour of the liquid in the test bottles dosed with C.I. Reactive Red 141 turned from a red/pink to a brown/yellow colour after 2 d. Similar results were observed by Carliell (1993), where, under anaerobic conditions, the C.I. Reactive Red 141 underwent partial degradation. It was thought that only one of the two azo bonds in the dye was cleaved and that the remaining azo bond or degradation products, such as aniline, resulted in the yellow to brown colour. For coloured wastewaters of varying hue, *Standard Methods* (1989) recommends the American Dye Manufacturers Institute (ADMI) Method for a representative measure of the colour. Measurement on the Hazen scale (at 400 nm) is not designed to be specific with respect to hue and, therefore, it would be expected that a brown/yellow colour would result in elevated colour measurements as would a pink/red colour.

The rate of decolourisation of C.I. Reactive Red 141 observed in the test bottles was lower than that found by Carliell (1993). Carliell (1993) found that C.I. Reactive Red 141 would be ca. 98 % decolourised in ca. 9 h whereas the samples from the experiment at HWWTP showed 60 % decolourisation in ca. 29 h. The low rate and the incomplete decolourisation of C.I. Reactive Red 141 in the test bottles may have been as a result of the experimental conditions. The sludge in the bottles was exposed to air during sampling and shaking (due to the head space) which may have inhibited decolourisation of the C.I. Reactive Red 141 due to oxygen contamination and subsequent inhibition of the facultative anaerobic pathways.

The experiment was performed in this manner to simulate the conditions of the HWWTP reactors which are exposed to the atmosphere. Carliell (1993) demonstrated that the degradation of C.I. Reactive Red 141 was influenced by the degree of anaerobicity of the solution. A strongly anaerobic system (low redox potential) would result in cleavage of the azo bond and removal of the colour from the solution. However, a weaker anaerobic system may only result in saturation of the azo bond, which would result in colour removal, but due to the reversibility of the reaction the colour would reappear on exposure to oxygen.

The experiment was conducted at room temperature (24 °C) while the Bardenpho reactors generally operate in the range 30 to 34 °C. A lower temperature retards the microbial activity and thus the rate of decolourisation.

In the work conducted by Carliell (1993) and other researchers (Zaoyan, 1992; Seshadri, 1994; Carliell, 1994; Knapp, 1995), the experimental conditions were controlled and either strictly anaerobic or strictly

aerobic. The test dyes were exposed to selected bacterial populations (mostly from domestic anaerobic treatment facilities) which were maintained under ideal growth conditions, i.e. grown in a defined media, with a known substrate at an ideal temperature of approximately 35 °C.

These screening tests showed that decolourisation of C.I. Reactive Red 141 was possible in HWWTP sludge, although the decolourisation was not proved to be complete. The extent, rate and factors affecting decolourisation were further investigated in subsequent tests. The removal mechanisms (anaerobic, aerobic and adsorption) were investigated separately to determine the colour removal potential of each mechanism. These experiments are discussed in the following sections.

4.2.2 Anaerobic Decolourisation Experiments

The literature supporting anaerobic decolourisation is extensive in comparison to the literature on aerobic methods for colour removal. Previous research (Brown and Laboureur, 1983) has indicated that, to achieve aerobic decolourisation, specialised populations of bacteria and/or long periods of acclimatisation are generally required. Anaerobic decolourisation has shown the potential for non-specific decolourisation of a wide range of textile dyes. Anaerobic decolourisation was, therefore, the first mechanism investigated. The method used to assess the anaerobic biodegradability of C.I. Reactive Red 141 followed Carliell (1993).

4.2.2.1 Method

Serum bottles (125 mℓ) were inoculated with sludge which was collected from the return activated sludge (RAS) pumps at the HWWTP before being over gassed with oxygen free nitrogen (OFN) for 10 min. A composite raw feed sample was collected from the splitter box (primary sedimentation tank) at the HWWTP. Varying ratios of the raw feed, a glucose solution (10 gℓ) and nutrient medium (**Appendix D**) were added to the serum bottles to give a total working volume of 100 mℓ (**Table 4.1**). Two inoculum concentrations were investigated, viz. 2.4 and 1.3 %. The sludge was thickened by centrifugation. Duplicate samples were prepared to test for reproducibility.

Table 4.1 : Composition of the four batches used in the anaerobic decolourisation test.

Test Batch	Inoculum		Raw Feed (mℓ)	Nutrient medium (mℓ)	Glucose solution (mℓ)
	Solids Concentration (%)	Volume (mℓ)			
I	2.4	50	50	-	-
	1.3				
II	2.4	50	-	50	-
	1.3				

III	2.4	30	40	30	-
	1.3				
IV	2.4	30	-	40	30
	1.3				

The sample bottles were over gassed (OFN) for 15 min and sealed with butyl rubber septa and aluminium caps. The sample bottles were incubated, in a water bath, at a constant temperature of 30 °C. After 24 h the gas pressure in the sample bottles was equilibrated, using a hypodermic syringe, and then dosed with a 1 g/ℓ C.I. Reactive Red 141 dye stock solution (10 mℓ) to give a concentration of ca. 46 mg/ℓ in each bottle. Each test batch had a control that was not dosed with the dye solution.

Samples (10 mℓ) were withdrawn every 2 h, with a hypodermic syringe. The withdrawn volume was replaced with OFN. The samples were centrifuged at 3 000 rpm for 15 min and the absorbance of the centrate was measured at the wavelength of the maximum absorbance of C.I. Reactive Red 141, 525 nm (Ultrospec II Model 4050). Distilled water was used as a reference.

4.2.2.2 Results and Discussion

The serum bottle tests were used to determine whether HWWTP sludge could decolourise textile dyes if strictly anaerobic. If decolourisation of C.I. Reactive Red 141 was successful then the rate of decolourisation and the factors affecting the decolourisation could also be derived from these tests. The results for Batches I to IV are presented in **Figure 4.2**. In the plot, the symbols represent the results of the duplicate samples for the 1.3 % and 2.4 % solids concentrations.

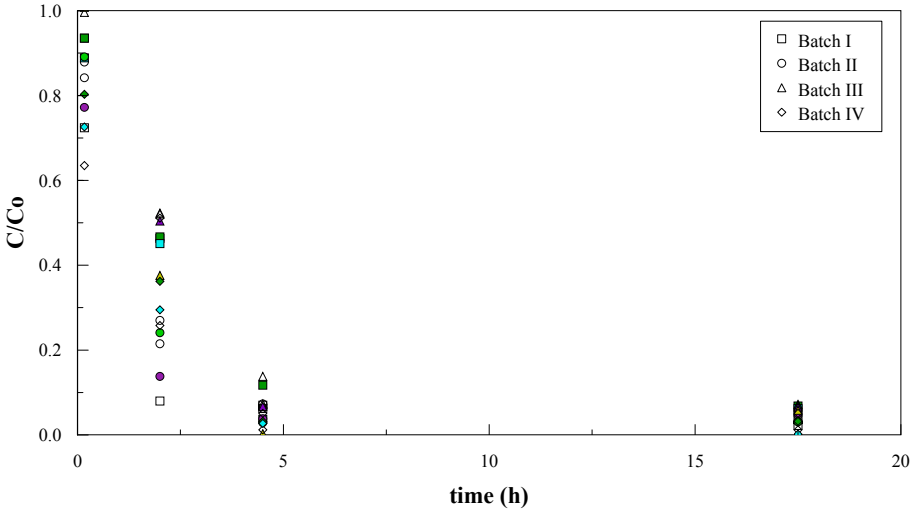


Figure 4.2 : Degradation of C.I. Reactive Red 141 in Batch I to IV for both 1.3 % and

2.4 % solids concentrations.

The results demonstrated that C.I. Reactive Red 141 was decolourised in Batches I to IV. There was some scatter of the results caused by inaccurate measurement of the absorbance of those Batches containing raw feed. This was due to solid material not being effectively removed during the centrifuging.

Batch I simulated conditions most representative of the HWWTP operation (raw feed and RAS only). Batch IV was representative of the situation whereby the feed sewage contained a high concentration of readily biodegradable COD (RBCOD), i.e. glucose. The results of Batch I (**Figure 4.3a**) were compared to the results for Batch IV (**Figure 4.3b**) to determine the effect of increasing the fraction of RBCOD.

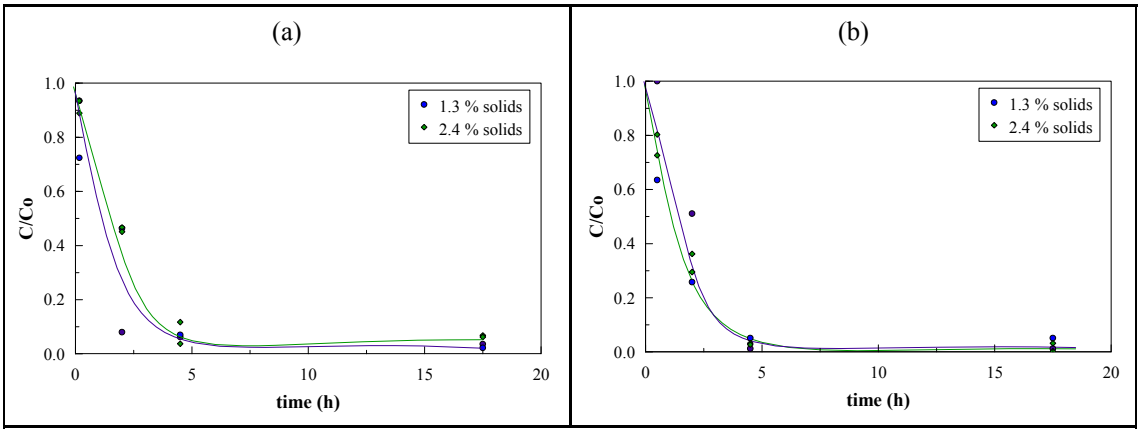


Figure 4.3 : Degradation of C.I. Reactive Red 141 in (a) Batch I and (b) Batch IV for both 1.3 % and 2.4 % solids concentrations.

Figure 4.3 shows that there was little change in the rate of decolourisation when the source of feed COD was increased by the addition of glucose. The results for Batch II and III were similar to those presented in **Figure 4.3** (**Appendix B**). The percentage decolourisation of C.I. Reactive Red 141 ranged between 95 and 98 %. There was over 92 % colour removal in the first 4.5 h in all four Batches.

To better indicate the comparison between the various assay conditions, the rates of decolourisation for each test batch was calculated in terms of *half-life*. The half-life is the time required for the dye concentration to reach half its initial value, i.e. $C = ½C_o$. These values were determined by fitting a curve to each set of results, by eye, and then reading the value from the plot. These results are shown in **Figure 4.4**.

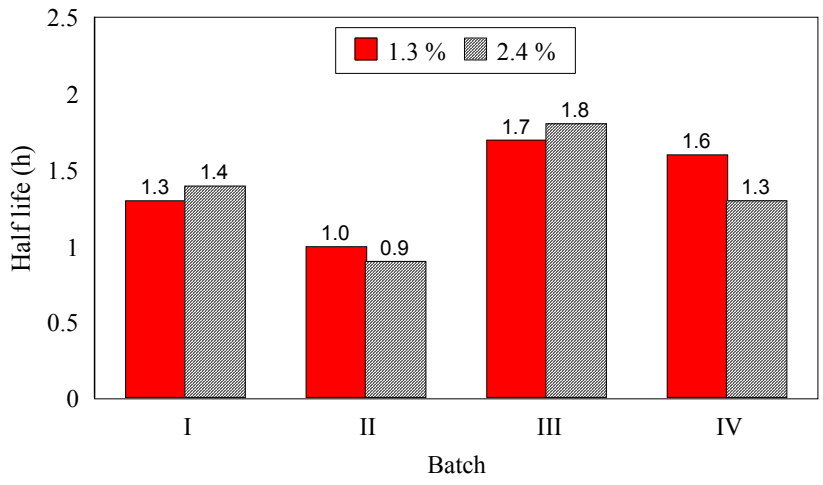


Figure 4.4 : Half lives for C.I. Reactive Red 141 under anaerobic conditions and various assay conditions.

Figure 4.4 shows the time required for the microorganisms to reduce the dye concentration to half its initial value which is indicative of the rate of decolourisation. Therefore, a lower half-life indicates a higher rate of decolourisation. The results were inconclusive with Batch II and IV showing an increased rate with increased solids concentration and Batch I and III showing a decreased rate with increased solids concentration. It was expected that, at higher solids concentrations, the rate of decolourisation would increase due to the increased contact between microorganisms and the dye resulting in an greater number of sites at which the dye was being reduced.

The assay conditions in Batch I were the most representative of the HWWTP process, however, the ratio of sludge to raw feed in the HWWTP reactors is 1.5:1 (RAS : raw feed) as opposed to the assay conditions of 1:1. The results show that the dye is 50 % reduced in ca. 1.3 h and 1.4 h for the 1.3 % and 2.4 % solids concentrations, respectively. There was little variation in the results for different solids concentration indicating that thickening of the sludge at the HWWTP would have little effect on the rate of decolourisation. The experiment did, however, show that decolourisation in HWWTP sludge was possible without addition of an external source of carbon or nutrients.

The rate of colour removal in Batch II, containing RAS and nutrient medium, was relatively higher than that of the other Batches. This Batch contained a lower COD concentration and a considerably lower fraction of RBCOD since no additional substrate (glucose or raw feed) was added. It was expected that the increased RBCOD would increase the rate of decolourisation by promoting microbial activity and thus result in an increased rate of reduction of the available electron acceptors. This would then have driven the redox potential of the system lower and thus reduced the dye. This was not the case however. Instead, those bottles

containing the higher COD concentration showed a marginally decreased rate of decolourisation, i.e. increased half-life.

A test using similar conditions to those used for Batch I (raw feed and HWWTP sludge) was repeated one week later. The absorbance was measured at the wavelength of the maximum absorbance of the test dye, 525 nm, and at the wavelength used to determine colour on the Hazen scale, 400 nm (**Figure 4.5**). The latter wavelength was used to compare the results with those obtained at the HWWTP during the daily analyses where the absorbance of the sludge liquor and effluent is measured at 400 nm and the colour determined on the Hazen scale (Standard Methods, 1989).

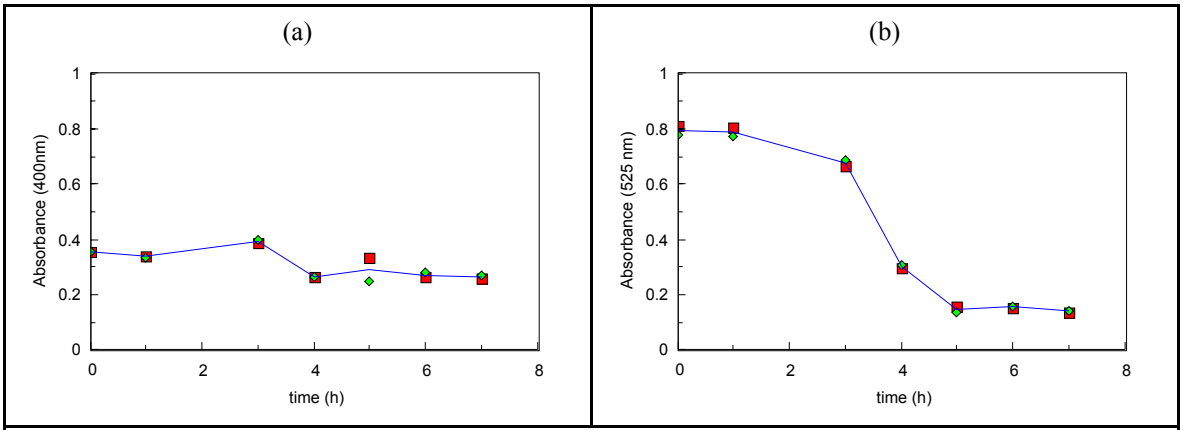


Figure 4.5 : Degradation of C.I. Reactive Red 141 in HWWTP sludge and raw feed at (a) 400 nm and (b) 525 nm, the wavelength of the maximum absorbance of the test dye.

The absorbance, measured at 525 nm, of the samples after 5 h for this test and that measured for Batch I were similar (ca. 0.06 in Batch I compared to ca. 0.13). From **Figure 4.5** it can be seen that although the decolourisation of C.I. Reactive Red 141 is 90 % complete within 5 h, the absorbance of the solution, measured at 400 nm, does not change significantly (ca. 25 %). This suggested that the colours normally detected at lower wavelengths (yellows and browns), were not completely decolourised under anaerobic conditions.

Previous tests (**Section 4.2.1**) indicated that, at 400 nm, the absorbance of the controls was approximately 0.140 and decreased to 0.100 after two days. The latter is indicative of the background absorbance at the

HWWTP. Addition of the test dye caused the absorbance of the solution to increase to ca. 0.400 when measured at 400 nm. Measurement of the absorbance of the dye at 525 nm is specific to C.I. Reactive Red 141 in any solution. Therefore, measuring the colour of the solution at 400 nm would not give an accurate indication of the degree of colour resulting from the dye.

4.2.3 Aerobic Biodegradation and Adsorption

Adsorption to biomass and aerobic biodegradation, although not as effective as anaerobic degradation, are documented mechanisms of decolourisation (Frostell, 1981; McKay, 1980; El-Geundi, 1990; Zaoyan, 1992; Seshadri, 1994). Colour removal by aerobic biodegradation and/or adsorption by the HWWTP sludge was investigated in order to assess the efficacy of these mechanisms.

A screening test method was developed to determine whether significant decolourisation occurred under aerobic conditions. If the experiment proved successful then further investigations would be implemented to determine the extent of each removal mechanism individually.

To determine the degree of adsorption of the dye to the HWWTP sludge, the colour of the raw feed had to be determined. The raw feed contains colloidal material which causes inaccuracies in the spectrophotometric determination of colour. After the raw feed has been mixed with the RAS, the colloidal material is precipitated by the alum present in the RAS and causes no further interference. Alum is dosed to the HWWTP process at the RAS pumps, between the clarifier to the anaerobic zone (**Chapter 3**), and at the maturation river following the reactors.

Due to the presence of suspended solids and colloidal material in the raw feed, the standard methods of colour measurement are inadequate. The colloidal material cannot be removed by filtration through 45 µm filter paper. Concomitantly, the removal of the colloidal material from the raw feed may result in removal of some of the colour since some textile dyes are present as dispersed suspensions. To eliminate the interference caused by the solid material in the raw feed it was decided to completely remove the solids and artificially add the colour by dosing the raw feed with textile dye. This procedure and the sample preparation method is discussed in the following section.

4.2.3.1 Sample Preparation and Method

An overview of the sample and experiment preparation is shown in **Figure 4.6** and the numerals in the method description refer to those in **Figure 4.6**. Sludge (RAS) and raw feed samples were collected as described in **Section 4.2.1.1**. The raw feed and RAS were centrifuged at 4 000 rpm for 20 min and the solids were retained (I). The raw feed was filtered (II) through a series of sintered glass filters (pore size 5 to 250 µm) and then through a Celite filter aid (Standard Methods, 1989). The filtration was repeated until the turbidity of the raw feed was zero or until the lowest turbidity was attained. The turbidity was determined

(III) using a turbidimeter (HACH Model 16 800). The centrate from the RAS (600 mℓ) was mixed with the filtered raw feed (400 mℓ) (IV) and the absorbance was measured at 400 and 525 nm (V). The test dye, C.I. Reactive Red 141, was dosed to a concentration of ca. 46 mg/ℓ (VI) and the absorbance measured at 400 and 525 nm (VII). The absorbance of the sample measured at step (VII) represented the absorbance of the solution at time t = –1 h. The solids removed in step (I) were resuspended in the mixture (VIII) and a sample (25 mℓ) was withdrawn. The absorbance of this sample, representing the absorbance of the solution at t = 0 h, was measured at 400 and 525 nm (IX). The sampling procedure commenced at this point in the method.

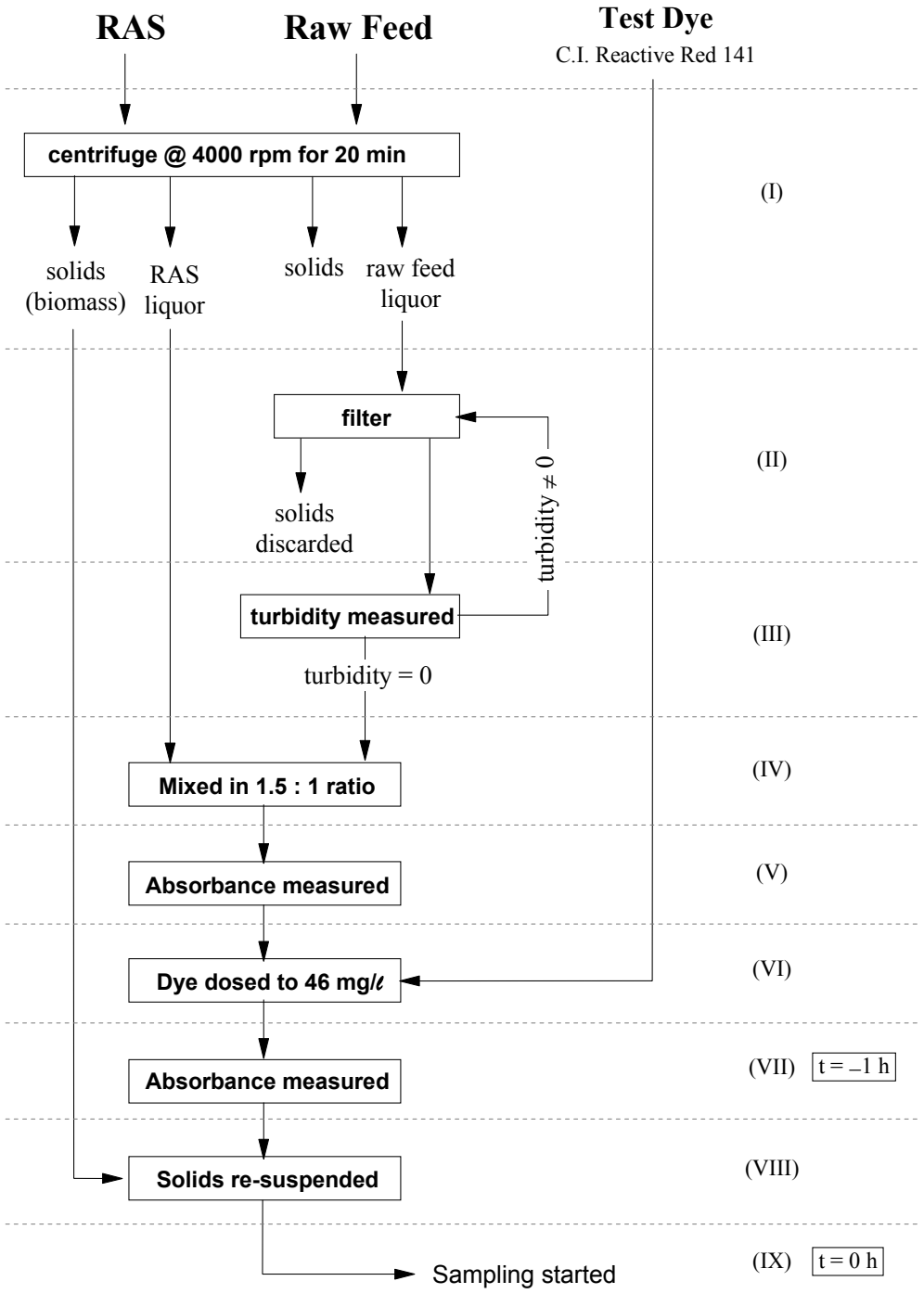


Figure 4.6 : Flow diagram of the method for measurement of decolourisation of C.I. Reactive Red 141 by aerobic degradation and/or adsorption. The diagram shows the method from sample collection to the start of sampling.

The sludge, which was continually mixed, was sparged with air at a rate of 6 ℓ/min. The dissolved oxygen (DO) concentration was measured to ensure that the system was fully aerobic. Samples were taken every 5 min, for the first 15 min, and then at hourly intervals. The sampling interval was increased when there was

no observable change in colour. Samples (10 mℓ) were centrifuged at 4000 rpm for 20 min and the absorbance of the centrate was measured at 525 nm and 400 nm, respectively. The test continued for 5 d.

4.2.3.2 Results and Discussion

The results of the experiment (**Figure 4.7**) demonstrated that there was no significant colour removal by aerobic degradation or adsorption.

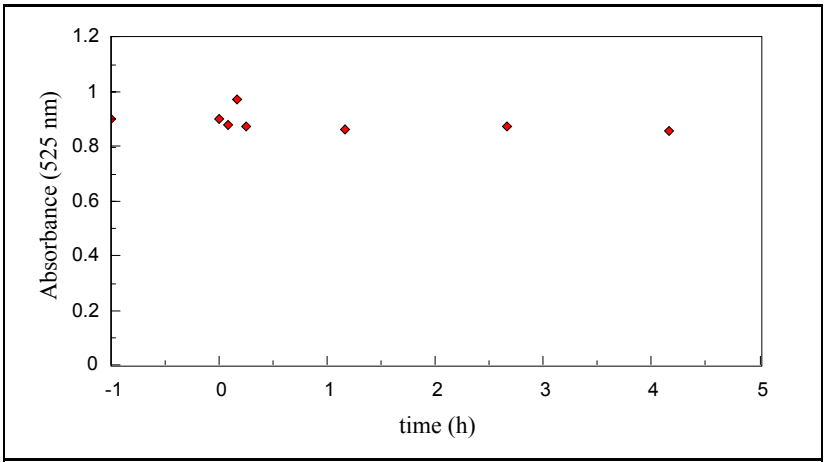


Figure 4.7 : Aerobic degradation test results. The colour of the sludge liquor prior to dosing of the dye is represented by the result at time = –1 h.

The absorbance of the samples decreased from ca. 0.90 to 0.86 after approximately 4 h. For the remainder of the experiment (5 d) the colour of the liquor did not change significantly (less than 1 % reduction in absorbance). The colour of the liquor, at t = –1 h, was the colour of the liquid after dosing with C.I. Reactive Red 141 dye, i.e. the starting colour. The colour of the solution was seen to decrease marginally (ca. 2 %) after the addition of the solids (biomass) which suggested that the degree of colour removal due to sudden adsorption of the dye to the biomass was not significant.

The correct procedure to monitor aerobic activity is to measure the oxygen uptake rate (OUR) of the bacteria. It was suggested (DeHaas, personal communication, 1996) that measurement of the DO in the sludge would give a sufficient indication of the OUR. The DO should decrease on addition of the raw feed and then steadily increase to some equilibrium value where aerobic activity should be prevalent, i.e. O_2 is the primary electron acceptor.

The DO increased from 5.4 mg/ℓ, at the start of the test, to 6.7 mg/ℓ in 10 min, where it remained constant for the duration of the test. It was therefore assumed that the bacteria were fully aerobic 10 min after the start of the aeration.

The results presented in Section 4.2 demonstrated that aerobic treatment was not an effective treatment for azo dyes, but that anaerobic treatment was. This confirmed the findings of Carliell (1993) and Mphephu (1996) that reducing conditions (anaerobic) were required to decolourise azo dyes.

4.3 REDOX POTENTIAL AND COLOUR REMOVAL

Previous work has shown that the colour caused by C.I. Reactive Red 141 was removed by reduction of the dye chromophore, i.e. breaking the azo bond (Carliell, 1993). This led to the conclusion that reducing conditions were conducive to dye degradation and that redox potential, also termed oxidation reduction potential (ORP), could be used as an indicator for determining the potential of a solution or bacterial environment to degrade textile dyes. In order to determine the reducing potential of the HWWTP sludge and the effect of redox potential on the degradation of dyes in anaerobic environments a series of experiments were conducted. A discussion on redox potential and these experiments is presented in the following section.

4.3.1 Redox Potential Measurement in Natural Waters and Wastewaters

Oxidation reduction potential (ORP) is a measure of the electron activity in an aqueous environment (Gupta, 1994). In a reducing environment there is a tendency to donate electrons and the ORP is low or negative, e.g.

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{2+} \qquad [4.1]$$

In the oxidation reduction reaction of iron and cerium the Fe^{2+} ion is oxidised to Fe^{3+}. The electron activity of the solution in equation 4.1 will be determined by :

(i) the ease with which the electron can be removed from the atom or ion, and,

(ii) the relative proportions of Fe^{3+} and Fe^{2+}. The more Fe^{3+} ions that are present, the greater the affinity of the solution for electrons and the lower the ORP.

Direct ORP measurements, used to determine the reducing or oxidising capability of a solution, are commonly made in polluted streams, chlorinated waters and industrial wastewaters (Orion, 1982). ORP is usually a useful control parameter in water and wastewater treatment and the equipment required is more robust and generally less expensive than the laboratory equivalents. With a good understanding of the ORP one may efficiently control such operations as disinfection, biocide treatment, odour and colour control, organics destruction and dechlorination (Gray, 1993).

There are many redox reactions occurring simultaneously in groundwaters and wastewaters (Strand, 1995; personal communication). The resulting potential of the solution is a weighted average, based on molar activity, of all the electroactive components. Since ORP responds to chemical activity and not simply

concentration it is usually only useful as a qualitative indicator. A change in the ORP will indicate a change in *content* and thus indicate the condition of the solution.

The use of ORP measurement as a control parameter in activated sludge treatment is well documented. When compared to DO measurement, ORP can be used for a complete range of redox conditions, i.e. aerobic and anaerobic environments (Gupta, 1994). However, measurements made in anaerobic environments are complicated by the possibility of oxygen contamination of the sample. Although many researchers have measured ORP in anaerobic environments (Koch, 1985; Srivinas, 1988; Charpentier, 1989; Gray, 1993; Gupta, 1994; Heduit, 1994), there is no standard protocol. The best results generally come from in situ placement of the ORP electrode, but this can lead to probe fouling and inaccurate measurements. For grab sampling, immediate measurement is recommended and the lowest value should be recorded as the final value (Mountford and Asher, 1979). The most suitable method of measuring ORP in anaerobic environments is, therefore, a flow through type system which isolates the probe from the bulk solution to allow for periodic removal for cleaning and eliminates the possibility of oxygen contamination (Gray, 1993; Gupta, 1994; Heduit, 1994).

4.3.2 ORP Measurement and Colour Removal

Carliell (1993) found that C.I. Reactive Red 141 would be degraded in an anaerobic environment provided a source of labile carbon was available and that no competitive electron acceptors such as oxygen and nitrate were present. Decolourisation was achieved by the cleavage of the azo bond in the dye chromophore. It was further concluded that the cleavage of the azo bond was a reduction reaction and that the entire bacterial system represented a redox system.

Carliell (1993) conducted an experiment to determine whether redox potential had any effect on the decolourisation of C.I. Reactive Red 141 in an anaerobic environment. Anaerobic seed sludge from a local domestic sewage works and a glucose solution (the labile carbon source) were placed in a glass digester (2 ℓ) and kept fully mixed using a magnetic stirrer. Online ORP measurements were made using a platinum/calomel electrode (Radiometer PK 1401) and a data logging computer. The C.I. Reactive Red 141 was dosed to the system to give a concentration of 100 mg/ℓ. Sodium nitrate and sodium sulphate were dosed to the system in various concentrations to act as competitive electron acceptors. The results of the experiment with sodium nitrate are shown in **Figure 4.8**.

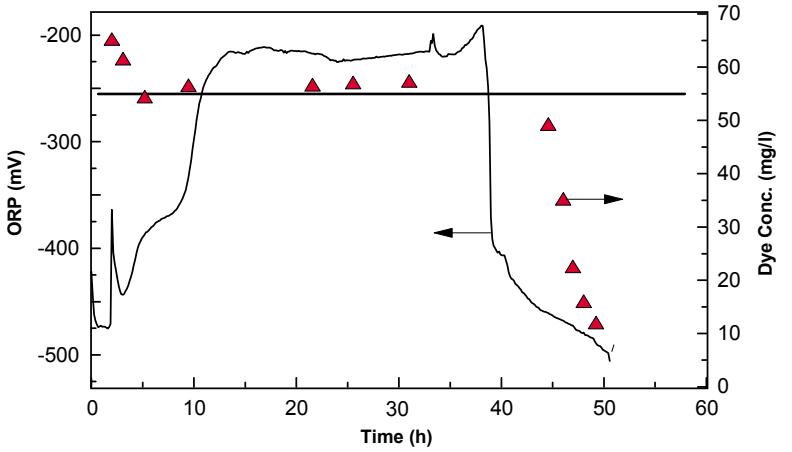


Figure 4.8 : Degradation of C.I. Reactive Red 141 in the presence of nitrate with online ORP measurement relative to the standard calomel electrode (Carliell, 1993).

Decolourisation of the dye was noticed in the first few hours of the experiment and the ORP was low at around -450 mV (SCE), or -200 mV (SHE). With the addition of sodium nitrate the ORP increased to the reduction potential of nitrate, approximately -200 mV (SCE), and the decolourisation process stopped. After a period of ca. 40 h the reduction potential decreased to -450 mV (SCE) and decolourisation of the dye recommenced.

It was concluded that the nitrate was reduced preferentially to the dye because the nitrate reduction potential is greater than that of the dye. Once the nitrate in the system had been reduced, the ORP of the system decreased to that of the reduction of the azo dye, ca. -450 mV (SCE), and the dye was decolourised. No noticeable effect on decolourisation was noted in the presence of sodium sulphate since the reduction potential of the sulphate ion is lower than that of the dye, therefore the dye would be reduced preferentially to sulphate.

Weber and Wolfe (1987) found that the reduction potential of azobenzene by anaerobic sediments varied between -220 and -300 mV (SCE) and the reduction exhibited psuedo-first-order kinetics. Each of the four sediments tested contained different amounts of organic matter and exhibited different half-lives for the disappearance of azobenzene. The half-lives were also affected by the change of season. Although low ORP values resulted in reduction, Weber and Wolfe (1987) found no conclusive evidence that the rate of reduction of azobenzene could be predicted by means of the ORP of the sediment.

It follows that low ORP's are conducive to the decolourisation of azo dyes. The HWWTP sludge was assessed to determine the ORP of the sludge under anaerobic conditions and during the decolourisation of dyes.

4.3.3 Measurement of the HWWTP Sludge Redox Potential

A sample (300 mℓ) of sludge (RAS) from HWWTP was placed in a 2 ℓ glass digester (**Figure 4.9**). The sludge was gently mixed and maintained at a constant temperature (35 °C) using a combination mixer/heater.

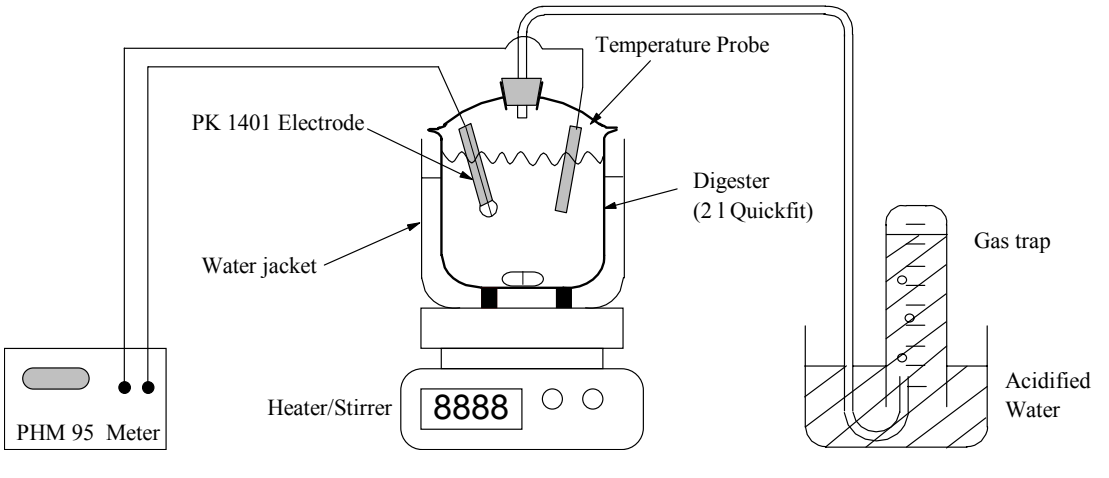


Figure 4.9 : Schematic diagram of the equipment used to measure the ORP of the HWWTP sludge under anaerobic conditions.

An ORP electrode (Radiometer PK1401) was inserted into the sludge through a port in the lid. The sludge was over gassed with OFN and the vessel sealed. Raw feed (1 ℓ) was added to the glass digester while overgassing with OFN. The ORP and temperature measurements were logged on a computer. After ca. 60 h into the experiment, a nutrient medium, containing glucose, was introduced to the system. The results are shown in **Figure 4.10**.

After an initial increase, during the first few hours, the ORP showed a steady decrease and reached a final value of ca. -370 mV at around 50 h. The addition of a nutrient medium (**Appendix D**) and glucose solution at around 64 h caused an increase in the ORP. The ORP remained stable at -200 mV for a further ca. 100 h and then decreased to ca. -370 mV.

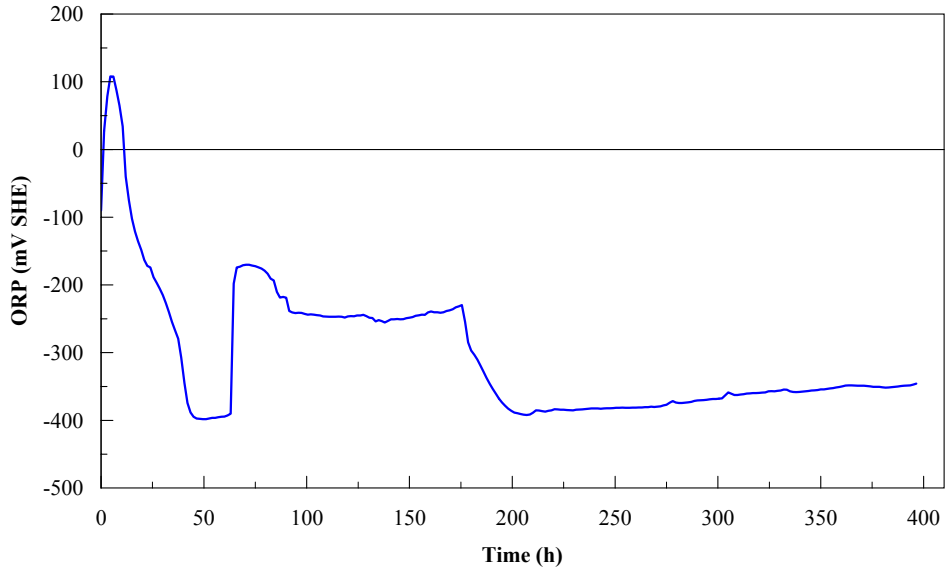


Figure 4.10 : ORP measurement, referred to the standard hydrogen electrode (SHE), of the HWWTP sludge under anaerobic conditions.

It was assumed that the initial increase in the ORP was associated with the oxygen content of the raw feed and the mineral salts solution. The raw feed was added to the digester after the sludge so that the effect, on the ORP, of adding raw feed to the sludge could be monitored. The experiment demonstrated that, under anaerobic conditions, the HWWTP sludge can maintain a potential low enough (-370 mV) to be conducive to decolourisation (Carliell, 1993; Reife, 1995).

4.3.4 Determination of the Required ORP for Decolourisation of C.I. Reactive Red 141

The next experimental step was to determine the potentials at which decolourisation would begin. Since ORP is a composite measure, it was not expected to find an exact potential at which decolourisation began; a so called *breakpoint* ORP.

The same apparatus (**Figure 4.9**) was used and samples of sludge and raw feed were collected as previously (**Section 4.2**). The sludge (900 mℓ) and raw feed (600 mℓ) were both over gassed with OFN before mixing them in the glass digester. OFN was bubbled through the mixture prior to sealing the vessel. The C.I. Reactive Red 141 dye was dosed to a concentration of ca. 85 mg/ℓ through a sampling port in the lid of the digester. Samples (25 mℓ) were withdrawn, by pipette, through the sampling port every 30 min for the first 3 h and every hour thereafter. A portion of the samples were centrifuged at 4 000 rpm for 25 min and the absorbance of the centrate measured at the wavelength of the maximum absorbance of the test dye, 525 nm. The remainder of the sample was refrigerated for COD determination. The pH of the sludge was measured periodically during the experiment (Orion Model 201). The COD of each sample, the raw feed and the RAS was determined by dichromate oxidation of the samples followed by colourimetric determination of the COD.

4.3.5 Results and Discussion

The aim of the experiment was to determine whether there was a correlation between the ORP of the HWWTP sludge and the rate of colour removal. The results of the decolourisation of C.I. Reactive Red 141 and the ORP of the sludge during the experiment are shown in **Figure 4.11**.

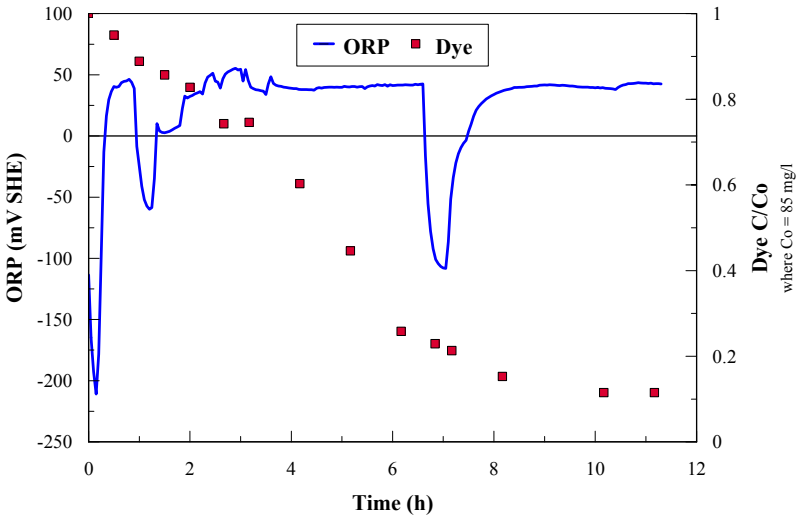


Figure 4.11 : Degradation of C.I. Reactive Red 141 in HWWTP sludge under anaerobic conditions with simultaneous ORP measurement.

The first observation was that decolourisation was occurring at redox potentials as high as 50 mV (SHE) which was greater than that recommended by Carliell (1993) and Mphephu (1996). The ORP was initially low at ca. -200 mV (SHE), rapidly increased to ca. 50 mV due to the addition of the raw feed (see **Section 4.3.3**). At this point the ORP varied between -50 to 50 mV and eventually stabilised at ca. 45 mV after approximately 3.5 h and remained there for a further 3 h. During this period the rate of decolourisation was greatest. From **Figure 4.11** it was apparent that there were two different rates of decolourisation during the first 6.5 h of the experiment. **Figure 4.12** shows these two distinct rates.

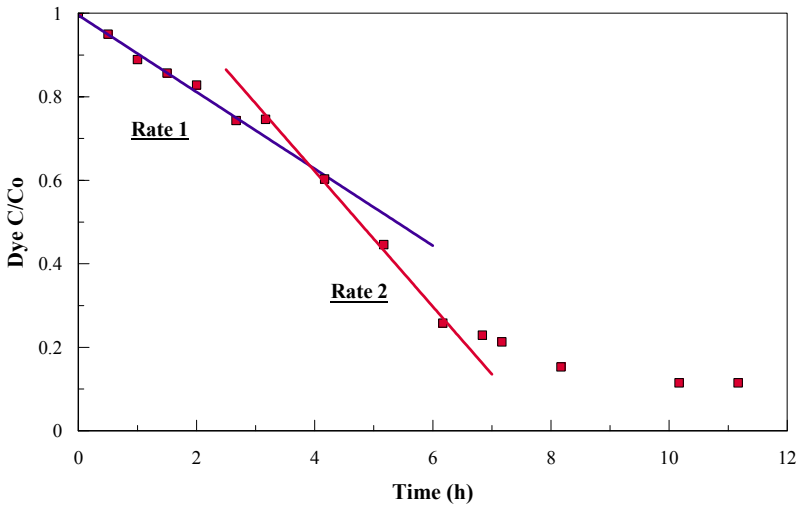


Figure 4.12 : Two-rate decolourisation of C.I. Reactive Red 141 in HWWTP sludge under anaerobic conditions.

Rate 1 : $C/C_o = 0.995 - 0.092t$ ($R^2 = 0.987$)

Rate 2 : $C/C_o = 1.27 - 0.162t$ ($R^2 = 0.996$)

Rate 1 and Rate 2 (**Figure 4.12**) were linear with respect to time which suggested that the decolourisation of C.I. Reactive Red 141 in HWWTP sludge was a second order reaction. The RAS, raw feed and dye were added simultaneously at t = 0 h, i.e. there was no period of incubation. The two rates may have been due to the reduction of different components in the raw feed. The processes that occur in the reduction of the raw feed are (i) hydrolysis of the complex organic polymers (fats, carbohydrates and proteins) to their simple organic monomer structures (lipids, sugars and amino acids), (ii) reduction of the monomers to volatile fatty acids (VFA's) and (iii) uptake of the VFA's by *Acinetobacter* with a simultaneous release of phosphorus.

4.4 CONCLUSIONS

The decolourisation of C.I. Reactive Red 141 was investigated under various biological conditions in a series of laboratory experiments. The following conclusions were made regarding the results of these laboratory experiments :

- C.I. Reactive Red 141 was decolourised in HWWTP sludge under anaerobic conditions. It was concluded that the dye was decolourised by cleavage of the azo bond (the dye chromophore) under reducing conditions created by the anaerobic bacteria.

- The rate and extent of the decolourisation was affected by the presence of oxygen in the anaerobic system (**Section 4.2.1.2**). It was concluded that the presence of oxygen increased the bulk oxidation reduction potential (ORP) of the solution thus inhibiting the reduction of the dye molecule.

- Decolourisation of C.I. Reactive Red 141 in HWWTP sludge was greater than 92 % complete under anaerobic conditions in approximately 4.5 h.

- In the anaerobic serum bottle tests (**Section 4.2.2**), similar results were obtained for all test conditions. There was little effect on the rate of decolourisation when the solids concentration was increased or when an additional source of readily biodegradable COD (glucose) was added to the anaerobic system.

- The initial rate (within the first 4.5 h) of decolourisation of C.I. Reactive Red 141 was observed to be approximately linear with respect to time which suggested that the decolourisation of the dye in HWWTP sludge was a second order reaction with respect to dye concentration (**Section 4.2.2**).

- The decolourisation of C.I. Reactive Red 141 was not observable when the absorbance of the solution was measured at 400 nm (wavelength for measurement on the Hazen scale). The Hazen scale measurement is a measure of the *yellowness* of a solution and, therefore, is not suitable for solutions of varying hue. To appropriately assess the colour removal performance of the HWWTP sludge, it was necessary to measure the absorbance of the solutions at the wavelength of the maximum absorbance.

- Decolourisation of C.I. Reactive Red 141 did not occur by aerobic biodegradation or by adsorption of the dye molecule to the sludge.

- The ORP of the HWWTP sludge was observed to be lower than that recommended (Carliell, 1993) for the reduction of C.I. Reactive Red 141 in anaerobic sludge after a period of approximately 100 h, i.e. less than -250 mV (SHE).

- The ORP of the sludge was observed to increase when raw feed or a glucose solution was added to the anaerobic system. It was suspected that the addition of the feed substrate resulted in an increase in the concentration of components that were reduced at relatively higher ORP's, e.g. nitrates, oxygen or possibly some organic compound.

- Decolourisation of C.I. Reactive Red 141 was observed to occur at higher redox potentials than that suggested by Carliell (1993) and Mphephu (1996); ca -50 to 50 mV (SHE) as opposed to -250 mV (SHE). A distinct plateau in the ORP (at ca. 50 mV) corresponded with the maximum rate of decolourisation of the dye.

- Two linear rates of decolourisation were observed during the first 6 h of the decolourisation experiment.

➢ The lack of correlation of these results with those found by Carliell (1993) was attributed to the difference in the origins of the inocula and the difference in the composition of the feed substrates. This difference may also have resulted in a different mechanism of dye decolourisation. Further investigation is required before a conclusion can be made.

Chapter Five

Assessment of the Hammarsdale Activated Sludge Reactors

The majority of the textile industries in the Hammarsdale region make use of balancing tanks and pH control to reduce the impact of their effluent on the local wastewater treatment plant (HWWTP). Waste minimisation and some in-house recycling also reduce the effect of *shock loading* the HWWTP with a waste that is both high in colour and salinity. Apart from this pre-treatment the textile industries in Hammarsdale discharge their effluent directly to the HWWTP. The result is a highly coloured influent to the works with a high conductivity due to the high concentration of dissolved salts. A description of the Hammarsdale Wastewater Treatment Plant (HWWTP) and the industries in the Hammarsdale region is presented in **Chapter 3**.

The operation of the HWWTP reactors was assessed to determine the extent of colour removal in the reactors and to identify options for improvement. Firstly it had to be determined in which zone the majority of the colour was being removed (**Section 5.2**). As discussed in **Section 4.3**, previous research indicated that ORP plays a role in colour removal, therefore, the ORP of the HWWTP reactors was measured (**Section 5.3**). **Section 5.4** describes a dye tracer test that was performed to determine the effect of shock-loading an azo dye, C.I. Reactive Red 141, in the HWWTP anaerobic zone. A residence time distribution (RTD) test was performed on the anaerobic zone of one of the HWWTP reactors and these results are presented in **Section 5.5**. **Section 5.6** is a summary of the results of a Computational Fluid Dynamics (CFD) study where the fluid flows within the anaerobic zone of the HWWTP reactors were modelled and the results compared with those obtained in the RTD.

5.1 INTRODUCTION

In order to achieve colour removal in a biological system certain requirements have to be met. Based on the results obtained in the laboratory tests (**Chapter 4**) and previous research (Brown and Laboureur, 1983; Carliell, 1993; Knapp, 1995; Mphephu, 1996; Naidoo, 1995) the requirements for the biological system for efficient colour removal were identified as the following :

(i) the system should be anaerobic,
(ii) a readily biodegradable source of carbon should be available,
(iii) no competitive electron acceptors should be present,
(iv) the system should be a reducing environment or have a low ORP, and

(v) the system should allow for sufficient residence time.

Textile dyes were successfully degraded in the laboratory using HWWTP sludge as the inoculum (**Chapter 4**). The objective of these full-scale tests was to determine whether the conditions in the HWWTP reactors were similar to those in the laboratory and thus conducive to colour removal. An assessment of the current operation of the reactors was obtained from the daily analyses over a period of 6 months and is detailed in **Chapter 3** and **Appendix A**. Further experiments were conducted to determine the other factors which could affect the colour removal potential of the Bardenpho reactors. These experiments are discussed in the following sections.

5.2 COLOUR REMOVAL IN EACH ZONE OF THE BARDENPHO REACTORS

The decolourisation potential of each zone in the Bardenpho reactors was assessed to determine which zone was responsible for colour removal. This was achieved by measuring the colour at various points in the reactor. The test was performed on reactors 2 and 4 on the 20th March 1996. The method and results are discussed.

5.2.1 Method

A submersible pump, suspended from a length of rope, was used to draw samples from various points in reactor 4. Samples were taken from the anaerobic zone, primary anoxic zone and from the clarifier overflow in reactor 4. A more detailed sampling procedure was performed in reactor 2 to determine whether there was variation in colour through each zone as well as from zone to zone. The sampling positions are shown in **Figure 5.1**. A composite sample of the raw feed was collected from the overflow of the primary sedimentation tank (splitter box). The colour of the raw feed was also measured during the course of the sampling to monitor variations in the colour of the feed. The samples collected from the reactors were filtered (Whatman 45 μm). The absorbance of the filtrate was measured at 400 nm and the results were reported in Hazen units. Triplicate samples were taken and the reported result was the calculated average.

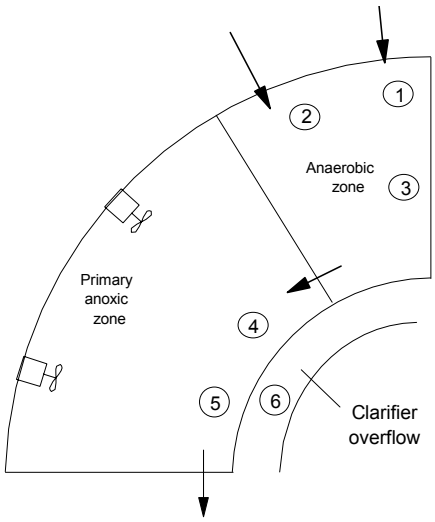


Figure 5.1 : Cropped drawing of 5-stage Bardenpho showing sample positions. All samples were taken at about 3 m depth.

5.2.2 Results and Discussion

The colour of the raw feed remained fairly constant during the sampling period (990 to 1 050 °H). From a visual inspection, the colour varied from a dark blue to a dark green colour with some of the colour being caused by suspended materials, possibly disperse dyes. The raw feed at the HWWTP contained suspended material (colloidal solids and some insoluble dyes). It was not possible to remove this material by filtration through 45 µm filter paper. Therefore, the determination of the absorbance (and the colour) of the raw feed was inaccurate due to the interference of the solid material (see **Section 4.2.3**). The measured colour of the raw feed was assumed to be the *best estimate* obtainable with the equipment at the HWWTP. The majority of the suspended material could, however, be removed by filtration (45 µm), but this also involved a concomitant removal of some of the raw feed colour since some of the dyes were present as insoluble or semi-soluble solids. It is expected that these would be removed by flocculation, early in the HWWTP process, and their effect was assumed to be insignificant.

The colour of the samples was low in comparison to the colour of the raw feed. The results are shown in **Table 5.1**.

Table 5.1 : Results of the colour measurements of the samples drawn from reactors 2 and 4.

Zone	Position	Colour (°H)	
		Reactor 2	Reactor 4
Anaerobic	1	117	-
	2	123	-
	3	130	270
Primary Anoxic	4	115	-
	5	113	253
Clarifier	6	115	106

The colour in the anaerobic zone of reactor 2 was relatively uniform and ranged from 117 to 130 °H. The colour did not decrease any further through reactor 2 and the final effluent colour (position 6) was 115 °H. The results from the sampling of reactor 4 showed that the colour decreased by 17 °H between the anaerobic and primary anoxic zone and by a further 147 °H after the clarifier. As both reactors receive identical feed, it would be expected that similar colour measurements would be obtained, however this was not observed. The difference in the colour of the samples from reactors 2 and 4 may have been due to the layer of scum on the surface of the anaerobic zone. The scum layer is as a result of the build up of fats and other colloidal material. The anaerobic and anoxic zones in reactor 2 were covered by a thick scum layer which was not present on reactor 4. It is suspected that this layer creates a barrier to the ingress of air to the anaerobic and anoxic zones, thus tending the facultative bacteria towards more anaerobic activity and, hence, a more conducive environment for colour removal.

Further colour removal was noticed in the maturation river; the reported value for the colour of the works effluent is generally around 60 °H (**Appendix A**). Previous research (DeHaas, 1993) has shown that colour was removed from the HWWTP wastewater when flocculants such as ferric chloride ($FeCl_3$) and alum ($Al_2(SO_4)_3$) were added. Alum, which is dosed to the HWWTP process at the RAS pumps and at the settling tank before the maturation river, could account for some of the colour removal, by both flocculation and/or chemical reaction, in the HWWTP process.

From the results for reactor 4, it was apparent that some mechanism of colour removal was occurring in the clarifier. Laboratory experiments (**Section 4.2**) showed that the primary mechanism of colour removal in the HWWTP was anaerobic degradation, thus the colour removal demonstrated in the results may be due to anaerobic activity in the clarifier.

From **Table 5.1**, the colour in the anaerobic zone is ca. 120 °H. The colour in the feed to the anaerobic zone (raw feed and RAS) can be estimated by the ratio of the flow rates, approximately 1.5 : 1, RAS to raw feed. If it is assumed that the colour of the liquor in the RAS was the same as that leaving the clarifier, about 115 °H,

and that the minimum and maximum values for the raw feed colour were 1 500 °H and 900 °H, respectively, the colour in the anaerobic zone should, therefore, be between :

$$(\tfrac{1.5}{2.5} \times 115) + (\tfrac{1}{2.5} \times 1500) = 669\ ^\circ\text{H, and} \qquad [5.1]$$

$$(\tfrac{1.5}{2.5} \times 115) + (\tfrac{1}{2.5} \times 900) = 429\ ^\circ\text{H} \qquad [5.2]$$

This represented a colour removal of up to 80 % in the anaerobic zone (with the assumption that the colour measurement of the raw feed was accurate).

If the anaerobic zone was not the primary colour removal zone then a colour gradient, from the anaerobic zone to the clarifier over flow, would be evident in the sampling results. However, from the estimates (Equations 5.1 and 5.2) and the sampling results (**Table 5.1**) it is clear that the anaerobic zone was responsible for the majority of the colour removal in the Bardenpho system.

5.3 REDOX POTENTIAL PROFILE THROUGH THE ANAEROBIC ZONE

Carliell (1993) found that reactive dyes used in the Hammarsdale textile mills could be decolourised under reducing conditions produced by anaerobic digester sludge. This suggested that oxidation reduction potential (ORP) may be useful as an indicator of colour removal potential. The ORP of the anaerobic zone of the HWWTP reactors was measured to determine whether the biological decolourisation of textile dyes was possible. This test also aimed to provide more information on the uniformity of mixing in the anaerobic section of the Bardenpho reactor.

5.3.1 Method

The ORP profile of reactor 2 was measured on two occasions, viz. the 17th April 1996 and 19th June 1996. A pump (Mono Pump S32M) was used to draw samples from the anaerobic zone via a 20 m (12 mm diameter) suction pipe (**Figure 5.2**). A flow cell was fitted in-line to house the ORP electrode. It was fitted on the suction side of the pump because ORP measurements are sensitive to the ingress of air into the system (Gray, 1993; Gupta, 1994; Heduit, 1994). Samples were taken from the discharge side of the pump.

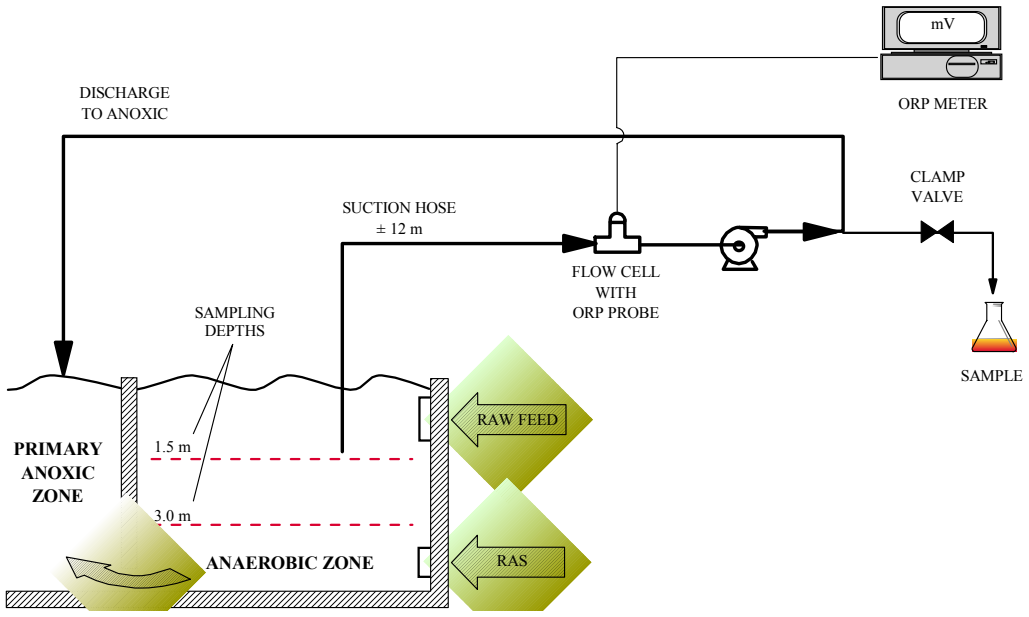


Figure 5.2 : A schematic of the ORP sampling rig used to measure the ORP profile in the anaerobic zone. A cross-sectional view of the anaerobic zone is shown indicating the sampling depths of 1.5 and 3.0 m. The positions of the raw feed and RAS inlets are also indicated.

Twelve sampling points were selected to determine the ORP profile in the anaerobic zone (**Figure 5.3**). The pump was started and the ORP was allowed to stabilise to within approximately 1 mV/min. Once a stable reading was obtained, the ORP was recorded and a sample was collected from the discharge side of the pump. The same procedure was repeated for all 12 sampling points. The samples were filtered (Whatman 45 μm) and the absorbance of the filtrate was measured at 400 nm.

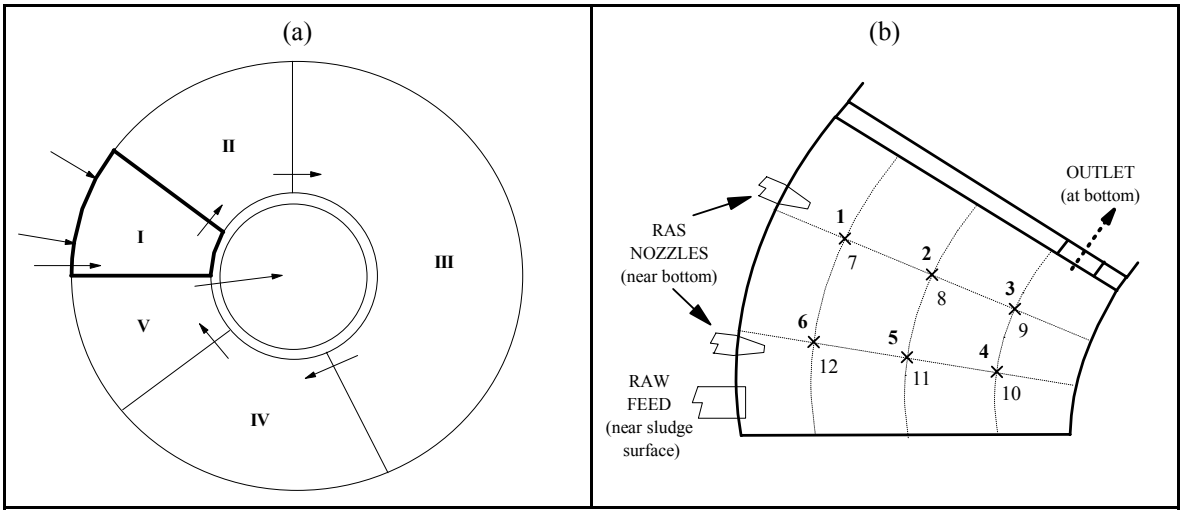


Figure 5.3 : A plan view (a) of the 5-stage Bardenpho reactor and the direction of the flow through the reactor. A magnified plan view (b) of the anaerobic zone (zone 1) of the Bardenpho reactor

shows the 12 sampling points. Sample points 1 to 6 (in bold) were at **1.5 m** depth and points 7 to 12 were at **3.0 m** depth.

The raw sewage inlet pipe was located just below the sludge surface and the RAS nozzles were located at the bottom of the anaerobic zone (**Figure 5.2**). The RAS nozzles were installed to keep the sludge in the anaerobic zone fully suspended. The nozzles throttled the flow of the RAS which produced sufficient kinetic energy to maintain the suspension (**Chapter 3**). The outlet for this compartment was a 1 m x 0,5 m opening situated at the bottom of the anaerobic zone (**Figure 5.3b**).

5.3.2 Results and Discussion

Prior to measuring the ORP profile the equipment was tested to determine the stabilisation time of the electrode, the effect of the sampling rig on the ORP and the effect of the variation in the raw feed flow on the ORP and colour results.

5.3.2.1 Variation of ORP with Time

The specifications of the electrode (Polymetron Ag/AgCl electrode) stated that it should reach 95 % of the reading within 1 min. The ORP was monitored to asses its variation with both position and time. The sampling pipe was placed at a point in the anaerobic zone and the pump allowed to run continuously. The ORP was recorded at regular intervals until a stable reading was obtained. The results are shown in **Figure 5.4**.

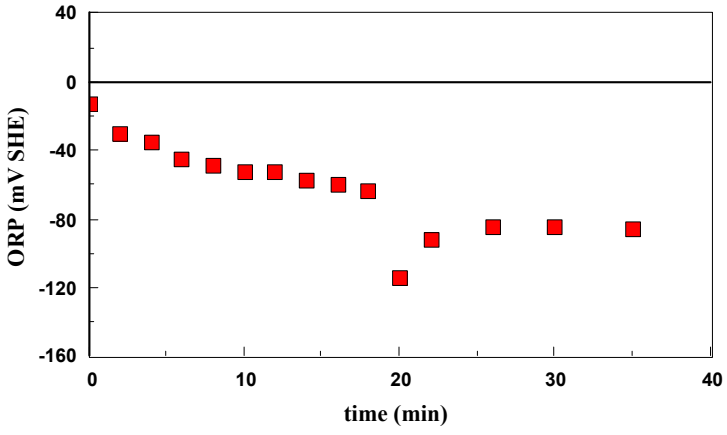


Figure 5.4 : Variation of ORP at a single point in reactor 2.

The ORP decreased steadily for the first 10 min and then decreased rapidly to ca. -110 mV. The final value (-90 mV) was obtained after 30 min. The final value was taken when the ORP variation was less than 1 mV/min. The significant negative spike measured at approximately 20 min occurred regularly during subsequent sampling at various points in the reactor. This phenomenon was due to the variable nature of the

raw feed and possibly also due to *pockets* of sludge of low redox potential. Unless this phenomenon occurred, the final value of the ORP was recorded after approximately 30 min.

Due to the size of the sampling rig and the length of the sampling pipe, it was necessary to stop the flow through the flow cell to move the sampling pipe to another position. This resulted in the flow reversing direction, air being drawn into the flow cell (through the bearings and glands in the pump) and consequently, interference with the measurement of the sludge ORP. This effect is shown in **Figure 5.5**.

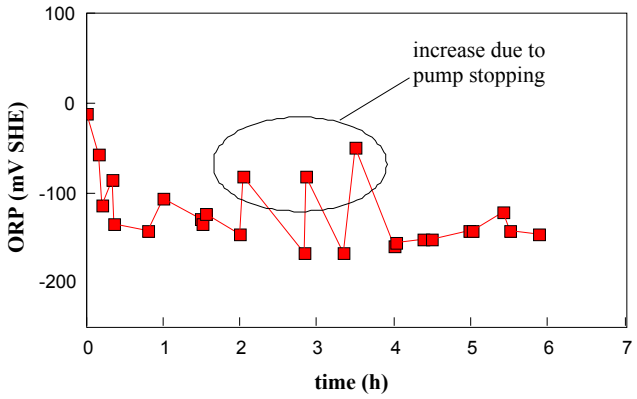


Figure 5.5 : Variation of ORP due to stopping and starting the pump.

The experiment was, therefore, structured to minimise the necessity to stop the pump and thus obtain the most representative measurement of the ORP of the sludge in the anaerobic zone.

Standard electrodes obtain direct potentials of electroactive solutions with respect to a standard electrode (**Section 4.3**). For this reason, ORP electrodes do not need to be calibrated and are relatively easy to maintain. The ORP electrode used (Polymetron Ag/AgCl gel electrode) was, however, checked against a standard solution.

The ORP profile was measured once all the equipment was confirmed to be operating within specifications. The results of the ORP profiles and the simultaneous colour measurements are presented in the following sections.

5.3.2.2 ORP Profile

The results of the ORP measurements, for the twelve sampling points, are shown in **Figure 5.6**.

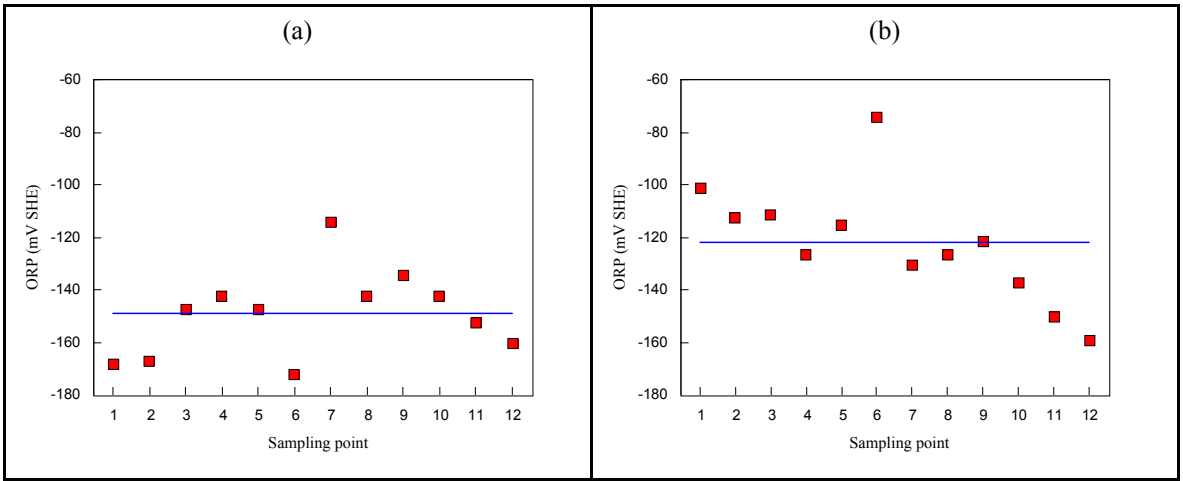


Figure 5.6 : ORP profiles for the anaerobic zone of reactor 2 as measured on (a) 17/4/96, and (b) 19/6/96.

In the following discussion Profile 1 and Profile 2 refer to **Figure 5.6 (a)** and **(b)**, respectively. In both profiles the ORP was below -60 mV (SHE) and the average, represented by the straight line in **Figure 5.6**, was between -120 and -140 mV (SHE). Carliell (1993) found that a potential of -450 mV (SCE) was required for *rapid* biological decolourisation of C.I. Reactive Red 141. This corresponds to a potential of -250 mV (SHE). Based on this conclusion, the limited decolourisation in the Bardenpho reactors could have been due to the relatively high ORP of the anaerobic zone (ca. -120 to -150 mV(SHE)). However, laboratory tests (**Section 4.3.4**) showed that, to decolourise C.I. Reactive Red 141 in HWWTP sludge and raw feed, the ORP should be between -50 and 50 mV. As described previously (**Chapter 4**), ORP was merely a qualitative indication of the colour removal potential of a biological system, i.e. the lower the ORP, the greater the affinity of the system to reduce dyes.

The range (minimum to maximum) of the ORP in the anaerobic zone was ca. 90 mV. The ORP gradient through the reactor was expected to be greater due to the stagnant areas identified by a visual inspection of the surface of the zone.

With reference to **Figure 5.6**, the results for **points 1** to **3** did not correlate for the two profiles. It is suspected that this region of the reactor was complex with respect to mixing and composition. The return sludge causes swirling in this area which could lead to surface aeration and thus an unpredictable ORP. Furthermore, there

could have been stagnant regions in the corner of the zone, around **points 1** and **6,** which could have affected the ORP measurements.

Similar ORP's, and a similar trend, were observed at **points 8** to **12** in both profiles. There was a steady increase in potential from **points 7** to **9** in profile 2 (**8** and **9** in Profile 1) followed by a steady decrease in potential from **points 10** to **12**, where the raw influent sewage was directly above the return sludge and flowing in the same direction (**Figure 5.3**). The ORP at **points 10** to **12** was associated with the ORP of the return sludge which had undergone significant denitrification in the clarifier. It was expected that the ORP of this sludge would be low, or at least lower than the ORP of the reduction of nitrates (around 20 mV (SHE) as indicated by (Carliell, 1993)). The steady increase towards the inner wall of the reactor was due to the mixing of the RAS with the raw sewage before the RAS contacted the inner wall. **Points 7** to **9** did not show the same effect since there was only one raw inlet and two sludge return inlets (**Figure 5.3**).

The disagreement in the results for **point 6** on the two separate sampling days could be attributed to either the variable nature of the HWWTP influent, or the length of time that the ORP electrode was exposed to the HWWTP sludge. In profile 1, **point 6** was the last point to be sampled (approximately 6 h exposure) whereas in profile 2, **point 6** was the first point to be sampled. It was suspected that the ORP electrode was prone to poisoning or polarisation during the experiment which would have lead to inaccurate measurements towards the end of the experiment. Attempts to simulate this effect in the laboratory were unsuccessful and it was speculated that the ORP probe measurements were affected by the sampling rig, i.e. there was a slow ingress of air into the flow cell or stagnation in the flow cell was occurring. Further investigations were conducted on the anaerobic zone using the ORP probe as an immersion probe. This eliminated the possibility of interference by the sampling rig. The results of the test (**Appendix C**) with the immersion probe correlated with those obtained with the sampling rig. This confirmed that the sampling rig was not responsible for signal interference and that the fluctuating ORP and slow response experienced by the ORP probe may have been due to the sludge characteristics.

The results of the measurements with the immersion probe showed that the ORP in the anaerobic zone of reactor 2 varied between -50 and -110 mV (SHE) with the response time being reduced marginally. The variation in ORP around **point 6** (below the raw feed inlet) was noticed with the immersion probe. Another observation was that the ORP fluctuated by ca. 100 mV when raw feed was introduced to the reactor (pulsed raw feed flow) which, again, demonstrating the variation in the composition of the sludge in the anaerobic zone. The lowest, stable ORP was measured around **point 1** where stagnation of the sludge was suspected.

The ORP of the individual feed components, viz. the raw feed from the splitter box and the RAS from the clarifier underflow, were measured with the immersion probe. The ORP of the RAS was measured at the RAS pumps initially, by bleeding a stream of the RAS into a 2 l beaker and allowing the RAS to overflow. The flow into the beaker was throttled to avoid excessive agitation, but the readings were unstable due to

oxygen contamination possibly from air entering the pump through cracks, faulty seals, etc. Later the immersion probe was lowered into the clarifier to a depth of approximately 4 m, i.e. below the sludge line. The ORP of the raw feed was measured at the splitter box by lowering the immersion probe into the tank to a depth of approximately 2 m. The ORP of the raw feed and the RAS was determined to be -100 to -150 mV (SHE) and 0 to 50 mV (SHE), respectively. It was expected that the ORP of the RAS would be lower than that of the raw feed due to the suggested denitrification that takes place in the clarifier (**Chapter 3**). The low ORP in the raw feed may be as a result of primary fermentation occurring in the splitter box, i.e. reduction of the organic compounds in the feed. For example, the reduction of pyruvate to lactate has a standard electrode potential of E_0 = -190 mV (SHE) (Keunen, 1997). The relatively higher ORP of the RAS may have been as a result of oxygen contamination caused by breaches in the RAS pump and pipe network.

From the data presented, it was concluded that the area around points 8, 9, 10, 11 and 12 was predominantly of low potential due to the denitrified return sludge from the clarifier and it was in this region that the majority of the decolourisation would have taken place. Based on the data from the immersion probe, it was concluded that there was stagnation, or a lower intensity of mixing, in the area around points 1 and 7 since the ORP in this region was consistently lower than that measured at other points in the reactor.

Further information regarding the mixing characteristics and the flow distributions within the reactor were required to determine the fate of dyes in the anaerobic zone. It was anticipated that the ORP profile would elude to the uniformity of mixing in the anaerobic zone. Tentative conclusions were made regarding the stagnation of the sludge around point 6 (**Figure 5.3**), but these would have to be confirmed by more appropriate tests. These tests are discussed in **Section 5.5** and **5.6**.

5.3.2.3 Colour Measurement

For each ORP measurement a liquid sample was taken from the discharge side of the pump and from the primary settling tank (i.e. the raw feed). The samples were filtered, visually inspected and the absorbance measured at 400 nm to obtain a colour measurement in degrees Hazen. **Figure 5.7** shows the results of these colour measurements.

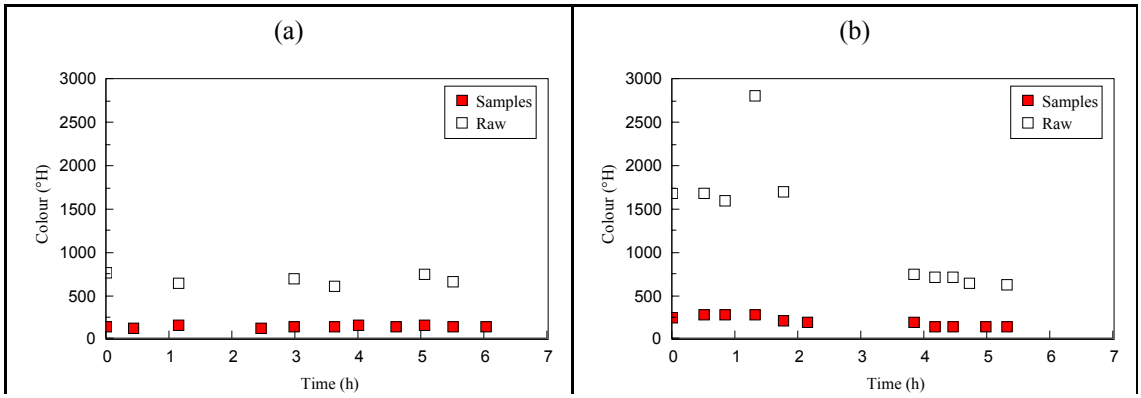


Figure 5.7 : Colour measurements during the measurement of (a) Profile 1 and (b) Profile 2.

On the first sampling day (Profile 1 in **Figure 5.7(a)**) the colour in the feed was not measured as frequently as the colour in the anaerobic zone. There was a correlation between the colour in the raw and the colour in the reactor for Profile 2. As the colour in the feed decreased, so the colour in the anaerobic zone decreased. It should be noted that the colour in the samples from the anaerobic zone were taken from the *ORP Profile sampling points* and did not represent the colour of the bulk sludge in that zone.

Similar experiments were conducted during the textile industry shutdown in December 1995. The colour in the anaerobic zone during this period was between 110 and 160 °H (**Appendix B**). This was regarded as the background colour in the anaerobic zone without the contribution of textile industry effluents.

There was no apparent correlation the between colour in the reactor and the ORP of the sludge. It was expected that the colour intensity would be lower in those regions where the ORP was low. It is more likely that the colour would vary with the bulk solution ORP and not the ORP of one specific point. However, from the experiments performed by Carliell (1993), the ORP would have to decrease to ca. -200 mV (SHE) to cause any decolourisation.

5.3.2.4 Surface Oxygen Mass Transfer Effects

The anaerobic zone of the Bardenpho system is not a true anaerobic reactor. As described in **Chapter 3**, the function of the anaerobic zone is to hydrolyse the long chain organic molecules in the feed and produce the VFA's necessary for the metabolism of the polyphosphate accumulating bacteria. The reactor is mixed by the raw feed and RAS inlet streams. It is open to the atmosphere, therefore, the anaerobic activity of the facultative anaerobes could be affected by the ingress of air from the surface of the reactor. To investigate this effect, the surface mass transfer of air on the ORP of the bulk solution was determined.

The sampling rig used for the test was similar to that used in the ORP profile experiment (**Figure 5.2**). The suction pipe was placed at a depth of approximately 3 m and slowly raised until the end of the hose was at the sludge surface. Care was taken to prevent air entering the system and to reduce the agitation at the surface. The results showed that the ORP decreased as the hose approached the surface. The ORP ranged from 33 to -97 mV (SHE) and the lowest potential was recorded just below the surface of the sludge liquor.

It was concluded that the surface oxygen mass transfer effects in the anaerobic zone were insignificant and there was little effect on the ORP of the bulk solution.

5.4 DYE TRACER TEST

To determine the effect of a colour *shock load* on the operation of the reactors, specifically the anaerobic zone, a dye tracer test was performed on reactor 2 at HWWTP. The tracer test involved dosing a relatively high concentration of dye to the input of the reactor and then monitoring the output of the anaerobic zone to determine the quantity of dye that passes through the process untreated. One may thus determine the removal efficiency of the treatment process.

5.4.1 Method

Dry, powdered C.I. Reactive Red 141 (7.5 kg) was dissolved in tap water and dosed to the inlet of reactor 2 at the splitter box (primary sedimentation tank). The same sampling rig (**Figure 5.2**) was used to collect samples (ca. 200 mℓ) from the outlet of the anaerobic zone. The ORP was measured at the sampling point. The samples were filtered (Whatman 45 µm) and the colour of the filtrate determined by measurement of the absorbance at 400 nm and conversion to Hazen units. This test was performed during the December 1995 textile industry shutdown.

5.4.2 Results and Discussion

The colour in the anaerobic zone was first observed at the raw feed inlet pipe ca. 10 min after the dye was dosed. The expected dye concentration in the anaerobic zone, based on the design volume of the anaerobic zone of 300 m³, was ca. 25 mg/ℓ. The results of the experiment are given in **Figure 5.8**.

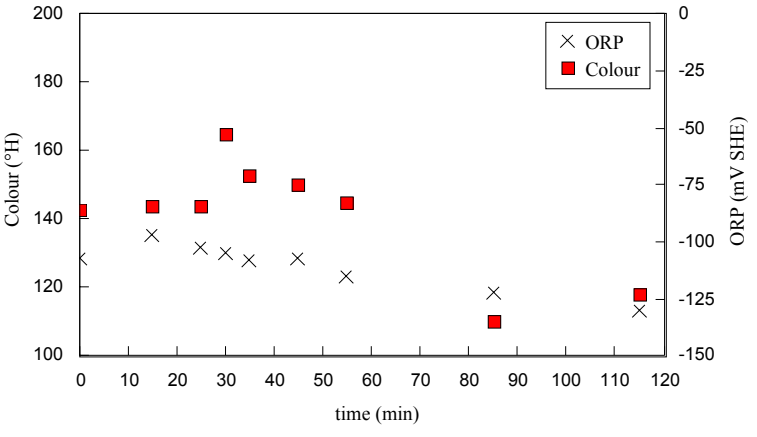


Figure 5.8 : Colour and ORP measurements at the outlet of the anaerobic zone after dosing 7.5 kg C.I. Reactive Red 141.

A distinct peak in colour (165 °H) was observed after ca. 35 min. The initial lag time was due to the residence time in the inlet pipe and the anaerobic zone. The colour then decreased, almost linearly ($R^2 = 0.962$), to a value of ca. 110 °H after ca. 90 min. During this period the ORP did not vary significantly. A peak value of ca. -100 mV (SHE) was observed at ca. 15 min after the dye was dosed. The ORP then also decreased approximately linearly ($R^2 = 0.97$) to -130 mV (SHE). The change in ORP with respect to the change in colour in the anaerobic zone was not significant (ca. -25 mV). The ORP was seen to decrease with decreasing colour at the exit of the zone which suggested that the reduction potential of the dye was higher than that of the sludge in the zone, i.e. the dye would be reduced in this zone provided there was a sufficient residence time.

Based on the design volume of the anaerobic zone (300 m^3), the expected concentration of C.I. Reactive Red 141 was 25 mg/ℓ. In laboratory tests (**Chapter 4**) conducted concurrently with the dye tracer test, the colour of a ca. 25 mg/ℓ solution of C.I. Reactive Red 141 in HWWTP sludge and raw feed was approximately 310 °H. However, the maximum colour at the exit of the anaerobic zone was 165 °H which suggested a colour removal of ca. 47 % in the anaerobic zone. Although this was a significant removal efficiency, the experiment demonstrated that a shock load of colour would not be fully decolourised in the anaerobic zone.

5.5 RESIDENCE TIME DISTRIBUTION

In order to determine the residence time distribution of the anaerobic zone of the 5-stage Bardenpho reactor, a lithium chloride tracer test was performed on reactor 2 at the HWWTP.

5.5.1 Introduction

Mixing in any biological system, or any reactor, is vital to the operation of the process. In biological systems, mixing increases the overall rate of biological activity by promoting contact between the microorganisms and the substrate (Sacks, 1997). Most reactors operate between two mixing regimes : perfectly mixed and plug flow, i.e. a perfectly stirred tank reactor or a perfect tubular reactor (Barona and Prengle, 1973). The degree of mixing, or rather the deviation from ideal mixing, can be estimated by injecting a tracer into the inlet of the reactor and then monitoring the concentration of the tracer at the outlet with time. Analysis of this data permits calculation of the actual hydraulic retention time in the reactor, a parameter controlled by the extent of mixing (Tenney and Budzin, 1972).

5.5.2 Method

A simulation was performed using IMPULSE (Baddock, 1992) to determine the expected residence time distribution in the anaerobic zone of the Bardenpho reactor, i.e. the profile and peak value. A 250 m^3, constant volume CSTR was modelled with constant inlet flows of 70 m^3/h and 160 m^3/h raw feed and RAS, respectively. The amount of Li added to the input was varied in the simulation in order to determine the

minimum amount required. It was determined that 5 kg LiCl would produce a peak of approximately 5 mg/ℓ which is 100 times the stipulated detection limit of 0.05 mg/ℓ.

A submersible pump was positioned at the outlet of the anaerobic zone of reactor 2, inside the anaerobic zone. The 5 kg of LiCl was dissolved in tap water by an outside party to avoid contamination of the samples during the test.

The LiCl was dosed to the section feeding reactor 2 at the splitter box at 11h00 and dosing took approximately 10 s. At 11h02 duplicate samples were collected from the submersible pump. Sampling began at 11h05. Samples were taken every 1 min for 30 min, then every 2 min for 10 min and then every 3 min for the remainder of the first hour. In the second hour, samples were taken every 5 min and at 10 min intervals for the third hour. The test ran for a total of 3 h.

Prior to dosing the LiCl to the splitter box, two samples of the raw feed were collected and marked as background samples B1 and B2. The raw feed was sampled periodically during the test to monitor the background concentration of LiCl. The samples were sealed and analysed for Li concentration by Umgeni Water.

5.5.3 Analysis

Instrumentation used:

- Varian SpectrAA 400 Series Flame Spectrometer
- Varian Mark VI Burner Head (N_2O-Air/Air-CH_2-CH_2)

Instrument Method/Setup:

- Instrument mode: Flame emission
- Calibration mode: Concentration
- Measurement mode: Peak height
- Slit width: 0.1 nm, Slit height: Normal
- Wavelength: 670.8 nm
- Replicates: 2
- Measurement time: 2.0 s
- Delay time: 0 s
- Air flow: 13.5 ℓ/min

- Acetylene flow: 2.00 ℓ/min

Chemicals used:

- Saarchem UnivAR Lithium solution 1000 ppm. Batch 33644A

Sample and standard preparation:

(i) Samples B1 and B2 (background samples) were filtered through Whatman GF/A glass micro fibre filters. The filtrates were combined. This solution was then filtered through 0.45 μm millex filters, manufactured by Millipore. (These filters contained a cellulose acetate/cellulose nitrate mixture.)

(ii) This solution formed the blank, and all standards were prepared from it. The samples were allowed to stand to settle out the solid matter would settle out. They were also filtered through the millex filters prior to analysis.

5.5.4 Results

The results from the laboratory analysis, referred to as experimental data in this report, are shown in **Figure 5.9**. The data shows an initial dead-time or lag period of ca. 10 min, a peak of ca. 2,5 mg/ℓ and then an exponential decay indicative of a mixed flow reactor (MFR).

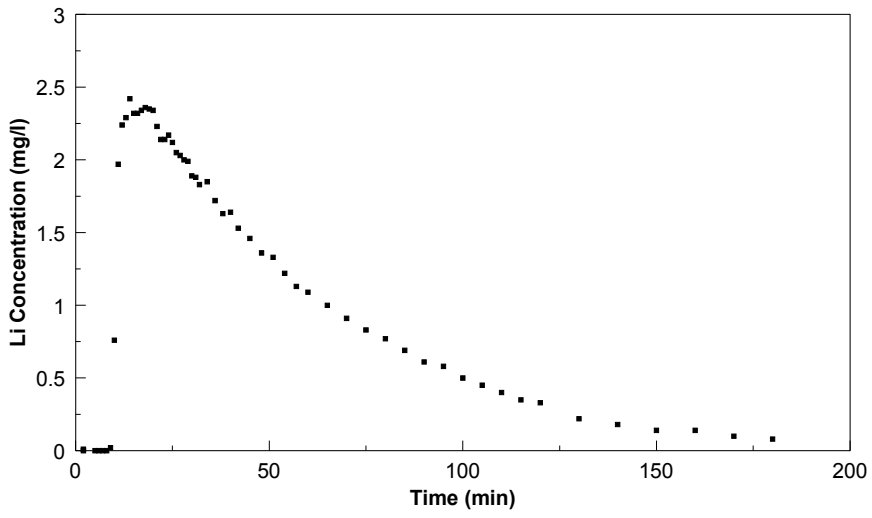


Figure 5.9 : Experimental data shows for the Li tracer test showing an initial lag time, a sudden peak and then an exponential decay.

The experimental data were imported into IMPULSE and a mixed flow reactor model with an initial dead time was modelled (**Figure 5.10**). The raw feed inlet pipe and the initial dead time in the reactor were

modelled as plug flow reactors (PFR) and the reactor was modelled as an MFR or CSTR. Later the MFR was modelled as a tanks in series model (MFR's in series).

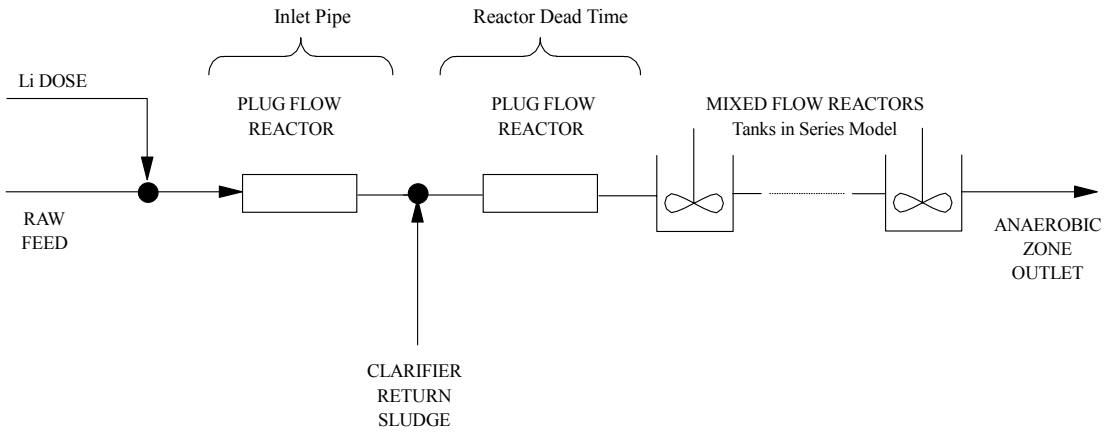


Figure 5.10 : The model chosen to fit the experimental data incorporated two *plug flow* reactors (PFR's) and a *tanks in series* model of mixed flow reactors. The PFR's represent the raw feed inlet pipe from the splitter box to the reactor and the initial dead time in the reactor .

The IMPULSE simulation program allows one to fit a model curve to the experimental tracer test data (**Figure 5.9**). Certain volumes, flow rates or concentrations are assigned as variables and the model parameters are regressed to fit the experimental data. By comparing the model parameters with the physical reactor parameters the flow characteristics and mixing efficiency of the reactor may be determined.

It was found that there could be two possible models which fit the experimental data. One model (Model 1) assumed that the inlet flows, the raw feed and the RAS from the clarifier, were constant and the reactor volumes and input salt concentration were allowed to vary. The second model (Model 2) allowed the flows to vary and the reactor volume and the amount of salt dosed were fixed at the experimental value. Both models are presented in this in the following discussion.

It should be noted that the *input spike* was physically a square wave peak of width 10 s and height ca. 3.8 g/ℓ. The peak value of Li, the concentration value associated with the unit DOSE (**Figure 5.10**), was entered into IMPULSE in such a way as to obtain a spike with the area below the spike curve equal to the initial amount of Li dosed, over one time step (1 min) (**Appendix C**, **Section C.3.3** shows this calculation).

5.5.4.1 Model 1

Model 1 assumed that the inlet raw feed flow rate was the same as the hourly measured flow rate at the head of the works, which remained constant from 11h00 to 13h00 at 1 305 ℓ/min and then increased to 1 416 ℓ/min at the 14h00 reading. The raw feed flow was measured, ultrasonically, before it flowed into the sump at the head of the works. From the sump it was pumped to the crossflow screens and into the splitter box. The hourly raw feed measurement is, therefore, indicative of what was flowing into the reactors. The RAS flow rate from the clarifier was determined, from pump sizing exercises, to vary between 150 and 170 m³/h and was assumed to be 160 m³/h or 2 667 ℓ/min. Based on these fixed parameters the following results were obtained from the IMPULSE model fit :

Table 5.2 : Summary of the IMPULSE results for Model 1.

Unit (IMPULSE name)	**Parameter**	**Result**	**Units**
Anaerobic zone (Zone1)	Volume	187	m³
	No. MFR's in series	1.4	
Reactor dead-time (Pipe2)	Volume	2	m³
Inlet pipe dead-time (Pipe)	Volume	3	m³
Total Volume of reactors (Anaerobic zone)		**192**	**m³**
Salt concentration (Dose)	Concentration	1 638	g/ℓ
	Scaling factor	0.67	
Raw feed (InletRaw) [1]	Flow rate	1 305 to 1 416	ℓ/min
RAS (ReturnSludge) [1]	Flow rate	2 667	ℓ/min

[1] Fixed Parameters

The normalised residence time distribution curve is shown in **Figure 5.11**. The area below the curve between any time t and t + Δt is the fraction of the tracer at the outlet stream with age between t + Δt. Average residence time is given by :

$$\tau = \frac{\sum t_i c_i \Delta t_i}{\sum c_i \Delta t_i} \qquad [5.3]$$

and then the reduced time is :

$$T_i = \frac{t_i}{\tau} \qquad [5.4]$$

where, c_i = concentration at time t_i

T = reduced time,

t = time (min), and,

τ = average residence time.

The residence time distribution function is calculated in reduced time :

$$C(T) = \tau \frac{c_i}{\sum c_j \Delta t_j} \qquad [5.5]$$

The tail of the curve was estimated by IMPULSE.

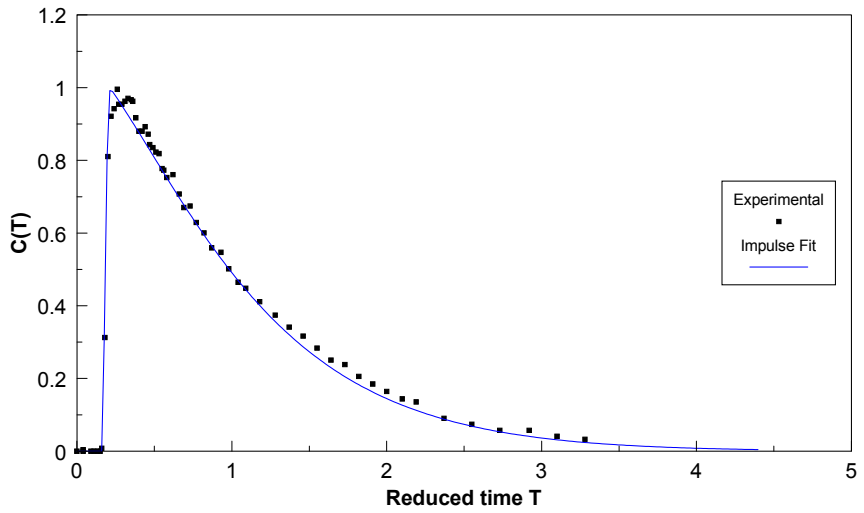


Figure 5.11 : The normalised RTD for the experimental data and Model 1.

The average residence time for the anaerobic zone was determined from the experimental data and the curve from Model 1, produced by IMPULSE, by a numerical integration method and was determined to be **57** and **55 min**, respectively.

The total volume was the sum of all reactor volumes used in the model, i.e. the MFR's in series and the two inlet PFR's. The volume determined by IMPULSE in Model 1 was 192 m³ which was 36 % smaller than the actual volume of the anaerobic zone, 300 m³, as determined from the design drawings.

5.5.4.2 Model 2

Model 2 assumed that the volume of the anaerobic zone and the salt added to the raw feed inlet remained constant, i.e. full salt recovery. The inlet flows and the initial dead-time volumes were allowed to vary in order fit the model data to the experimental data. The results are summarised in **Table 5.3**.

Table 5.3 : Summary of the IMPULSE results for Model 2.

Unit (IMPULSE name)	**Parameter**	**Result**	**Units**
Anaerobic zone (Zone1)	Volume [1]	282	m³
	No. MFR's in series	1.4	
Reactor dead-time (Pipe2)	Volume	2.6	m³
Inlet pipe dead-time (Pipe)	Volume	3.1	m³
Total Volume		**288**	**m³**
Salt concentration (Dose) [1]	Concentration	1 638	g/ℓ
	Scaling factor	1	
Raw feed (InletRaw)	Flow rate	1 305 to 1 416	ℓ/min
	Scaling factor	0.99	
RAS (ReturnSludge)	Flow rate	2 667	ℓ/min
	Scaling factor	1.72	

[1] Fixed Parameters

Figure 5.12 shows the normalised RTD for Model 2.

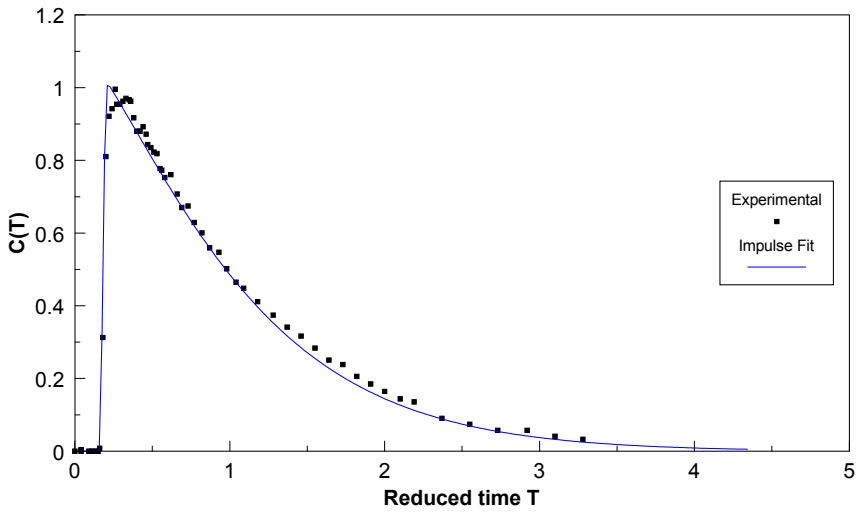


Figure 5.12 : The normalised RTD for the experimental data and Model 2.

The average residence time for Model 2 was calculated to be **56 min**. The average residence time calculated from the experimental data was **57 min** and is, therefore, in close agreement with the IMPULSE model residence times.

Since the salt concentration, reactor volume and flow rates are all dependent on each other in the modelling, it is difficult to conclude which parameter is in error without further investigation.

5.5.5 Discussion of the RTD Results

IMPULSE produced a good fit to the experimental data in both models, however the model parameters needed to be scaled in order to achieve this. In Model 1 the flows were fixed which forced the reactor volume and salt concentration to decrease to compensate for this, i.e. to fit the experimental data. The result was that the reactor volume estimated was 36 % smaller than that specified in the design drawings. This effectively meant that the average residence time was lower than designed, assuming the flow data was correct.

In Model 2, the raw feed flow rate did not vary noticeably, but the RAS flow rate was scaled up 1.7 times during the regression in order to obtain the fit. This implied that the RAS flow had been under estimated. Prior to the test the flow rate produced by the RAS pumps was checked by pumping into the sludge sump, i.e. approximately 0 m head on the discharge side. The pumps were rated at approximately 153 m^3/h, but this could have varied between 150 to 170 m^3/h depending on the specific pump. One would then assume that the return sludge flow rate would be a fixed parameter in the model.

From the experimental data it was apparent that the anaerobic zone behaved as an MFR, but not ideally since the model calculated that there were 1.4 MFR's in series. The tanks in series model allows for sequential mixing through the reactor. A visual inspection of the anaerobic zone showed that there were different mixing regimes due to the geometry and the position of the inlet pipes.

The design residence time of a reactor can be estimated by dividing the total reactor volume by the total flow rate into the reactor. Assuming the flow and volume estimates were correct, i.e. 300 m^3, 1 305 ℓ/min for the raw feed and 2 667 ℓ/min for the RAS, then the average residence time should be **78 min**. The residence time calculated from the modelling results was ca. 56 min which was lower than the design value. An increased residence time would be beneficial to decolourisation and VFA production and could ultimately enhance the phosphorus removal (P-removal) in the Bardenpho reactor. Increasing the residence time would require either increasing the size of the anaerobic zone or decreasing the flow to the reactor. Since increasing the volume of the reactor is not feasible, a decrease in the flow to the reactor by modifying the splitter box, or by re-routing one of the RAS jets, could achieve this goal. Although an increase in the residence time in the reactor would have a beneficial effect on the decolourisation of the highly coloured textile effluents that enter the works, there may be other implications associated with it. In order to keep the substrate to micro-organism (S/X) ratio the same the raw feed flow and the return sludge flow would have to be scaled down proportionately. The return sludge could be scaled down by diverting one of the return sludge jets to the primary anoxic zone. This would allow for the same flow through the reactor, yet simultaneously decrease the flow through the anaerobic zone.

The extrapolation of the tail of the RTD curve was dependent on the IMPULSE model. The model only reflected the RTD of the raw feed flow since this was the stream to which the salt was dosed. Both models allowed for the prediction of the effect of changing operating conditions as well as the RTD of the RAS flow although this was dependent on the reliability and similarity of the models to reality. An accurate model could be used to investigate the changes in operating conditions which could be effected to obtain maximum decolourisation. Laboratory studies (**Chapter 4**) showed that some textile dyes were decolourised in HWWTP sludge within 4 h, which is longer than the current residence time of the anaerobic zone (< 1 h). The effect of an increased residence time could then be assessed by the model.

The two models presented are both feasible, but there is not enough information to select the most likely scenario, and one can argue as to the validity of each. The design drawings show that the anaerobic zone volume is 300 m^3, but the drawings are not the most recent and modifications may have been made before construction of the reactor. Based on recent measurements, the flow data for the sludge return is reliable to within approximately 10 %, but the raw flow data is assumed to be the same as that measured before the sump. Model 2 was considered to be the most feasible since the flow measurement of the raw feed is undetermined and the drawings of the reactor should be accurate unless there have been any modifications made or if solids are occupying some of the volume (dead volume). Another factor supporting the validity of Model 2 is the mass balance on the Li. The mass balance was determined by numerical integration of the experimental data and was dependent on the flow rates (**Appendix C**). The percent salt recovery was ca. 65 % for Model 1 and ca. 96 % for Model 2 (with the scaling of the flow rates being taken into account). The higher salt recovery therefore suggests that Model 2 was the more reliable of the two models presented.

5.5.6 Possible Errors with the RTD

The results from the analysis may have been subject to some error. The standards for the analysis were made up using the raw feed samples B1 and B2. Sample B2 was taken, from the splitter box, 30 min after dosing and may have contained some lithium which would have offset the results. Samples B1 to B5 (samples B3 to B5 were collected from the splitter box during the course of the sampling) were intended as background samples, but unfortunately the levels of Li in these were not determined.

Another factor influencing the results could have been the inconsistencies associated with measuring the raw feed flow rate to the anaerobic zone. The raw feed flow is measured at the head of the works before it flows into the sump. The sump is level-controlled and the raw feed is fed from here to the fine mesh screens and then to the splitter box. The flow to the reactor was assumed to be the flow into the works. The latter could also account for the low recovery of the salt since the salt recovery is calculated as a function of the inlet flows.

The pump used for sampling was a small submersible pump which was positioned inside the anaerobic zone as close as possible to the outlet hole. The samples may have been diluted by either the pump drawing from the anoxic zone or from a less concentrated position in the reactor resulting a decreased salt recovery.

5.5.7 Recommendations based on the RTD

The average residence time of the anaerobic zone was less than 1 h. It would be beneficial to the decolourising potential of the reactor to increase this retention time by decreasing the flow into the anaerobic zone. To achieve this, one could turn off the RAS for a period or redirect one of the RAS flows to the primary anoxic zone. There may be some complications associated with this though due to increasing the substrate to micro-organisms (S/X) ratio. The increased residence time would improve the VFA production and improve the P-removal. Further investigation into this is required.

The IMPULSE program and the Residence Time Distribution theory only take into account a single input and a single output. This test involved dosing to one of the three inlet pipes to the anaerobic zone, namely the raw feed inlet. In order to better understand the flow characteristics of the anaerobic zone it is recommended that a second RTD be performed with the tracer being dosed to the RAS pipes and possibly a second type of salt being dosed to the raw feed simultaneously. The flow characteristics of each component flow could then be determined independently. If there is short circuiting or bypassing of the return sludge via the nozzles at the bottom of the reactor the tracer test would detect this. To confirm this prior to a second RTD, it is recommended that the outlet of the anaerobic zone be sampled to determine the solids concentration. If bypassing or short circuiting is occurring, then the solids concentration at the outlet would be greater than that of the bulk solution.

5.6 FLUID DYNAMICS MODELLING OF THE ANAEROBIC ZONE

In conjunction with the work discussed previously, a separate study was undertaken to model the flow patterns in the anaerobic zone of the HWWTP reactors using Computational Fluid Dynamics (CFD). A background to CFD and the results of this study are presented in the following section.

5.6.1 Background

The physical aspects of any fluid flow are governed by three fundamental principles :

(i) mass is conserved,
(ii) Newton's second law, and,
(iii) energy is conserved.

These fundamental principles can be expressed in terms of mathematical equations, which in their most general form are usually partial differential equations. Computational Fluid Dynamics (CFD) is the science of

determining a numerical solution to the governing equations of fluid flow whilst advancing the solution through space or time to obtain a numerical description of the complete flow field of interest.

The governing equations for Newtonian fluid dynamics, the unsteady Navier-Stokes equations, have been known for over a century. However, the analytical investigation of reduced forms of these equations is still an active area of research, as is the problem of turbulent closure for the Reynolds averaged form of the equations. For non-Newtonian fluid dynamics, chemically reacting flows and multiphase flows theoretical developments are at a less advanced stage.

The steady improvement in the speed of computers and the available memory size since the 1950s has led to the emergence of computational fluid dynamics. This branch of fluid dynamics complements experimental and theoretical fluid dynamics by providing an alternative cost effective means of simulating real flows. As such it offers the means of testing theoretical advances for conditions unavailable on an experimental basis (Rubini, 1998).

5.6.2 Results and Discussion

The geometry of the anaerobic zone and the location of the inlets and outlets were configured in a CFD program called FLUENT. The flow rates for the raw feed were obtained from historical data at the HWWTP and the RAS flows were reported as being 160 m^3/h (from recent pump sizing exercise). With this information the FLUENT program was able to model the flow vectors in the anaerobic zone. Once the model was determined a tracer input was injected into the raw feed inlet and the concentration of tracer was monitored at the outlet of the anaerobic zone. The results were compared with those obtained from the RTD test (**Section 5.5**) and are shown in **Figure 5.13**.

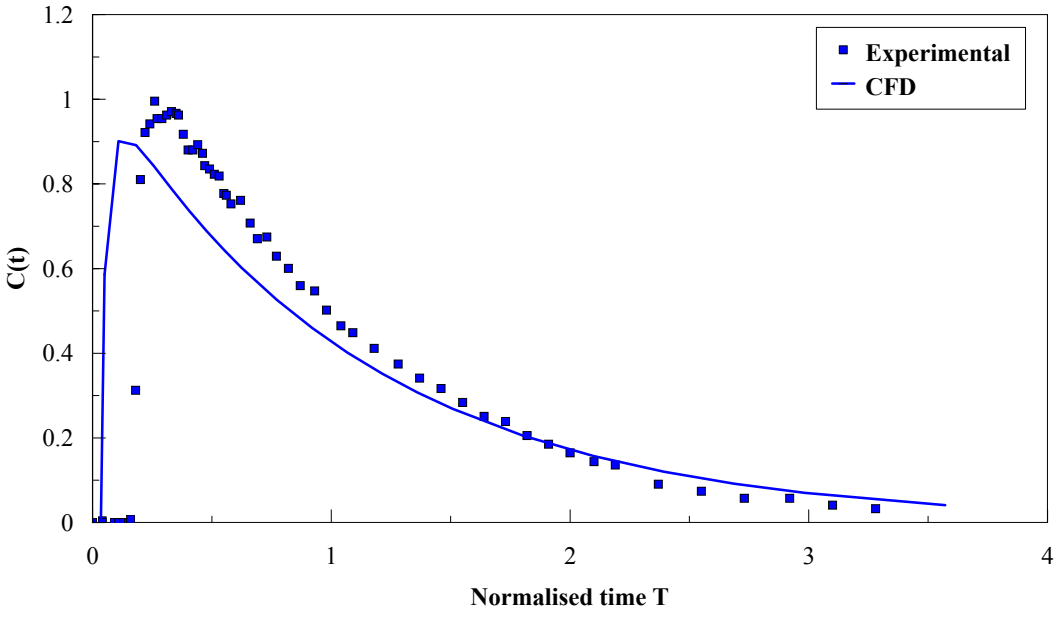


Figure 5.13 : Normalised RTD results from the experimental data (**Section 5.5**) and from the CFD model.

There was a reasonably good comparison between the results from the RTD test and the CFD modelling. The peak in the experimental data was greater than that from the CFD result which indicated that the flows in the CFD model were greater, or rather, the flows for the RTD had been under-predicted. However, there was a discrepancy between the average residence times for the experimental data and that predicted by the CFD model. As discussed previously, the RTD test determined that the average residence time in the anaerobic zone was ca. 55 min, but the CFD model predicted the residence time to be approximately 68 min which is closer to the design value of 78 min. This was contradictory since an increased flow rate should result in a decreased residence time.

To understand why this was occurring it was necessary to construct a profile of the tracer concentration through the anaerobic zone. The locations and flow directions of the three inlets and the location of the outlet are indicated by **Figure 5.14**. The tracer simulation made it possible to track the movement of the tracer with respect to time and position. A *slice* of this profile is shown in **Figure 5.15** where the mass fraction of tracer is shown as contours in the anaerobic zone. The slices where taken on a vertical plane near the outlet (y = 24) and on a horizontal plane near the bottom of the anaerobic zone (z = 1).

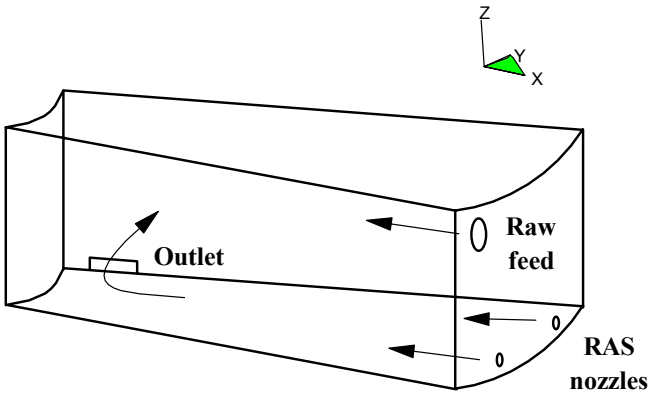


Figure 5.14 : A 3-dimensional perspective of the anaerobic zone indicating the raw feed, RAS nozzles and outlet.

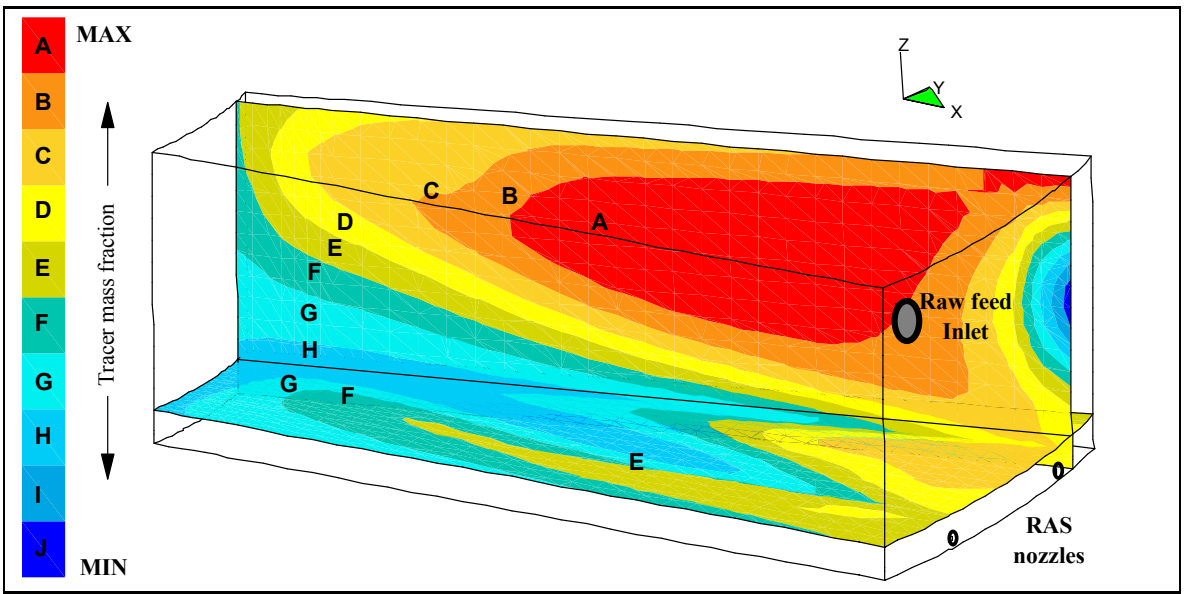


Figure 5.15 : Concentration profile at the y = 24 and z = 1 planes as generated by the FLUENT simulation. The raw feed and RAS jets are indicated on the figure.

The slices through the concentration profile (**Figure 5.15**) show the influence of the RAS flow on the overall flow characteristics in the anaerobic zone. What was evident from **Figure 5.15** was the relatively large accumulation of tracer near the middle of the reactor. This was effectively the raw feed since the tracer was injected into that inlet and is assumed to represent the fluid. The CFD model (**Figure 5.15**) also showed short circuiting of the RAS flows (especially the one below the raw feed inlet) which was not detected by the RTD model. The RAS flows were characterised by lower concentrations of tracer which was clearly visible in the profile.

Although the CFD and RTD model residence times did not agree, they were reasonably similar. The disagreement between the CFD and the RTD models may have been due to the fact that it was difficult to

model three inlet flows when the tracer was injected to only one inlet; the raw feed. However, the CFD model was able to demonstrate that the average residence time of the fluid components in the anaerobic zone was a function of all three inlet flows, i.e. the individual residence times of the inlet components (raw feed and two RAS inlets) were not comparable to the overall average residence time. The hold-up of the raw feed resulted in the residence time of this component being greater than that of the bulk liquid, but short circuiting caused the residence time of the RAS to be lower than that of the bulk liquid. This would be advantageous to the operation of the anaerobic zone and to decolourisation since an increased holding time would (i) result in an increase in the production of VFA's and ultimately improve the P-removal, and, (ii) increase the amount of time the dyes, in the raw feed, reside in a reducing environment. After the anaerobic zone the DO in the sludge increases and, hence, the concentration of nitrate increases due to nitrification. This causes the redox potential of the sludge to increase and produce an environment unsuitable for decolourisation.

The CFD results confirmed the recommendations of the RTD model (**Section 5.5.7**). To obtain a representative model of the anaerobic zone it is necessary to model all inlet flows, i.e. a tracer should be injected to each inlet to model all fluid components. For this reason, the RTD model could only be regarded as being representative of the raw feed flow and information regarding the two RAS flows may only be inferred.

5.7 CONCLUSIONS

The HWWTP Bardenpho reactors were assessed to determine their performance with respect to the decolourisation of textile dyes. The following conclusions were drawn from the results of the full-scale tests :

- ➢ It was concluded that decolourisation was occurring mainly in the anaerobic zone of the HWWTP reactors since there was little decrease in colour between the anaerobic zone and the clarifier overflow, i.e. there is little or no decolourisation occurring in the anoxic and aerobic zones.
- ➢ The colour reduction in the anaerobic zone may be as high as 80 % in the anaerobic zone.
- ➢ The oxidation reduction potential (ORP) in the anaerobic zone ranged between -60 and -180 mV (SHE).
- ➢ Addition of raw feed to the anaerobic zone resulted in variations in the ORP of the sludge of up to 100 mV.
- ➢ The ORP of the raw feed in the splitter box was observed to be of lower potential than that of the RAS. It is suspected that the RAS is exposed to air in the pipe network prior to entering the anaerobic zone.

- Variations in the ORP in the anaerobic zone near the outer wall was observed and led to the conclusion that this are of the anaerobic zone was characterised by complex mixing patterns and possibly an accumulation of raw feed, i.e. this area was suspected to be less well mixed than the remainder of the zone.

- The effect of surface aeration on the ORP in the anaerobic zone was observed to be negligible.

- Colour removal of a shock load of dye (C.I. Reactive Red 141) was observed to be ca. 47 % in the anaerobic zone.

- The RTD model showed that the anaerobic zone was well mixed by the three inlet streams.

- The average residence time of the anaerobic zone was determined to be 57 min as opposed to the design value of 78 min.

- The RTD model developed for the anaerobic zone showed that the reported flow rates of the RAS into the anaerobic zone were questionable.

- It was concluded that injection of the tracer to the raw feed stream and not the RAS streams provided insufficient information regarding the flow patterns in the anaerobic zone. The RTD could only be related to the flow of the raw feed stream since the tracer was injected into this stream and not the RAS streams. Therefore, it would be required to inject known quantities of tracer (possibly distinct tracers) into each inlet in order to obtain a representative RTD of the anaerobic zone.

- The computational fluid dynamics (CFD) modelling produced similar results to that obtained in the RTD test. The tracer profiles (concentration with respect to time at the outlet) were similar, however, the CFD model showed that the peak concentration of the tracer was less than that determined in the RTD test and the average residence time of the fluid components in the anaerobic zone were greater than the RTD test determined; 68 min as opposed to 57 min, respectively.

- The CFD model indicated that there may have been short-circuiting of the RAS feed occurring in the anaerobic zone which would have influenced the residence time of the bulk solution and possibly the operation of the anaerobic zone.

- A concentration profile of the tracer across the anaerobic zone demonstrated that the residence time of the raw feed may have been greater than the residence time of the RAS feed and, thus, greater than the residence time of the bulk solution in the anaerobic zone since the residence time will be a function of the three inlet feed streams.

- It was concluded that the majority of the conditions required for decolourisation of textile dyes was being met by the HWWTP reactors, viz.

(i) decolourisation was most prevalent in the anaerobic zone as indicated by previous research,

(ii) the concentration of competitive electron acceptors, such as nitrates and oxygen, in the feed to the anaerobic zone was low, however, some oxygen contamination was suspected to be occurring in the RAS feed lines,

(iii) there is a readily biodegradable source of carbon available in the feed, due to the relatively high COD of the raw feed, to promote microbial activity and thus decolourise the dyes.

➢ However, there were some of the criteria that were not met, viz.

(i) The ORP of the bulk solution in the anaerobic zone appeared to be greater than that suggested for reduction of some textile dyes; -120 to -140 mV compared to the required -250 mV.

(ii) The residence time in the anaerobic zone is less than that recommended, by the laboratory experiments (**Chapter 4**), for effective decolouisation of the dyes; 57 min compared to the recommended 4.5 h.

The results from **Chapter 4** and **Chapter 5** are discussed in detail in **Chapter 6**.

Chapter Six

Discussion and Conclusions

Laboratory and full-scale experiments were performed to assess the capability of the Hammarsdale Wastewater Treatment Plant (HWWTP) to decolourise textile dyes. The purpose of this chapter is to summarise and compare the results of the laboratory and full-scale experiments in order to assess their applicability to the operation of the HWWTP reactors and thereby propose recommendations for the improvement of the decolourising performance of the reactors. **Section 6.1** discusses the factors affecting decolourisation including physical, chemical and electrochemical factors. In **Section 6.2** the applicability of the laboratory experimental results are assessed in conjunction with the results of the full-scale experiments performed. The conclusions from the comparison of the laboratory and full-scale experiments is presented in **Section 6.3**.

6.1 FACTORS AFFECTING DECOLOURISATION

The decolourisation of a target dye, C.I. Reactive Red 141, was investigated under anaerobic and aerobic biological conditions. Return activated sludge (RAS) from the HWWTP was used as the inoculum and various organic compounds, including raw HWWTP sewage, as the feed substrate. The method of preparation of the experiments and the conditions under which the experiments were maintained proved to affect the rate of decolourisation of the dye. These factors are discussed in the following sections.

6.1.1 Physical Factors

Carliell (1993) determined that C.I. Reactive Red 141 would be decolourised in an anaerobic system if a source of labile carbon was available, no competitive electron acceptors were present and if the ORP (oxidation reduction potential) of the system was below -250 mV (SHE). These experiments were conducted in the absence of oxygen. Even if the serum bottles were exposed to oxygen during the preparation, the pre-incubation period was sufficient to ensure that any oxygen present was eliminated or consumed within the first day. The experimental conditions were considered to be *strongly* anaerobic and provided the required reducing environment for the cleavage of the azo bond chromophore in the dye molecule.

The screening test method, described in **Section 4.2.1**, demonstrated that relatively small amounts of oxygen contamination resulted in significant reduction of the rate of decolourisation of C.I. Reactive Red 141. In these experiments, the sludge was exposed to air during sampling. At each sample interval the bottles were

shaken by hand, opened, a sample withdrawn by pipette and then resealed. This procedure allowed air to enter the head space of the bottles at each interval and resulted in dissolution of a portion of that air during shaking. The results showed only 60 % decolourisation of the dye in ca. 29 h (taking into account the background colour of the control) whereas Carliell (1993) showed that the same dye would be 98 % decolourised in ca. 9 h. The first, and most significant, difference between these experimental procedures was the presence of oxygen. Dissolution of oxygen would have resulted in the ORP of the system increasing and, thus, reduced the decolourising potential of the system. The second difference was the origins of the two inocula used. Carliell (1993) used an inoculum from an anaerobic digester treating domestic sewage with a small quantity of textile dyes. The experiments in **Section 4.2.1** used the RAS from the HWWTP process as the inoculum which is a mixed culture of facultative bacteria. Bacterial populations and their kinetics can vary significantly between treatment facilities and it is thus not appropriate to assume that the rate of degradation of a particular compound at one plant will be equivalent to the rate at another.

The adverse effect of oxygen contamination on decolourisation was further illustrated by the successful decolourisation (over 92 % colour removal) of C.I. Reactive Red 141, with HWWTP sludge, under anaerobic conditions. The procedure for these experiments (**Section 4.2.2**) was similar to that used by Carliell (1993). The HWWTP sludge was over gassed with oxygen free nitrogen and incubated for one day prior to dosing of the dye. These experiments demonstrated that effective colour removal, over 92 % referenced to distilled water, was achieved within 4.5 h. This experiment was repeated using RAS (inoculum) and raw feed (substrate) from HWWTP with the only difference being that the method of pre-incubation was not used. The results (**Figure 4.5b**) correlated well with that of the previous experiment and showed a lag phase where little or no decolourisation took place in the first 2 h of the experiment.

Therefore, oxygen contamination should be minimised in order to achieve an increased rate of decolourisation in HWWTP sludge. This factor is significant in terms of the design and operation of the HWWTP reactors since the 5-stage Bardenpho process is an *extended aeration activated sludge system* and dissolved oxygen plays an important role in the process for carbon, nitrogen and phosphorus removal. The anaerobic zone of the reactor is also an open reactor and subject to surface aeration, although this effect was determined to be negligible in terms of ORP (**Section 5.3.2.4**); the ORP gradient towards the surface of the sludge in the anaerobic zone was determined to be negligible. It was concluded, however, that there was oxygen contamination of the RAS feed streams due to breaches in the pumping and piping system. This resulted in an increase in the ORP of the RAS stream thus increasing the ORP of the bulk solution in the anaerobic zone thereby reducing the decolourising performance of the anaerobic zone.

Pagga and Brown (1986) concluded that short term biodegradation of dyes in activated sludge systems was unlikely and that the primary mechanism of removal would be adsorption of the dye to the sludge. McCurdy et al. (1991) found that water soluble dyes such as reactive dyes would pass through activated sludge treatment systems. **Section 4.2.3** demonstrated, conclusively, that decolourisation of C.I. Reactive Red

141 by aerobic biodegradation and/or adsorption of the dye molecule to the biomass did not occur in the HWWTP sludge. Therefore, the primary mechanisms of decolourisation occuring at the HWWTP were identified as being anaerobic biological decolourisation and decolourisation due to the addition of alum.

Thickening of the sludge to improve decolourisation was investigated in **Section 4.2.2**. It was expected that this would increase decolourisation due to the increased concentration of biomass and thus the increased number of sites at which decolourisation would occur. However, the results (**Figure 4.4** in **Section 4.2.2**) demonstrated that there was a negligible effect on the rate of decolourisation when the solids concentration was approximately doubled from 1.3 to 2.4 % solids.

6.1.2 Variations in the Feed Substrate

To investigate the effect of adding an additional or alternate carbon source to the HWWTP sludge on the rate of decolourisation, glucose was introduced in the anaerobic serum bottles tests described in **Section 4.2.2**. The concentration of the COD due to the addition of the glucose (ca. 10 000 mg/ℓ) was approximately four times that of the raw feed (ca. 2 200 to 2 500 mg/ℓ). The increase in COD had a negligible effect on the rate of decolourisation of C.I. Reactive Red 141. It was concluded that the bacteria were accustomed to growth in a medium containing a relatively high influent COD due to the chicken abattoir effluent. The additional COD (which would have been inhibitory to some types of sludge according to Owen et al. (1979)) had no effect on the microbial activity or the mechanisms taking place.

6.1.3 The Effect of Redox Potential on Decolourisation

Mphephu (1996) demonstrated that Reactive Red 2, an azo reactive dye, would be decolourised by bulk electrolysis of the solution when exposed to a potential of -715 mV (SHE) at a pH value of 7.06. Similar results were obtained by Carliell (1993), using anaerobic digester sludge, whereby C.I. Reactive Red 141 was decolourised when the ORP decreased to -250 mV (SHE) and a source of labile carbon was available. This reduction exhibited first order kinetics. Weber and Wolfe (1987) found that the reduction potential of azobenzene by anaerobic sediments varied between -20 and -100 mV (SHE) and the reduction exhibited psuedo-first-order kinetics. Therefore, azo reduction exhibits differing reduction potentials in different environments. This may be due to the complexity of a biological redox system. As mentioned in **Section 4.3.1**, the ORP of the bulk solution of a biological system is the weighted average, based on molar activity, of all of the electroactive components. There are many redox reactions occurring simultaneously in biological systems and the reduction potentials vary for each reaction. Therefore, the reduction potential of the azo bond in a biological system will be the apparent reduction potential of the bulk solution and not necessarily that of the azo bond.

An investigation of the ORP of the HWWTP sludge (**Section 4.3.3**) and the ORP of the sludge in the anaerobic zone (**Section 5.3**) was undertaken. In conjunction with this, the decolourisation of C.I. Reactive Red 141 in HWWTP sludge was investigated with respect to time and with simultaneous ORP measurement (**Section 4.3.4**). The intention was to develop a relationship between decolourisation and ORP. The initial measurement of the HWWTP sludge in laboratory experiments (**Figure 4.10** in **Section 4.3.3**) showed that potentials as low as -400 mV (SHE) were obtainable over extended periods of time (ca. 50 h). It was observed that the addition of raw feed to the sludge resulted in an increase in the bulk ORP. The addition of the raw feed, and thus addition of a source of readily biodegradable COD (RBCOD), would have resulted in a shift in the metabolism of the microorganisms from strong reducing conditions (possibly sulphate reduction or methanogenesis) to relatively higher reducing conditions created by processes such as hydrolysis, reduction of the monomers (sugars, amino acids, etc.) or production of VFA's. The shift in metabolism and the resultant increase in the ORP does not imply that the other reactions like sulphate reduction and even dye reduction cease. These reactions may still occur, but in smaller quantities, i.e. the number of dye reduction reactions occurring decreases when the ORP of the solution increases.

The results of the decolourisation experiment (**Figure 4.11** in **Section 4.3.5**) with simultaneous ORP measurement showed that C.I. Reactive Red 141 was decolourised in HWWTP sludge at redox potentials between ca. -50 to 50 mV (SHE) . This was 200 to 300 mV greater than that suggested by Carliell (1993). The ORP was unstable during the initial 3 h of the experiment owing to the concentration of RBCOD in the feed. At ca. 3 h the ORP stabilised at ca. 50 mV and the rate of decolourisation increased. After ca. 6 h the rate of decolourisation began to decrease and there was a simultaneous step-down in the ORP to ca. -100 mV. Although there was no direct relationship between decolourisation and ORP, the changes in the ORP were indicative of changes in the composition of the system and possibly changes in the metabolism of the microorganisms. Two distinct rates of decolourisation were noticed during the initial stages of the experiment (first 7 h) and these corresponded with definite changes in the ORP of the system (**Figure 4.12** in **Section 4.3.5**). It was concluded that these rates corresponded with different microbiological processes and that both were favourable to decolourisation of C.I. Reactive Red 141. It was not possible to identify these different processes but they were assumed to be :

(i) hydrolysis of the complex organic polymers (fats, carbohydrates and proteins) to their simple organic monomer structures (lipids, sugars and amino acids),
(ii) reduction of the monomers to volatile fatty acids (VFA's) and
(iii) uptake of the VFA's by *Acinetobacter* with a simultaneous release of phosphorus.

Therefore, ORP may be useful in determining the decolourisation of dyes. However, the particular characteristics of the dyes in that particular sludge, in terms of ORP, first need to be determined.

6.2 OPERATION OF THE BARDENPHO REACTORS FOR DECOLOURISATION

The 5-stage Bardenpho nutrient removal reactors at the HWWTP were investigated in order to assess their performance in terms of decolourisation of textile dyes. The performance of the reactors was then compared with the results obtained in the laboratory experiments to determine methods of improving decolourisation. The following section summarises the results from the full-scale tests (Chapter 5) and discusses the applicability of the laboratory results to the full-scale operation of the HWWTP.

6.2.1 Anaerobic Conditions in the Reactors

The Bardenpho reactors incorporate an anaerobic, two anoxic and two aerobic zones to achieve carbon, nitrogen and phosphorus removal (see **Section 2.4.2.3**). This arrangement of reactors would be suitable for treatment of textile dyes since primary degradation would take place in the anaerobic section (according to Zaoyan, 1992; Seshadri, 1994; Carliell, 1993; Carliell, 1994; Carliell, 1994; Knapp, 1995) and the metabolites (generally aromatic amines) would be further degraded in the aerobic section by hydroxylation and ring opening (Malaney, 1960; Dagley, 1975). However, primary degradation in the anaerobic section is required otherwise the dye passes through the aerobic sections untreated (Pagga and Brown, 1986; Barclay, 1996). This was confirmed by the experiments described in **Chapter 4** whereby C.I. Reactive Red 141 was decolourised in HWWTP sludge under anaerobic conditions and not affected when exposed to HWWTP sludge under aerobic conditions. Sampling from different zones in the Bardenpho reactor demonstrated that this was also true for the full-scale (see **Section 5.2**). The colour change from the outlet of the anaerobic zone to the overflow over the clarifier was negligible in most cases indicating that the majority of the colour was being removed in the anaerobic zone. An initial estimate revealed that the colour removal in the anaerobic zone may have been as high as 80 % (**Section 5.2**), but the measurement of the colour in the raw feed was not reliable. Measurement of the raw feed colour was complicated by colloidal material. The raw feed had to be filtered to remove all colloidal material and this may have resulted in removal of some of the colour due to dyes in the wastewater. Therefore, it was concluded that the colour of the filtered sample of the raw feed was not representative of the colour entering the anaerobic zone.

The HWWTP process is a facultative one incorporating both anaerobic and aerobic processes in succession and these processes do not have defined boundaries, i.e. where they start and stop. There exists, rather, different *degrees of anaerobicity* and *aerobicity*. This, therefore, means that the anaerobic zone may become more anaerobic or less anaerobic according to the operation of the process as a whole. The degree of anaerobicity, in terms of the rate of decolourisation, was demonstrated by the results in **Section 4.2** and **Section 4.3**. The rate of decolourisation is affected by the presence of competitive electron acceptors in the sludge such as oxygen and nitrate. These components would be reduced in preference to the dye due to their higher reduction potential. Therefore, if oxygen is injected into the anaerobic zone via either the raw feed or the RAS feeds, then the rate of decolourisation would be expected to decrease. As mentioned previously in

Section 6.1.1, it was suspected that air was being entrained into the RAS lines via breaches in the pumps (e.g. faulty seals), but this could not be quantified. Another possibility of introducing inhibitors to the decolourisation process would result from sludge that has not been fully denitrified in the secondary anoxic zone and the clarifier. Nitrification of nitrite to nitrate takes place in the primary and secondary aerobic zones after which the secondary anoxic zone, and possibly the clarifier, denitrify the wastewater to free nitrogen. Denitrification in the clarifier is not desirable due to the effect on the settling of the solids, therefore, the process is controlled to minimise this and as a result some of these nitrates are recycled to the anaerobic zone via the RAS. Due to the relatively low concentration of nitrogen entering in the raw feed at HWWTP, this was not thought to be a significant factor in the performance of the anaerobic zone in terms of decolourisation.

Furthermore, samples drawn from the anaerobic zones of two different reactors, simultaneously, showed a significant variation in colour. The only notable difference between the two anaerobic zones was the presence of a thick layer of scum on the surface of the anaerobic zone with the relatively lower colour. It was concluded that this scum layer increased the anaerobicity of that zone and thereby reducing the redox potential of the sludge and, thus, creating a more conducive environment for decolourisation. Unfortunately, this scum layer is a nuisance effect and is regularly removed, but the effect of enclosing the anaerobic zones should be investigated further to determine its feasibility. The strictly anaerobic serum bottle tests discussed in **Section 4.2** would also suggest further investigation into the degree of anaerobicity in the anaerobic zones of the HWWTP reactors.

6.2.2 Redox Potential of the Anaerobic Zone

The ORP of the anaerobic zone was measured in order to determine whether the redox conditions within this zone were suitable for decolourisation (see **Section 5.2**). Since it was suspected that the mixing in the anaerobic zone was non-ideal, it was decided to measure the ORP at various points in the anaerobic zone to construct a ORP profile of that zone. It was determined that the ORP in the anaerobic zone varied between -60 and -180 mV (SHE) over the twelve points at which it was measured. The lowest potentials were measured in a region near the outer wall of the anaerobic zone (see **Figure 5.3** in **Section 5.2**) where the mixing was suspected to be less intense that the remainder of the zone. This region also showed the greatest variation in ORP results which indicated the complexity of the sludge in this region. The average ORP of the sludge in the anaerobic zone was determined to be between -120 and -140 mV (SHE) which is higher than that recommended by Carliell (1993) and Mphephu (1996) for the reduction of azo dyes. However, the results from **Section 4.3.5** demonstrated that C.I. Reactive Red 141 would be decolourised in HWWTP sludge under anaerobic conditions when the ORP was between -50 and 50 mV (SHE). This leads to the conclusion that the redox conditions in the anaerobic zone of the Bardenpho reactor at the HWWTP are conducive to decolourisation of most azo dyes.

The colour in the anaerobic zone was measured at the same points the ORP was measured during the construction of the ORP Profile. The colour did not vary considerably and it was concluded that the colour of the bulk solution would vary as opposed to varying from point to point as the ORP did.

It was clear from the ORP Profile experiments that the mixing in the anaerobic zone due to the three inlet streams, viz. the raw feed and the two RAS feeds, was complex and needed further investigation. To determine the flow characteristics in the anaerobic zone a residence time distribution study was performed.

6.2.3 Residence Time Distribution in the Anaerobic Zone

In order to determine the residence time distribution of the anaerobic zone of the 5-stage Bardenpho reactor a lithium chloride tracer test was performed on reactor 2 at the HWWTP. The results of the tracer test were used to determine the residence time distribution (RTD) of the anaerobic zone and to construct a model of the flow patterns in this zone. A locally developed computer program called IMPULSE was used to model the RTD (**Section 5.5**). The modelling determined that the anaerobic zone was operating as a mixed flow reactor (MFR) and produced two feasible results : Model 1 which assumed that the flow rates were fixed parameters and the salt concentration and the volume of the reactor as variables, and, Model 2 which assumed that the volume of the reactor was and the salt added to the raw feed remained constant. Model 2 was chosen in preference to Model 1 due to the difference in the Li recovery calculated; 65 % for Model 1 as opposed to 96 % for Model 2.

Model 2 determined that the RAS flows were underestimated by as much as 1.7 times. The average residence time was determined to be ca. 57 min which was lower than the design value of ca. 78 min. An increase in the residence time in the anaerobic zone would be beneficial to processes such as decolourisation and VFA production and hence phosphorus removal. Increasing the residence time in the anaerobic zone would imply a reduction in the flows, or at least a reduction in the flow of the raw feed, i.e. increase the residence time of the raw feed components.

The RTD experiment was not complete, however, since the tracer was only injected into one of the three inlet streams. The IMPULSE program makes use of the classical RTD theories and equations, but is only intended for single-input, single-output systems. Since the lithium salt was only dosed to the raw feed inlet, the RTD can only be regarded as being representative of the raw feed and any information regarding the other components (two RAS flows) must be inferred (see **Section 5.5.5**). Further tests would be required in order to obtain a representative RTD and model of the anaerobic zone.

6.2.4 Implications of the Residence Time Distribution

Laboratory experiments in **Section 4.2.2** suggested that over 92 % decolourisation of C.I. Reactive Red 141 could be achieved within 4.5 h in an anaerobic environment using HWWTP RAS as the inoculum and raw

feed as the substrate. The RTD experiment demonstrated that the average residence time of fluid components in the anaerobic zone was ca. 57 min. In order to achieve maximum decolourisation, the residence time of the anaerobic zone would have to be increased. It was suggested in the previous section that throttling of the raw feed flow would produce the required result since the residence time of the RAS was not considered to be critical. However, it would be critical if it resulted in an imbalance in the food to microorganism (S/X) ratio and disturbed the normal operation of the Bardenpho reactors, i.e. the microbial activity under normal operating conditions. Further research into this aspect would be required before implementing these changes.

6.2.5 Computational Fluid Dynamics of the Anaerobic Zone

In conjunction with the work discussed in the previous sections, a separate study was undertaken to model the flow patterns in the anaerobic zone of the HWWTP reactors using Computational Fluid Dynamics (CFD). A propriety computer program called FLUENT was used to model the flow vectors of the raw feed flow and the two RAS feed flows. Later, a tracer was injected into the raw feed inlet and the residence time distribution of the FLUENT simulated anaerobic zone was determined. The results (**Section 5.6.1**) correlated fairly well with the actual RTD results, but the simulated model determined that the residence time was 68 min which is closer to the design value of 78 min. The CFD model demonstrated that the RAS flows were short-circuiting through the zone and that the residence time of the raw feed appeared to be greater than that of the bulk solution, i.e. the apparent residence time of the bulk solution was a function of the RAS and raw feed residence times and the apparent residence time of the bulk would have remained fairly constant while those of the RAS and raw feed varied. These conclusions were qualitatively confirmed by a concentration profile (**Figure 5.14** in **Section 5.6.1**) of the anaerobic zone which showed a large *pocket* of relatively high tracer concentration towards the outer wall of the anaerobic zone. This demonstrated that the holding time of the raw feed was in fact greater than the average residence time (57 min) would suggest. However, to confirm this, it would be required to perform a tracer test by injecting tracer to all three inlets to the anaerobic zone.

6.3 CONCLUSIONS

The experimental results presented in **Chapter 4** and **Chapter 5** were compared in order to determine methods of improving the decolourisation performance of the HWWTP Bardenpho reactors. The following conclusions were made :

- The presence of dissolved oxygen reduced the rate of decolourisation of C.I. Reactive Red 141 in HWWTP sludge under anaerobic conditions.

- In order to improve the decolourising performance of the anaerobic zone, the concentration of dissolved oxygen in the feed should be minimised. It was suspected that oxygen entrainment was occurring in the RAS feed lines, but this was not quantified.
- The colour removal in the anaerobic zone may have been as high as 80 %, but this would have to be revaluated when a representative measure of the raw feed colour was obtained.
- The presence of a layer of scum on the surface of the anaerobic zone appeared to improve the decolourising potential of the Bardenpho reactors.
- The ORP of the anaerobic zone created by the microorganisms was concluded to be conducive to the decolourisation of azo dyes.
- The ORP of the bulk solution of the anaerobic zone would determine the rate of decolourisation.
- The residence time of the anaerobic zone in insufficient for effective decolourisation of textile dyes.
- The residence time of the raw feed appears to be greater than that of the bulk solution.
- Further experimentation and modelling is required to obtain a representative model of all three inlet flows to the anaerobic zone.

Chapter Seven

Recommendations

The work presented in the previous chapters described an evaluation of the Hammarsdale Wastewater Treatment Plant (HWWTP) process for the decolourisation of textile dyes. The purpose of the evaluation was to determine the decolourising performance of the Bardenpho reactors and to propose modifications to improve this performance. The following recommendations are proposed :

(i) The effect of covering or enclosing the anaerobic zone of the Bardenpho reactor should be investigated to determine its effect on the decolourisation performance of the reactor. This could possibly be achieved by covering the zone temporarily, with foam rubber sheets for example, and then measuring the ORP of the sludge. A decrease in the ORP would indicate an increase in the decolourising performance of the anaerobic zone.

(ii) The residence time in the anaerobic zone should be increased to allow for effective decolourisation. This may be achieved by redirecting one of the RAS flows to the primary anoxic zone thereby halving the RAS flow. It is further recommended that the RAS flow directly below the raw feed inlet be the flow that is redirected since it is this flow that is suspected to be short-circuiting to the anoxic zone.

(iii) A second option for increasing the residence time in the anaerobic zone is to make use of one of the six Bardenpho reactors at HWWTP as a dedicated *decolourising* reactor. The CONNEPP (Consultative National Environmental Policy Process) White Paper on Environmental Management Policy which states for Waste Avoidance and Minimisation : *Waste management must minimise and avoid the creation of waste at source, especially in the case of toxic and hazardous wastes. Government must encourage waste recycling, separation at source and safe disposal of unavoidable waste*. Bearing this in mind, the volumes of trade effluent from the Hammarsdale region are expected to decrease thereby reducing the already below design inflow to the HWWTP. In terms of Section 4/6, (2)a of the Durban Metro Sewage Diposal Bylaws (1997), which states : ... *technology used by the applicant represents the best available to the applicants industry*..., using the available capacity at the works for process improvement would be advantageous in terms of the relaxations granted the HWWTP, specifically those for colour and conductivity.

Further experimentation is also proposed :

- A laboratory digester experiment, similar to that in **Section 4.3.4**, should be performed with a stepped feed of dye and continuous ORP monitoring. This would elucidate the relationship between dye decolourisation and redox potential. The control of nutrient removal systems using ORP is an established principle and could prove useful for colour removal.

- The above experiment could be combined with bulk electrolysis, i.e. applying a known voltage across the solution. Electrolysis has proved successful in the past, but there is the requirement of secondary wastewater treatment. Therefore, a combination of electrolysis and conventional wastewater treatment, whether anaerobic, aerobic or both, could prove feasible if the running costs could be minimised.

- Serum bottle experiments similar to those in **Section 4.2** should be performed using other test dyes, preferably those used in the Hammarsdale textile mills, to identify recalcitrant, problematic dyes.

- The residence time distribution test described in **Section 5.5** should be repeated, but with tracer injected into all of the inlets. If possible, distinct tracers should be injected into the raw feed line and the MLR line simultaneously to obtain separate RTD's for each flow component.

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Appendix A

Hammarsdale WWTP Data

The data in **Appendix A** is presented and discussed in **Chapter 3**.

A.1 INFLUENT FLOW DATA

Table A.1 : Daily Average flows during the period November 1995 to December 1997

Month	Daily Flow (m^3)		
	High	**Low**	**Average**
Nov 95	14670	4910	11533
Dec 95	14300	3110	7763
Jan 96	13460	2390	8845
Feb 96	14180	5050	10621
Mar 96	20760	4710	11692
Apr 96	13860	2270	9453
May 96	12920	2360	9931
Jun 96	12670	3170	9029
Jul 96	16250	5190	10311
Aug 96	12950	4470	9980
Sep 96	13400	5030	10340
Oct 96	14970	5720	11724
Nov 96	14350	5960	11077
Dec 96	13790	2080	6212
Feb 97	15770	5990	10871
Mar 97	14450	3610	10064
Apr 97	13700	4450	10744
May 97	14070	6310	11096
Jun 97	13370	4120	10586
Jul 97	13920	5890	11090
Aug 97	32230	4810	10193
Sep 97	15490	4970	10743
Oct 97	15170	6220	11556
Nov 97	16950	6060	12247
Dec 97	14390	2780	8002
Average	**15282**	**4465**	**10228**

The data in **Table A.1** is presented in **Figure 3.3** in **Section 3.3**.

Table A.2 : Total daily flows during the period November 1995 to December 1997

Month	Flow (m^3)				
	Chicken Abattoir	**Textile Industry**	**Buckman**	**Other**	**Total**
Nov 95	103663	250620	800	6537	361620
Dec 95	114837	154070	0	7420	276327
Jan 96	73983	196841	0	8864	279688
Feb 96	120146	185608	0	7139	312893
Mar 96	90064	206811	0	7237	304112
May 96	102076	185689	0	8457	296222
Jun 96	78672	199722	0	5893	284287
Jul 96	87832	228903	0	8790	325525
Aug 96	86419	174705	0	6844	267968
Sep 96	90226	227913	0	6957	325096
Oct 96	90314	242766	0	7667	340747
Nov 96	88398	248942	0	9264	346604
Dec 96	86558	122000	0	7168	215726
Feb 97	79035	232202	7450	0	318687
Mar 97	93017	220881	0	5851	319749
Apr 97	67509	245920	0	6957	320386
May 97	85133	270266	0	7880	363279
Jun 97	80483	251898	0	8740	341121
Jul 97	76282	228433	0	7789	312504
Aug 97	87226	246795	0	8031	342052
Sep 97	85340	239179	0	7676	332195
Oct 97	88907	286977	80	10368	386332
Nov 97	81715	246756	220	9671	338362
Dec 97	88575	179090	250	10333	278248
Average	**88600**	**219708**	**367**	**7564**	**316239**

The data in **Table A.2** is presented in **Figure 3.4** in **Section 3.3**.

A.2 EFFLUENT QUALITY AND REMOVAL PROFILES

Table A.3 : Profile of removals across the HWWTP. The data represents averages for the period November 1995 to December 1997

	units	Raw	R1	R2	R3	R4	R5	R6	Final	% Rem.
pH		7.4	7.4	7.3	7.4	7.4	7.4	7.4	7.2	
Colour	°H	ND	80	84	80	80	84	97	61	-
COD	mg/ℓ	2375	84	85	88	87	87	112	58	98
SS	mg/ℓ	541.28	ND	ND	ND	ND	ND	ND	15.37	97
MLSS	mg/ℓ	ND	10670	10034	9894	9782	10491	11732	ND	-
VSS	%	ND	79.9	81.2	79.3	79.9	80.3	82.1	ND	-
Alkalinity	mg/ℓ	318.9	170.4	172.9	169.5	167.4	169.3	187.1	155.2	51
Nitrate	mg/ℓ	0.712	0.736	0.728	0.744	0.788	0.8	0.884	0.984	-38
Conductivity	mS/m	258	ND	ND	ND	ND	ND	ND	234	9
SRP	µg/ℓ	6848	540	598	553	545	574	823	515	92

A.3 CHEMICALS USED

The chemicals used at the HWWTP are presented in **Table A.4** and **Table A.5** since the use of alum at the works is a significant running cost.

Table A.4 : Daily average mass of chemicals used during the period November 1995 to December 1997

Chemical	**Mass (kg)**		
	Average	**Minimum**	**Maximum**
Alum	52 891	26 573	85 723
Chlorine	784	500	1 200
ZETAG 57	597	150	1 300
Lime	220	0	1 700
Chloride of lime	37.5	0	150

Table A.5 : Daily average dosing concentration of chemicals used during the period November 1995 to December 1997

Chemical	**Dose concentration (mg/ℓ)**		
	Average	**Minimum**	**Maximum**
Alum	170	110	258
Chlorine	3	1	5
ZETAG 57	5	3	7
Lime	ND	ND	ND
Chloride of lime	ND	ND	ND

A.4 EFFLUENT QUALITY

The quality of the HWWTP effluent is reflected in **Figure A.1(a)** to **Figure A.1(c)**.

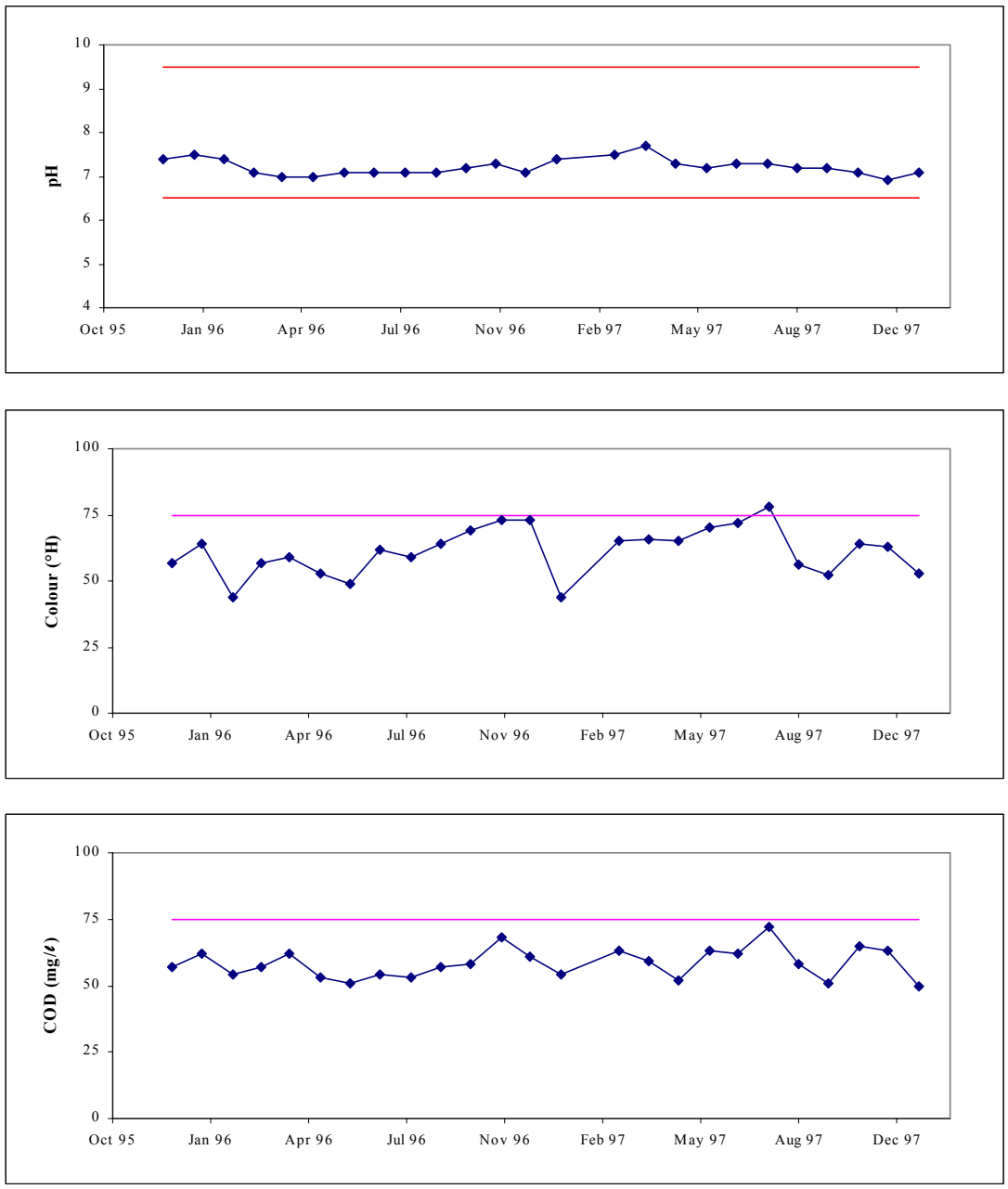

Figure A.1a : Effluent quality data for the period November 1995 to December 1997. The General Standard is shown as the straight line.

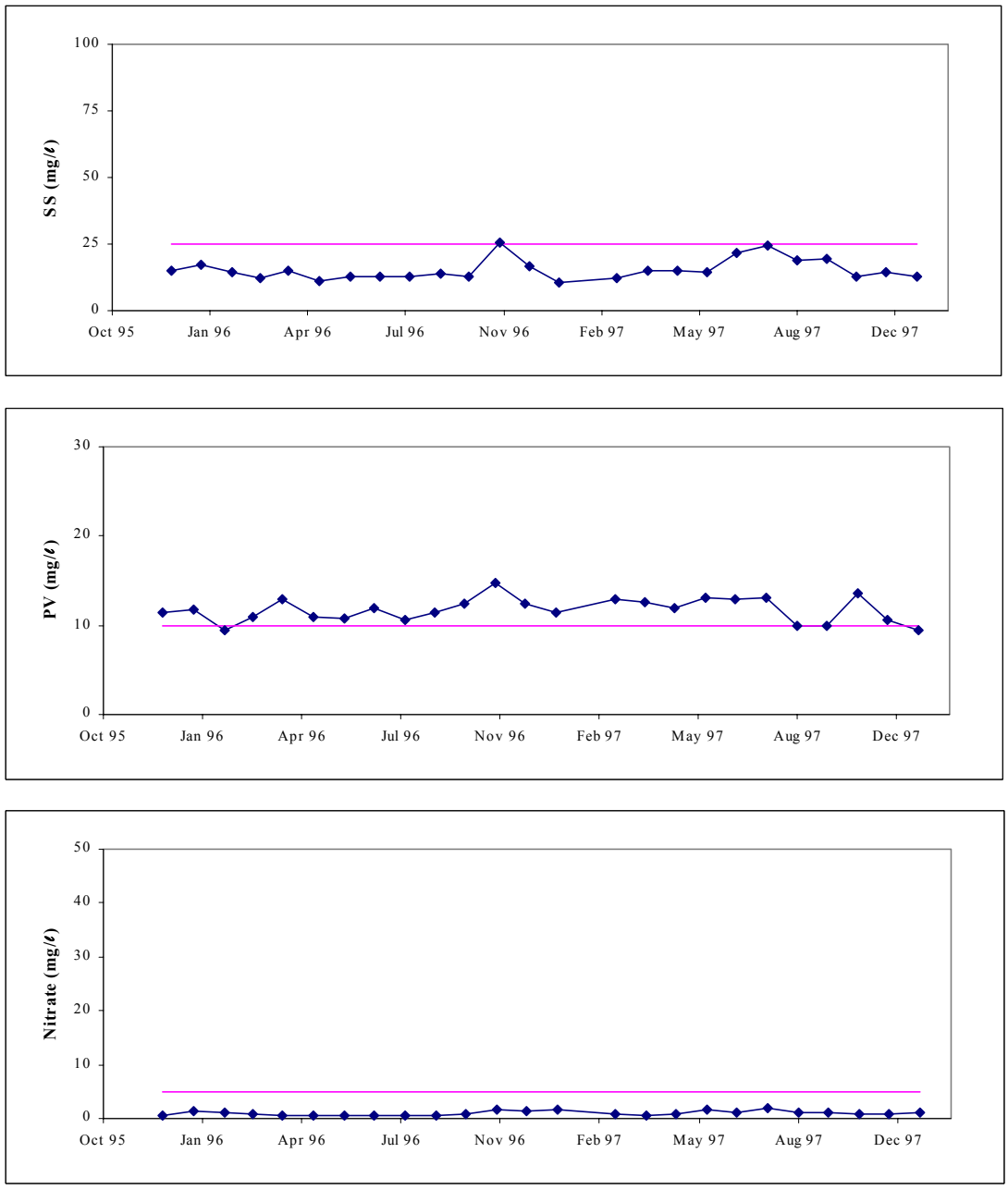

Figure A.1b : Effluent quality data for the period November 1995 to December 1997. The General Standard is shown as the straight line.

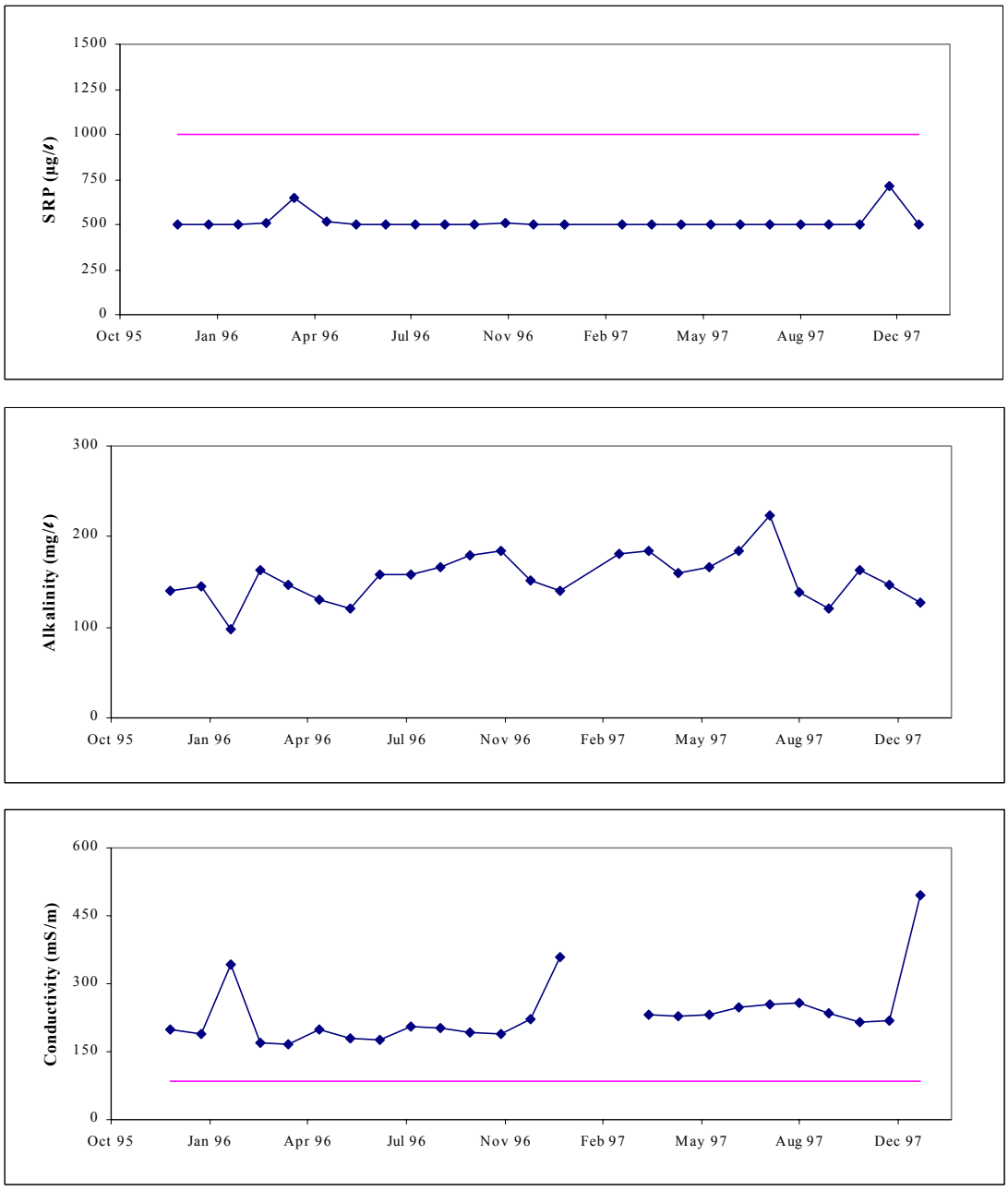

Figure A.1c : Effluent quality data for the period November 1995 to December 1997. The General Standard is shown as the straight line.

A.5 ANALYTICAL DATA

Table A.6 : Daily average pH of samples from the raw feed, reactors and final effluent during the period November 1995 to December 1997

Month	pH							
	Raw	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**Final**
Nov 95	7.3	7.3	7.4	7.4	7.4	7.4	7.4	7.4
Dec 95	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.5
Jan 96	6.7	7.3	7.2	7.3	7.3	7.3	7.3	7.4
Feb 96	7.7	7.3	7.4	7.5	7.5	7.5	7.5	7.1
Mar 96	7.2	7.2	7.3	7.3	7.3	7.3	7.3	7.0
Apr 96	7.7	7.2	7.3	7.3	7.3	7.3	7.4	7.0
May 96	8.0	7.1	7.2	7.3	7.3	7.3	7.3	7.0
Jun 96	7.6	7.2	7.3	7.3	7.4	7.4	7.5	7.1
Jul 96	7.5	7.2	7.2	7.3	7.3	7.3	7.3	7.1
Aug 96	7.6	7.2	7.3	7.3	7.4	7.4	7.4	7.1
Sep 96	7.3	7.4	7.4	7.5	7.5	7.6	7.6	7.2
Oct 96	7.4	7.5	7.5	7.5	7.6	7.6	7.6	7.3
Nov 96	7.3	7.3	7.4	7.5	7.5	7.5	7.6	7.1
Dec 96	7.1	7.2	7.2	7.2	7.3	7.2	7.3	7.4
Feb 97	7.1	7.4	7.5	7.5	7.4	7.4	7.4	7.5
Mar 97	7.2	7.6	7.6	7.6	7.6	7.6	7.6	7.7
Apr 97	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.3
May 97	7.4	10.8	7.4	7.4	7.4	7.4	7.4	7.2
Jun 97	7.5	7.4	7.4	7.4	7.4	7.4	7.4	7.3
Jul 97	8.2	7.4	7.4	7.4	7.4	7.5	7.5	7.3
Aug 97	7.4	7.2	7.3	7.3	7.3	7.3	7.3	7.2
Sep 97	7.3	7.2	7.3	7.3	7.2	7.2	7.2	7.2
Oct 97	7.1	7.3	7.4	7.4	7.4	7.4	7.4	7.1
Nov 97	7.2	7.2	7.3	7.3	7.3	7.3	7.3	6.9
Dec 97	7.0	7.1	7.2	7.3	7.3	7.2	7.2	7.1
Average	**7.4**	**7.4**	**7.3**	**7.4**	**7.4**	**7.4**	**7.4**	**7.2**

Table A.7 : Daily average colour of samples from the raw feed, reactors and final effluent during the period November 1995 to December 1997

Month	Colour (°H)							
	Raw	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**Final**
Nov 95	NM	81	83	87	89	89	97	57
Dec 95	NM	89	88	92	98	91	107	64
Jan 96	NM	63	53	57	58	58	67	44
Feb 96	NM	88	90	94	97	103	191	57
Mar 96	NM	91	95	95	97	99	180	59
Apr 96	NM	80	82	83	84	83	128	53
May 96	NM	82	84	90	83	86	97	49
Jun 96	NM	88	93	90	87	139	96	62
Jul 96	NM	85	86	87	82	89	93	59
Aug 96	NM	85	75	73	76	80	92	64
Sep 96	NM	94	93	93	93	98	107	69
Oct 96	NM	90	91	97	105	112	113	73
Nov 96	NM	87	89	92	96	101	104	73
Dec 96	NM	73	47	54	45	51	58	44
Feb 97	NM	83	78	80	81	84	90	65
Mar 97	NM	80	81	80	83	86	91	66
Apr 97	NM	78	79	81	82	84	87	65
May 97	NM	88	84	86	84	88	91	70
Jun 97	NM	91	88	88	87	88	95	72
Jul 97	NM	87	87	91	98	96	96	78
Aug 97	NM	63	78	66	65	68	73	56
Sep 97	NM	58	88	61	60	62	75	52
Oct 97	NM	68	101	61	66	65	66	64
Nov 97	NM	62	101	61	56	53	67	63
Dec 97	NM	56	78	49	49	50	53	53
Average	**-**	**80**	**84**	**80**	**80**	**84**	**97**	**61**

The average data from **Table A.7** was presented in **Table 3.3** in **Section 3.4.1**.

Table A.8 : Daily average COD of samples from the raw feed, reactors and final effluent during the period November 1995 to December 1997

Month	COD (mg/ℓ)							
	Raw	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**Final**
Nov 95	1888	86	90	92	92	96	110	57
Dec 95	1989	82	101	97	87	87	116	62
Jan 96	2933	82	82	80	84	84	84	54
Feb 96	2994	89	88	93	109	92	275	57
Mar 96	2284	100	106	128	122	98	243	62
Apr 96	2240	77	82	80	82	83	127	53
May 96	2155	79	89	98	85	92	116	51
Jun 96	2189	72	74	99	83	87	80	54
Jul 96	1911	78	75	76	80	81	90	53
Aug 96	2371	78	73	73	71	81	95	57
Sep 96	2227	90	86	87	79	87	107	58
Oct 96	2248	103	104	125	119	128	136	68
Nov 96	2364	89	83	89	92	109	106	61
Dec 96	3015	101	62	90	63	75	76	54
Feb 97	2323	97	82	97	88	97	109	63
Mar 97	2408	85	70	81	74	83	96	59
Apr 97	2238	73	65	81	74	72	87	52
May 97	2459	94	83	91	95	84	103	63
Jun 97	2637	91	91	90	96	93	112	62
Jul 97	2296	108	89	91	151	116	115	72
Aug 97	2183	66	87	72	61	69	84	58
Sep 97	1995	64	106	74	65	71	87	51
Oct 97	2707	95	104	82	91	92	104	65
Nov 97	2619	67	82	67	67	69	80	63
Dec 97	2691	57	73	61	60	59	59	50
Average	**2375**	**84**	**85**	**88**	**87**	**87**	**112**	**58**

The average data from **Table A.8** was presented in **Table 3.3** in **Section 3.4.1**.

Table A.9 : Daily average suspended solids and conductivity of samples from the raw feed and final effluent during the period November 1995 to December 1997

Month	Suspended Solids (mg/ℓ)		Conductivity (mS/m)	
	Raw	**Final**	**Raw**	**Final**
Nov 95	391	15	192	200
Dec 95	529	17	168	190
Jan 96	965	14	351	341
Feb 96	457	12	179	169
Mar 96	383	15	216	165
Apr 96	350	11	208	199
May 96	500	13	195	179
Jun 96	375	13	171	175
Jul 96	577	13	198	204
Aug 96	466	14	208	203
Sep 96	452	13	207	193
Oct 96	445	26	230	190
Nov 96	531	16	226	223
Dec 96	824	11	265	359
Feb 97	500	12		
Mar 97	708	15	244	233
Apr 97	535	15	246	229
May 97	566	15	256	232
Jun 97	588	22	270	247
Jul 97	523	24	244	255
Aug 97	481	19	240	258
Sep 97	578	19	228	234
Oct 97	474	13	228	214
Nov 97	452	15	315	220
Dec 97	882	13	900	496
Average	**541**	**15**	**85**	**88**

Table A.10 : Daily average Alkalinity of samples from the raw feed, reactors and final effluent during the period November 1995 to December 1997

Month	Alkalinity (mg/ℓ)							
	Raw	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**Final**
Nov 95	242	177	172	167	174	176	189	140
Dec 95	282	178	168	166	167	167	194	145
Jan 96	337	131	110	123	130	131	152	98
Feb 96	302	195	193	199	205	203	293	163
Mar 96	339	193	188	192	185	199	271	147
Apr 96	275	160	149	146	156	155	185	131
May 96	319	159	149	154	165	160	163	120
Jun 96	285	189	184	189	187	199	192	158
Jul 96	291	186	183	187	183	183	195	158
Aug 96	300	184	179	184	179	178	188	167
Sep 96	267	197	188	198	188	193	204	179
Oct 96	342	190	189	208	206	214	208	185
Nov 96	362	154	149	159	154	175	174	151
Dec 96	289	148	115	136	121	121	139	141
Feb 97	366	201	194	210	190	193	209	181
Mar 97	412	180	175	187	173	175	199	185
Apr 97	395	158	158	166	172	154	162	160
May 97	425	191	180	180	184	179	188	166
Jun 97	398	187	178	180	182	183	195	185
Jul 97	370	242	222	227	228	231	234	224
Aug 97	256	129	182	138	126	138	157	139
Sep 97	257	114	184	118	115	101	137	121
Oct 97	290	172	207	154	170	168	181	163
Nov 97	294	138	178	140	129	143	150	146
Dec 97	278	106	149	130	116	113	119	127
Average	**319**	**170**	**173**	**170**	**167**	**169**	**187**	**155**

Table A.11 : Daily average nitrate of samples from the raw feed, reactors and final effluent during the period November 1995 to December 1997

Month	Nitrate (mg/ℓ)							
	Raw	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**Final**
Nov 95	0.5	0.5	0.6	0.5	0.5	0.5	0.5	0.5
Dec 95	4.7	1.8	1.0	0.8	1.1	1.2	1.5	1.4
Jan 96	0.6	0.6	0.7	1.0	1.0	1.1	0.9	1.1
Feb 96	0.5	0.5	0.5	0.5	0.5	0.5	0.8	0.8
Mar 96	0.5	0.5	0.5	0.5	0.5	0.5	0.8	0.6
Apr 96	0.6	0.5	0.6	0.5	0.5	0.5	0.7	0.6
May 96	0.5	0.5	0.5	0.6	0.7	0.5	0.7	0.6
Jun 96	0.7	0.5	0.5	0.5	0.5	0.5	0.6	0.6
Jul 96	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Aug 96	0.5	0.5	0.5	0.5	0.5	0.5	0.6	0.5
Sep 96	0.5	0.5	0.5	0.5	0.5	0.6	0.8	0.9
Oct 96	0.5	1.1	1.1	1.8	2.1	2.3	2.6	1.6
Nov 96	0.5	0.8	1.0	0.8	1.2	1.3	1.4	1.5
Dec 96	0.5	0.7	0.5	1.2	1.0	1.1	0.6	1.6
Feb 97	0.5	0.6	0.7	0.5	0.6	0.9	1.1	0.8
Mar 97	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5
Apr 97	0.5	0.9	0.7	0.6	0.6	0.6	0.6	0.9
May 97	0.5	0.8	0.8	0.7	0.7	0.7	0.9	1.6
Jun 97	0.5	0.8	0.6	0.9	0.9	0.8	0.9	1.1
Jul 97	0.6	1.7	1.6	1.5	1.6	1.8	1.5	1.9
Aug 97	0.5	0.7	0.6	0.6	0.6	0.5	0.8	1.2
Sep 97	0.6	0.7	1.0	0.7	0.7	0.7	0.8	1.1
Oct 97	1.0	0.9	0.9	0.7	0.9	0.7	0.7	0.8
Nov 97	0.5	0.5	0.9	0.6	0.5	0.5	0.6	0.8
Dec 97	0.5	0.7	0.9	1.1	1.0	0.7	0.6	1.1
Average	**0.7**	**0.7**	**0.7**	**0.7**	**0.8**	**0.8**	**0.9**	**1.0**

Table A.12 : Daily average soluble reactive phosphate of samples from the raw feed, reactors and final effluent during the period November 1995 to December 1997

Month	Soluble Reactive Phosphate (mg/ℓ)							
	Raw	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**Final**
Nov 95	7481	500	500	500	500	500	500	500
Dec 95	15428	500	500	500	500	500	500	500
Jan 96	4930	500	500	500	500	500	500	500
Feb 96	9003	637	662	740	716	1008	3691	506
Mar 96	7636	1110	1304	1394	1215	1503	4130	646
Apr 96	6503	541	566	556	549	557	1128	513
May 96	6717	502	505	501	581	558	1009	500
Jun 96	6191	500	500	500	500	500	500	500
Jul 96	6370	500	500	500	500	500	500	500
Aug 96	5762	500	500	500	500	500	500	500
Sep 96	5352	500	500	500	500	500	500	500
Oct 96	6096	517	515	521	520	527	538	505
Nov 96	7419	500	500	500	500	500	500	500
Dec 96	3200	500	500	500	500	500	500	500
Feb 97	6657	500	500	500	500	500	500	500
Mar 97	7591	500	500	500	500	500	500	500
Apr 97	7114	500	500	500	500	500	500	500
May 97	8538	501	500	505	503	500	503	500
Jun 97	8382	500	500	500	500	500	500	500
Jul 97	8030	500	500	500	500	500	500	500
Aug 97	8513	500	500	500	500	500	500	500
Sep 97	7605	500	500	500	500	500	500	500
Oct 97	2915	500	795	500	500	500	500	500
Nov 97	2950	696	853	580	530	700	586	710
Dec 97	4819	500	1242	537	500	500	500	500
Average	**6848**	**540**	**598**	**553**	**545**	**574**	**823**	**515**

A.6 SLUDGE HANDLING

Table A.13 : Sludge age during the period November 1995 to December 1997

Month	Sludge Age (d)					
	R1	**R2**	**R3**	**R4**	**R5**	**R6**
Nov 95	36	36	35	36	38	ND
Dec 95	55	67	64	57	63	ND
Jan 96	55	49	51	46	56	53
Feb 96	55	56	48	48	47	ND
Mar 96	32	35	37	32	32	ND
Apr 96	52	39	30	44	44	ND
May 96	90	76	26	64	72	75
Jun 96	79	78	28	78	78	78
Jul 96	90	87	51	80	85	90
Aug 96	53	54	70	50	49	53
Sep 96	61	56	62	56	62	50
Oct 96	110	117	125	95	107	90
Nov 96	86	80	86	80	79	75
Dec 96	70	82	77	74	84	62
Feb 97	83	81	84	85	80	73
Mar 97	69	75	83	69	80	82
Apr 97	100	98	86	77	96	86
May 97	73	76	76	84	66	82
Jun 97	76	80	76	76	75	74
Jul 97	82	97	74	77	76	65
Aug 97	ND	ND	40	42	34	35
Sep 97	ND	ND	42	45	42	39
Oct 97	ND	ND	41	34	32	36
Nov 97	ND	ND	44	35	40	40
Dec 97	109	108	91	96	101	99
Average	**69**	**67**	**58**	**62**	**66**	**70**

A.7 PHOTOGRAPHS OF THE HWWTP

Figure A.2 : A view of one of the 5-stage Bardenpho reactors with the anaerobic and primary anoxic zones to the right of the picture.

Figure A.3 : A view of the anaerobic and primary anoxic zones with the central clarifier to the left of the picture.

Appendix B

Laboratory Experimental Data

Raw and processed data from laboratory experiments (**Chapter 4**) are presented in the following sections.

B.1 SCREENING TEST DATA

Raw data for the batch experiments performed at the HWWTP laboratory is given in **Table B.1**. The results of this experiment are presented in **Section 4.2.1**.

Table B.1 : Colour measurement of the samples during the batch tests at HWWTP. The colour at *t = 0 min* represents the colour of the solutions prior to dosing the test dye.

time (min)	Colour (°H)				
	Control	Mixed Batches		Unmixed Batches	
0	136	104	118	120	121
0.25	136	390	380	402	386
0.58	140	418	408	403	383
1.5	135	402	409	391	374
2.5	129	363	357	348	338
3.83	121	348	357	355	340
4.83	136	352	344	320	342
24.83	156	280	270	230	242
26.17	120	274	245	220	262
29.33	123	247	262	221	294
121.33	102	240	234	234	269

B.2 ANAEROBIC SERUM BOTTLE TESTS

B.2.1 Decolourisation of C.I. Reactive Red 141 and Determination of Factors Affecting Decolourisation

Data shown in **Table B.2 to B.5** is presented and discussed in **Section 4.2.2**. A curve was fitted to each of the data sets to make comparisons between Batches. However, the number of data points were not sufficient to obtain representative curves. The data for the curves are shown in this section, but have been ommitted from the discussion in **Chapter 4**.

Table B.2 : Data for measurement of decolourisation of C.I. Reactive Red 141 in HWWTP sludge and raw feed

Raw Data						
time (h)	**C.I. Reactive Red 141 (mg/ℓ)**					
	1.3 % solids			**2.4 % solids**		
	Rep 1	**Rep 2**	**Average**	**Rep 1**	**Rep 2**	**Average**
0.17	42.53	32.93	37.73	42.53	40.45	41.49
2.0	3.64	21.06	12.35	21.26	20.51	20.88
4.5	2.83	3.18	3.01	5.30	1.67	3.48
17.5	1.62	1.01	1.31	3.08	2.83	2.95
Normalised Data						
time (h)	**C/C_o** where C_o = 45.5 mg/ℓ					
	1.3 % solids			**2.4 % solids**		
	Rep 1	**Rep 2**	**Average**	**Rep 1**	**Rep 2**	**Average**
0.17	0.935	0.724	0.829	0.935	0.889	0.912
2.0	0.080	0.463	0.271	0.467	0.451	0.459
4.5	0.062	0.070	0.066	0.117	0.037	0.077
17.5	0.036	0.022	0.029	0.068	0.062	0.065
	$R^2 = 0.939$ **$C/C_o = 0.26t^{-0.74}$**			$R^2 = 0.918$ **$C/C_o = 0.54 - 0.20\ln t$**		

Table B.3 : Data for measurement of decolourisation of C.I. Reactive Red 141 in HWWTP sludge and nutrient medium.

Raw Data						
time (h)	**C.I. Reactive Red 141 (mg/ℓ)**					
	1.3 % solids			**2.4 % solids**		
	Rep 1	**Rep 2**	**Average**	**Rep 1**	**Rep 2**	**Average**
0.17	26.01	24.90	25.45	26.36	22.83	24.60
2.0	6.36	7.98	7.17	7.12	4.09	5.61
4.5	1.87	2.17	2.02	0.86	1.11	0.98
17.5	1.36	0.96	1.16	0.91	1.46	1.19
Normalised Data						
time (h)	**C/C_o** where C_o = 29.6 mg/ℓ					
	1.3 % solids			**2.4 % solids**		
	Rep 1	**Rep 2**	**Average**	**Rep 1**	**Rep 2**	**Average**
0.17	0.879	0.842	0.861	0.891	0.772	0.832
2.0	0.215	0.270	0.242	0.241	0.138	0.190
4.5	0.063	0.073	0.068	0.029	0.038	0.033
17.5	0.046	0.032	0.039	0.031	0.050	0.040
	$R^2 = 0.955$ **$C/C_o = 0.27t^{-0.69}$**			$R^2 = 0.882$ **$C/C_o = 0.42 - 0.18\ln t$**		

Table B.4 : Data for measurement of decolourisation of C.I. Reactive Red 141 in HWWTP sludge raw feed and nutrient medium.

Raw Data						
time (h)	**C.I. Reactive Red 141 (mg/ℓ)**					
	1.3 % solids			**2.4 % solids**		
	Rep 1	**Rep 2**	**Average**	**Rep 1**	**Rep 2**	**Average**
0.17	33.38	29.44	31.41	30.30	29.80	30.05
2.0	15.40	15.45	15.43	14.90	11.11	13.01
4.5	2.17	4.09	3.13	1.97	0.10	1.04
17.5	2.02	2.12	2.07	1.92	1.72	1.82
Normalised Data						
time (h)	**C/C_o** where C_o = 29.6 mg/ℓ					
	1.3 % solids			**2.4 % solids**		
	Rep 1	**Rep 2**	**Average**	**Rep 1**	**Rep 2**	**Average**
0.17	1.129	0.996	1.062	1.025	1.008	1.016
2.0	0.521	0.523	0.522	0.504	0.376	0.440
4.5	0.073	0.138	0.106	0.067	0.003	0.035
17.5	0.068	0.072	0.070	0.065	0.058	0.061
	$R^2 = 0.931$ **$C/C_o = 0.63 - 0.23\ln t$**			$R^2 = 0.905$ **$C/C_o = 0.57 - 0.22\ln t$**		

Table B.5 : Data for measurement of decolourisation of C.I. Reactive Red 141 in HWWTP sludge nutrient medium and glucose solution**.**

Raw Data						
time (h)	**C.I. Reactive Red 141 (mg/ℓ)**					
	1.3 % solids			**2.4 % solids**		
	Rep 1	**Rep 2**	**Average**	**Rep 1**	**Rep 2**	**Average**
0.17	30.45	18.79	24.62	23.74	21.46	22.60
2.0	15.10	7.63	11.36	10.71	8.74	9.72
4.5	0.35	1.52	0.93	0.96	0.81	0.88
17.5	0.35	1.52	0.93	0.96	0.05	0.51
Normalised Data						
time (h)	**C/C_o** where C_o = 29.6 mg/ℓ					
	1.3 % solids			**2.4 % solids**		
	Rep 1	**Rep 2**	**Average**	**Rep 1**	**Rep 2**	**Average**
0.17	1.030	0.635	0.833	0.803	0.726	0.764
2.0	0.511	0.258	0.384	0.362	0.295	0.329
4.5	0.012	0.051	0.032	0.032	0.027	0.030
17.5	0.012	0.051	0.032	0.032	0.002	0.017
	$R^2 = 0.954$ **$C/C_o = 0.45 - 0.23\ln t$**			$R^2 = 0.969$ **$C/C_o = 0.40 - 0.21\ln t$**		

The above experiments were repeated using HWWTP sludge and raw feed only. The results are shown in **Table B.7** and **B.8** and the data is presented and discussed in **Section 4.2.2**.

Table B.7 : Data for the comparison between absorbance measurements at 400 and 525 nm.

time (h)	Absorbance					
	400 nm			525 nm		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
0	0.353	0.355	0.354	0.808	0.779	0.794
1	0.342	0.335	0.339	0.804	0.775	0.790
3	0.390	0.399	0.395	0.664	0.687	0.676
4	0.264	0.267	0.266	0.298	0.308	0.303
5	0.333	0.248	0.291	0.156	0.136	0.146
6	0.265	0.279	0.272	0.154	0.157	0.156
7	0.259	0.272	0.266	0.138	0.142	0.140

Table B.8 : Anaerobic decolourisation of C.I. Reactive Red 141 in HWWTP sludge and raw feed (repeat test)

time (h)	C.I. Reactive Red 141 (mg/ℓ)			C/C_o where C_o = 47.6 mg/ℓ		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
0	39.844	38.333	39.089	0.837	0.805	0.821
1	39.635	38.125	38.880	0.833	0.801	0.817
3	32.344	33.542	32.943	0.679	0.705	0.692
4	13.281	13.802	13.542	0.279	0.290	0.284
5	5.885	4.844	5.365	0.124	0.102	0.113
6	5.781	5.938	5.859	0.121	0.125	0.123
7	4.948	5.156	5.052	0.104	0.108	0.106

B.3 AEROBIC/ADSORPTION EXPERIMENTAL DATA

The data for the determination of the aerobic degradation and adsorption of C.I. Reactive Red 141 are shown in **Table B.9**. This data is presented and discussed in **Section 4.2.3**.

Table B.9 : Decolourisation of C.I. Reactive Red 141 in HWWTP sludge and raw feed under aerobic conditions

time (h)	C.I. Reactive Red 141 (mg/ℓ)	Dissolved O_2 (mg/ℓ)
-1.00	46.93	4.7
0.00	45.68	5.5
0.08	50.78	6.2
1.08	45.05	6.7
2.58	45.47	6.6
4.08	44.53	6.7
48.00	44.17	6.8

B.4 DETERMINATION OF THE ORP OF HWWTP SLUDGE

The raw data for this experiment have not been included since there are in excess of 500 data points.

B.5 2 ℓ ANAEROBIC TEST

Table B.10 : ORP Data from the 2 ℓ anaerobic decolourisation experiment (**Section 4.3.5**).

time (h)	ORP (mV SHE)
0.00	-113.60
0.05	-164.70
0.10	-192.80
0.15	-211.00
0.20	-178.30
0.25	-95.60
0.30	-13.10
0.35	16.40
0.40	29.80
0.45	36.40
0.50	40.40
0.55	39.80
0.60	40.50
0.65	43.60
0.70	44.70
0.75	45.00
0.80	46.30
0.85	43.90
0.90	38.90
0.95	-8.50
1.00	-25.20
1.05	-41.10
1.10	-52.00
1.15	-57.30
1.20	-59.80
1.25	-58.50
1.30	-34.70
1.35	10.10
1.40	4.10
1.45	2.90
1.50	2.70

time (h)	ORP (mV SHE)
1.55	3.20
1.60	3.80
1.65	5.10
1.70	6.30
1.75	7.30
1.80	8.50
1.85	22.50
1.90	32.60
1.95	31.00
2.00	32.40
2.05	33.20
2.10	34.50
2.15	35.30
2.20	36.30
2.25	34.40
2.30	43.30
2.35	48.20
2.40	49.60
2.45	51.30
2.50	44.80
2.55	44.10
2.60	39.20
2.65	46.70
2.70	50.50
2.75	52.40
2.80	53.40
2.85	54.60
2.90	55.40
2.95	53.90
3.00	54.50
3.05	44.90

time (h)	ORP (mV SHE)
3.10	54.30
3.15	45.50
3.20	39.90
3.25	38.70
3.30	37.80
3.35	37.50
3.40	37.00
3.45	36.70
3.50	33.90
3.55	42.50
3.60	48.40
3.65	43.00
3.70	41.50
3.75	40.90
3.80	40.60
3.85	40.00
3.90	39.60
3.95	39.30
4.00	39.00
4.05	38.70
4.10	38.80
4.15	38.10
4.20	38.00
4.25	38.00
4.30	38.00
4.35	37.80
4.40	37.90
4.45	37.40
4.50	39.00
4.55	39.50
4.60	39.20
4.65	39.70
4.70	39.80
4.75	40.00

time (h)	ORP (mV SHE)
4.85	39.80
4.90	40.00
4.95	39.80
5.00	39.80
5.05	40.60
5.10	40.20
5.15	40.10
5.20	40.50
5.25	40.40
5.30	40.00
5.35	40.30
5.40	40.50
5.45	38.80
5.50	40.20
5.55	40.90
5.60	41.20
5.65	40.90
5.70	42.10
5.75	41.50
5.80	41.20
5.85	42.00
5.90	40.70
5.95	41.90
6.00	41.20
6.05	41.40
6.10	41.60
6.15	41.60
6.20	41.70
6.25	41.90
6.30	41.80
6.35	41.70
6.40	41.60
6.45	42.20
6.50	41.90

4.80	40.00

6.55	42.20

time (h)	ORP (mV SHE)
6.60	42.60
6.65	-16.50
6.70	-55.30
6.75	-77.90
6.80	-92.10
6.85	-101.00
6.90	-104.30
6.95	-106.70
7.00	-107.80
7.05	-108.30
7.10	-86.50
7.15	-51.70
7.20	-34.00
7.25	-22.10
7.30	-14.50
7.35	-9.50
7.40	-6.00
7.45	-3.50
7.50	4.00
7.55	9.40
7.60	16.20
7.65	21.20
7.70	24.10
7.75	26.50
7.80	28.40
7.85	30.20
7.90	31.60
7.95	32.80
8.00	33.90
8.05	34.90
8.10	35.70
8.15	36.50

time (h)	ORP (mV SHE)
8.35	38.70
8.40	39.60
8.45	39.60
8.50	39.80
8.55	39.80
8.60	39.90
8.65	40.30
8.70	40.50
8.75	40.60
8.80	40.90
8.85	40.90
8.90	41.50
8.95	41.70
9.00	41.80
9.05	41.70
9.10	41.90
9.15	41.80
9.20	41.70
9.25	41.40
9.30	41.20
9.35	41.50
9.40	41.30
9.45	41.10
9.50	40.90
9.55	40.90
9.60	40.60
9.65	40.20
9.70	40.10
9.75	40.00
9.80	40.00
9.85	39.90
9.90	39.70

8.20	37.30
8.25	37.80
8.30	38.30

9.95	39.60
10.00	39.40
10.05	39.70

time (h)	ORP (mV SHE)
10.10	39.30
10.15	39.50
10.20	39.10
10.25	38.90
10.30	38.80
10.35	38.40
10.40	38.00
10.45	39.70
10.50	40.90
10.55	41.60
10.60	42.00
10.65	42.80
10.70	42.90

time (h)	ORP (mV SHE)
10.75	43.00
10.80	43.20
10.85	43.60
10.90	43.30
10.95	43.10
11.00	43.10
11.05	43.00
11.10	43.20
11.15	42.70
11.20	42.90
11.25	42.80
11.30	42.60

B.5.1 Decolourisation of C.I. Reactive Red 141

Table B.11 : Decolourisation of C.I. Reactive Red 141 in HWWTP sludge and raw feed using a 2 ℓ digester

time (h)	C.I. Reactive Red 141 (mg/ℓ)	C/C_o where C_o = 90.9 mg/ℓ
0.00	84.34	0.928
0.50	80.10	0.881
1.00	74.95	0.825
1.50	72.17	0.794
2.00	69.75	0.767
2.67	62.47	0.687
3.17	62.73	0.690
4.17	50.61	0.557
5.17	37.22	0.409
6.17	21.31	0.234
6.84	18.84	0.207
7.17	17.42	0.192
8.17	12.37	0.136
10.17	9.09	0.100
11.17	9.09	0.100

B.5.2 Chemical Oxygen Demand (COD)

The results of the COD determination were inaccurate due to difficulties encountered with the blank. It was only possible to obtain a COD relative to the raw feed COD, i.e. a percentage reduction in COD relative to the raw feed. The data showed vaery little variation for the duration of the experiment and were thus not presented in **Chapter 4**.

Table B.12 : Percent COD reduction of samples during decolourisation of C.I. Reactive Red 141

time (h)	% Reduction
0.00	24.73
0.50	NM
1.00	NM
1.50	17.34
2.00	NM
2.67	NM
3.17	NM
4.17	29.44
5.17	35.48
6.17	26.41
6.84	30.44
7.17	24.73
8.17	26.08
10.17	27.76
11.17	21.03

NM = Not Measured

B.6 C.I. REACTIVE RED 141 CALIBRATION CURVE

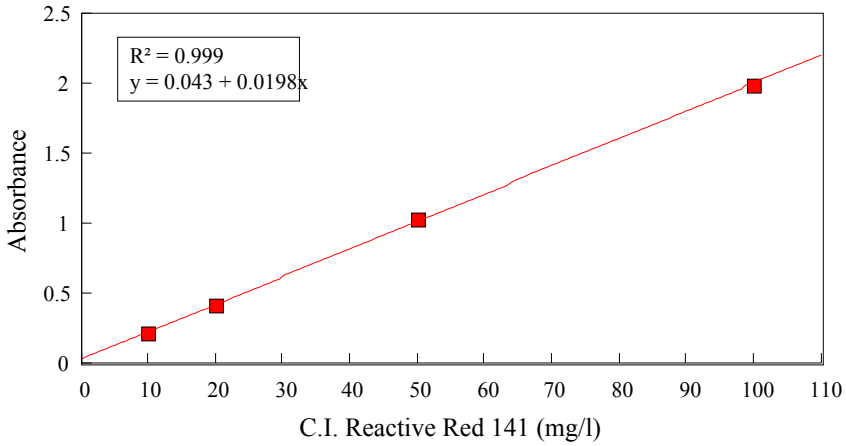

Figure B.1 : Calibration curve for C.I. Reactive Red 141 in distilled water measured at 525 nm.

Appendix C

Full Scale Experimental Data

The data shown in **Appendix C** is presented and discussed in **Chapter 5**.

C.1 ORP AND COLOUR DATA FOR THE ANAEROBIC ZONE

C.1.1 ORP and Colour with respect to Position

ORP measurements were made relative to the silver/silver chloride (Ag/AgCl) reference electrode and converted to ORP values relative to the standard hydrogen electrode (SHE) according to equation C.1.

$$ORP_{SHE} = ORP_{Ag/AgCl} + 198 \text{ mV} \qquad [C.1]$$

Table C.1 : ORP and colour measurements in the anaerobic zone

Sampling Position	Profile 1			Profile 2		
	ORP (mV)		Colour (°H)	ORP (mV)		Colour (°H)
	(Ag/AgCl)	(SHE)		(Ag/AgCl)	(SHE)	
1	-366	-168	150	-299	-101	192
2	-365	-167	138	-310	-112	155
3	-345	-147	140	-309	-111	150
4	-340	-142	168	-324	-126	280
5	-345	-147	150	-313	-115	289
6	-370	-172	140	-272	-74	248
7	-312	-114	146	-328	-130	147
8	-340	-142	131	-324	-126	140
9	-332	-134	168	-319	-121	140
10	-340	-142	145	-335	-137	281
11	-350	-152	162	-348	-150	224
12	-358	-160	146	-357	-159	204

C.1.2 ORP with respect to Time

Table C.2 : Data for the determination of the change in ORP in the anaerobic zone with respect to time

Profile 1			Profile 2		
time (h)	ORP (mV)		time (h)	ORP (mV)	
	(Ag/AgCl)	(SHE)		(Ag/AgCl)	(SHE)
0.00	-210	-12	0.00	-89	109
0.17	-255	-57	0.42	-272	-74
0.22	-312	-114	0.48	-283	-85
0.33	-283	-85	0.92	-313	-115
0.37	-333	-135	1.00	-292	-94
0.80	-340	-142	1.25	-324	-126
1.00	-305	-107	1.37	-325	-127
1.50	-328	-130	1.75	-335	-137
1.52	-332	-134	1.83	-333	-135
1.55	-321	-123	2.20	-348	-150
2.00	-345	-147	2.30	-350	-152
2.03	-280	-82	2.58	-357	-159
2.83	-365	-167	2.88	-254	-56
2.85	-280	-82	4.25	-299	-101
3.35	-366	-168	4.27	-300	-102
3.50	-248	-50	4.58	-310	-112
4.00	-358	-160	4.65	-313	-115
4.03	-354	-156	4.88	-309	-111
4.38	-350	-152	4.92	-311	-113
4.50	-350	-152	5.15	-319	-121
4.98	-340	-142	5.18	-321	-123
5.02	-340	-142	5.40	-324	-126
5.42	-320	-122	5.45	-324	-126
5.50	-340	-142	5.75	-328	-130
5.88	-345	-147			
6.00	-355	-157			
6.40	-370	-172			

C.1.3 Colour with respect to Time

Table C.3 : Data for the determination of the colour in the anaerobic zone with respect to time

time (h)	Colour (°H)	
	samples	raw feed
Profile 1		
0.00	146	768
0.43	131	-
1.15	168	642
2.47	138	-
2.98	150	710
3.63	146	608
4.02	162	-
4.62	145	-
5.05	168	751
5.52	150	661
6.03	140	-
Profile 2		
0.00	248	1690
0.50	289	1690
0.83	280	1600
1.33	281	2820
1.78	224	1710
2.17	204	-
3.83	192	750
4.17	155	720
4.47	150	720
4.73	-	650
4.98	140	-
5.33	147	630

C.2 DYE TRACER TEST

Table C.4 : Data for the determination of the decolourisation of C.I. Reactive Red 141 in the anaerobic zone

time (min)	Colour (°H)	ORP (mV)	
		(Ag/AgCl)	(SHE)
0	143	-305	-107
15	144	-295	-97
25	144	-300	-102
30	165	-303	-105
35	153	-306	-108
45	150	-305	-107
55	145	-313	-115
85	110	-320	-122
115	118	-328	-130

C.3 RESIDENCE TIME DISTRIBUTION TEST ON THE ANAEROBIC ZONE

C.3.1 Experimental Data

Table C.5 : Lithium concentration measured at the outlet of the anaerobic zone for the RTD

time (min)	Li concentration (mg/l)
0	0.00
2	0.01
2	0.00
5	0.00
6	0.00
7	0.00
8	0.00
9	0.02
10	0.76
11	1.97
12	2.24
13	2.29
14	2.42
15	2.32
16	2.32
17	2.34
18	2.36
19	2.35
20	2.34
21	2.23
22	2.14
23	2.14
24	2.17
25	2.12

time (min)	Li concentration (mg/l)
26	2.05
27	2.03
28	2.00
29	1.99
30	1.89
31	1.88
32	1.83
34	1.85
36	1.72
38	1.63
40	1.64
42	1.53
45	1.46
48	1.36
51	1.33
54	1.22
57	1.13
60	1.09
65	1.00
70	0.91
75	0.83
80	0.77
85	0.69
90	0.61

time (min)	Li concentration (mg/l)
95	0.58
100	0.50
105	0.45
110	0.40
115	0.35
120	0.33

time (min)	Li concentration (mg/l)
130	0.22
140	0.18
150	0.14
160	0.14
170	0.10
180	0.08

C.3.2 Flow Data

Table C.6 : Inlet flow rates for each HWWTP reactor

time (min)	Flow (m^3/h)	
	raw feed	MLR
0	78.33	160
60	78.33	160
120	78.33	160
180	85.00	160

C.3.3 Calculation of Input Spike Concentration

(a) Actual concentration

The input concentration is a function of the flow rate to which the salt is dosed :

5 kg LiCl dosed over ca. 10 min, ∴ 0.819 kg Li dosed over ca. 10 min.

$$\text{Concentration of input spike} = \frac{\text{mass}}{(\text{flow})(\text{time})}$$

$$= \frac{819\ 000\ \text{mg}}{(1305.5\ \text{l/min})(0.167\ \text{min})}$$

$$= \mathbf{3764\ mg/\ell}$$

(b) Simulated concentration

The time step for the IMPULSE simulation was 1 min. Therefore, the input concentration had to be determined for this time step. The actual input was a step input of 3 764 mg/ℓ height and 0.167 min width (**Figure C.1**). The simulated concentration is the input concentration for the spike input where the base length is 1 min.

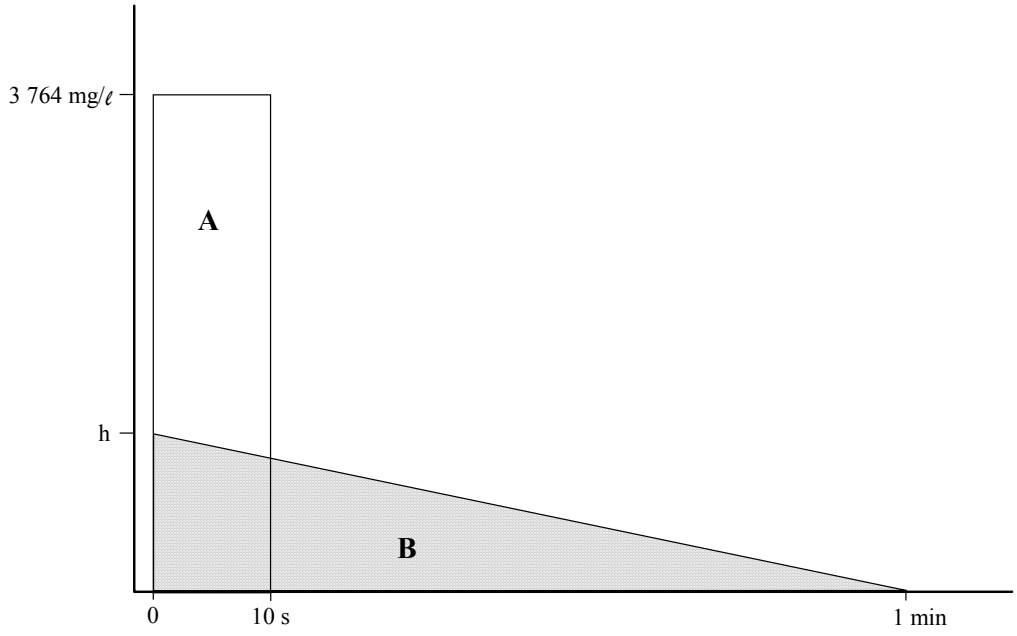

Figure C.1 : Graphical representation of the actual and simulated input spikes for the RTD test

∴ The area **A** should equal the area **B** for the amount of salt to be equal.

Area **A** = l x b = (0.167)(3 764)

= **628.588 mg.min/ℓ**

Area **B** = ½ x b x h = Area **A** = 628.588

∴ h = **1 257 mg/ℓ**

C.3.4 Impulse Output - Model 1

IMPULSE calculated the following according to the parameters for **Model 1** (Fixed Flow Model) :

Dose
Flow rate (Scale : 1)
0 1
180 1
Concentration (Scale : 0.669)

0 1638000
1 0
180 0

Mix2
Pipe:1

Mixer
Pipe2:1

Pipe
DeadVol : 3043.257

Pipe2
DeadVol : 2088.414

Zone1
Vol : 187105.468
num : 1.403

ReturnSludge
Flow rate (Scale : 1)
0 2667
250 2667
Concentration (Scale : 1)
0 0
180 0

InletRaw
Flow rate (Scale : 1)
0 1305.5
60 1305.5
120 1305.5
180 1416.67
250 1416
Concentration (Scale : 1)
0 0
0 0

Out

Connectors

Pipe2	->	Zone1
Mixer	->	Pipe2
Zone1	->	out
ReturnSludge	->	Mixer
Pipe	->	Mixer
mix2	->	Pipe
InletRaw	->	mix2
Dose	->	mix2

C.3.5 Impulse Output - Model 2

IMPULSE calculated the following according to the parameters for **Model 2** (Full Recovery Model) :

Dose
Flow rate (Scale : 1)
0 1
180 1
250 1
Concentration (Scale : 1)
0 1638000
1 0
180 0
250 0

Mix2
Pipe : 1

Mixer
Pipe2 : 1

Pipe
DeadVol : 3132.922

Pipe2
DeadVol : 2662.105

Zone1
Vol : 282259.048
num : 1.38

ReturnSludge
Flow rate (Scale : 1.72)
0 2667
250 2667
Concentration (Scale : 1)
0 0
250 0

InletRaw
Flow rate (Scale : 0.997)
0 1305.5
60 1305.5
120 1305.5
250 1416.67
Concentration (Scale : 1)
0 0
250 0

out

Connectors
Pipe2 -> Zone1
Mixer -> Pipe2
Zone1 -> out
ReturnSludge -> Mixer
Pipe -> Mixer

mix2	->	Pipe
InletRaw	->	mix2
Dose	->	mix2

C.3.6 Lithium Recovery Calculation

The mass recovery of Li was calculated as a function of the flow rate and the concentration of Li measured at the outlet of the reactor (anaerobic zone). The incremental mass recovered with time was calculated according to equation C.2 :

$$m_i = QC_i\Delta t_i \qquad [C.2]$$

where m_i = incremental mass at time i (kg)

Q = flow rate (ℓ/min)

C_i = Li concentration at time i (mg/ℓ)

Δt_i = difference between time t_i and t_{i-1} (min)

The total mass (M) of Li recovered was then :

$$M = Q\Sigma C_i\Delta t_i \qquad [C.3]$$

Table C.7 : Lithium recovery results for Model 1 (Fixed Flow) and Model 2 (corrected flows)

		Model 1		Model 2	
time (min)	**Li Concentration (mg/ℓ)**	**Flow rate (ℓ/min)**	**Li recovery (kg)**	**Flow rate (corrected) (ℓ/min)**	**Li recovery (corrected) (kg)**
0	0.00	3972.17	0.00000	5888.25	0.00000
2	0.01	3972.17	0.00008	5888.25	0.00011
2	0.00	3972.17	0.00000	5888.25	0.00000
5	0.00	3972.17	0.00000	5888.25	0.00000
6	0.00	3972.17	0.00000	5888.25	0.00000
7	0.00	3972.17	0.00000	5888.25	0.00000
8	0.00	3972.17	0.00000	5888.25	0.00000
9	0.02	3972.17	0.00008	5888.25	0.00011
10	0.76	3972.17	0.00302	5888.25	0.00447
11	1.97	3972.17	0.00783	5888.25	0.01160
12	2.24	3972.17	0.00890	5888.25	0.01319
13	2.29	3972.17	0.00910	5888.25	0.01348

14	2.42	3972.17	0.00961	5888.25	0.01425

time (min)	Li Concentration (mg/ℓ)	Flow rate (ℓ/min)	Li Recovery (kg)	Corrected flow rate (ℓ/min)	Corrected Li Recovery (kg)
15	2.32	3972.17	0.00922	5888.25	0.01366
16	2.32	3972.17	0.00922	5888.25	0.01366
17	2.34	3972.17	0.00929	5888.25	0.01377
18	2.36	3972.17	0.00937	5888.25	0.01389
19	2.35	3972.17	0.00933	5888.25	0.01383
20	2.34	3972.17	0.00929	5888.25	0.01377
21	2.23	3972.17	0.00886	5888.25	0.01313
22	2.14	3972.17	0.00850	5888.25	0.01260
23	2.14	3972.17	0.00850	5888.25	0.01260
24	2.17	3972.17	0.00862	5888.25	0.01277
25	2.12	3972.17	0.00842	5888.25	0.01248
26	2.05	3972.17	0.00814	5888.25	0.01207
27	2.03	3972.17	0.00806	5888.25	0.01195
28	2.00	3972.17	0.00794	5888.25	0.01177
29	1.99	3972.17	0.00790	5888.25	0.01171
30	1.89	3972.17	0.00751	5888.25	0.01112
31	1.88	3972.17	0.00747	5888.25	0.01107
32	1.83	3972.17	0.00727	5888.25	0.01077
34	1.85	3972.17	0.01470	5888.25	0.02178
36	1.72	3972.17	0.01366	5888.25	0.02025
38	1.63	3972.17	0.01295	5888.25	0.01919
40	1.64	3972.17	0.01303	5888.25	0.01931
42	1.53	3972.17	0.01215	5888.25	0.01801
45	1.46	3972.17	0.01740	5888.25	0.02579
48	1.36	3972.17	0.01621	5888.25	0.02402
51	1.33	3972.17	0.01585	5888.25	0.02349
54	1.22	3972.17	0.01454	5888.25	0.02155
57	1.13	3972.17	0.01347	5888.25	0.01996
60	1.09	3972.17	0.01299	5888.25	0.01925
65	1.00	3972.17	0.01986	5888.25	0.02944

time (min)	Li Concentration (mg/ℓ)	Flow rate (ℓ/min)	Li Recovery (kg)	Corrected flow rate (ℓ/min)	Corrected Li Recovery (kg)
70	0.91	3972.17	0.01807	5888.25	0.02679
75	0.83	3972.17	0.01648	5888.25	0.02443
80	0.77	3972.17	0.01529	5888.25	0.02267
85	0.69	3972.17	0.01370	5888.25	0.02031
90	0.61	3972.17	0.01212	5888.25	0.01795
95	0.58	3972.17	0.01152	5888.25	0.01707
100	0.50	3972.17	0.00993	5888.25	0.01472
105	0.45	3972.17	0.00894	5888.25	0.01324
110	0.40	3972.17	0.00794	5888.25	0.01177
115	0.35	3972.17	0.00695	5888.25	0.01030
120	0.33	3972.17	0.00655	5888.25	0.00971
130	0.22	3972.17	0.00874	5888.25	0.01295
140	0.18	3972.17	0.00715	5888.25	0.01059
150	0.14	3972.17	0.00556	5888.25	0.00824
160	0.14	3972.17	0.00556	5888.25	0.00824
170	0.10	3972.17	0.00397	5888.25	0.00588
180	0.08	4083.33	0.00327	5999.08	0.00479
TOTAL (kg)			**0.53010**		**0.78576**
Initial mass Li = 0.819 kg					
% RECOVERY			**64.72**		**95.94**

C.4 ORP SAMPLING RIG CALIBRATION AND TESTING DATA

C.4.1 Immersion Probe Data

The Polymetron Ag/AgCl electrode was converted into an immersion probe to determine the ORP at various points in the anaerobic zone (**Figure C.2**). The results are shown in **Table C.8**.

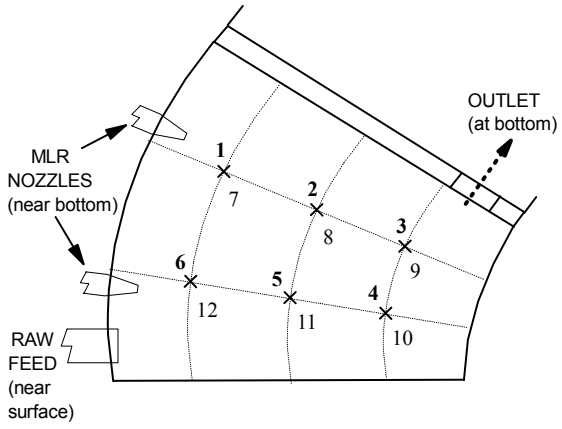

Figure C.2 : Plan view of the anaerobic zone showing the ORP profile points. Points 1 to 6 were at a depth of 1.5 m and points 7 to 12 at 3.0 m.

Table C.8 : Results of the ORP measurement in the anaerobic zone of reactor 2 using the immersion probe

Sampling Position	ORP (mV)	
	(Ag/AgCl)	(SHE)
1	-310	-112
2	NM	NM
3	-260	-62
4	-260	-62
5	-250	-52
6	-250 to -350 [1]	-52 to -152 [1]
7	-310	-112
8	NM	NM
9	-250	-52
10	-260	-62

11	-260	-62
12	-280	-82

[1] Consistent variation in the ORP caused by the pulsed raw feed flow. The ORP was observed to decrease sharply when the raw feed flowed into the reactor

C.4.2 ORP Variation with Time

The sampling rig was used to draw sludge from one point in the anaerobic zone and the variation of the ORP was recorded with respect to time.

Table C.9 : Variation of ORP with time at a single point in the anaerobic zone

time (min)	**ORP (mV)**	
	(Ag/AgCl)	**(SHE)**
0	-210	-12
2	-228	-30
4	-233	-35
6	-242	-44
8	-246	-48
10	-250	-52
12	-250	-52
14	-255	-57
16	-257	-59
18	-261	-63
20	-312	-114
22	-290	-92
26	-282	-84
30	-282	-84
35	-283	-85

C.5 COMPUTATIONAL FLUID DYNAMICS DATA

The flows in the anaerobic zone were modelled using a CFD package called FLUENT. The results are presented in **Chapter 5**. In the CFD model, an arbitrary amount of tracer (67.8 kg) was injected into the inlet. The results were then scaled according to the actual amount of tracer injected (0.819 kg) in the RTD test. Table C.10 shows the modelled and scaled results of the CFD model.

Table C.10 : Results from CFD flow model with a tracer injection into the raw feed inlet

Time (min)	Mass fraction tracer ($\times 10^4$)	Total flow (kg/s)	Mass tracer (g)	Mass tracer (scaled) (g)
0	0.00	99.14	0.000	0.000
1	1.14	99.14	11.339	0.137
5	1.76	99.14	17.423	0.210
10	1.74	99.14	17.238	0.208
15	1.64	99.14	16.297	0.197
20	1.54	99.14	15.259	0.184
25	1.44	99.14	14.260	0.172
30	1.34	99.14	13.323	0.161
35	1.26	99.14	12.451	0.150
40	1.17	99.14	11.637	0.141
50	1.03	99.14	10.170	0.123
60	0.90	99.14	8.890	0.107
70	0.78	99.14	7.773	0.094
80	0.69	99.14	6.797	0.082
90	0.60	99.14	5.943	0.072
100	0.52	99.14	5.197	0.063
120	0.40	99.14	3.975	0.048
140	0.31	99.14	3.040	0.037
160	0.23	99.14	2.325	0.028
180	0.18	99.14	1.778	0.021
200	0.14	99.14	1.359	0.016
240	0.08	99.14	0.795	0.010

The average residence time and the normalised residence time distribution curve was obtained using the same method as for the RTD test (**Section 5.5.4.1**) and determined to be :

Average residence time = <u>67.9 min</u>

The Normalised data are shown in **Table C.11**.

Table C.11 : Normalised data from the CFD model.

Normalised time T	Normailised function C(T)
0.0351	0.0000
0.0499	0.5863
0.1088	0.9009
0.1825	0.8914
0.2562	0.8427
0.3298	0.7890
0.4035	0.7374
0.4772	0.6889
0.5509	0.6438
0.6246	0.6017
0.7719	0.5259
0.9193	0.4597
1.0666	0.4019
1.2140	0.3515
1.3614	0.3073
1.5087	0.2687
1.8034	0.2055
2.0982	0.1572
2.3929	0.1202
2.6876	0.0919
2.9823	0.0703
3.5718	0.0411

Appendix D

Nutrient Medium

The decolourisation of C.I. Reactive Red 141 was investigated in Chapter 4 using a series of batch experiments. The inoculum was obtained from the HWWTP return activated sludge pumps. The anaerobic experiments were made in 125 ml serum bottles and some made use of a defined mineral salts medium. The recipe for this defined medium is given in the following section.

D.1 PREPARATION OF NUTRIENT MEDIUM

A defined solution containing trace elements, minerals and vitamins was prepared according to Owen et al. (1979) with some modifications. The stock solutions for preparation of the nutrient medium are presented in **Table D.1** and the method for preparation is presented in **Table D.2**.

TABLE D.1: Stock solutions for preparation of mineral salts solution.

Stock solution	Composition	Concentration (g/ℓ)
S2	Resazurin	1
S3	$(NH_4)_2HPO_4$	26.7
S4	$CaCl_2.2H_2O$	16.7
	NH_4Cl	26.6
	$MgCl_2.6H_2O$	120
	KCl	86.7
	$MnCl_2.4H_2O$	1.33
	$CoCl_2.6H_2O$	2
	H_3BO_3	0.38
	$CuCl_2.2H_2O$	0.18
	$Na_2\ MoO_4.2H_2O$	0.17
	$ZnCl_2$	0.14
S5	$FeCl_2.4H_2O$	370
S6	$Na_2S.9H_2O$	500
S7	Biotin	0.002
	Folic acid	0.002
	Pyridoxine hydrochloride	0.01
	Riboflavin	0.005
	Thiamin	0.005
	Nicotinic acid	0.005
	Panthothenic acid	0.005
	p-aminobenzoic acid	0.005
	Thioctic acid	0.005

Due to the unavailability of the two vitamins, *p*-aminobenzoic acid and thioctic acid, these were omitted from the stock solution, S7. *p*-aminobenzoic acid is a member of the vitamin B group. The stock solutions were stored at 4 °C.

TABLE D.2 : Preparation of the defined mineral salts solution.

Step	Method	Volume (ml)	Mass (g)
1	1 l of deionised water was added to a 2 ℓ Pyrex vessel		
2	The following were added :		
	Stock solution S2	1.8	
	Stock solution S3	5.4	
	Stock solution S4	27.0	
3	Deionised water was added up to 1.8 l		
4	Boiled for 15 min whilst flushing with OFN gas (1 l/min)		
5	Cooled to room temperature		
6	The following were added:		
	Stock solution S7	18.0	
	Stock solution S5	1.8	
	Stock solution S6	1.8	
7	$NaHCO_3$ was added as powder		8.4
8	Flushed with OFN until pH stabiliseed around 7.1		
9	Autoclaved (30 min at 121 °C)		
10	Stored at 4 °C until use.		